GC/MS ANALYSIS OF CHLORINATED ORGANIC COMPOUNDS IN MUNICIPAL WASTEWATER AFTER CHLORINATION

DISSERTATION

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A study has been conducted for the qualitative and quantitative analysis of chlorinated organic compounds in water. The study included the adaptation of Amberlite XAD macroreticular resin techniques for the concentration of municipal wastewater samples, followed by GC/MS analysis. A new analytical method was developed for the determination of volatile halogenated organics using liquid-liquid extraction and electron capture gas chromatography. And, a computer program was written which searches raw GC/MS computer files for halogen-containing organic compounds.

Municipal wastewater samples which had been subjected to high chlorine doses were concentrated using XAD-2 resin. After concentration, the samples were subjected to analysis by both gas chromatography and gas chromatography/mass spectroscopy. The gas chromatograph was equipped with a halogen-specific detector. Survey chromatograms indicated that over thirty halogen-containing organic compounds had formed by the action of chlorine on the wastewater. The GC/MS studies resulted in the identification of over

thirty-five compounds representing a variety of chemical classes.

A new analytical method was developed for the determination of volatile halogenated organic compounds. The method utilizes a pentane extraction of the volatile halogenated organics from the water sample followed by electron capture gas chromatographic analysis. The technique is equally precise and more sensitive than conventional methodology using a purge-and-trap approach. The method shows virtually no matrix dependence and good linear dynamic range.

A computer program was written which searches raw GC/MS data for specific mass spectral peak patterns characteristic of halogen-containing organic compounds. An important feature of the program is that it is not mass specific and thus has the potential of identifying most compounds having a specific combination of chlorine or bromine atoms. The program has two parameters which are assignable by the operator prior to beginning the data search. Selection of these parameters allows the operator to adjust the decision process to best fit the quality of the GC/MS data.

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INTRODUCTION

Molecular chlorine was first used in water treatment as a wastewater disinfectant around the turn of the century. Shortly thereafter, drinking water supplies began to be disinfected with chlorine. At that time, strong objections were raised regarding the potential dangers of such widespread use of relatively untested new technology. Sir Alexander Houston (1), Director of Water Purification, Metropolitan Water Board of London, said that many prominent thinkers of the day felt, "the use of chemicals for (water) purification purposes is worse than playing with black magic." Houston, however, went on to explain the necessity for chlorination concluding, "there is absolutely no convincing evidence that a properly chlorinated water is any way injurious to health."

Thus scientific opinion was swayed for almost half a century. In recent years, however, opinion has come full circle with new doubts arising among investigators such as Brungs (2) who states:

> The present emphasis on environmental preservation and human health is resulting in an increased use of chlorine for disinfection and waste treatment. Few efforts, if any, are being made by those proposing such procedures to determine the adverse impact of increased usage.

This study addresses one such impact, the possible formation of new chlorinated organic compounds as a result of the disinfection of municipal wastewaters with chlorine.

History and Scope of Chlorination

Gaseous molecular chlorine had been vaguely recognized as an interfering by-product of various chemical processes for hundreds of years. However, Carl W. Scheele (3) is credited with its formal discovery in 1774. He first produced chlorine by heating manganese dioxide with hydrochloric acid:

$$MnO_2 + 4HCl \xrightarrow{heat} MnCl_2 + Cl_2 + 2H_2O$$

In 1810, Humphry Davy recognized the elemental nature of gaseous chlorine. By the mid-nineteenth century, the industrial utility of chlorine had been recognized. Two procedures were developed for commercial production (4). The first was a catalytic chemical reaction:

$$4HCl + O_2 \xrightarrow{heat + catalyst} 2Cl_2 + 2H_2O \ .$$

An electrolytic process was also developed:

$$2NaCl + 2H_2O + \text{electric current} \longrightarrow 2NaOH + Cl_2 + H_2 \ .$$

At that time, the primary commercial use of chlorine was as a bleaching agent. About 1854, the Royal Sewage Commission recognized that chlorine was useful as a

wastewater deodorant. By 1880, biologists had correlated the occurrence of certain diseases with specific bacterial strains. Within a few years (1893), chlorine was being used as a drinking water and wastewater disinfectant. A year later, Brewster, New York became the first American city to use chlorine as a wastewater disinfectant to protect against potential contamination of the New York City drinking water supply.

In 1929, Bunker (1) indicated the worldwide recognition of the importance of chlorination for disease control, primarily amoebic dysentery and typhoid:

> I am of the opinion that the disinfection of water supplies by the application of liquid chlorine and calcium hypochlorite is established on such a firm basis that it is unnecessary to defend it against the attacks to which it is occasionally subjected in every country.

By 1945, Enslow (5) had defined properly effective wastewater treatment as a three-stage process including terminal chlorination for disinfection. Active interest in terminal wastewater chlorination grew rapidly across the United States. This interest culminated in the Federal Water Pollution Control Act of 1970 (6) that requires all wastewater effluents to be disinfected. Although chlorination is not specified as the only acceptable disinfection technique, in the United States it is used almost exclusively.

In 1975, approximately 10^{10} kilograms of chlorine were distributed in the United States. Of this amount, 80 percent was consumed by the chemical industry for plastics, pesticides, antifreeze fluids, synthetic fibers, gasoline additives, solvents, and paint removers. Sixteen percent was consumed by the pulp and paper industry, and about 4 percent was used for "sanitary" purposes that included potable water and wastewater treatment, swimming pools, household use, cooling-water circuits, food packaging, and process-water finishing.

Terminal chlorination of wastewater effluents is emphasized to achieve the following objectives (8):

1. Prevention of the spread of disease;
2. Protection of potable water supplies, bathing beaches, receiving waters used for boating and water-contact sports; and
3. Protection of shellfish growing areas.

The minimum effective chlorine dosage necessary to achieve the above objectives was thoroughly evaluated by the California State Department of Health, Bureau of Sanitary Engineering and later by the U.S. Environmental Protection Agency (9). The studies were based on the number of fecal coliforms contained in residual effluents. The Environmental Protection Agency's temporary commitment of 200-400 bacteria per 100 mL of effluent, depending on the nature

of the receiving waters, is the national maximum allowable limit although some states have set more stringent requirements (10).

Chemistry of Chlorine

When molecular chlorine is dissolved in water, it is hydrolyzed (11) according to the equation:

$$Cl_2 + H_2O \longrightarrow HOCl + HCl \ .$$

This reaction is 99 percent complete in only seconds, and thus the aqueous chemistry of chlorine is in fact the chemistry of hypochlorous acid. Indeed, chlorination reactions can be effected with equal efficiency by the use of solutions of hypochlorite salts.

Hypochlorous acid is a weak acid which dissociates according to the equation:

$$HOCl \rightleftharpoons H^+ + OCl^- \ .$$

The dissociation constant for HOCl is 2.95×10^{-8} at 18°C (12); thus, at a pH of 7.5 there are approximately equimolar amounts of HOCl and OCl^- present in aqueous solutions.

Kinetic studies have shown aqueous chlorination reactions to be extremely complicated. Reviews have been published by Jolley (13), Morris (14), Carlson (15), and Pierce (16). For many reactions, the pH dependence of the

reaction rates suggests that hypochlorous acid, HOCl, is the reactive species or is involved directly in the generation of the principal reactive species. Hypochlorous acid is reported (17) to be 10^4 times more reactive as a chlorinating agent than the hypochlorite ion, OCl^-. However, other authors have determined the reactive species to be the hypochloronium ion, H_2OCl^+, the free chloronium ion, Cl^+ (18), and the chlorine radical, $Cl^\cdot$ (15). Carlson (15) states that chlorine-containing organic products will be derived from the attack of electrophilic species such as H_2OCl^+ or $Cl^\cdot$ in a free radical process. The former process will generate products by aromatic substitution or addition reactions, while the less-likely radical process may occur with reactants which will give a stable radical intermediate. De la Mare (19) studied aromatic halogen substitution using low concentrations of HOCl in the presence of perchloric acid and silver perchlorate. He concluded that the measured rate was determined by the generation of Cl^+ according to the following sequence:

$$HOCl \longrightarrow Cl^+ + OH^-$$

$$HOCl + H^+ \longrightarrow H_2OCl^+$$

$$H_2OCl^+ \longrightarrow Cl^+ + H_2O$$

$$Cl^+ + ArH \longrightarrow ArCl + H^+ .$$

However, in the absence of low pH and silver ion, the

system became much more complicated. Chloride and hypochlorite ions that were present in solution could react to form new chlorinating species, Cl_2 and Cl_2O:

$$H_2OCl^+ + Cl^- \longrightarrow Cl_2 + H_2O$$

$$ClOH_2^+ + OCl^- \longrightarrow ClOCl + H_2O$$

These products have been shown to be potent chlorinating species (20). Furthermore, at concentrations above about 0.001 M HOCl, the kinetic form showed partial dependence on the square of the HOCl concentration indicating other reactions produce even more powerful chlorinating species.

Hine (18) has presented evidence that the hypochloronium ion, H_2OCl^+, is less reactive than the chloronium ion Cl^+, but the former may still be an important species in the chlorination of the very reactive substrates such as anisole and phenol. Still, it is safe to say at this point that few definitive mechanistic studies have been reported, and much uncertainty remains regarding the mechanisms of aqueous chlorination processes.

At very high concentrations of chlorine, e.g., above one gm/L and at low pH, it is possible that molecular chlorine may be an important, kinetically active species. Such solutions have a characteristically yellow color which may be attributed to molecular chlorine (21).

Other important reactive species in the chlorination of natural water and wastewater are chloramines, the products of reactions of ammonia (and its derivatives) with HOCl:

$$NH_3 + HOCl \longrightarrow NH_2Cl + HOH$$

$$NH_2Cl + HOCl \longrightarrow NHCl_2 + HOH$$

$$NHCl_2 + HOCl \longrightarrow NCl_3 + HOH \ .$$

Studies of the reactive nature of chloramines have been extensive. This work was reviewed in detail by Kovacic (22) and Jolley (23). Jolley calculated the concentrations of active chlorinating species based on equilibrium constants for the appropriate reactions. For example, a system at a pH of 7.5 containing Cl_2 and Cl^- at concentrations of 1 and 10 mg/L as Cl equivalent, and containing ammonia at 1 mg/L, resulted in the following concentrations of the chlorinating species:

Species	Concentrations, mg/L (as Cl equivalent)
$HOCl + OCl^-$	0.0004
NH_2Cl	0.9729
$NHCl_2$	0.0264
NCl_3	trace .

It is important to note, however, that the specific reactivity of monochloramine is approximately 10^4 less

than that of HOCl (24), thus offsetting much of its concentration advantages. Also, monochloramine is an effective amminating reagent (25), and ammination reactions may effectively compete with chlorination reactions. The following (26) may also be a competitive reaction:

$$NH_2Cl + NHCl_2 + HOCl \longrightarrow N_2O + 4HCl \ .$$

This type of reaction occurs when the free available chlorine, HOCl and OCl^-, approaches a value of approximately eight times by weight that of the available nitrogen. The mechanistic chemistry for this reaction is unclear. One should recognize that, while chloramine formation reactions produce new chlorinating reagents, break-point chlorination results in a reduction in the total amount of chlorinating species. Break-point chlorination (27) is defined as the point at which the amount of chlorine added is equal to the stoichiometric quantity required for complete conversion of ammonia to nitrogen according to the following equation:

$$3Cl_2 + 2NH_3 \xrightarrow{H_2O} N_2 + 6HCl \ .$$

In practice, break-point chlorination refers to the introduction of chlorine until free available chlorine is observed by some analytical method. This indirectly indicates the complete conversion of ammonia to chloramines or

other forms. Thus, break-point chlorination results in a reduction of the total available chlorine whereas chloramine formation simply produces a shift in the ratio of free available chlorine versus combined available chlorine. In systems containing ammonia and chlorine, the following definitions apply to active chlorine species present. Free available chlorine is defined as hypochlorous acid in its various forms including hypochlorite ion and chlorine, if present. Combined available chlorine is defined as chloramines in all their forms which will oxidize iodide ion to iodine.

Chemical Reactions of Chlorine

In discussing the chemical reaction of chlorine, the primary reactive species considered here is hypochlorous acid, HOCl. The reactions of this species have been reviewed recently by Jolley (28), who classifies them into three categories:

1. Oxidation;
2. Substitution,
    a. Formation of N-Cl compounds,
    b. Formation of C-Cl compounds,
    c. Haloform reaction;
3. Addition.

Oxidation Reactions

Some of the most important oxidation reactions occur with other inorganic species. This class includes the following reactions:

$$HOCl + H_2SO_3 \longrightarrow H_2SO_4 + HCl$$

$$H_2O + 4HOCl + H_2S_2O_3 \longrightarrow 2H_2SO_4 + 4HCl \ .$$

Sulfite (29) and thiosulfate (3) react instantaneously and quantitatively with all chlorinating species and thus are often used as quenching reagents in chlorination studies. Nitrite (31) reacts with aqueous chlorine to form nitrate according to the following equation:

$$HNO_2 + HOCl \longrightarrow HNO_3 + HCl \ .$$

Other species which serve as reducing agents for hypochlorous acid include Fe^{++}, Mn^{++}, H_2O_2 (31), and organic compounds. The chemistry of these reactions is not straight forward and has not been described in detail. These oxidation reactions probably constitute the largest category in terms of total chlorine consumption. As Jolley indicated, as much as 99 percent of the reacted chlorine ends up as reduced organic chloride (23).

Substitution Reactions

Reactions of HOCl with ammonia have been discussed previously. HOCl also reacts with organic amines to displace a proton and form the corresponding N-Cl bond. The reaction rate depends, in general, on the nucleophilicy of the nitrogenous substrate (24). Reactions of HOCl with amides (17) usually require more vigorous conditions than those available under normal wastewater chlorination. Most N-Cl bonds are relatively unstable in aqueous media. For example, dichloroamines and trichloramines are reported to decompose to nitrogen and hypochlorous acid (27):

$$2NHCl_2 + H_2O \longrightarrow N_2 + HOCl + 3HCl \ ,$$

and dichloroamino acids decompose to nitriles and chloride ion (32):

$$R\text{-}\underset{\displaystyle NCl_2}{\underset{|}{CH}}COOH \longrightarrow RCN + CO_2 + 2NCl \ .$$

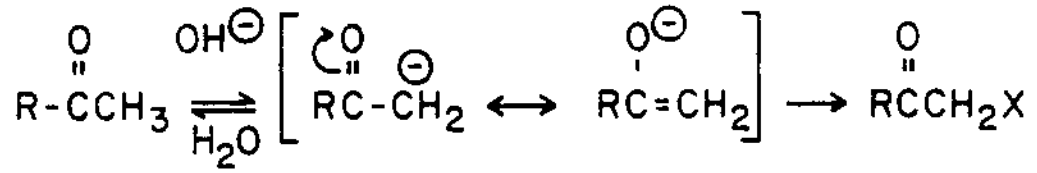
The second and most important group of substitution reactions are characterized by displacement of a proton in a carbon-hydrogen bond to form a carbon-chlorine bond. These reactions usually require activation of the leaving proton before the reaction will proceed under typical wastewater chlorination conditions. Substrates such as activated aromatic systems, or alpha, alpha'-diketomethylene

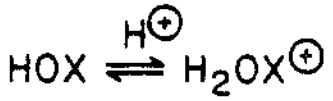
groups, are required for successful reaction. Soper (33), who described phenolic reactions with chlorine in 1926, was one of the earliest to study such a mechanism.

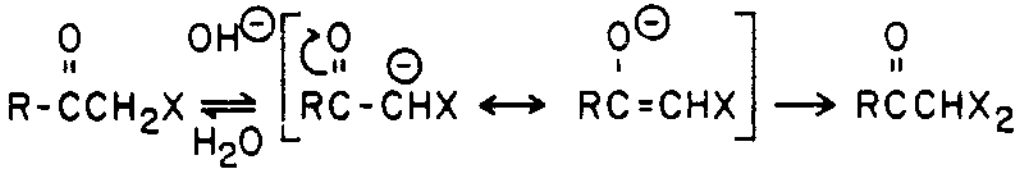
More extensive investigations which followed have shown that the chloronium ion, Cl^+, is the likely intermediate in aromatic substitution reactions (18). Electron donating aromatic substituents such as hydroxy-, alkoxy-, and amino-groups activate the rings to chlorination. Electron withdrawing groups such as nitro, carbonyl, cyano, and positively charged ions retard the chlorination process (34).

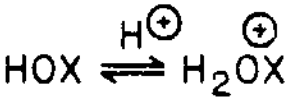
Haloform Reaction

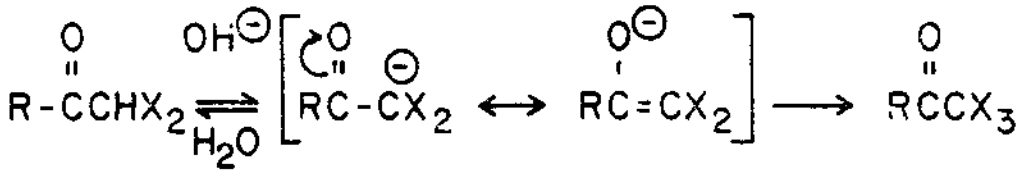
An especially important group of substitution reactions, haloform reactions, has been known since 1822 (35). These are complex reactions which ultimately yield trihalomethanes such as chloroform. Morris (14,36), and Pierce (16) have reviewed the basic chemistry of haloform formation. Several types of substrates are known, most commonly those which contain the methyl keto group, $CH_3C = O$, and those which can be easily oxidized to methyl keto groups such as secondary alcohols. The mechanism proposed (36) to account for chloroform formation from a methyl ketone is shown in Figure 1. In fact, as shown by Morris (36), the haloform reaction is possible with any

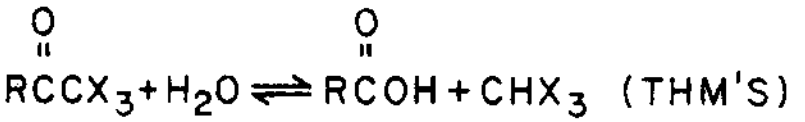








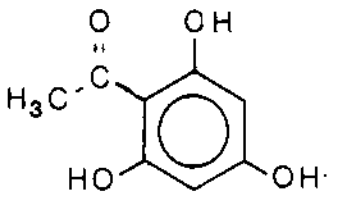




X=Cl, Br, or I

Fig. 1--Formation of chloroform from a methyl ketone

of a number of substrates such as the β-diketones and pyrolles. Rook (37) has shown that 1,3-cyclohexadione, resorcinol, and other 1,3-dihydroxy aromatic compounds also are active haloform precursors. Morris (36) has shown that acetogenins (natural pigments) such as phloro-acetophenone are potent haloform precursors.



phloroacetophenone

More recently, Arguello (38) lists a total of thirty-four substances which give low-to-high yields of chloroform upon aqueous chlorination.

Rook (37) proposed the following mechanism for the formation of chloroform from m-dihydroxy aromatic compounds, a variation of a mechanism by Moye (39) shown in Figure 2. It should be noted that rapid electrophilic substitution produces the initial intermediate I that opens under the influence of base. Morris (36) pointed out that stable carbonion formation is a prerequisite for haloform production, and that precursors such as m-dihydroxy

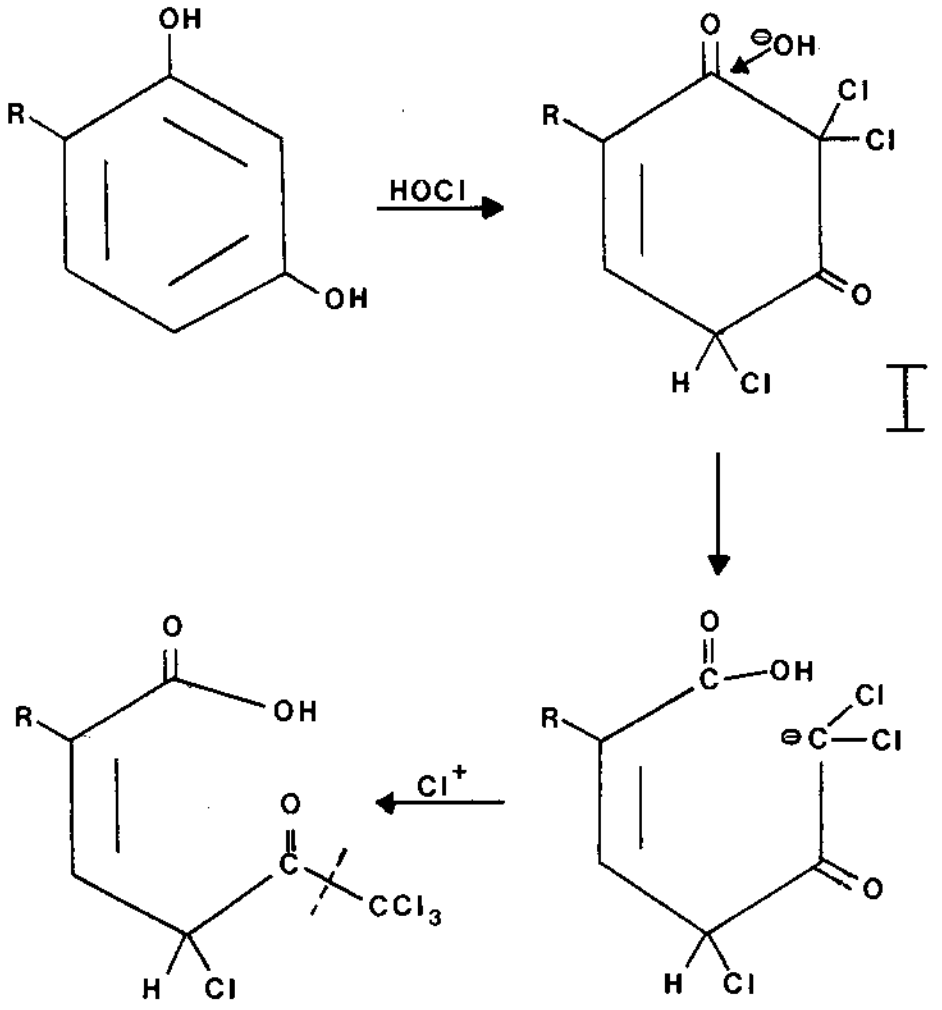


Fig. 2--Formation of chloroform from a m-hydroxy aromatic compound.

aromatic compounds are more reactive than simple methyl ketones for this reason.

The presence of haloforms generated by water chlorination was first reported by Glaze (40). The first extensive study of the presence of haloforms was conducted by Rook (41). He introduced the convention of classifying all reactions which produced haloforms as haloform reactions. This includes not only the traditional haloform reaction but also the polychlorination of aromatic systems, followed by ring rupture to result in haloform production.

Rook (42) initially recognized the correlation of the bleaching effect of water chlorination with the appearance of haloforms. He noted that the coloration of the water was caused by

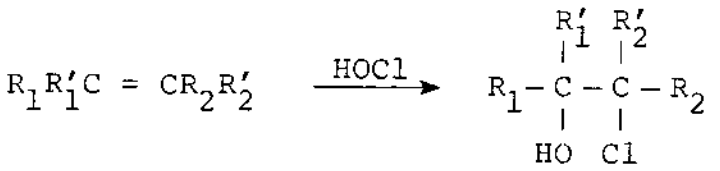
> humic substances which are very stable to biological decay and do not appreciably diminish in concentration during impoundment (of the water supply). These substances are the products of plant decay and include macromolecules which are condensation products of quinones and polyhydroxybenzenes, with substituent NH_2 groups.

His laboratory experiments demonstrated that the chlorination of purified humic substances dissolved in doubly distilled water produced haloforms. Recently, Glaze (43) and Schnoor (44) have shown that fractionated fulvic acid from natural waters yield trihalomethanes. Glaze (43) showed that other halogenated organic compounds are also produced because the yield of organically bound halogen

is greater than that found in the trihalomethanes. It is significant that the Moye-Rook mechanism predicts the formation of these substances. The fate and occurrence of these products in the aquatic environment, or their effects on man or other species who consume them, is unknown at the present time.

Addition Reactions

Hypochlorous acid may add to olefinic double bonds to yield chlorohydrins as shown in the following equation:



Carlson (15) has shown that aqueous chlorination of oleic acid produces a mixture of 9-chloro-10-hydroxystearic acid (III) and 10-chloro-9-hydroxystearic acid (IV).

III: $CH_3-(CH_2)_7-\underset{\displaystyle HO}{\underset{|}{CH}}-\underset{\displaystyle Cl}{\underset{|}{HC}}-(CH_2)_7-COOH$

IV: $CH_3-(CH_2)_7-\underset{\displaystyle Cl}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{HC}}-(CH_2)_7-COOH$

Others (16) consider this type of reaction too slow to be important in dilute aqueous solutions, but Carlson's data contradicted their expectations. It should be noted, however that few examples of addition products have been

observed in surveys of chlorination products from wastewaters or municipal drinking waters.

Toxicity of Chlorinated Wastewater Effluents

As a general class of compounds, chlorinated organic compounds have been shown to exhibit significant hazardous properties including acute and chronic toxicity, mutagenicity, carcinogenicity and teratogenicity. Therefore, their presence in wastewater effluents could pose a threat to life forms in the receiving streams, rivers and lakes. Furthermore, many drinking water supplies, especially those which originate from surface waters, are also threatened. As Bunch (45) pointed out, the surface waters are often composed of some fraction of reconditioned sewage. Each time the water is recycled, the treated effluent can sustain an increase as high as 100 mg/L of organic materials, including chlorinated organics, as measured by the chemical oxygen demand of the water. To compound this problem, many areas are recycling the same water several times. This practice will increase with time as will the danger from the resulting organic load.

Because of the dangers posed by the presence of toxic compounds in wastewater effluents, Garrison (46) stated:

> Knowledge of the specific compounds discharged is needed to study health effects of pollutants, to help determine the sources of compounds found in

drinking water surveys and to establish effluent guidelines.

Some chlorinated organic compounds exhibit acute toxicity at relatively low concentrations as indicated by their oral lethal dosages for 50 percent of the test species, the LD_{50}, values. Examples include pesticides such as aldrin with an LD_{50} of 50 mg/kg, endrin with an LD_{50} of 7.5 mg/kg, dieldrin with an LD_{50} of 46 mg/kg, all determined in rats (47). Because of the extremely low concentrations of chlorinated organics in municipal effluents (40), the threat of acute toxicity is probably minimal. Chronic toxicity poses a more realistic health threat.

Examples of chronic symptoms caused by chlorinated organics include liver dysfunctions such as cirrhosis and abnormal enlargement which are caused by compounds such as lindane (48), polychlorinated biphenyls (49), carbon tetrachloride (50), and chloroform (51). Various cutaneous abnormalities have been attributed to contact with chlorinated organics. For example, hexachlorobenzene has been shown to cause cutaneous porphyria and skin lesions (52). Another classic example of chronic effects caused by chlorinated organics is the reduced thickness of bird shells which is attributed to DDT contamination in the food chain (53).

Many examples of carcinogenic effects caused by chlorinated organic compounds can also be found in the literature. For example, tetrachloroethylene (54), chloroform (55), and polychlorinated biphenyls (PCBs) (56), have been shown to cause hepatocellular carcinomas. Hexachlorobenzene (57) has been shown to cause alveolar adenomas, and several hexachlorocyclohexane isomers have been shown to cause liver tumors (58).

Another area of increasing concern regarding potential health effects is the mutagenic nature of some chlorinated organics. The concern relates to the positive correlation between mutagenicity and carcinogenicity (59). Examples of chlorinated organic compounds which are mutagenic include most of the volatile chlorinated organics discussed in Chapter III, such as 1,2-dichloroethane (60), chlordibromomethane, bromodichloromethane and bromoform (61).

Of special interest are the health problems related to the compound 2,3,7,8-tetrachlorodibenzeno-p-dioxin (TCDD). This compound has been documented to cause chronic degenerative health effects such as liver and thymus abnormalities in rats at oral dose rates as low as 0.1 μg/kg of body weight (62). It has been shown to be a vicious teratogen which can cause such abnormalities as cleft palate, fetopathy, and skeletal anomalies (63). It is also considered to be the primary cause of teratogenic

effects exhibited by the herbicides, 2,4-dichlorophenoxyacetic acid (64) and 2,4,5-trichlorophenoxyacetic acid (65).

Characterization and Identification of Specific Organic Compounds in Wastewaters

A very large number of organic species with widely divergent structures combine to produce an incredibly complex organic mixture in wastewater effluents. Only ten years ago, Feng (66) indicated that the study of the chlorination of sewage would perhaps always be impossible because of the complexities of such systems. This problem was compounded by the fact that until recently (c. 1960s), the available analytical techniques were hopelessly inadequate both in terms of species separation and identification at ultratrace concentrations. Giger (67) recently emphasized the point:

> Such investigations are hindered by two intrinsic properties of organic water constituents. First, the organic assemblages in environmental samples are an extraordinarily high compositional complexity; and second, single components occur in trace quantities only.

Organic content was historically evaluated in terms of gross parameters such as solids, suspended solids, dissolved solids, biological oxygen demand (BOD), or chemical oxygen demand (COD) (68). Unfortunately, these parameters do not always provide a true indication of the potential

hazard. In referring to the BOD test, Carlson (69) points out:

> . . . at low concentrations the chlorophenols are not significantly metabolized over the test period and at high concentrations the chlorophenols are actually adversely affecting the microbiol population [and therefore] . . . qualitative criteria such as reduction of BOD upon chlorination must be viewed with some suspicion.

Later, some crude separation techniques were used to differentiate between classes of compounds such as humic substances (70). Much of these data show poor correlation with any potential health hazards associated with wastewater effluents. Extensive microbial data have been collected (71) and show good correlation with some disease potentials. However, the discovery of some effluents containing certain chemicals with high toxicities has resulted in subsequent extensive surveys that identified additional compounds in both wastewater effluents and their receiving streams.

Several works have been published which utilize various chromatographic and spectroscopic methods for the determination of specific chemical constituents of wastewaters. The advent of combined gas chromatography/mass spectroscopy, GC/MS (72), greatly enhanced the ability to separate and identify volatile components. Budde (72), Keith (73), and Garrison (46) are among several groups who have utilized GC/MS for the identification of specific

compounds in environmental samples. However, as Jolley (23) indicates, only about one-half of the volatile (gas chromatographable) organic materials in wastewater effluents have been adequately characterized.

The remainder of the volatile organics are comprised of a myriad of compounds whose individual concentrations are below the detection limits of analytical methods. Moreover, volatile compounds are said to make-up only about 5 to 10 percent of the total organic carbon in drinking water (74), and the same must surely hold for wastewater effluents. Thus, our knowledge of wastewaters is limited at this time to only a portion of a minor fraction of the constituents.

Recently, a new group parameter, total organic halogen (TOX), has been proposed which may relate more directly to the toxicity of chlorinated water supplies and wastewaters. Two methods for the measurement of TOX have been proposed (75,76); both use an adsorption step for sample concentration and a pyrolysis microcoulometric method for measurement of organic halide. One method uses synthetic resins with solvent elution (75), while the other uses granular activated carbon (76) that is completely burned in the pyrolysis step.

Effect of Chlorination on the Constituents in Municipal Wastewater Effluents

The general toxicity of carbon-bound chlorine has been known for many years. Investigators have clearly shown the harmful effects of environmental contamination by chlorinated insecticides (77), polychlorobiphenols (78), and chlorophenols (79). In 1966, Ingols (80) evaluated the toxicity of carbon-bound, chlorine-containing compounds that are known to form upon wastewater chlorination. Although carbon-chlorine bond formation during wastewater chlorination had been recognized for many years, Ingols' work was the first experimental effort which indicated potentially harmful effects from the use of chlorine as a disinfectant.

With the advent of the first gas chromatograph/mass spectrometer system in 1957 (81), the analysis of aqueous micropollutants became possible. However, it was not until 1973 that Glaze (40) addressed the problem of the potential hazards of wastewater chlorination using this technique. About the same time, Jolley (13,23) developed an analytical procedure using high-pressure liquid chromatography and ^{36}Cl to identify polar or ionic compounds containing carbon-bound chlorine formed by water chlorination.

Several chlorination studies have been done whereby compounds known to occur in prechlorinated municipal

wastewater (secondary effluents) were subjected to chlorination in distilled water under various treatment conditions. Using paper chromatography and various spectroscopic techniques, Burttschell (82) elucidated the mechanistic pathway for the chlorination of phenols in waters and identified the chlorophenols responsible for taste and odor problems.

Carlson (34) demonstrated facile chlorine up-take by such compounds as phenol, anisole, and acetanilide. In the same report, Carlson also demonstrated that biphenyl formed various chlorinated analogues upon aqueous chlorination. Increased chlorine doses resulted in formation of increasing polychlorinated analogues. Also found were chlorohydrins formed upon chlorination of some olefinic systems such as oleic acid.

Objectives of the Present Study

It is unlikely that the precise composition of municipal wastewater effluents will ever be known. Indeed, the major components on a mass basis are probably intractable, non-volatile materials, including biodegradation products, which have very complex structures. What is most important is that methods be derived to measure the potential toxicities of these effluents to maximize the efficiency of treatment processes and to determine the potential dangers associated with water treatment and disposal practices.

In this connection, careful attention must be paid to the use of chlorine as a wastewater disinfectant and as an oxidant.

In this work, new techniques are utilized for the isolation and identification of new chlorinated organics formed in wastewater chlorination. It is hoped that the information gained as a result of this work will be of ultimate benefit in determining the safe treatment of water.

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CHAPTER II

THE GC/MS ANALYSIS OF CHLORINATED ORGANIC COMPOUNDS IN MUNICIPAL WASTEWATERS

Introduction

The hazardous nature of chlorinated organic compounds was discussed in the previous chapter. Because of the harmful potential of these compounds, any source that discharges them into the environment poses a threat to all forms of life, including human life, which might be exposed to them. This study of municipal wastewater treatment plants was conducted in order to determine if the action of chlorine on wastewater does indeed produce chlorinated organic compounds, and, if so, what are the nature and amounts of these species. Such information is necessary and important before an accurate assessment of the environmental danger can be made.

Chlorination of Denton, Texas, Municipal Wastewater

Most of the water samples used in this study were collected at the Denton, Texas, Municipal Wastewater Treatment Plant. This plant utilizes a biologically activated sludge treatment process as shown in Figure 3. The treatment process includes the following:

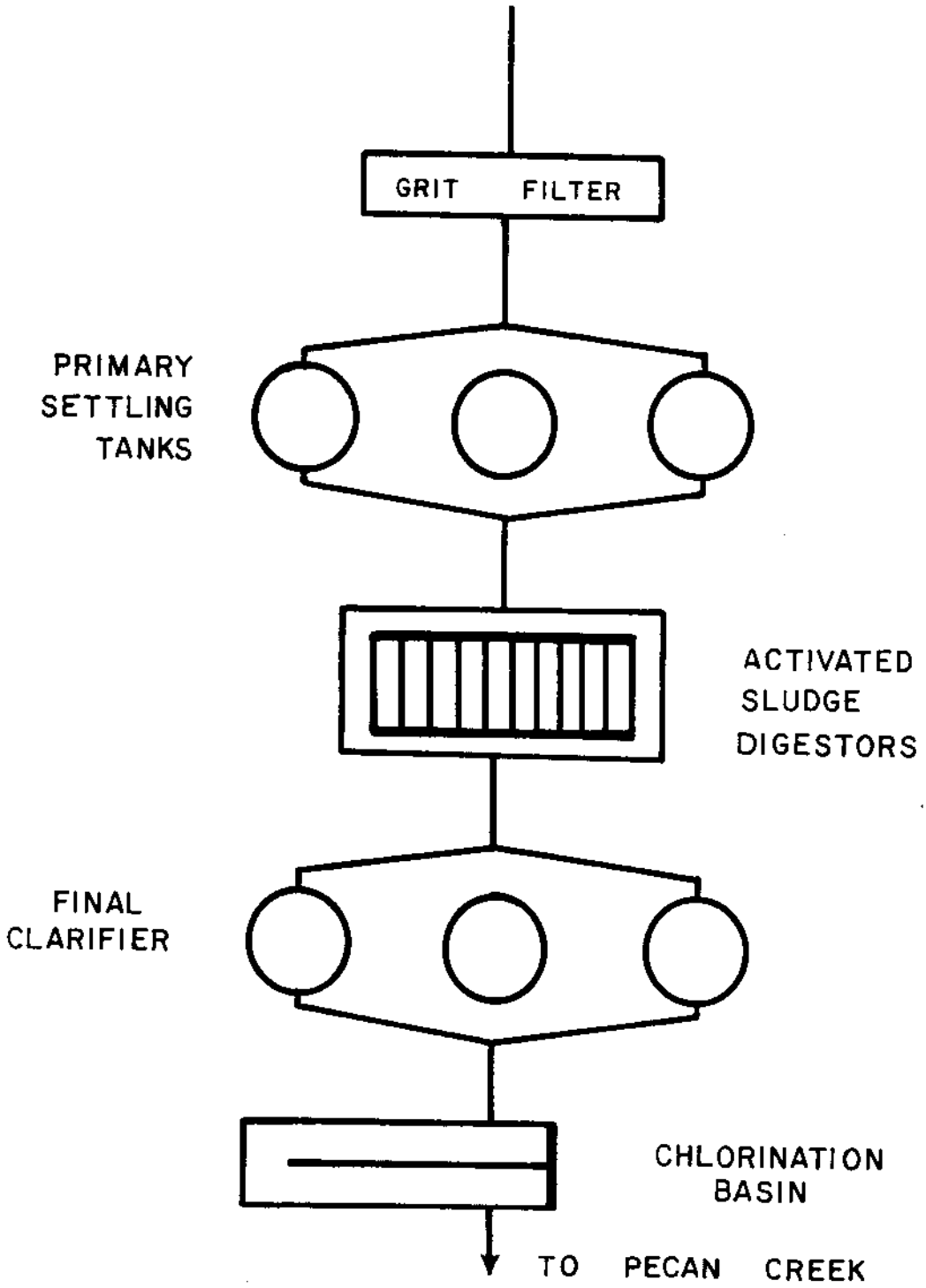


Fig. 3--Denton, Texas, Municipal Wastewater Treatment Plant.

1. primary clarification;
2. digestion by activated sludge;
3. secondary clarification; and
4. terminal disinfection by chlorination.

During most of the sampling, the plant was operating near capacity at approximately 5.7 million gallons per day. BOD levels of the final plant effluent before chlorination averaged approximately 19 mg/L during most of the sampling period, although records were not kept.

In the earliest studies, samples were collected before and after the chlorination process. The specific sampling point for the chlorinated sample was at a spillway at the effluent end of the chlorination basin. The unchlorinated control sample was collected at the effluent point of one of the secondary clarifiers.

Later, however, only the unchlorinated sample was collected and transported in a metal container to the laboratory where the actual chlorination was conducted. This alternative procedure allowed the chlorinated and control sample background matrices to be identical prior to beginning the experimental procedure. The alternative procedure also allowed quality control procedures to be performed on all reagents used in the experiments.

The general approach used to demonstrate the formation of new organochlorine compounds was to subject the

chlorinated water extracts to gas chromatography and to utilize a halogen-specific detector, the Coulson electrolytic conductivity detector. This profile chromatogram could then be compared to a chromatogram of the unchlorinated control sample extract. The additional peaks seen in the chlorinated extract chromatogram represented the formation of new halogen-containing species.

These experiments clearly demonstrated that new chlorinated organic compounds were generated using wastewater disinfection procedures. The experiments were followed with another series of experiments to identify the new chlorinated species. The same sampling procedure was used, but the chlorine doses were raised to 1,000 to 4,000 mg/L. These large chlorine doses increased the concentrations of the chlorinated species making their identifications easier.

A second reason for conducting these studies at such high chlorine doses was to simulate a newly-proposed treatment process that is described in a 1969 patent (1). This process uses pressurized chlorine at similarly high concentrations as a means of oxidizing and disinfecting wastewater and sludge by-products. The purpose of the process is to increase the settlability of the suspended materials as well as to disinfect the water or sludge. The process operates by pumping the substrate into a chamber that is

pressurized with chlorine. A portion of the supernatant is then pumped off into a second chamber where oxidation by chlorine is completed. The remainder of the reactor mixture, approximately 75 to 80 percent, is recycled into the first chamber where it is subjected to further oxidative chlorination. The process can be used in place of anaerobic digestors for sludge treatment, or it can even be used on the entire plant influent as an alternative to conventional treatment systems (i.e., activated sludge, trickling filter).

Experimental

Resin Preparation

The XAD-2 (20 to 50 mesh, Rohm and Haas Company) resin preparation techniques have been described previously in detail (2). Approximately 25 gm of resin was transferred from its shipping container to a 250 mL erlenmeyer flask. The resin was then covered with approximately one inch of reagent-grade methanol (Fisher, ACS Certified). The erlenmeyer was then swirled several times to remove unreacted monomer and suspended polymeric fines that were generated during manufacturing and shipment. The excess methanol was then removed by suction using a glass tube attached to an aspirator. Another portion of methanol was then

added to the erlenmeyer, and the process was repeated until the methanol remained clear upon vigorous swirling.

Following the washing, the resin was transferred to a soxhlet extractor and extracted sequentially with methanol (Baker, b.p. = 65°C), acetone (Baker, b.p. = 56°C), and diethyl ether (Mallinckrodt, b.p. = 34°C) for twenty-four hours with each solvent.

After the extraction process had been completed, the resin was washed into a clean erlenmeyer flask using methanol and was stored under a portion of methanol in the stoppered flask.

The apparatus used to contain the resin during the sample extraction process is shown in Figure 4. After cleaning the apparatus with chromic acid, a small plug of glass wool was placed in the bottom of the column as shown in the figure. Approximately 1 gm of the resin, in a methanol slurry, was then transferred into the column, and the methanol was removed by allowing approximately 0.5 L of distilled water to flow through the column. Next, the column was slowly and carefully backflushed by stoppering the top of the column, placing the effluent end of the column in a beaker of distilled water and attaching an aspirator to the takeoff arm on the column. The backflush flow rate could be controlled by manipulating the stopcock on the takeoff arm. This procedure suspended the resin

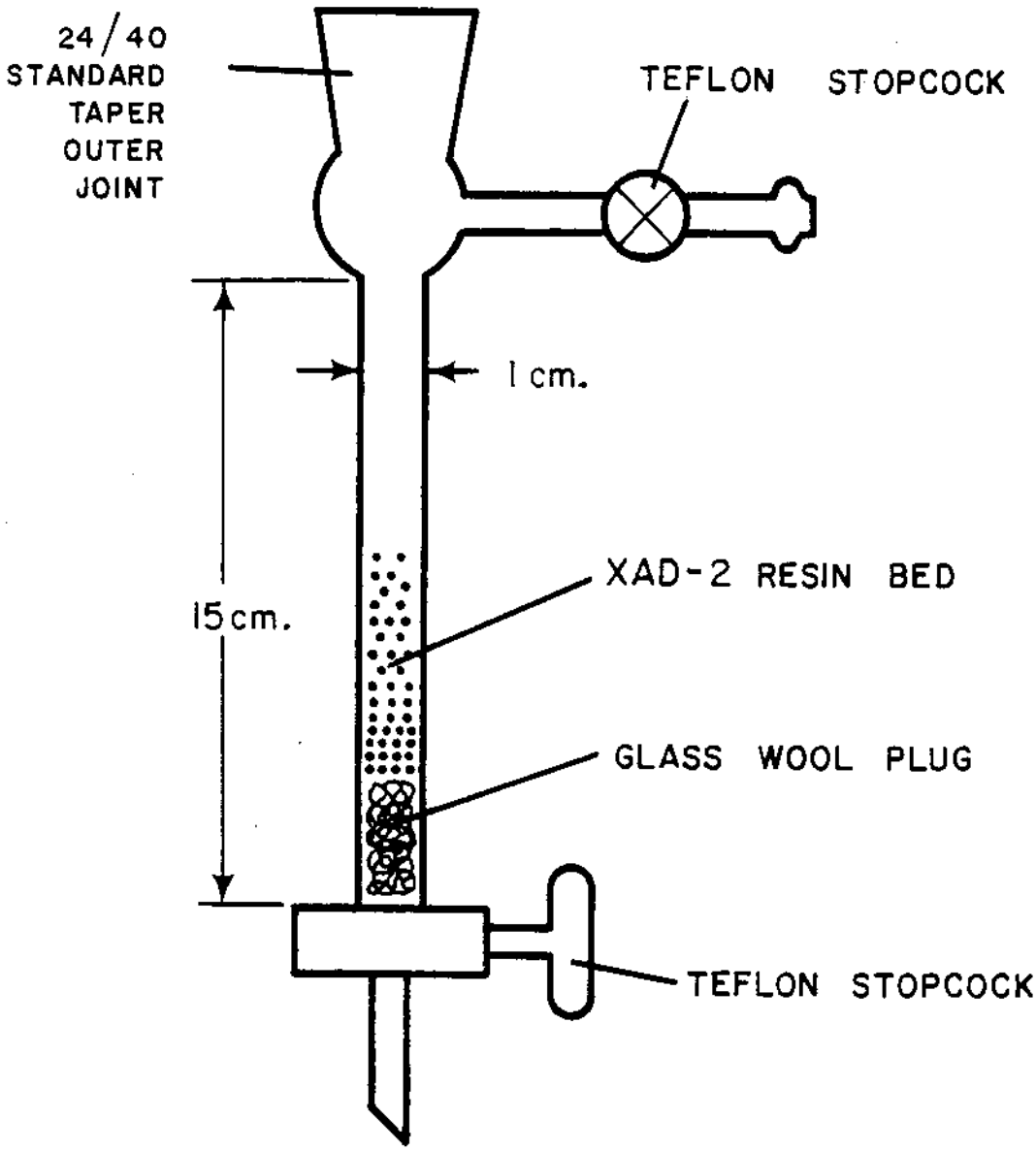


Fig. 4--XAD resin column

beads in the water in the column. The beads could then be packed in an extremely regular matrix with virtually no channeling effects, by quickly switching the aspirator from the takeoff arm to the effluent end of the column, removing the stopper at the top of the column, and momentarily opening the effluent stopcock. The column was then ready for use in the extraction process.

Wastewater Sample Processing

The wastewater samples were processed according to the protocol outlined in Figure 5. The samples were prefiltered using coarse, fluted filter paper (Whatman #41, Whatman, Limited), followed by suction filtration using Gelman #61694 glass fiber filters. Samples which ranged in volume from two to ten liters were then transferred into glass vats that were equipped with glass stirring mechanisms.

Chlorination of one of the aliquots was effected by bubbling chlorine gas (Dixie Chemical Company, 99.5 percent purity) into the water as it was stirred. The chlorine concentration was monitored by removing aliquots, making proper dilutions, and assaying for chlorine by using the orthotolidine arsenite method (3). The chlorine contact time was one hour, after which time excess granular sodium sulfite was added to both chlorinated and

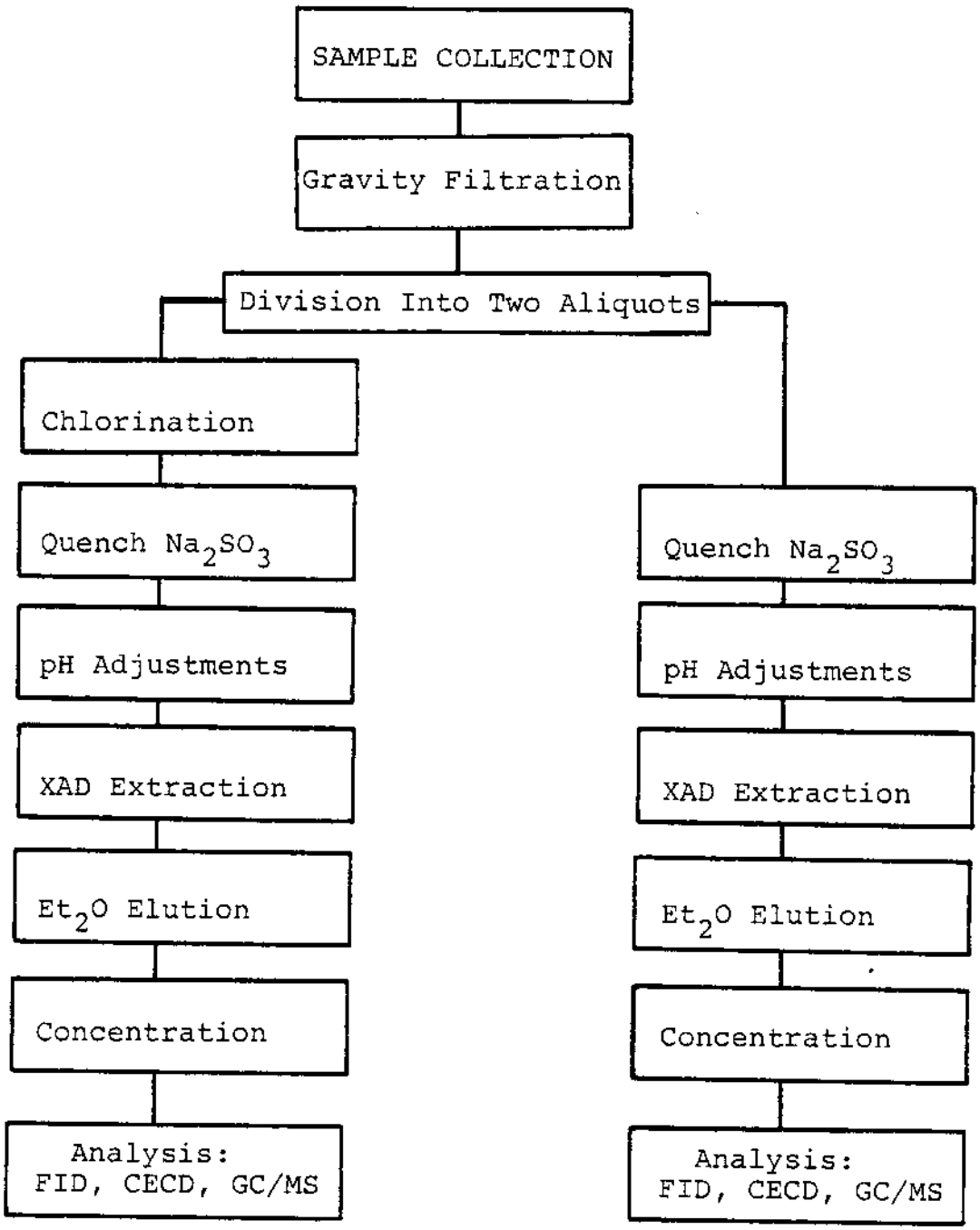


Fig. 5--Analytical methodology for wastewater samples.

control water portions. The pH was then adjusted to approximately seven prior to extraction.

The resin columns were attached to a glass siphon that descended from the glass vats. The water samples were allowed to flow through these columns at a rate of approximately 30 mL/min. The excess water was forced out of the column using a pipette bulb, and the resin was washed with 25 mL of diethyl ether (Mallinckrodt, pre-purified), which was glass-distilled in the laboratory prior to use. The diethyl ether extracts were concentrated to one mL using a modified Kuderna-Danish flask and a Snyder three-ball distillation column as described by Junk (4). A laboratory blank was routinely carried through elution, concentration, and analysis to detect possible laboratory contamination.

The survey chromatographic analyses were then performed on the concentrates, followed by further concentration to approximately 50 µL for gas chromatographic-mass spectrometric analysis.

Processing Samples from the Commercial Superchlorination System

Three sets of samples were obtained from commercial superchlorination systems, one each from Boston, Massachusetts, Ventura, California, and San Antonio, Texas. All systems used pressurized chlorination for oxidation and

disinfection of sludge and wastewater. The samples were filtered, transferred to the glass vats and percolated through the XAD-2 resin columns as described above. No chlorine was added to the samples prior to processing.

In addition to the use of XAD-2 columns, these samples were also analyzed for volatile organics using a new method which was not available during the period when the municipal wastewater samples were being analyzed. The method utilized the purge-and-trap concentration technique developed by Bellar (5) which is described in Chapter III.

Model Compound Recovery Efficiency Studies

Recovery efficiency studies were performed on final effluent wastewater samples to which was added a solution containing seven chlorinated organic compounds. Three replicate two-liter aliquots containing the chlorinated organics and one two-liter control aliquot were analyzed in parallel. The three aliquots containing chlorinated organics were prepared by putting the water samples into individual two-liter separatory funnels and adding 100 µL of an acetone solution containing the compounds to be tested. The concentration of the chlorinated organics in the wastewater was 50 µg/L for each compound. All compounds were reagent grade materials supplied in a kit

(Chem Services, Inc.). The control aliquot was prepared by adding 100 µL of the acetone solvent to the water.

The aliquots were then allowed to percolate through an XAD-2 column prepared as described above at a rate of approximately 30 mL/min. The columns were washed with 25 mL of diethyl ether and concentrated to 1 mL using Kuderna-Danish equipment.

An analytical standard was prepared by adding 100 µL of the acetone spiking solution described above to 900 µL of diethyl ether. The samples were analyzed by gas chromatography using a Coulson electrolytic conductivity detector as described below. The percent recovery efficiencies, R, for each compound were calculated according to the formula:

$$R = \frac{\text{(Peak Area of Sample)}}{\text{(Peak Area of Standard)}} \times 100$$

Gas Chromatographic Analysis of Wastewater Samples

The survey chromatographic analyses were performed on a Varian 1800 gas chromatograph that was equipped with a flame ionization detector (FID) and a Coulson electrolytic conductivity detector. The glass chromatographic column used was 6 feet by 2-mm i.d., packed with three percent Dexsil 300 GC and coated on 100/120 mesh Supelcoport. The helium carrier gas flow rate was 30 mL/min. The temperature program conditions were as follows:

1. Held isothermally at room temperature (approximately 27°C) for four minutes after injection;
2. Programmed at approximately 25°/minute from room temperature to 50°C;
3. Programmed from 50° to 300° at 6°/minute; and
4. Held isothermally at 300°C until no further peaks eluted.

The injector temperature was 225°, and the detector temperature was 300°C. The Coulson block temperature was 300°C, and the furnace temperature was 830°C. The detector was operated in the reductive mode with 80 mL/min of hydrogen added to the gas chromatographic column effluent before pyrolysis. The bridge current was thirty volts; the attenuation was X4 to X32. The FID detector was run at a range of 10^{-11} amp/mv, and an attenuation of X8 to X32.

Gas Chromatography/Mass Spectrometry/ Data System Analysis

Two gas chromatograph/mass spectrometer (ac/ms) systems were used for this study. The first was a Finnigan Model 1015 GC/MS controlled by a System Industries computerized data system. The second was a Finnigan Model 3200 controlled by a Finnigan Model 6100 computer. The chromatographic conditions were the same as those described for the survey analyses. Successive mass spectral scans

were acquired from m/e 35-450 at a scan rate of approximately one sec/decade (4 seconds/scan).

Quantification of Chlorinated Organic Compounds

Once a chlorinated organic compound had been identified, two methods of quantification were used. When the GC/MS chromatographic peak could be correlated to a specific peak in the Coulson chromatogram, quantification was effected by integration of the Coulson chromatographic peak using a digital electronic integrator (Columbia Scientific Industries, Inc.). When no correlation could be made, but a distinct GC/MS peak was identifiable, quantification was effected by integration of the GC/MS chromatographic peaks. In other cases, extreme interferences in both the GC/MS and Coulson chromatograms precluded quantification by either method.

Both analytical instruments were calibrated using the standard mixture shown in Figure 6. Both the peak area integrals and the concentrations of the standard compounds were then averaged and the following formula was used to obtain a quantitative value, X:

$$X = \frac{P_I}{P_S} \times C \times F$$

where P_I is the peak area integral for the identified chlorinated organic compound, P_S is the average peak area

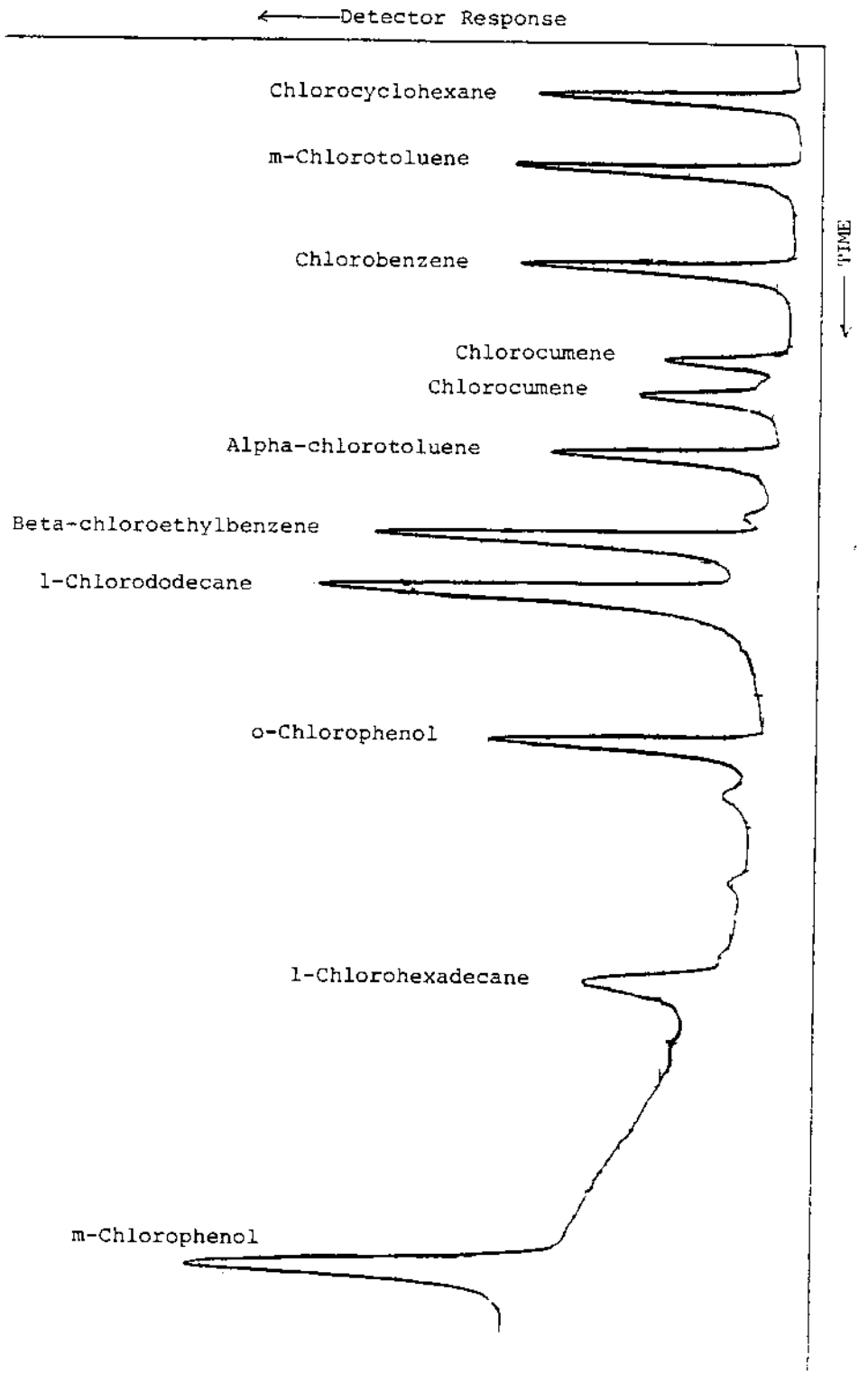


Fig. 6--GC and GC/MS calibration standard mixture

integral for the standard compounds, C is the average concentration of the standard compounds, and F is the concentration factor achieved by XAD sample processing.

Advantages of XAD-2 Adsorption as a Concentration Technique

The XAD-2 resin is a polystyrene/divinyl benzene copolymer that is manufactured in the form of spherical beads. The porous nature of the beads results in a fairly high surface area of 300 m^2/gm (2). The surface of the resin is extremely hydrophobic, which accounts for its affinity for nonpolar organics in waters. This means that very large volumes of water can be passed through XAD-2 columns with virtually no migration of nonpolar organics. Junk (4) demonstrated this volume to be greater than 100 liters of water to one gram of resin. Thus, loss of organics due to their elution through the entire column during the extraction step was no problem for the parameters selected for this study (two to ten liters/gram of XAD-2).

Desorption of organics from the XAD-2 resin proved to be a very facile process. Junk (4) demonstrated that 5 mL of diethyl ether eluant resulted in almost quantitative recovery for adsorbed organics. However, because of the disruptive effect which wastewater had on XAD-2, an eluant

volume of 25 mL was selected to ensure complete removal of organics from the resin.

The XAD-2 has been shown to be superior to activated charcoal for concentration of organics from wastewater producing higher recovery efficiencies for most compounds. Chriswell (6) tested 100 compounds representing thirteen chemical classes and found XAD-2 to produce higher recoveries for fifty-nine compounds while activated carbon produced high efficiencies for twelve compounds. In his study, the average percent recovery for all compounds using XAD-2 was 61 percent while activated carbon produced an average percent recovery of 24 percent.

The primary advantage of XAD-2 versus liquid-liquid extraction lies in the large water-to-solvent ratio which can be achieved with XAD in sample processing. The methodology described for this work involves the processing of up to ten liters of wastewater samples with 25 mL of diethyl ether or a 400:1 ratio. Liquid-liquid extraction of a ten liter wastewater sample would require at least one liter of organic solvent using extreme conditions such as extracting two liter portions of water at a time with two successive 100 mL portions of solvent. Thus, a water-to-solvent ratio of 10:1 can be achieved.

The importance of the water-to-solvent ratio is associated with solvent impurities and the analytical

methodology to be employed. The gas chromatographic techniques employed here are sensitive to concentrations of one to ten ppm injected into the instrument. If a solvent extract is going to be concentrated to a final volume of 1 mL, the XAD-2 method will require a solvent purity before extraction of 40 ppb or less for each impurity to produce a relatively clean solvent blank. However, the liquid-liquid extraction method will require a solvent purity before extraction of one ppb or less to obtain the same quality of solvent blank. This purity was difficult to achieve in our laboratory even with fractional distillation immediately prior to use.

A similar argument was put forth by Grob (7) when he selected an adsorption technique over extraction for the analysis of Zurich tapwater.

Model Compound Recovery Studies

Recovery efficiencies for seven compounds which were added to the wastewater samples are shown in Table I. The average percent recovery for all compounds was 39 $\pm$ 11 percent. An independent study performed by a commercial analytical laboratory on this same sample showed that the average percent recovery using a conventional solvent extraction procedure was 53 $\pm$ 26 percent (8). This independent study included data for twenty-two chlorinated and unchlorinated compounds spiked at various concentrations

TABLE I

RECOVERY EFFICIENCIES OF XAD-2 RESIN
USING SPIKED WASTEWATER EFFLUENT

Compound	Average Percent Recovery	Percent Relative Standard Deviation
1,4-Dichlorobenzene	37	18
hexachloroethane	44	8.6
hexachlorobutadiene	28	11
1,2,4-trichlorobenzene	35	14
2-chloronaphthalene	40	9.5
hexachlorobenzene	19	4.7
1,2,3,4,5,6-hexachlorocyclohexane	66	13
Totals	39	11

from 10 to 250 mg/L. Comparison of these data indicate that the XAD procedure may be slightly less efficient than the solvent extraction procedure.

Several recovery studies using XAD-2 to extract organic compounds added to distilled water have been reported in the literature. Webb (9) reported an average percent recovery of 71 percent for thirteen compounds spiked at concentrations of 50 g/L each. Junk's (10) latest studies reported an average percent recovery of 59 percent for 58 compounds at concentrations of 10 to 100 mg/L. These data indicate that XAD-2 procedures

are subject to considerable dependency on sample composition.

Analysis of Chlorinated Municipal Wastewater

Figure 7 shows survey gas chromatograms of the chlorinated and control wastewater extracts (chlorine dose, 2,000 mg/L) using a flame ionization detector (FID) which responds fairly uniformly to all compounds. The chromatograms are typical for a complicated matrix such as wastewater. Well over 100 peaks are identifiable, many of which are mixtures of two or more compounds. The complexity indicated by those chromatograms is consistent with the results of others (11).

Figure 8 shows typical Coulson (halogen-specific) survey chromatograms. More than thirty halogenated species detected in the chlorinated portion are not present in the control, or they are present at distinctly lower concentrations. Some of the chlorinated compounds are the same as those generated at chlorine concentrations in the one to ten mg/L range (12). The GC/MS chromatograms (Figure 9) are similar in complexity to the FID chromatograms. For this reason, it was extremely difficult to correlate the GC/MS chromatograms with the Coulson chromatograms.

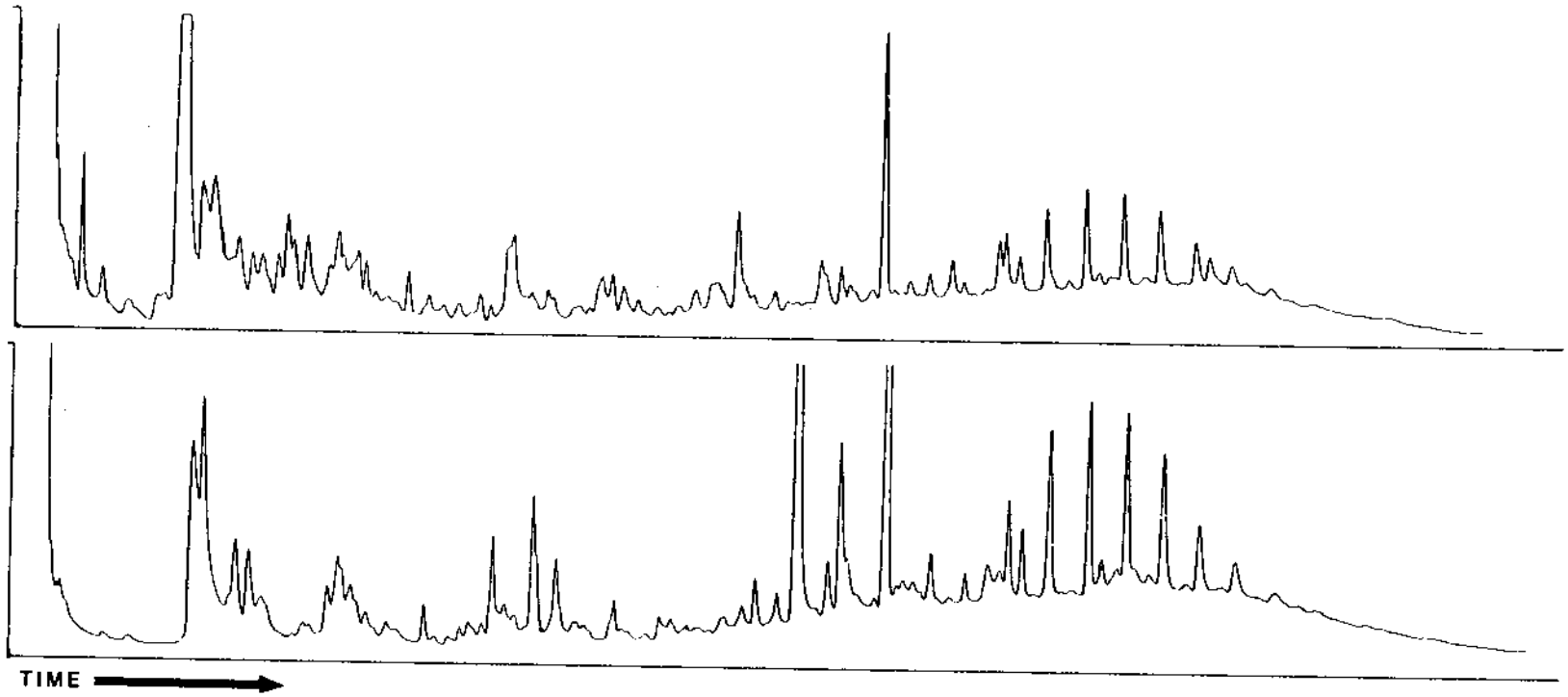


Fig. 7--Flame ionization gas chromatogram of a Denton, Texas Municipal Wastewater Treatment Plant extract.

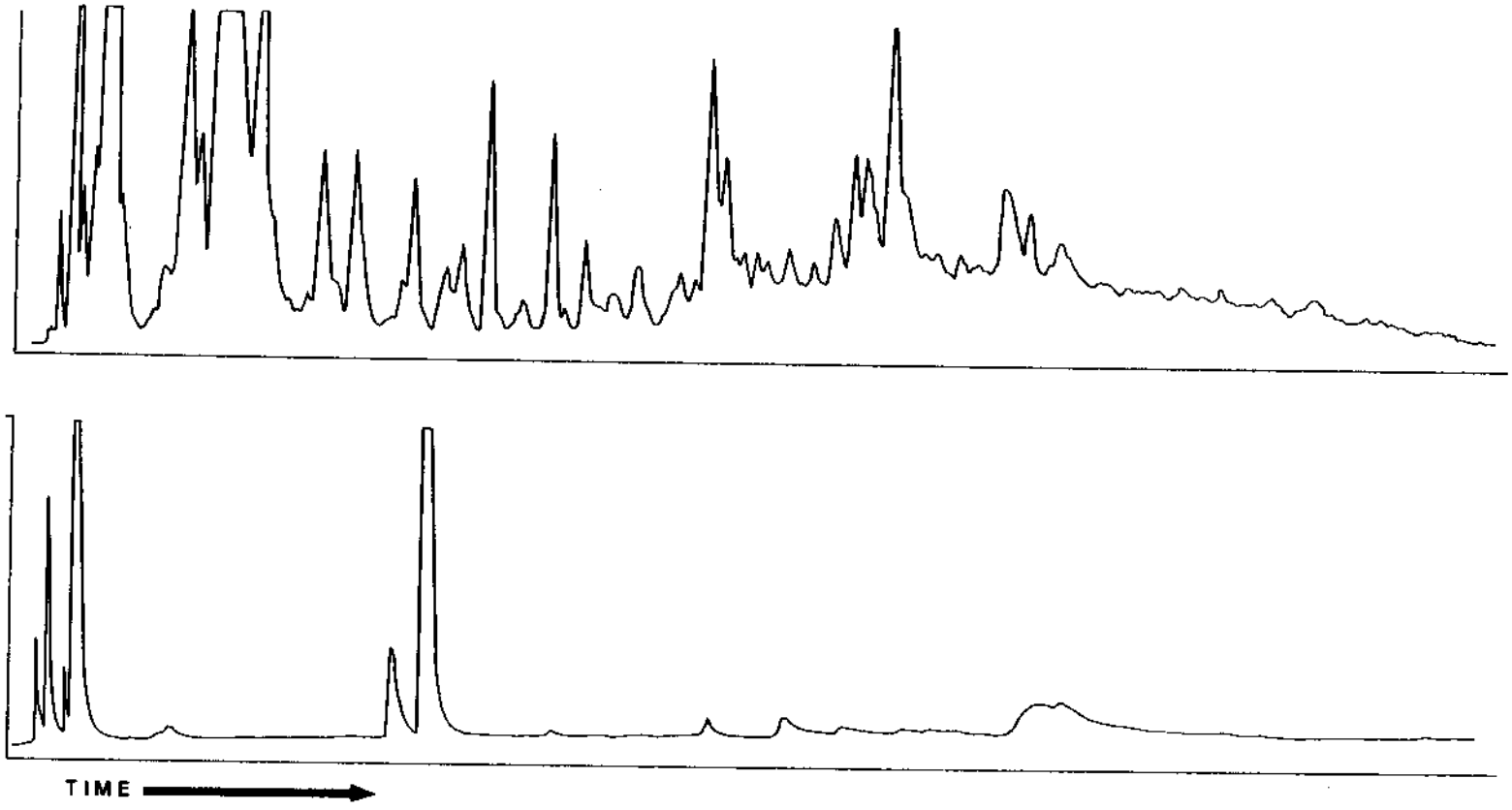


Fig. 8--Coulson electrolytic conductivity gas chromatogram of a chlorinated Denton, Texas Municipal Wastewater Treatment Plant extract.

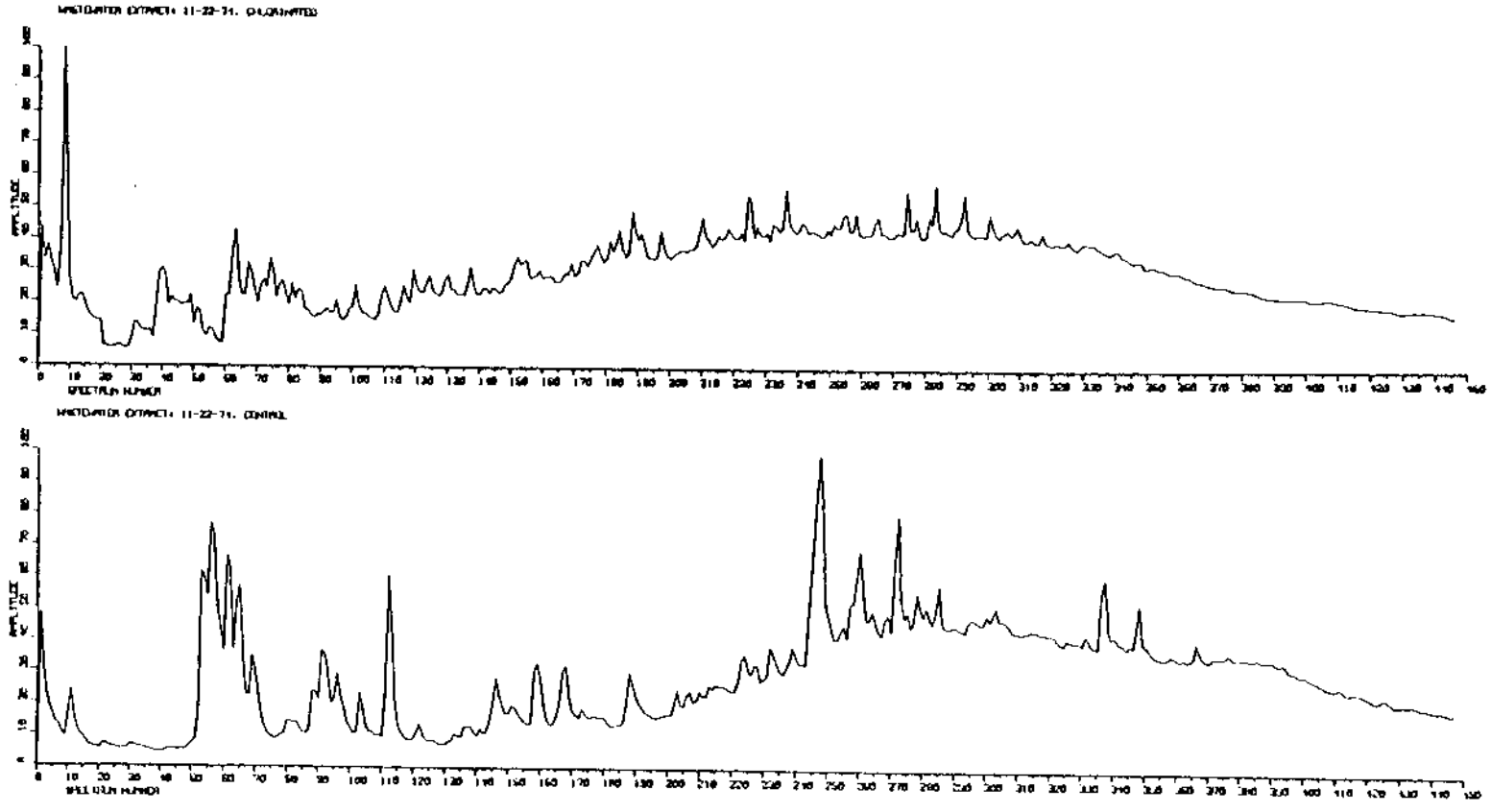


Fig. 9--GC/MS chromatogram of a Denton, Texas Municipal Wastewater Treatment Plant extract.

Interpretation of the Mass Spectra

The complexity of the GC/MS chromatograms makes the retrieval of the mass spectra for individual compounds extremely difficult. In some cases, the subtraction of a large background signal causes a skew in the relative peak intensities. In other cases, overlapping chromatographic peaks are impossible to separate, and thus the mass spectra represent mixtures of compounds. Nevertheless, most of the spectra can be interpreted by associating spectral peaks and clusters whose masses differ by amounts representing losses of common fragments such as 14 (methylene), 15 (methyl), 28 (carbonyl), and 35 (chlorine atom). Using this approach, a total of 31 chlorinated compounds representing more than ten chemical classes have been identified (Table II). Mass spectra from the analyses of chlorinated wastewater samples and, where available, library reference shown in Appendix A. Interpretations for each of the chemical classes are discussed below.

Benzenes.--Mass spectra of three identified chlorinated benzene homologs were easily recognized because the molecular ion isotopic clusters contained the base peak (most intense peak in the mass spectrum), and because no other plausible molecular structure would produce that particular cluster at that particular mass. For example, trichlorobenzene exhibited a molecular ion at m/e 180, and

TABLE II

IDENTIFICATION AND QUANTIFICATION OF CHLORINATED ORGANICS IN WASTEWATER

Compound Class/Names	Identification Status*	Library Reference Spectrum	Appendix A Figure Number	Concentration µg/L
Benzenes				
Chlorobenzene	Complete	No	1	--
Dichlorobenzene	Complete	Yes	2	--
Trichlorobenzene	Complete	Yes	3	20
Phenols				
Trichlorophenol	Complete	Yes	4	--
Tetrachlorophenol	Complete	Yes	5	30
Pentachlorophenol	Complete	Yes	6	--
Toluenes				
Chlorotoluene	Complete	Yes	7	--
Dichlorotoluene	Complete	Yes	8	--
Ethylbenzenes				
Chloroethylbenzene	Complete	Yes	9	20
Dichloroethylbenzene	Complete	Yes	10	20
Propylbenzenes				
γ-chloropropyl-dichlorobenzene	Speculative	No	11	--
α-chloropropylbenzene	Tentative	No	12	--
Ethylphenols				
Chloroethylphenol	Tentative	No	13	--
Dichloroethylphenol	Tentative	No	14	10
Trichloroethylphenol	Tentative	No	15	20
Tetrachloroethylphenol	Tentative	No	16	30
Acetones				
Tetrachloroacetone	Complete	No	17	10
Pentachloroacetone	Complete	Yes	18	30
Hexachloroacetone	Complete	Yes	19	30
Nitrogen-Containing				
Dichlorobenzamine	Speculative	No	20	--
Trichloro-N-methylbenzamine	Speculative	No	21	10
Purgeables				
Chloroform	Complete	Yes	22	--
Dibromochloromethane	Complete	Yes	23	--
Miscellaneous				
Dichloroethanal	Tentative	No	24	--
Chloromethylbutene	Tentative	Yes	25	300
Chloro-1-hexene	Tentative	No	26	20
Trichlorodihydroxyethylbenzene	Tentative	No	27	--
Chlorobis(chloromethyl)phenyl-dicarboxylate	Speculative	No	28	--
Dichloromethoxyphenol	Tentative	No	29	--
Dichlorodimethoxybenzene	Speculative	No	30	--
α,α-Dichloromethoxytoluene	Tentative	No	31	30

*Three categories of identification status are used:

Complete--the spectrum matches a library reference spectrum or is in excellent agreement with the fragmentation tendencies of the other homologous compounds in respective group.

Tentative--spectral interferences or lack of library reference spectra for the identified compound or or possible alternatives preclude unequivocal identification.

Speculative--extremely heavy spectral interferences were observed and/or not all of the spectral information was available to rationalize the identification.

the isotopic cluster had the 9:9:3:1 ratios which are characteric of a trichlorinated ion. Each homolog exhibits a strong $(M-Cl)^+$ ion and an $(M-Cl-HCl)^+$ ion for the dichloro- and trichloro- species.

Phenols.--Like the benzene homologs, the three identified chlorinated phenol homologs exhibit the base peak of the mass spectrum in the molecular ion isotopic cluster. This molecular ion mass plus the location of the base peak is virtually exclusive to phenols. All three homologs exhibit strong $(M-HCl)^+$ ions.

Toluenes.--Two chlorinated toluene homologs were identified. As with the benzenes and the phenols, the mass of the molecular ion for chlorinated toluenes is highly characteristic. The two homologs both exhibit base peaks at $(M-Cl)^+$. No $(M-CH_3)^+$ ions were observed indicating that the loss of chlorine is highly preferred to the loss of a methyl group.

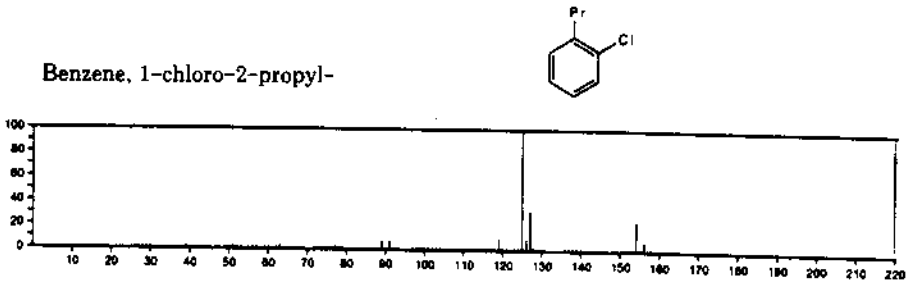
Ethylbenzene.--Two chlorinated ethylbenzenes were identified. Both homologs exhibit relatively strong molecular ion clusters. The base peaks for both compounds are at $(M-CH_3)^+$ indicating a strong preference to cleave the α-methyl moiety. Neither compound generates an $(M-CH_2CH_3)^+$ ion, but both compounds generate strong $(M-Cl)^+$ ions indicating a similar preference for chlorine

cleavage over alkyl group cleavage as was shown by the toluene species.

n-Propylbenzenes.--The mass spectrum identified as γ-chloropropyl-dichlorobenzene was listed as a speculative identification because of the heavy interferences in the spectrum. Of particular importance is the trichlorinated species at m/e 209. The identification was based on the absence of an ion representing the loss of a methyl group and the presence of a dichlorinated ion cluster beginning at m/e 159 which probably represents the loss of CH_2CH_2Cl. The intensity of this ion cluster indicates that the fragment was not cleaved directly off the aromatic ring, but was probably cleaved from a benzylic position. This indication is further strengthened by the absence of an ion representing the loss of CH_2Cl which should be prominent in a β-chloroethyl-methyl-benzene spectrum. It is possible that the ion cluster beginning at m/e 159 originates from the interference at m/e 209. However, if 209 is the molecular ion, the 159 fragment would represent the losses of CH_3 and Cl. This almost never occurs when there is no loss of only a methyl group as is indicated by the absence of a trichlorinated ion cluster at m/e 194.

α-chloropropylbenzene is identified as tentative because of the heavy interferences in the mass spectrum. The spectrum does, however, exhibit a monochlorinated

molecular ion cluster beginning at m/e 154, and clusters representing the loss of a methyl group at m/e 139 and the loss of an ethyl group at m/e 125. The high relative intensity of the ion at m/e 125 is a strong indication of the ethyl group being cleaved from a benzylic carbon. The α position was selected as the location of the chlorine atom because a mass spectrum of the other alternatives--a ring chlorinated isomer--was available and is shown below. This alternative was eliminated because the spectrum shows no loss of a methyl group.



Ethylphenols.--A group of four compounds were identified which form a homologous series of chlorinated ethylphenols. The molecular ion for each compound was clearly identifiable by the loss of a methyl group to form the isotopic cluster containing the base peak of the mass spectrum. The number of chlorine atoms in the homologous series ranged from one to four. The other common ions for the four spectra are shown in Table III. The mass spectrum of the monochlorinated homolog is partially masked by interferences including trichlorophenol and other minor

TABLE III

COMPARISON OF MASS SPECTRAL FRAGMENTS FOR CHLORINATED ETHYLPHENOL ANALOGS

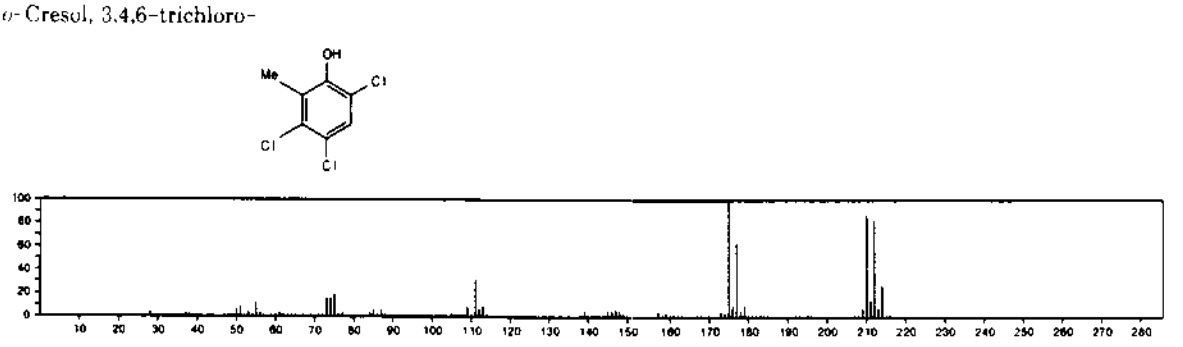
Loss From Molecular Ion (M), Mass Units	Probable Ion Fragment Lost	Mass of Fragment for Respective Chlorinated Analogs			
		Cl	Cl_2	Cl_3	Cl_4
M	--	156	190	224	258
M-15	CH_3	141	175	209	243
M-35	Cl	121	155	189	223
M-36	HCl	120	154	188	222
M-51	CH_3 + HCl	(105)	139	173	207
M-70	Cl_2	--	120	154	188
M-79	Cl + CH_3 + CO + H	77	111	145	179
M-99	Cl_2 + CO + H	--	91	125	159
M-115	HCl + Cl + CH_3 + CO + H	--	75	109	143
M-135	Cl_2 + HCl + CO + H	--	--	89	123
M-149	Cl_2 + Cl + CH_3 + H + CO	--	--	75	143
		Heavy Interference	Slight Interference		

(105) = No ion observed at mass 105.

-- = Ion formation involves loss of more chlorine atoms than are present in the molecule.

compounds (see the halogenated cluster at m/e's 209, 211, 213). However, the spectrum was identified as part of this series by the relative intensity of the molecular ion, 28 percent, which is in approximate agreement with the other molecular ion clusters, and by the identification of four of the five possible fragment ions observed in the other ethylphenol spectra. All of the spectra show relatively low ion intensity for the low mass range indicating aromaticity.

The basic structure for the homologous series was deduced by an elimination process. For the series of molecular weights indicated in Table III, nine reasonable basic structures are possible and are shown in Figure 10. Structures I, II, and III cannot lose a methyl group by any reasonable mechanism. Although no spectrum of IV was available, a spectrum was available for 3,4,6-trichloro-o-cresol (shown below) which shows no tendency to lose a



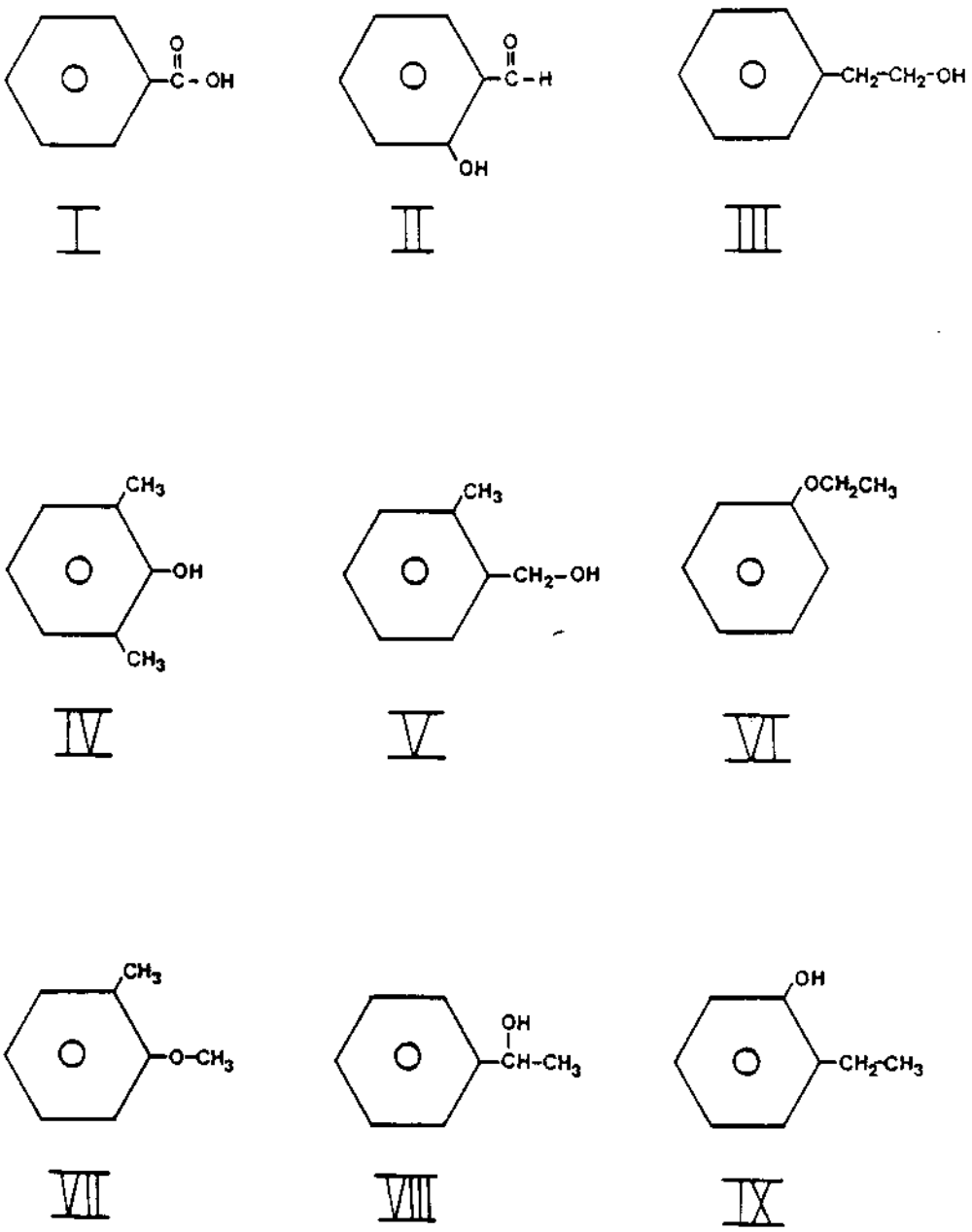
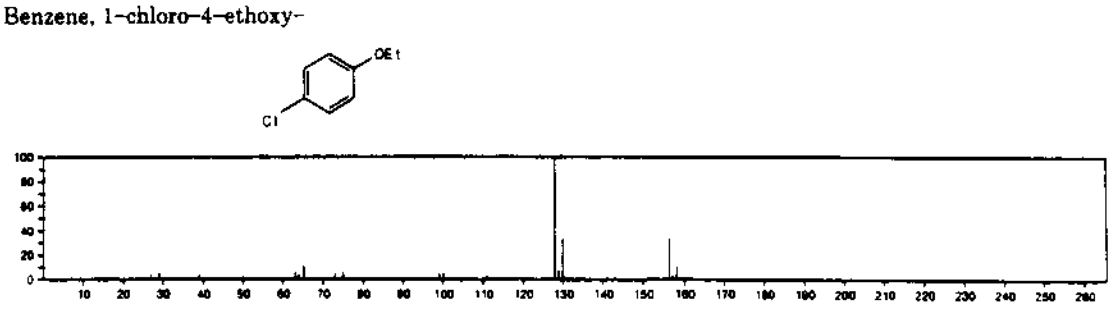
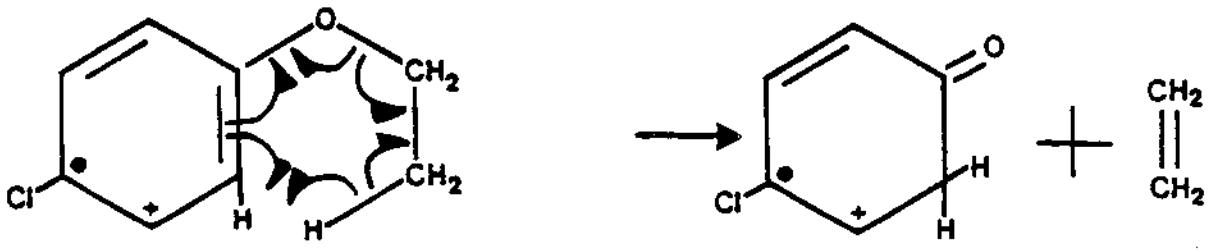


Fig. 10--Possible basic structures with molecular weights of 122.

methyl group. Therefore, IV was eliminated since its fragmentation processes should be similar to the cresol compound. Structure V was eliminated based on the same agrument that it should not show a strong inclination to lose a methyl group. A mass spectrum of the monochlorinated analog of VI was available (shown below) and showed

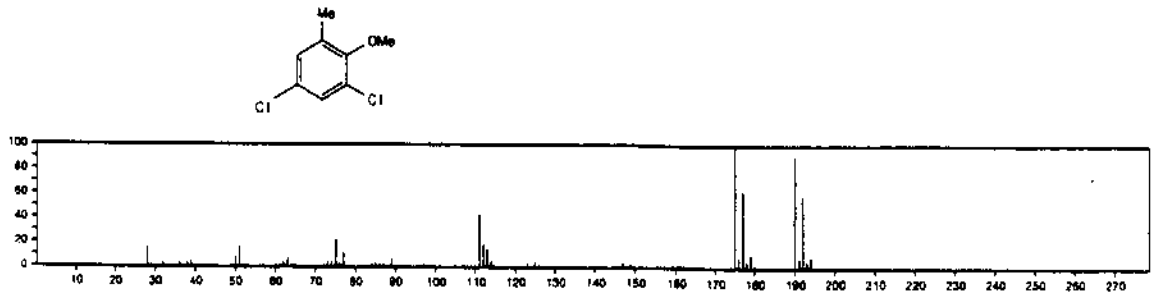


no ion at mass 141 (loss of a methyl group). The only significant fragment ion was formed by loss of $H_2C = CH_2$ as shown below:



A mass spectrum of the dichlorinated analog of structure VII was available (shown below) and showed no loss

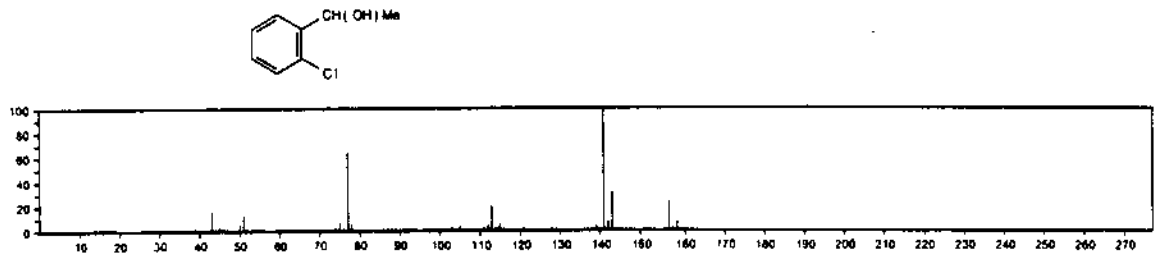
Benzene, 1,5-dichloro-2-methoxy-3-methyl-



of 35, 36, 51 or 70 representing the Cl, HCl (CH_3 + HCl) and Cl_2 moieties. In addition, the molecular ion is approximately 90 percent of the base peak which is clearly out of line with the spectra in question.

A monochlorinated analog of structure VIII was available for review (shown below). The spectrum showed a large

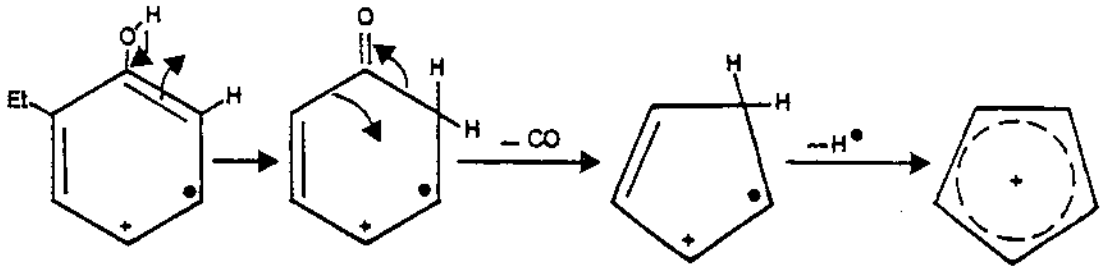
Benzenemethanol, 2-chloro-α-methyl-



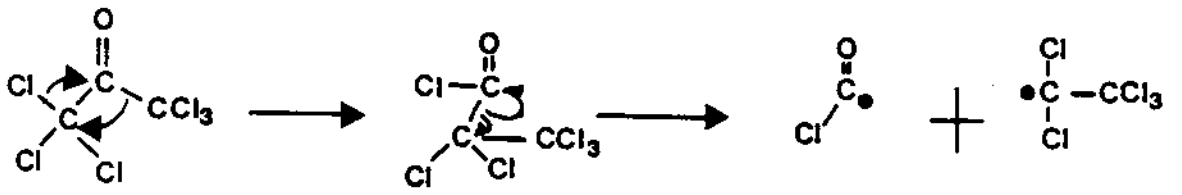
dichlorinated ion cluster beginning at m/e 147 representing the loss of 43 from the percent species. This loss does not occur in any of the mass spectra in question.

Although no reference spectra were available for chlorinated ethylphenols, all of the major fragments for

the series can be rationalized. Most fragments shown in Table III involve conventional losses of various combinations of Cl, CH_3 and/or H. The most important fragments, for identification purposes, include those fragments which involve the loss of CO and H. This loss was proposed to occur by the following mechanism (14):



Acetones.--Three chlorinated acetones were identified. The tetrachloroacetone mass spectrum exhibits the molecular ion at mass 194. Although some interfering peaks could be present, the ions at 131, 133, and 135 (very small) probably represent the loss of COCl, possibly formed by the mechanism shown below:



The dichlorinated ion cluster beginning at m/e 111 represents the loss of $CHCl_2$. The dichlorinated ion cluster beginning at m/e 83 represents the $CHCl_2$ ion. The monochlorinated ion clusters at m/e's 47 and 48 represent the ions CCl and HCCl, respectively.

The pentachloroacetone mass spectrum agrees well with the library reference spectrum. No molecular ion is visible at m/e 228. The largest visible ion cluster results from the loss of Cl and begins at m/e 193. The tetrachlorinated ion cluster beginning at m/e 165 can be attributed to the loss of COCl via the same mechanism described above for tetrachloroacetone. Loss of Cl from the ion represented at m/e 165 results in the ion at m/e 130. The trichlorinated cluster at m/e 117 represents the ion CCl_3^+. The dichlorinated clusters at m/e's 83 and 111 represent the ions $CHCl_2$ and $COCHCl_2$, respectively. The monochlorinated clusters at 35, 36, 47, 48, and 76 represent the ions Cl^+, HCl^+, CCl^+, $CHCl^+$, and $COCHCl^+$, respectively.

The hexachloroacetone mass spectrum exhibits no molecular ion at m/e 262, however a faint cluster can be seen at m/e 227 representing loss of Cl. Again, the loss of COCl occurs to produce the ion cluster beginning at m/e 199. The ion cluster at mass 162 is probably an interference since no combination of atoms contained in

hexachloroacetone could form a cluster with that mass. The ions beginning at m/e's 47, 82, 110, 117, and 145 represent the respective ions CCl^+, CCl_2^+, $COCCl_2^+$, CCl_3^+, and $COCCl_3^+$.

Nitrogen-containing compounds.--Two nitrogen-containing compounds were identified. Both compounds exhibited characteristic odd molecular weights, 161 and 209, respectively. The mass spectrum of the first compound, dichloroaniline, closely matches the corresponding library spectrum. However, no library spectrum was available for the isomeric series of compounds, the dichlorinated methylpyridines. It is suspected that these two compounds may produce similar spectra by first forming a seven membered ring species as shown in Figure 11. Hence, the identification status is listed as speculative. Note that the species shows little inclination to lose a hydrogen atom and form an ion similar to a tropylium ion as indicated by the relatively small ion at m/e 160.

The aniline mass spectrum exhibits conventional losses of Cl at m/e 126, HCl at m/e 125, Cl_2 at m/e 91, and HCl_2 at m/e 90. HCl_2 is probably lost as HCl followed by a second loss of Cl.

A dichlorinated ion at m/e 134 could be formed by the loss of HCN. The monochlorinated ion at m/e 99 could then be formed by the loss of Cl .

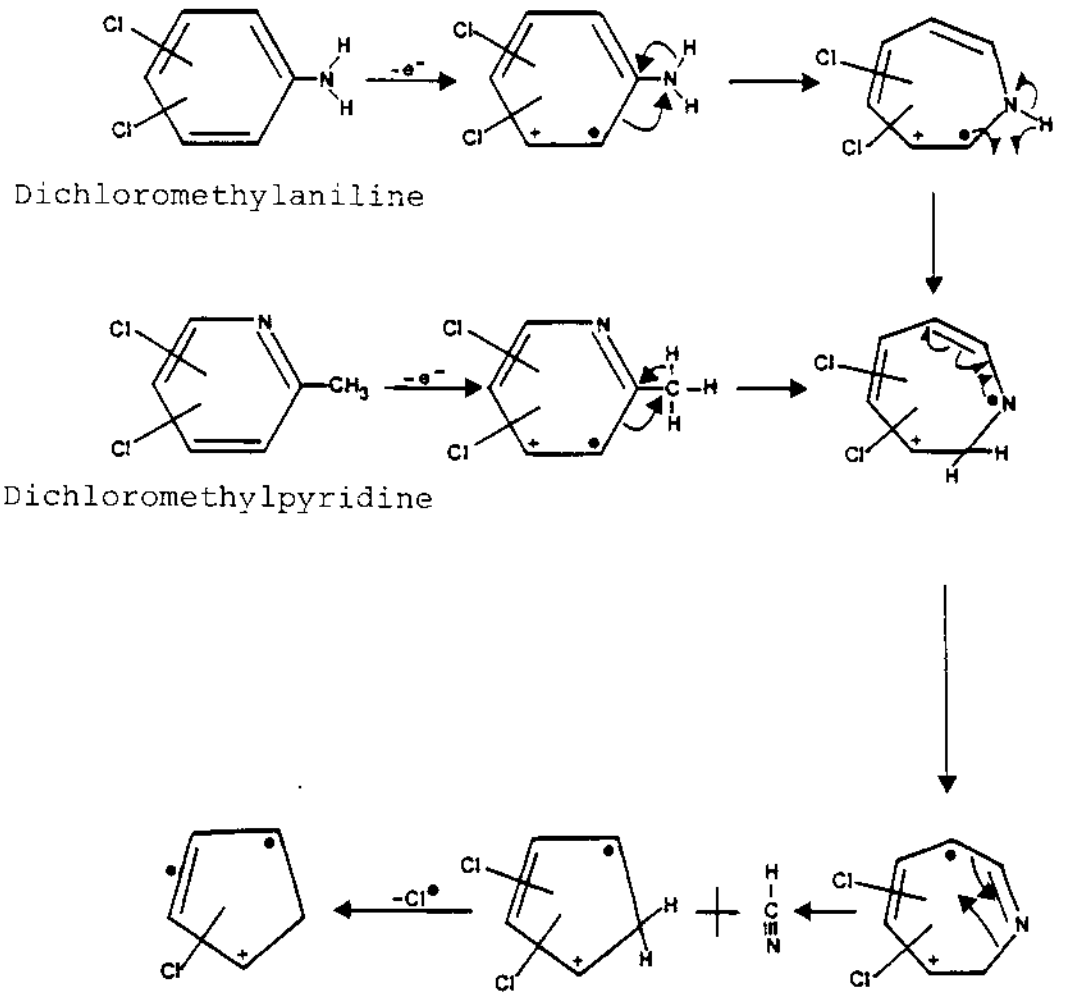
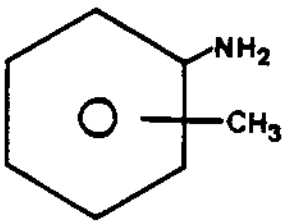
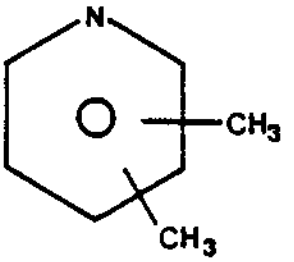
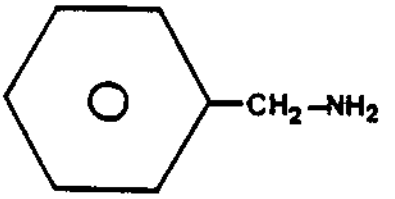


Fig. 11--Fragmentation mechanisms for dichloroaniline and dichloromethylpyridine.

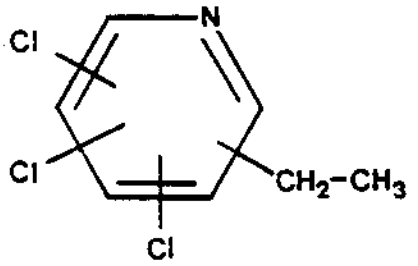
The second compound has a molecular weight of 209 as indicated by the ion at m/e 194 which represents a loss of a methyl group. No library spectrum matched this unknown. Of the five possible configurations which could exist, the three structures shown below would not produce a facile loss of a methyl group:

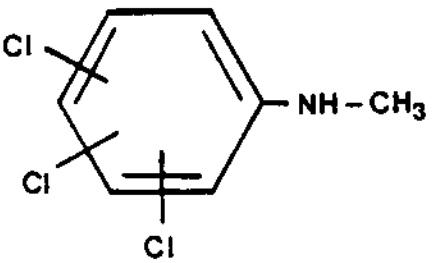




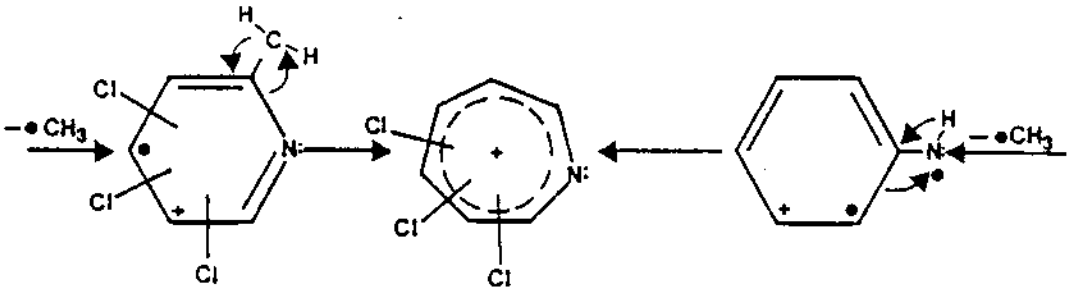


The remaining two isomers which might lose a methyl group easily are trichloro-N-methylaniline and a trichlorinated ethylpyridine shown below:





These two compounds could produce similar spectra by loss of a methyl group to form the stable ion below:



Stable Ion

The structure of a trichlorinated ethylpyridine was selected because the mass spectrum of unchlorinated N-methylaniline (Figure 12, top spectrum) does not show a tendency to lose a methyl group which would form an ion at m/e 92. The unchlorinated ethylpyridine mass spectrum does show a peak at 92 indicating little tendency to lose a methyl group. It is recognized, however, that the presence of three chlorine atoms may influence these tendencies, and thus the identification status for the trichlorinated ethylpyridine as shown in Table II is speculative.

In addition to the loss of a methyl group, the trichlorinated ethylpyridine mass spectrum also shows losses from the molecular ion of Cl at m/e 174, CH_3 and Cl at m/e 159, CH_3 and HCl at m/e 158, HCl and Cl at m/e 138, HCl, Cl, and CH_3 at m/e 123, and two HCl's and Cl at m/e 102.

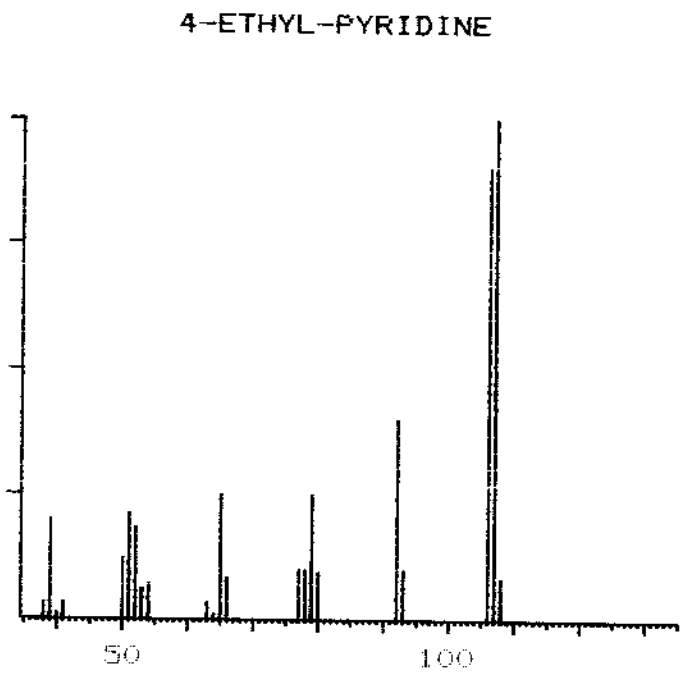


Fig. 12--Library reference spectra of 4-ethyl-pyridine and N-methyl aniline.

Purgeable organics.--Purgeable organics refer to an important class of compounds which can be analyzed using the Bellar purge-and-trap technique referenced in the experimental section for the analysis of commercially superchlorinated septage. Even though XAD-2 extraction was employed here, two purgeable organic compounds were identified. It should be noted, however, that since a concentration step involving solvent evaporation was included in the analytical procedure, the quantitative results will be subject to additional error due to volatilization.

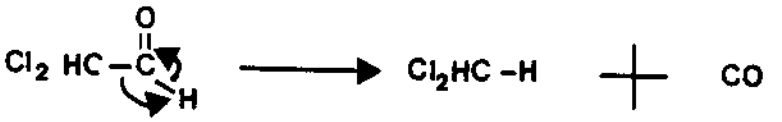
The two purgeable organics which were identified are haloform analogues (see the discussion section below). The chloroform spectrum shows the weak molecular ion at m/e 118. The trichlorinated isotopic cluster is barely visible as well as the (M-1) trichlorinated cluster beginning at m/e 117. The base peak is generated by the $(M-Cl)^+$ ion at m/e 83 showing the characteristic two-chlorine isotopic cluster. Also predominant is the $(M-Cl_2)^+$ ion with one chlorine atom at m/e 48 and a loss from that of a hydrogen atom at m/e 47.

The other haloform analogue is dibromochloromethane which exhibits a weak molecular ion at m/e 206. The base peaks result from the $(M-Br)^+$ ion. Other characteristic

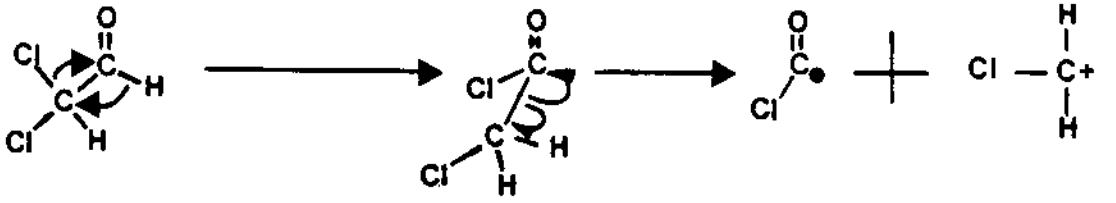
ions occur at m/e 91, CBr^+, m/e 79, Br^+, m/e 48, $CHCl^+$, and m/e 47, CCl^+.

Miscellaneous compounds.--Several compounds were identified which were not associated with a homologous series. These compounds have been grouped together as miscellaneous compounds.

The mass spectrum of dichloroethanal exhibits a distinct dichlorinated molecular ion cluster at m/e 112. This molecular weight limits the alternative structures to two possibilities, dichloropropane or dichloroethanal (assuming an epoxide would not exist in water). All of the four dichloropropane isomer mass spectra were available for review, and none matched the spectrum in question. The dichlorinated fragment cluster at m/e 84 is an important fragment cluster in terms of structural elucidation. This fragment is formed by the loss of CO as follows:

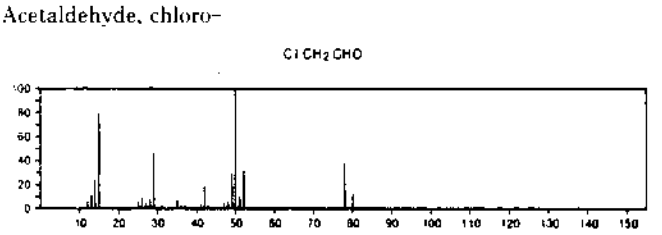


Another important fragment is the monochlorinated cluster beginning at m/e 49 representing the fragment CH_2Cl. This fragment is formed by the loss of COCl by a similar mechanism discussed for the chlorinated acetones above:



The CH_2Cl fragment then loses a hydrogen atom to form the CHCl ion cluster beginning at m/e 48.

Although a mass spectrum of dichloroacetaldehyde was not available for review, a mass spectrum of chloroacetaldehyde was available and is shown below.

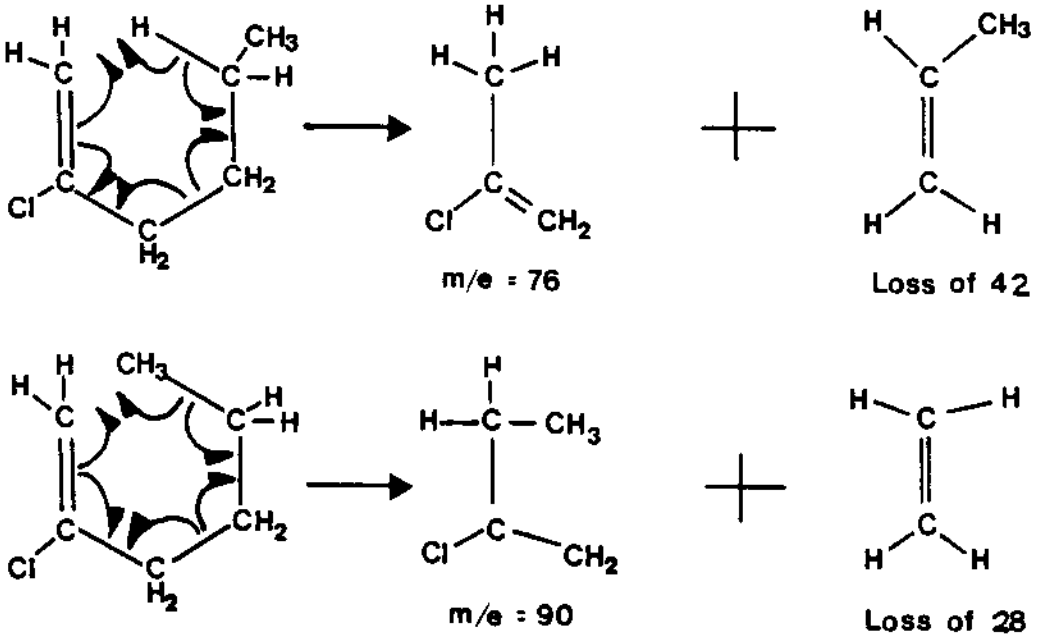


This spectrum exhibited many of the same characteristics as the spectrum of interest including virtually no loss of $H^{\bullet}$, strong ions representing loss of CO (m/e 50), weak ions representing the loss of HCO (m/e 49), and a strong ion representing the loss of COCl (m/e 15).

Chloromethylbutene was identified by comparison of the unknown spectrum with library spectra. Mass spectra were available for nine of the twelve isomers, exclusing cis/trans isomers. Two isomers matched well--3-chloro-2-methyl-2-butene and 3-chloro-2-methyl-1-butene--the latter

of which matched better and is offered as a library reference spectrum in the appendix.

No library spectrum was available for comparison with the spectrum identified as chloro-1-hexene, however the 1-hexene is the only basic structure which can account for both monochlorinated ion clusters beginning at m/e's 76 and 90. The even masses of these fragments indicate the breakage of two bonds (15) and can be reconciled by the following mechanisms:



Note that the chlorine atom could be located on the 1-, the 2-, or the 3- carbon and still produce the two important fragments discussed above.

Trichlorodihydroxyethylbenzene is listed as a tentative identification because of interferences in the mass spectrum. The identification is based on the high relative intensity of the ion cluster representing the loss of a methyl group, probably in a benzylic position.

The α-hydroxyethyl structure was eliminated because those types of structures usually produce a strong ion representing the loss of 43. This ion is not observed at m/e 197.

Chlorobis(chloromethyl)dicarboxylate is listed as a speculative identification because no library spectrum was available as a reference, and not enough information could be deduced from the interpretation of the mass spectrum to assure the structural elucidation. The compound appears to produce an unusually simple spectrum for a compound with such a large molecular weight of 296. The suggested identification does account for the two major fragments--loss of Cl to form the dichlorinated ion cluster beginning at m/e 261 and loss of $COOCH_2Cl$ to form the dichlorinated ion cluster beginning at m/e 203.

Dichloromethoxyphenol was identified based on the strong tendency to lose a methyl group indicated by the dichlorinated ion cluster beginning at m/e 177 as would be expected. This fragment then loses CO in a similar

mechanism as was discussed for the chlorinated ethylphenols to form the dichlorinated ion fragment at m/e 149.

The mass spectrum of dichlorodimethoxybenzene exhibits extremely heavy interferences. The speculative identification accounts for the primary ions which are attributed to loss of a methyl group at m/e 191 followed by loss of a carbonyl group at m/e 163.

The mass spectrum of α,α-dichloromethoxytoluene exhibits a strong inclination to lose a methyl group from the dichlorinated molecular ion cluster beginning at m/e 190. The strong dichlorinated ion cluster at m/e 83 is formed by the cleavage of the $CHCl_2$ group. A slight interference is observed from trichlorophenol (trichlorinated ion fragment beginning at m/e 196 and related fragment peaks and clusters).

Results of the Commercial Superchlorination Analyses

The XAD extracts of the commercial superchlorination samples proved to be even more complex than the superchlorinated municipal wastewater samples. Figure 13 shows a GC/MS chromatogram of a superchlorination extract. Most of the chromatographic peaks are grossly distorted indicating the overlap of several compounds. This complexity resulted in extremely poor mass spectral quality as a whole. The compound identifications were often based on

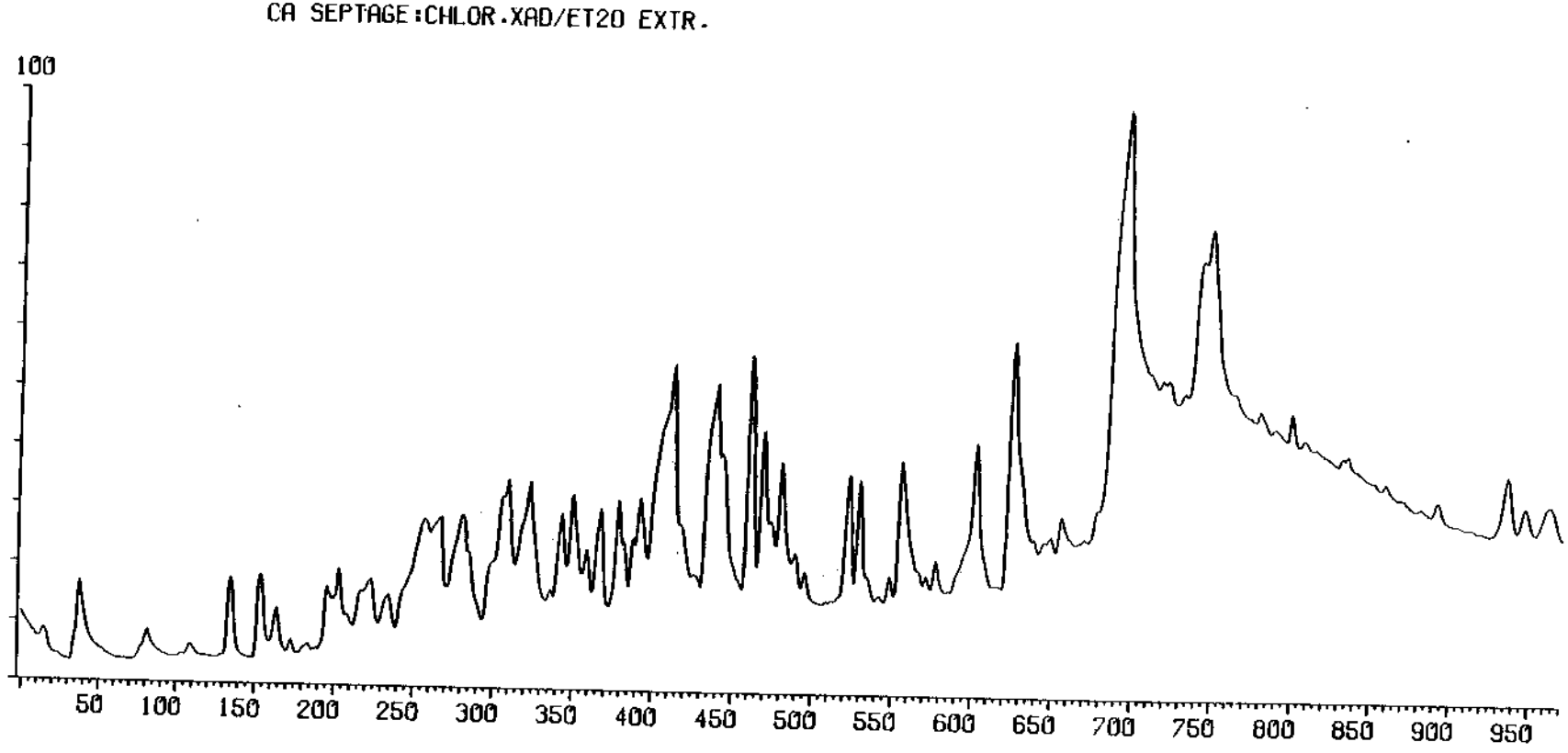


Fig. 13--GC/MS chromatogram of an XAD extract of a commercially superchlorinated municipal wastewater sample.

the location and number of chlorine atoms for a single isotopic cluster. Fortunately, many of the chlorinated aromatic compounds identified in the municipal wastewater samples as described above could be unequivocally identified based on a single isotopic cluster. The compounds which were identified are listed in Table IV. The mass spectrum for each compound is shown in the figures in Appendix B. Library reference spectra are included when available (13). Because of the complexity of the sample, no attempt could be made at quantitation.

1,1,1,4,4-pentachloro-2-butanone is listed as a suggested identification for several reasons. No library spectrum was available. No molecular ion was observed which is somewhat unusual for ketones although less so for polyhalogenated ketones. And, many interfering peaks were observed in the mass spectrum. However, most of the significant fragments can be accounted for by the proposed structure. The trichlorinated cluster beginning at m/e 117 represents cleavage of the trichlormethyl group adjacent to the carbonyl group. The rest of the fragmentation can be accounted for as follows:

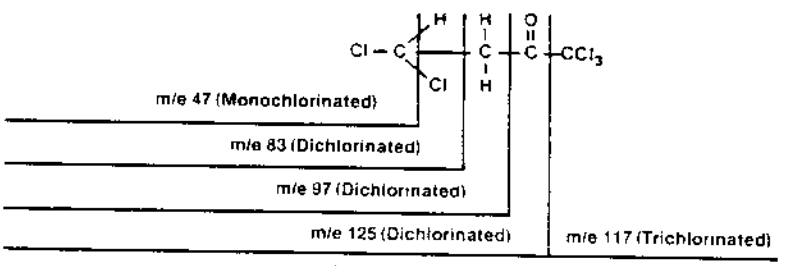


TABLE IV

CHLORINATED ORGANIC COMPOUNDS IDENTIFIED IN XAD-2 EXTRACTS OF COMMERCIALLY SUPERCHLORINATED WASTEWATER SAMPLES

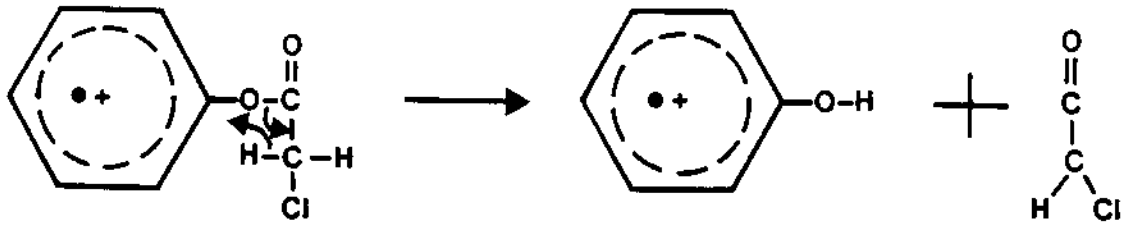
Compound Class/ Identification	Identification Status	Library Reference Spectrum	Appendix B Figure Number
Benzenes			
Dichlorobenzene	Complete	Yes	1
Trichlorobenzene	Complete	Yes	2
Phenols			
Dichlorophenol	Complete	Yes	3
Trichlorophenol	Complete	Yes	4
Ketones			
1,1,3,3-tetrachloro-propanone	Suggested	Yes	5
1,1,1,4,4-pentachloro-2-butanone	Suggested	No	6
3-chloro-2-pentanone	Suggested	No	7
Miscellaneous			
Dichloroacetonitrile	Tentative	No	8
Phenyl chloro-ethanoate	Tentative	No	9
Chlorocresol	Tentative	No	10

3-chloro-2-pentanone is also listed as a suggested identification because of the unavailability of a library reference spectrum and because of interferences in the mass spectrum. The molecule shows a similar fragmentation pattern to the pentachlorinated compound discussed above.

However, a molecular ion is observed, perhaps due to the lower degree of chlorination. The spectrum indicates the molecule has a strong tendency to lose 15 (methyl group), placing the oxygen on the second carbon. Loss of the methyl group is followed by loss of 28 (the carbonyl group). Thus, the chlorine atom was placed on the third carbon because no further loss of 14 (methylene group) was observed which would be expected if the chlorine were on the fourth or fifth carbon.

The dichloroacetonitrile spectrum shows a weak molecular ion at m/e 109 and a tendency to lose a hydrogen atom at m/e 108. The first significant fragment cluster is formed by the loss of HCN to form the dichlorinated isotopic cluster beginning at m/e 82. The other important ion cluster is formed by the loss of chlorine from the intact molecule to form the monochlorinated isotopic cluster beginning at m/e 74.

Phenyl chloroethanoate was identified based on the molecular ion at m/e 170, the monochlorinated ion at 93 representing $COOCH_2Cl$ and the nonchlorinated ion at m/e 121 representing the loss of CH_2Cl from the intact molecule. The acetate structure was selected because of the unusually large ion at m/e 94 caused by the loss of chloroketene:



The alternative structure, chloromethyl benzoate, would not form this m/e 94 ion, and it should form a very prominent ion at m/e 105 due to the loss of OCH_2Cl. This later ion was not, in fact, observed to any significance.

Chlorocresol is listed as tentative because, although the only two prominent peaks in the library spectrum match the identified spectrum well, it is clear that the later contains very heavy interferences. Spectra of the alternative structures--chloromethoxybenzene and chlorobenzyl alcohol--were available for review and did not match the unknown spectrum.

A GC/MS chromatogram of a purge-and-trap analysis of a commercially superchlorinated municipal wastewater sample is shown in Figure 14. Again, the many peaks in the chromatogram reflect the complexity of samples of this type. The conspicuous absence of chromatographic peaks in the first two hundred mass spectral scans (approximately ten minutes) probably indicates that some sample degradation

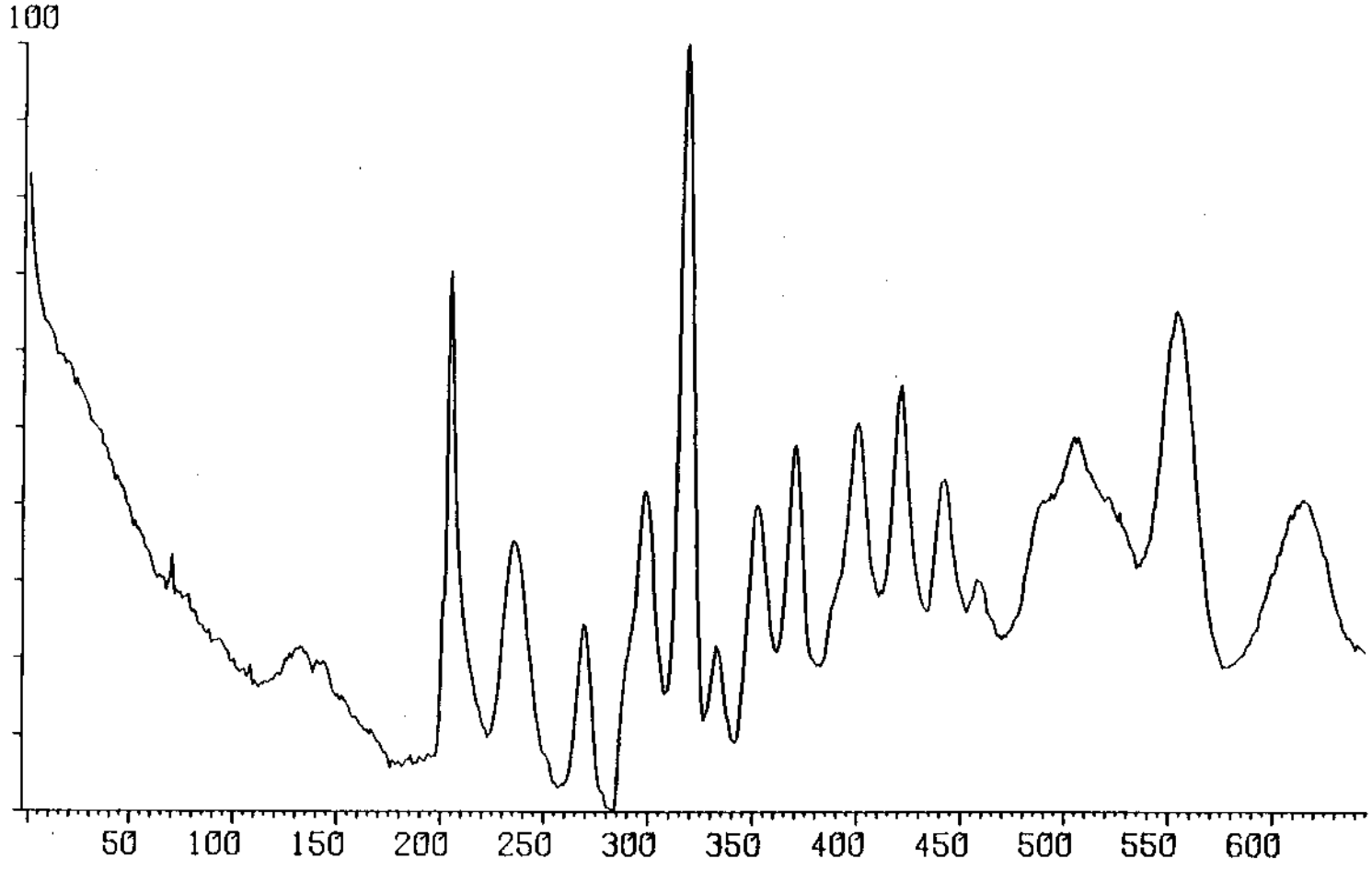


Fig. 14--Purge-and-trap GC/MS chromatogram of superchlorinated wastewater

has occurred in the form of losses due to volatilization. The compounds which were lost would typically have boiling points below that of methylene chloride (b.p. = 40°C) such as chloromethane, vinyl chloride, and others.

Table V lists the chlorinated organic compounds which were identified. Library reference spectra were available for all of the compounds. Spectra of both the identified compounds and the library references are shown in Appendix B.

TABLE V

CHLORINATED ORGANIC COMPOUNDS IDENTIFIED IN PURGE-AND-TRAP ANALYSES OF COMMERCIALLY SUPERCHLORINATED WASTEWATER SAMPLES

Compound Identification	Identification Status	Library Reference Spectrum	Appendix B Figure Number
Chloroform	Complete	Yes	11
Carbon Tetrachloride	Complete	Yes	12
1,1,1-Trichloroethane	Complete	Yes	13
Dichloroethanal	Tentative	No	14
1,1-Dichloroethane	Complete	Yes	15

Interpretation of Volatile Chlorinated Organics Forms From Chlorination of Wastewater Products

This research has shown that chlorination of wastewaters and other municipal waste products produces new chlorinated organic compounds. Although a total of 41 compounds were identified, many other spectra remain unelucidated at this time. There remain unanswered two questions regarding these new substances: what are their effects on the environment (including man) into which they are discharged, and what are their precursors?

The answer to the latter question is difficult to derive primarily because of the lack of knowledge of the molecular types present in municipal wastes. Undoubtedly, these wastes are extremely complex in regard to their molecular composition, and one may never know the source of the new chlorinated compounds.

It is striking to note, however, that many of these new halocarbons are similar to those found from laboratory chlorination of fulvic acid (16). Others can be rationalized by assuming that fulvic acid has the structure proposed by Christman (Figure 15). Results of the chemical degradation studies of aquatic humic matter have suggested that the core structure of humic and fulvic acids contain units which, upon oxidative degradation or hydrolysis, give resorcinol (X), catechol (XI), vanillic acid (XII),

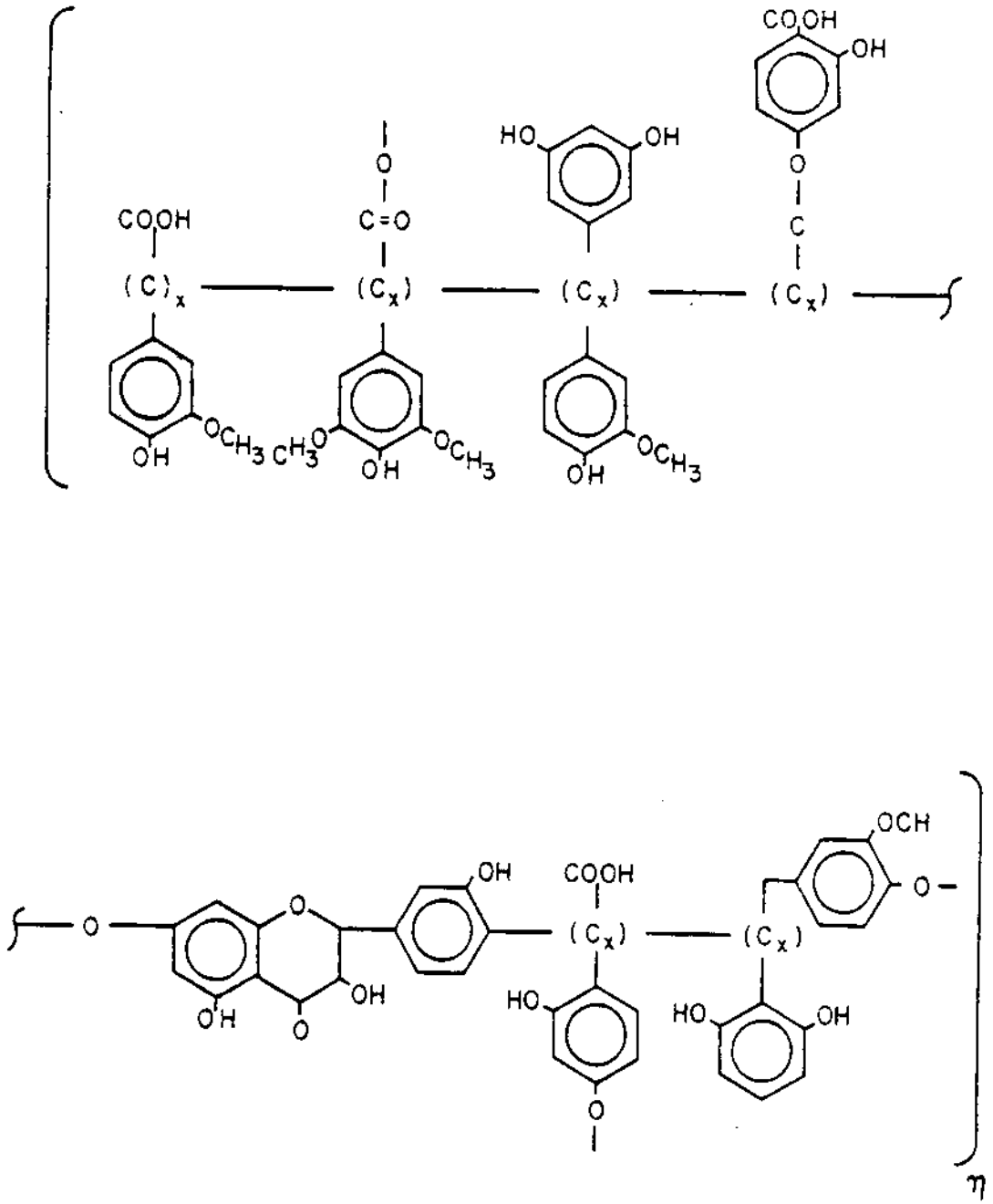
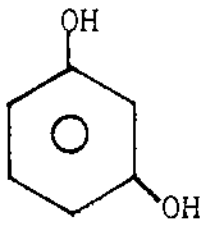
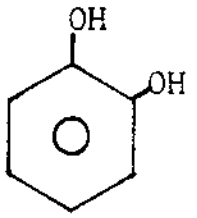


Fig. 15--Proposed composite structure of humic and fulvic acids.

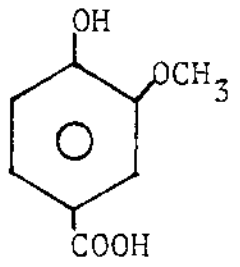
syringic acid (XIII), 3,5-dihydroxybenzoic acid (XIV), p-hydroxybenzoic acid (XV), and protocatechuic acid (3,4-dihydroxybenzoic acid (XVI) (17):



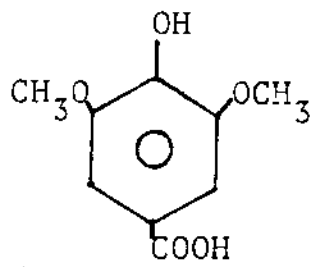
X.



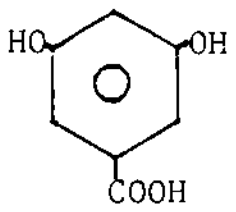
XI.



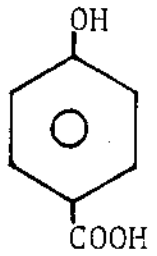
XII.



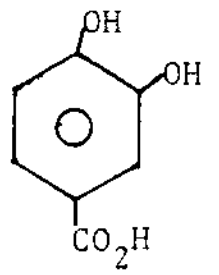
XIII.



XIV.



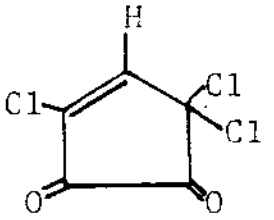
XV.



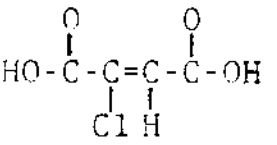
XVI.

Christman and coworkers have studied chlorine degradation products of compounds containing the several aromatic substitution patterns known to occur in humic degradation products, each with different C_3 side chain units (18). The C_3 side chain units were chosen because propyl side chains are thought to predominate in the structure of lignin, a possible precursor of humic matter (17). While not complete, this work has shown that resorcinol yields a new compound (XVII) which presumably is formed through a ring

cleavage and reclosure process. Other resorcinol products include chloroform, trichloracetic acid, unspecified ring chlorinated, and the chlorinated dicarboxylic acid (XVIII):



XVII.



XVIII.

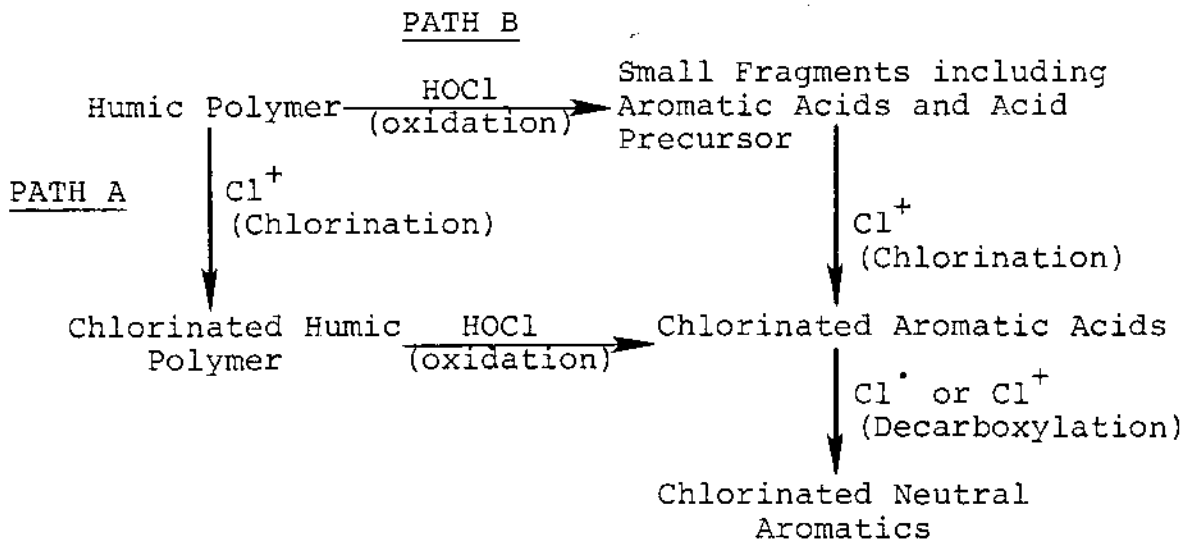
In a recent study, Christman and coworkers have observed a variety of small molecular weight compounds from the degradation of humic acid with chlorine (19). Earlier work by Rook (16) identified several compounds from the chlorination of peat extract and water from a storage reservoir of Rotterdam, Netherlands. Compounds from peat included chloroform, dichloromethane, chloral, dichloracetic acid, trichloropropylene, chloroisopentanol, tetrachloro- and pentachloroacetone. From the reservoir, several α-chlorinated C_4 and C_5 ketones, polychlorinated acetones, chloral, and chlorinated butanol were found. Of particular significance to this work was the detection of compounds such as the chlorinated propylbenzene isomers. It should be noted that several of these compounds are

listed in Tables II and IV along with others of similar structure.

Apparently, as Rook pointed out, "excessive chlorination of waters is just one more degradation method of humic substances," (16) the major organic component of natural waters. Moreover, the same types of compounds apparently are formed in the chlorination of wastewaters, although it is not established that humic substances are the major components of wastewater from municipal sources. It is reasonable to assume, however, that these biorefractory compounds survive activated sludge treatment and will be present in final clarified wastewater. Whether or not this is an accurate view, it is true that the compounds found in this work are structurally similar and, in many cases, identical to the compounds found by Rook and by Christman et al. from the chlorination of humic material.

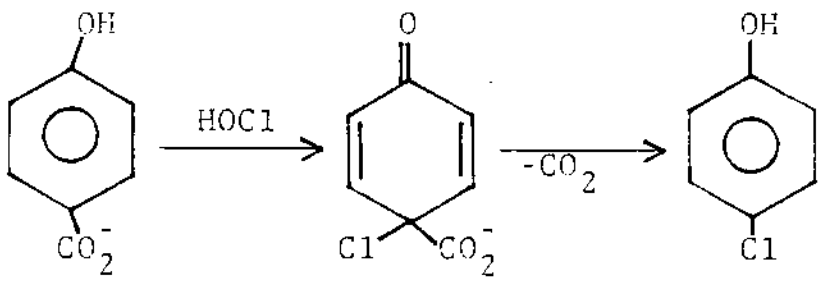
Three types of compounds listed in Tables II and IV deserve special attention: the polychlorinated propanones, chloromethylbutene, and several chlorinated alkylbenzenes. The latter include chlorinated benzene, toluene, ethylbenzene, and propylbenzenes. Direct chlorination of the corresponding aromatic compounds is unlikely since some type of activating substituent is usually required for facile chlorination in aqueous systems (20). More likely these neutral chloroaromatics result from the

decarboxylation of the corresponding aromatic acids that are formed during oxidative cleavage of the humic polymer (Scheme A).

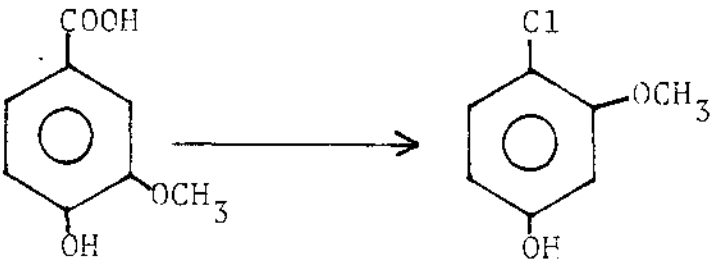


Scheme A

It is not clear whether chlorination occurs before or after oxidative degradation of the humic polymer (Path A and Path B, respectively). Nor it it clear that a radical chlorine intermediate is responsible for the decarboxylation process; however, other works have shown that this is a legitimate pathway for aqueous chlorination of carboxylic acids. For example, Rockwell (21) has shown that p-hydroxybenzoic acid gave 4-chlorophenol:



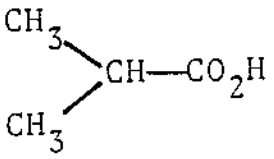
The absence of phenol, 2-chlorophenol, or 2,6-dichlorophenol suggests a two-step process with chlorination as the initial step. Vanillic acid (XVIV) yielded 4-chloro-2-methoxyphenol (XX), apparently by a similar process (21). Recently, Sievers (22) has observed the formation of toluene and several other aromatic hydrocarbons from the chlorination of municipal wastewater (23).



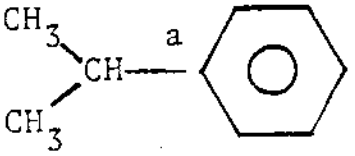
XIX. XX.

The compound identified as chloromethylbutene may be related to the compound chloroisopentanol which was observed by Rook (16). Both are isoprenoids and most probably result from the degradation of some aliphatic component of the humic polymer. Likewise, the polychlorinated acetone derivatives most probably arise from a cleavage of aliphatic side chains on the polymer before or after partial chlorination. The observation of 2-methyl-propionic acid (XXI) among the oxidative degradation products of humic acid (17) suggests that the 2-methylbutyl unit may be one of the aliphatic connecting

links in the humic polymer (XXII). Cleavage of this side group may result in the formation of acetone, and subsequently, their chlorinated derivatives.



XXI.



XXII.

In conclusion, the major chlorinated compounds from the chlorination of municipal wastewaters bear striking resemblance to the products obtained from natural and modic humics. Whereas the role of anthropogenic precursors cannot be neglected, it appears that this role is minor as compared to that of natural precursors.

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CHAPTER III

ANALYSIS OF VOLATILE HALOGENATED ORGANICS IN WATER BY LIQUID-LIQUID EXTRACTION

Introduction

One of the most important classes of chlorinated organic compounds generated during water chlorination appears to be the volatile halogenated organics (VHOs). The four most prominent compounds in this class are the trihalomethanes (THMs), chloroform, bromodichloromethane, chlorodibromomethane, and bromoform. They are important because recent data indicate that they comprise a significant portion of the total halogenated organic material generated by water chlorination (1), and because the VHOs are all known or suspected to have toxic (2) and/or carcinogenic (3) potential.

The relationship between water chlorination and the formation of these VHOs has only recently been recognized. Glaze (4) was the first to demonstrate that VHOs could be formed by the action of chlorine in water. They reported chloroform as a product of the chlorination of municipal wastewaters. However, the analytical techniques that he used were not designed to accurately quantitate such highly volatile compounds. J. J. Rook (5) adapted a closed

system headspace analytical procedure which was a more appropriate technique for volatile analytes. He later used this technique (6) to demonstrate the formation of all of the THMs during drinking water chlorination.

Concern about the presence of VHOs increased as more recent studies confirmed their occurrence in water supplies in other geographical areas. In 1973, a new analytical technique was developed by Bellar and Lichtenberg (7) which offers several advantages over the headspace technique. With the Bellar method, samples are collected in 125 ml serum bottles. Five ml aliquots are withdrawn for each analysis. Sample aliquots are purged with inert gas that entrains VHOs and transports them to a trap containing an adsorbent resin, usually Tenax-GC. Following adsorption, the gas flow is reversed, the trap is heated, and VHOs are desorbed onto the head of a GC column for subsequent analysis. The headspace procedure used by Rook requires large volumes of samples for analysis. This necessitates bulky sampling equipment and laboratory glassware. Also, the Bellar method requires only fifteen minutes for the concentration portion of the analytical procedure versus twelve hours for the compounds of interest to equilibrate between the liquid and gas phases in the headspace technique.

As a result, the Bellar method has been adopted by the United States Environmental Protection Agency, and

subsequently by VHO analysts in general. This method was used by the U.S. EPA for the National Organics Reconnaissance Survey (8) that showed the presence of various combinations and quantities of VHOs in all of the eighty cities in the United States that were sampled during the survey.

The impact of these recent studies on the water treatment field is already significant and will probably become more important in the near future. The role of chlorine in the water and wastewater treatment field is undergoing extensive reevaluation because of the potentially harmful side effects of chlorinated organics such as the THMs that are produced in the process. Mandatory VHO monitoring programs are already being proposed (1), and the EPA has promulgated maximum-allowable limits for THMs in drinking waters.

These developments imply that great numbers of VHO analyses will soon have to be run by water treatment facilities as well as by regulatory and surveillance authorities. Much manpower and equipment will be required if the Bellar method is used for routine screening. The alternative is to develop new and even more streamlined analytical techniques. Nicholson (9) recognized this and understood the importance of an analytical method which can "handle large numbers of samples in a relatively short period of

time" as well as be "highly specific for halogen-containing compounds."

In accordance with these requirements, two new analytical techniques have been developed. The first, developed by Nicholson (9), is a direct aqueous injection technique (DAI). This technique takes advantage of the high sensitivity of the electron capture gas chromatographic detector to circumvent any concentration step. The second technique, which was developed in this laboratory, is called the North Texas State University liquid-liquid extraction (NTSU/LLE) method. It utilizes a closed system extraction step followed by an electron capture gas chromatographic analytical procedure. This chapter describes in detail the NTSU/LLE method and compares it to the other two contemporary methods--the Bellar purging method and the DAI procedure.

Recently, important parameter critiques of the headspace, the Bellar, and the NTSU/LLE analytical methods have been published that have led to modifications in equipment and procedures. Kaiser (1) has reported a miniaturized headspace analysis system that requires only sixty milliliters of sample. Headspace analyses can be performed in approximately forty-five minutes using this system. The equilibration occurs in only thirty minutes. The small sample size requires the use of the more sensitive electron capture detector, but this small sample size makes Kaiser's

headspace method more specific for halogenated species than Rook's survey procedure. Kaiser's paper also reports the results of their study of the important parameters that control the headspace procedure. Although these data were collected using their new miniaturized headspace system, most of them are universally applicable to headspace procedures. Thus, they are cited below in comparing headspace procedures to the NTSU/LLE method.

Kuo (11) published a definitive analysis of the important parameters that control the performance of the purging method. Although his study included the evaluation of several purging systems of various configurations, he concluded that the Bellar system was the most effective. Therefore, the majority of the data reported in this work were collected using the Bellar apparatus. These data will be cited as representative of the purging method in comparing it to the NTSU/LLE method.

Liquid-liquid extraction techniques have been and still are the classical means of concentration of trace organic compounds in water. The most important area in which these techniques are currently being used is the analysis of pesticides, herbicides, and fungicides (12). These procedures typically call for a series of organic extractions followed by concentration of the extracting solvent before analysis. Such extensive handling and

transferring of the water sample and extraction solvents might be acceptable for analysis of non-volative compounds, but new interest in much more volatile analytes requires considerable modification of the classical procedures to avoid losses due to volatilization. Grob (13) was one of the first investigators to recognize this. In his liquid-liquid extraction procedure, a high ratio of water to organic solvent is used which eliminates the need for concentration. The organic layer is sampled directly out of the extraction vessel for chromatographic analysis.

Since the NTSU/LLE method was first reported (14), two other liquid-liquid extraction procedures have been published by Richard (15) and Meiure (16). Although neither procedure utilizes a closed extraction system, both procedures place heavy emphasis on the careful handling of both the water sample and the organic solvent in order to avoid losses due to volatilization. The advantages and disadvantages of these procedures will be compared to the NTSU/LLE procedure.

Experimental

Authentic samples used for experimental comparison of the NTSU/LLE, the Bellar, and the DAI procedures were collected and handled in identical manners. It has been recognized (17) that samples must be collected so as to

avoid air bubbles within the sampling container that could cause compound losses due to water/headspace partitioning. Therefore, samples were collected in 125 ml serum bottles that were filled to overflowing and then sealed with teflon-lined silicone septa which were crimped in place by aluminum outer sleeves (Figure 16). Before sampling, the bottles were cleaned with chromic acid, water, acetone, and then dried in an oven at 165°C for several hours. After sampling was completed, the bottles were transported to the laboratory for analysis. If more than a few hours had to elapse between sample collection and analysis, the sample bottles were chilled with ice and then warmed to room temperature before analysis.

Two reagents were added to the samples at the time of collection. Sodium sulfite (Baker analytical reagent grade) was added as a chlorine reducing agent in varying amounts depending on the anticipated chlorine residuals. This reduction of residual free chlorine to inorganic chloride prevented chlorination reactions from occurring subsequent to sampling (17). A buffer was also added to avoid possible extraction anomalies related to pH effects. The buffer added was 1.2 ml of a solution prepared from a 2:3 mixture of 1.0 M NaH_2PO_4 and 1.0 M Na_2HPO_4, pH 6.5. Although no pH effects were observed during preliminary tests, it was felt that not all possible matrix variations

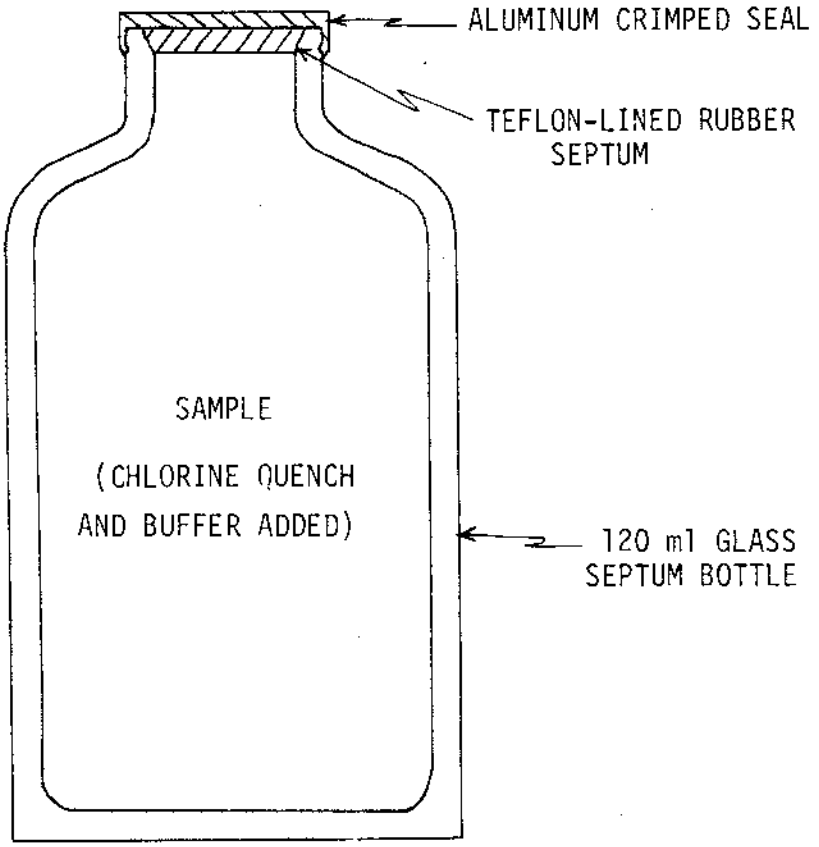

Fig. 16--Sampling bottle for water samples to be analyzed by the NTSU/LLE method.

could be anticipated; thus, the decision was made to continue to use the buffer despite the lack of any data indicating its usefulness.

NTSU/LLE Procedure

The LLE method basically involves a specialized closed system organic solvent extraction procedure followed by chromatographic separation and analysis. A schematic representation is shown in Figure 17.

Pentane Extraction Procedure

Normal pentane (Fisher, pesticide grade) is used as the extracting solvent. Chromatographic analysis of the pentane prior to use in the LLE procedure usually shows this grade of solvent to be of adequate quality as received. If purification is necessary, it is effected by fractional distillation from sodium metal or passage through an activated alumina column. The internal standard, 1,2-dibromoethane (Aldrich, reagent grade), is distilled and added to the solvent at a concentration of approximately 20 mg/L.

Three ml of this solvent/internal standard mixture is added in the manner shown in Figure 18 to the 125 mL water sample, using two 10 cc syringes. One syringe contains the solvent mixture while the other is empty. As the solvent mixture is injected into the inverted sample bottle, it

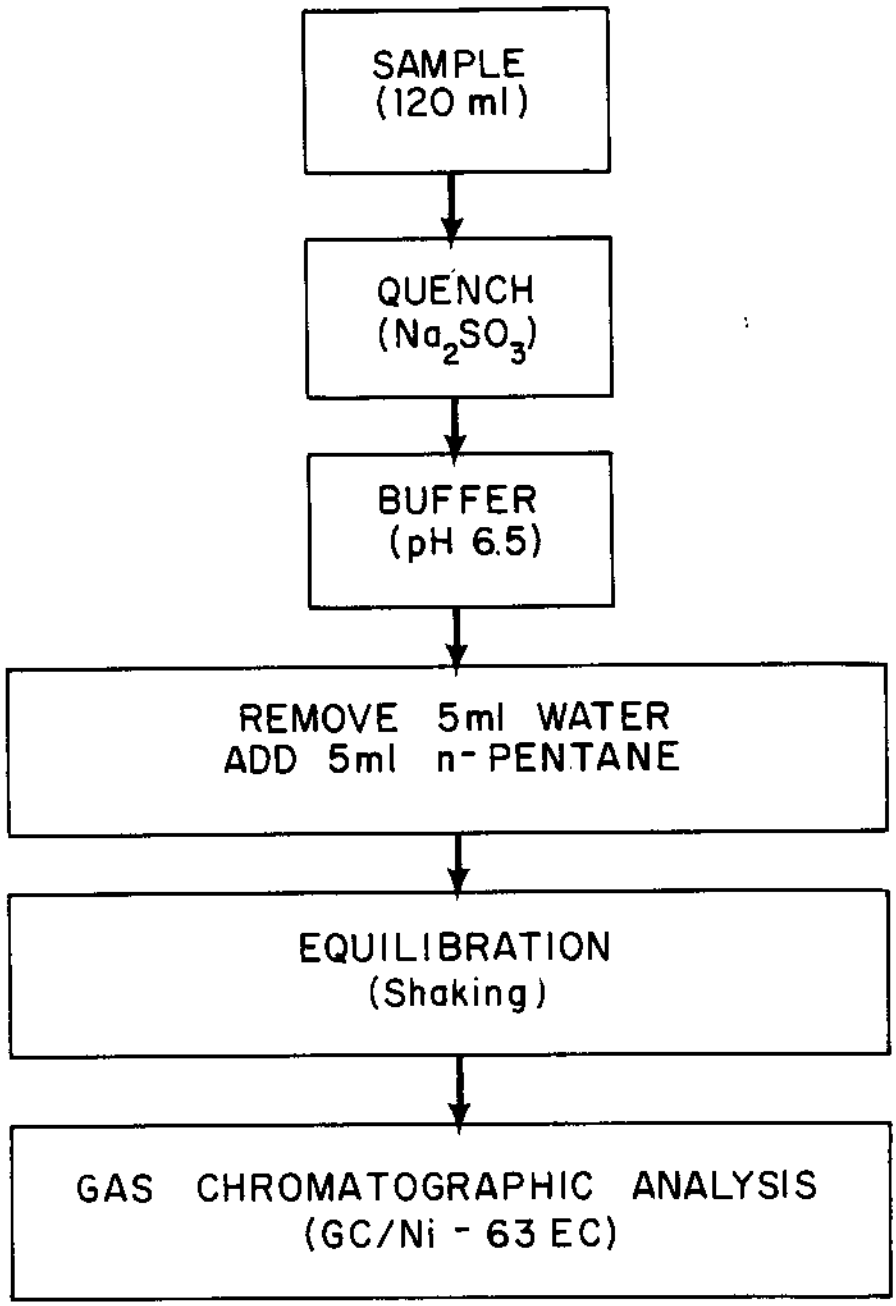

Fig. 17--Protocol used for the NTSU/LLE analysis of volatile halogenated organics.

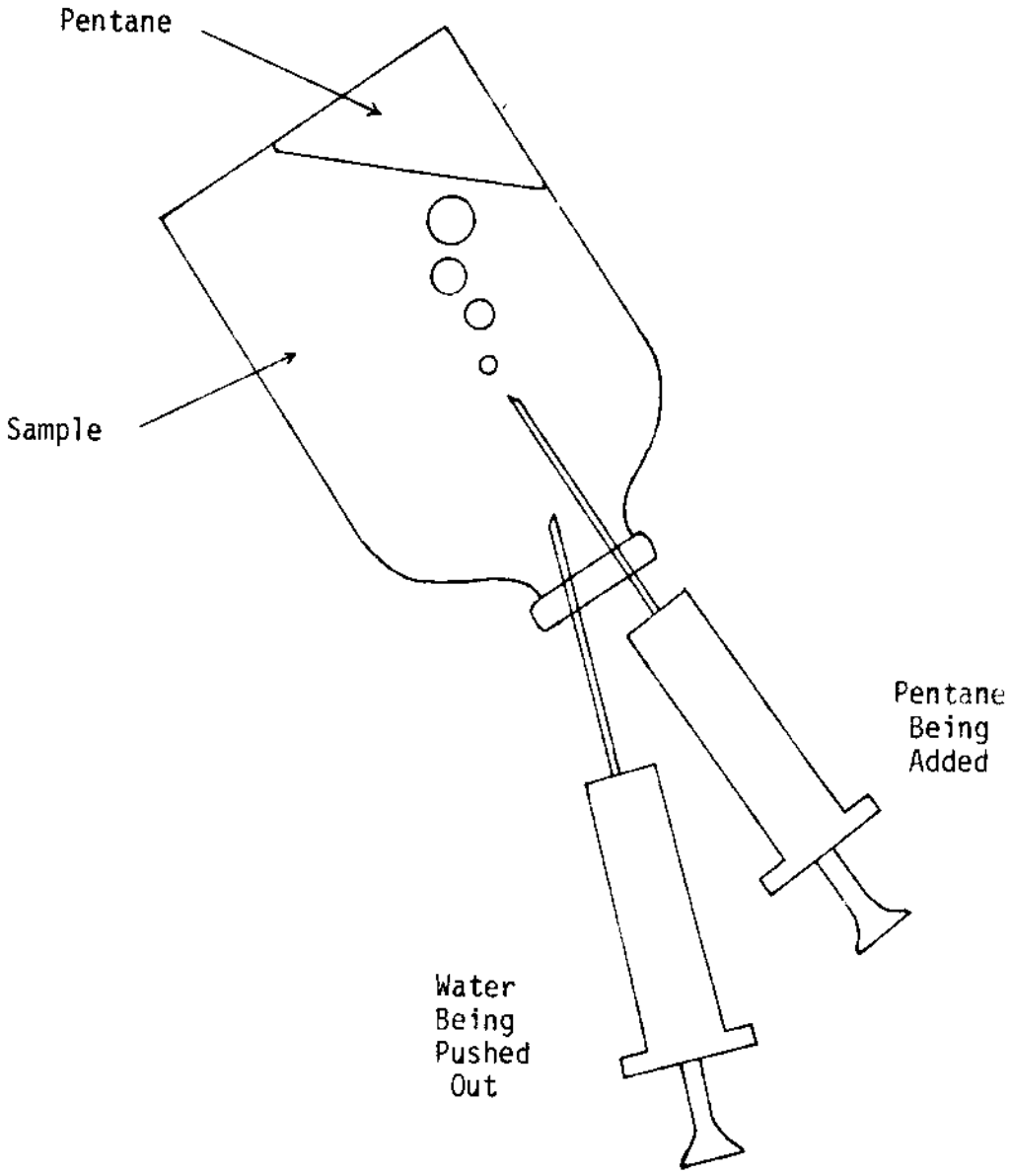

Fig. 18--Addition of pentane to the sample bottle

rises to the top of the bottle, and an equivalent amount of water is displaced into the empty syringe. The sample bottle is then strapped to the surface of a platform gyratory shaker (Junior Orbit Shaker, Labline Instruments, Inc.) and shaken at a speed of 400 rpm for twenty-five minutes. After shaking, the samples are ready for immediate analysis.

Chromatographic Analysis

A two-to-five microliter pentane aliquot is removed through the silicone septum with a Hamilton 801 ten-microliter syringe. This aliquot is injected into a Tracor 560 gas chromatograph equipped with a ^{63}Ni linearized electron capture detector. The glass chromatographic column is 183 cm by 2 mm I.D. It is packed with 10 percent squalane on 100/120 mesh Supelcoport (Supelco, Inc.). The carrier gas is a 95/5 percent argon/methane mixture. The column flow rate is 20 mL/min with 60 mL/min of makeup gas (the same argon/methane mixture) added to the GC column effluent to improve detector performance. The respective oven temperatures are injector, 100°C, column, 66°C, and detector, 300°C. An electronic digital integrator (Supergrator, Columbia Scientific Instruments) is used for quantification. Chromatograms are recorded on a Perkin Elmer 56 strip chart recorder.

Direct Aqueous Injection

The same chromatograph, integrator, and recorder are used for this procedure as were used for the NTSU/LLE procedure described above. The glass GC column used is 122 cm by 2 cm I.D.; it is packed with Chromosorb 102 60/80 mesh, a polystyrene/divinylbenzene copolymer adsorbant. The injector, column, and detector temperatures are 175°C, 135°C, and 300°C, respectively. The procedure followed is to remove a three-to-five microliter water aliquot directly from the VOA sample bottle and inject it into the chromatograph.

Bellar Purge and Trap Method

A schematic diagram of the procedure used in our laboratory is shown in Figure 19. The procedure is essentially the same as that outlined by Bellar et al. (7), with three important modifications (refer to Figure 19):

1. A liquid chromatograph sample loop injector (Altec, Inst. #568031) is used to accurately introduce reproducible aliquots of water samples into the purging device;
2. The analytical column serves as the adsorbing trap. Thus, the VHOs are purged directly onto the chromatographic column eliminating a significant source of erratic behavior;

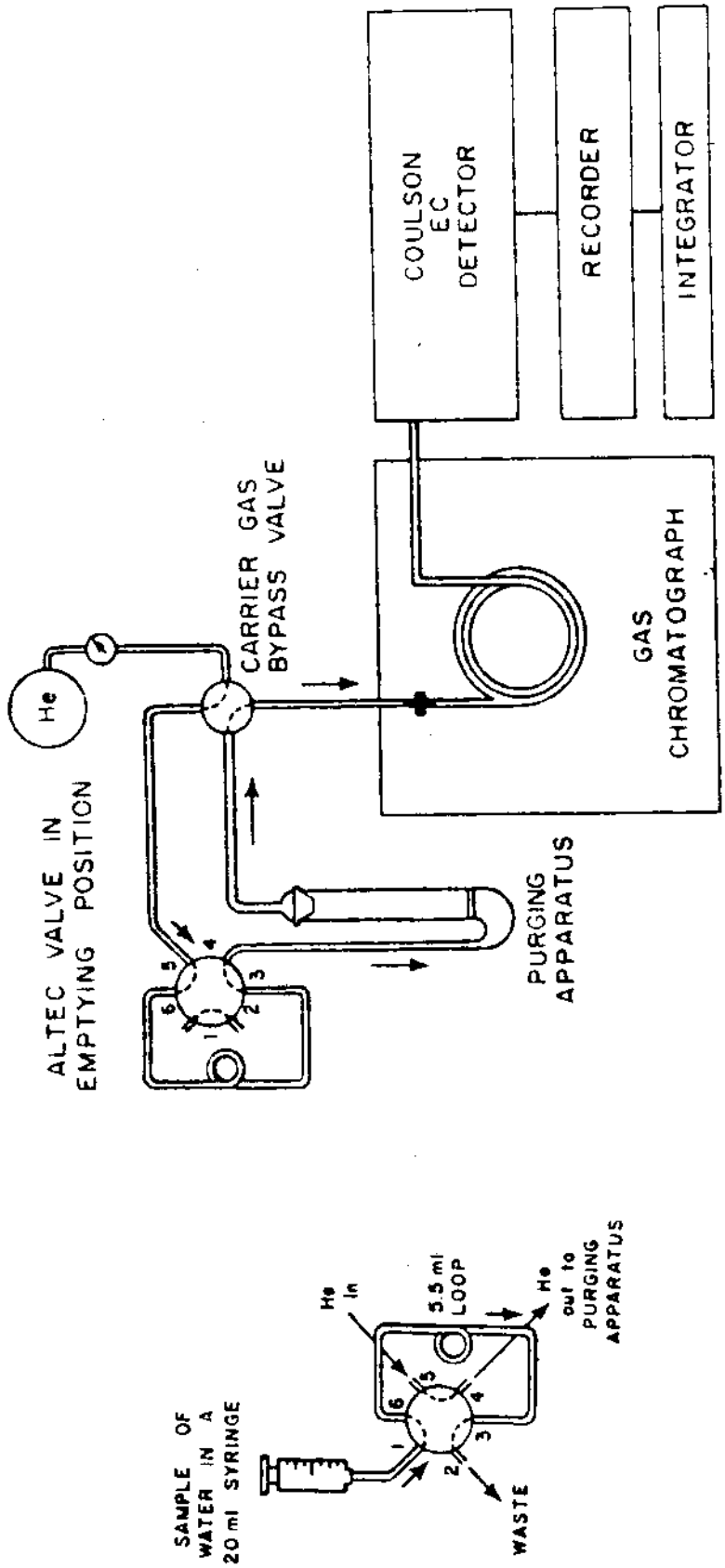

Fig. 19--Modified purge-and-trap aparatus with sample loop injector

3. The Chromosorb 102 analytical column that is used allows the separation of several other compounds such as carbon tetrachloride and 1,2-dichloroethane that could not be separated using Bellar's original analytical column.*

Purging Procedure

The 5.5 ml sample injector loop is filled to overflowing with the water sample using a 20 cc syringe. The valve is switched to the inject position and the sample is forced to flow into the purging device by the pressure of the helium carrier gas. As the pressure continued to build, the helium purges the volatile compounds from the water and sweeps them into the analytical column which is cooled to room temperature. A carrier gas bypass valve allows the purging equipment to be circumvented during chromatographic analysis thus avoiding possible problems due to water-saturated carrier gas.

Chromatographic Analysis

The gas chromatograph is a Hewlett-Packard 5700 that is equipped with a Coulson Electrolytic Conductivity Detector (CECD: Tracor Inst., Inc., Austin, Texas). The glass chromatographic column is 122 cm by 2 mm I.D. and

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*Recent improvements in the purge and trap GC procedure have eliminated this deficiency.

contains Chromosorb 102. The helium carrier gas flow is 20 mL/min. The injector temperature is 200°C, and transfer lines and venting value leading to the CECD are 275°C. After sample introduction, the GC column oven is programmed ballistically from ambient temperature to 60°C, then from 60°C to 220° at 8°/min. The CECD is operated in the reductive mode with 60 mL/min of hydrogen added to the GC effluent prior to the influent end of the pyrolysis furnace which is at 850°C. The recorder and integrator are the same as those used in the LLE and DAI procedures.

Ionic Strength Versus Recovery Efficiency

Three experiments were performed in parallel in an effort to determine possible matrix effects for the NTSU/LLE system. Laboratory water which had been deionized, distilled, and purged with nitrogen was used for all experiments. In the first experiment, nothing was added to the water sample. In the second, 0.5 gm of NaCl (Baker Chemical Co., reagent grade) was added to each water sample. In the third, 25 gm of NaCl was added to each water sample. Ten microliter of a methanol solution containing six compounds of interest was then added to each water sample. The final concentration of each of the compounds in the water samples is shown in Table V, the column on the left. Each experiment was performed using duplicate samples, and

each sample was analyzed in duplicate. A control containing no added NaCl and no added organic compounds was also analyzed and shown to contain no significant interferences.

The samples were then analyzed using the NTSU/LLE procedure described above with the following exceptions:

1. The quantification was performed by external standard calculation as no internal standard was available at that time.

2. The samples were analyzed on a Varian 3700 gas chromatograph equipped with a ^{63}Ni electron capture detector. The chromatographic peak areas were integrated by a Hewlett-Packard 3351 integrating computer.

An analytical standard was prepared by adding 10 uL of the methanol solution containing the compounds of interest to the same volume of pentane used in the water extractions.

The quantitative calculations were performed as follows:

1. The standard was analyzed in duplicate and the two resulting measurements, M_X's for each compound, X, were averaged to obtain A_X (standard).

2. Each sample was analyzed in duplicate and the two resulting measurements for each compound were averaged to obtain A_X (sample).

3. The percent recovery, $\%R_X$, for each compound, X, was determined according to the external standard formula:

$$\%R_X = \frac{A_X \text{ (Sample)}}{A_X \text{ (Standard)}} \times 100 \ .$$

4. For each compound, the two $\%R_x$ values for the duplicate samples in each experiment were averaged to obtain an average percent recovery, APR_x.

5. The system precision was expressed as a range value for each compound which was simply the absolute value of the difference of the two $\%R_x$ values for the duplicate samples, 1 and 2:

$$Range_x = |\%R_{x1} - \%R_{x2}| .$$

Results and Discussion

An extensive comparison has been made in the laboratory between the NTSU/LLE method and the Bellar method for VHO analysis. Although the direct aqueous injection technique was also evaluated relative to the NTSU/LLE method, the comparison was less extensive than with the Bellar method for reasons described below.

Typical chromatograms are shown in Figures 20 through 22 for the three analytical methods. The concentration of chloroform in all samples was about 40 ppb. Other compound concentrations were adjusted using the appropriate response factors (shown in Table VI) to produce peak heights approximately equal to that of chloroform. It is important to note that the response factors reflect concentrations which produce equal peak heights as opposed to equal areas. This approach was used because the classical (though less reliable) quantification of trace compounds by gas chromatography has usually been performed by manually measuring peak

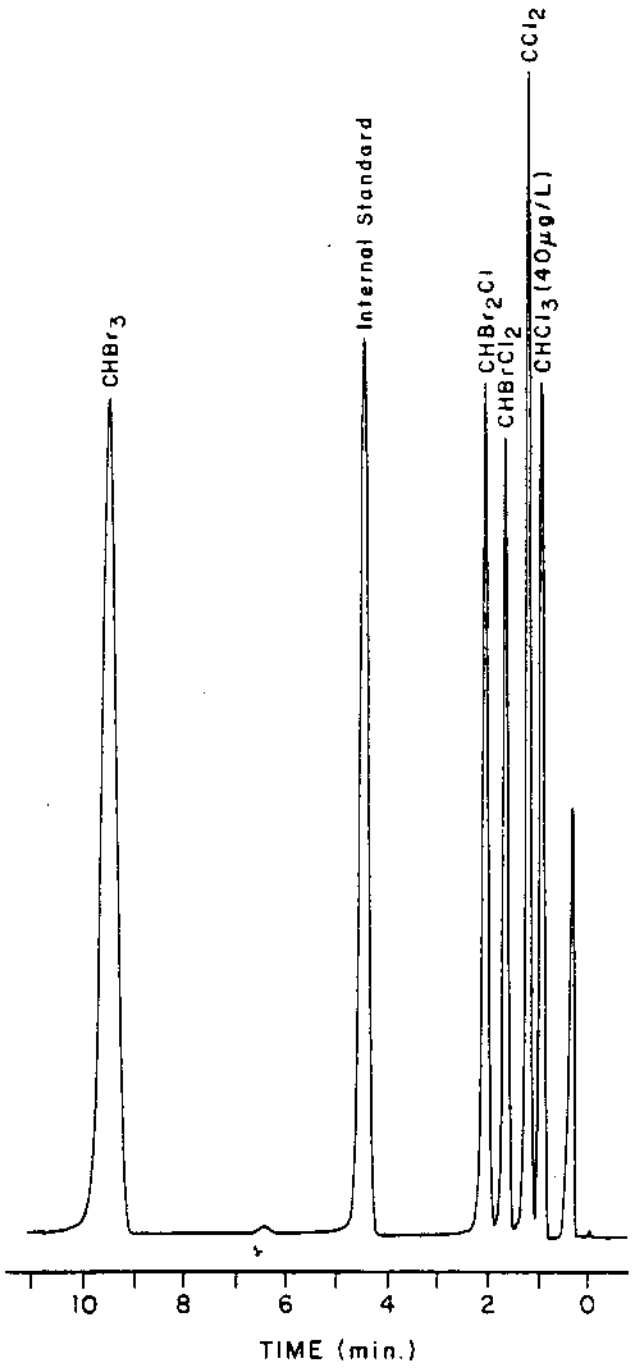

Fig. 20--Gas chromatogram using the NTSU/LLE protocol

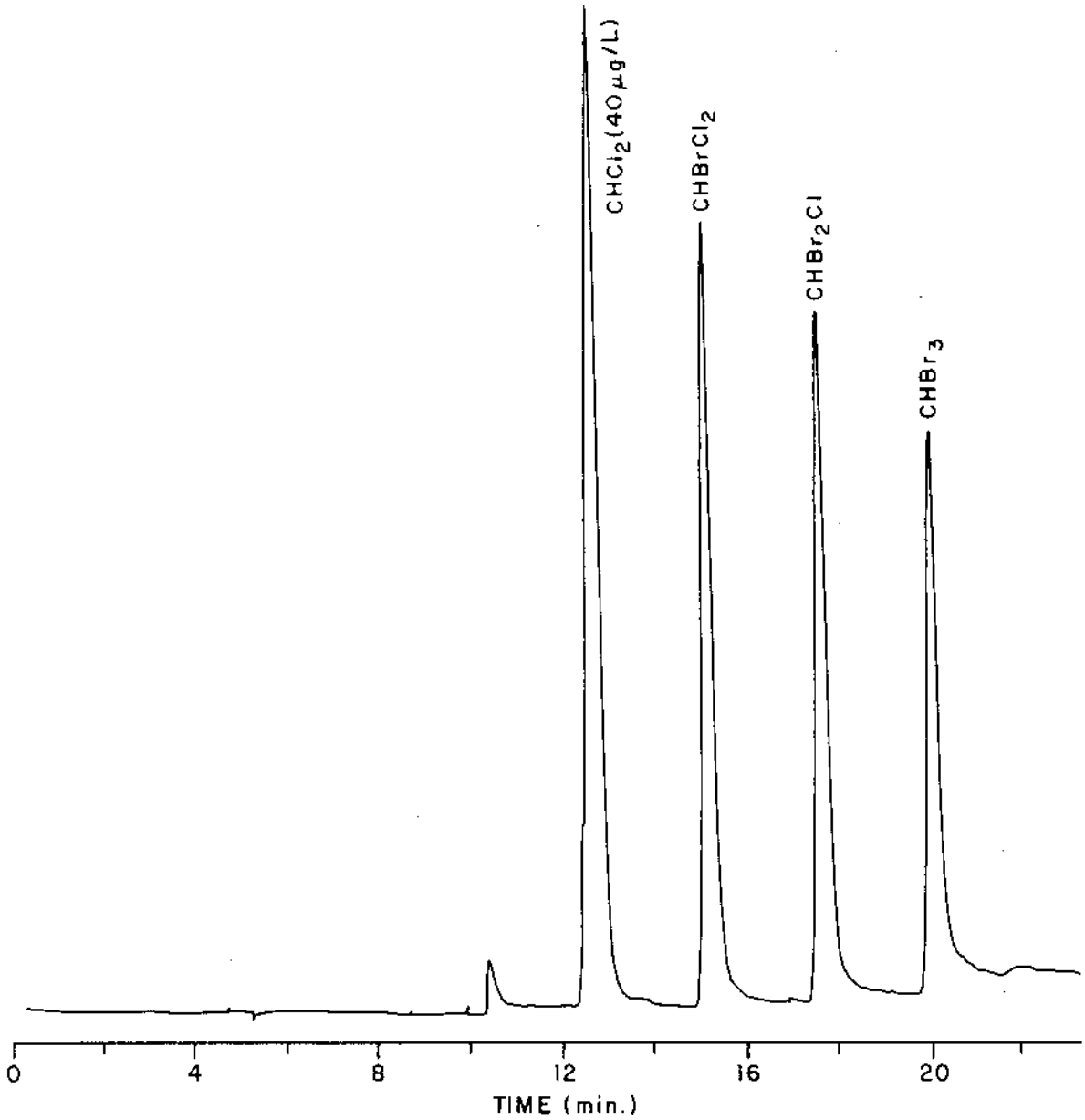

Fig. 21--Gas chromatogram using the modified purge-and-trap protocol.

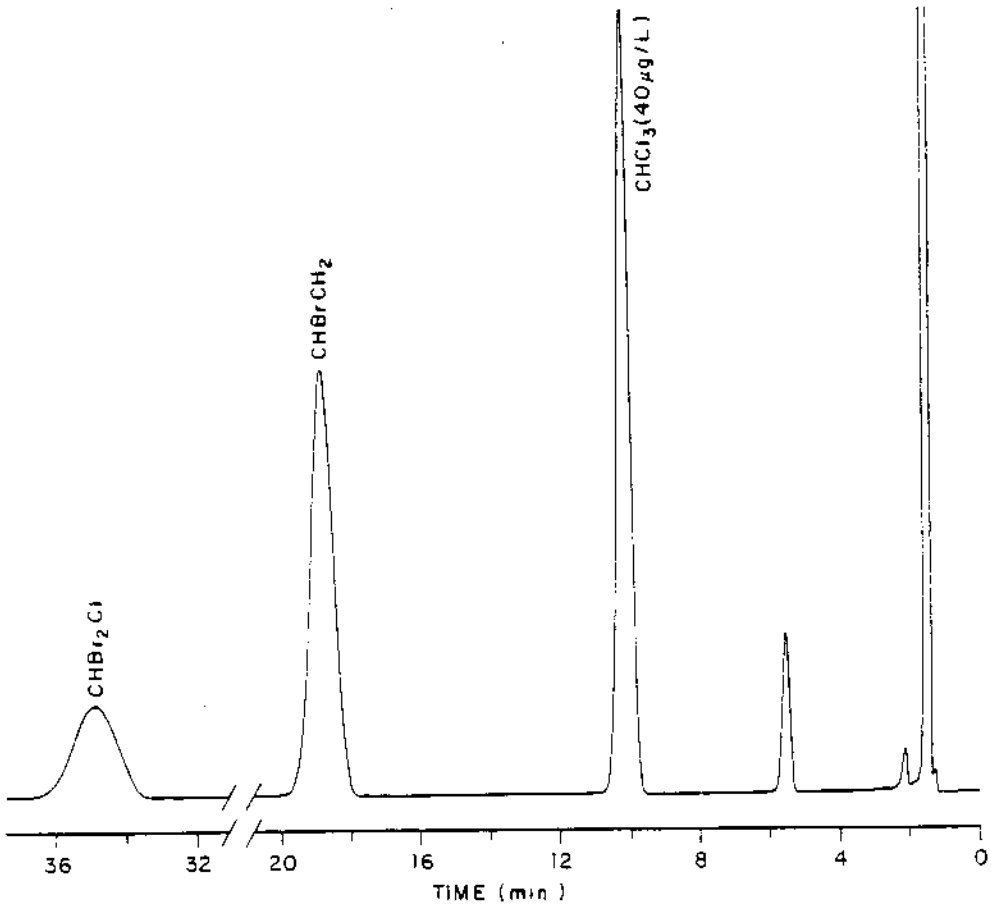

Fig. 22--Gas chromatogram using the direct aqueous injection protocol.

TABLE VI

RESPONSE FACTORS FOR VHOs USING DIFFERENT ANALYTICAL TECHNIQUES

Compound	NTSU/[a] LLE	Modified[b] Bellar P/T	Direct[a] Injection
$CHCl_3$	100	100	100
$C_2H_4Cl_2$	0.56	67	1
CCl_4	2000	67	1000
$CHBrCl_2$	500	50	200
$CHBr_2Cl$	333	40	100
$CHBr_3$	67	29	22

[a]Electron capture detection.

[b]Coulson electrolytic conductivity detection.

heights to calculate concentrations. This was the procedure originally used by Bellar (7) and is the procedure still being widely used today. Also, signal to noise ratios are related to peak heights rather than areas. Since the minimum detectable limit is a function of the signal to noise ratio, it is therefore also a function of peak height.

The digital electronic integrator used in our laboratories measures both peak heights and areas automatically. Therefore, either variable can be selected as the basis of quantification. The estimates of quantitative precision are shown in Table VII. For precision studies, the compound concentrations were all adjusted to a signal to noise ratio of approximately 20 to 200. Therefore, these

TABLE VII

PRECISION OF ANALYTICAL METHODS FOR ANALYSIS OF VHOs AT S/N 20-200 (PERCENT STANDARD DEVIATION)

Compound	NTSU/ LLE	Modified Bellar P/T	Direct Aqueous Injection
$CHCl_3$	1.9	1.8	1.5
$C_2H_4Cl_2$	3.8	2.2	--
CCl_4	2.1	5.2	--
$CHBrCl_2$	8.1	2.4	3.8
$CHBr_2Cl$	5.4	3.4	3.1
$CHBr_3$	4.7	6.6	--

precision values probably approach the optimum which can be produced for each respective method. Of particular interest is the fact that the internal standard quantification procedure used in the NTSU/LLE method produced values roughly comparable to the values for the Bellar method which used the usually less precise external quantification method. This is probably due to the use of the liquid chromatographic sample loop injector in the Bellar method which allows good reproducibility of sample sizes for successive analyses. The precision for all techniques is generally at or below the 5 percent level which is acceptable precision for a trace analytical technique of this type.

The minimum detectable limits for the three methods were determined by analyzing increasingly dilute standard mixtures until a signal to noise ratio of approximately 2

was reached. The resulting values are shown in Table VIII. The data indicate the LLE technique to be generally more sensitive than the DAI method or the Bellar method using the Coulson detector.*

TABLE VIII

MINIMUM DETECTABLE LIMITS FOR THE ANALYSIS OF VHOs BY LLE, BELLAR P/T, AND DAI METHODS

Compound	Detection Limit (μg/l in H_2O)		
	NTSU/ LLE	Modified Bellar P/T	Direct Aqueous Injection
$CHCl_3$	0.2	0.2	1
$1,2\text{-}C_2H_4Cl_2$	36	0.3	90
CCl_4	0.01	0.3	0.1
$CHCl_2Br$	0.04	0.4	0.5
$CHBr_2Cl$	0.06	0.5	1
$CHBr_3$	0.3	0.7	4.5

One should also recognize that minimum detectable limits for the Bellar method are close to the required analytical sensitivity limit necessary for water survey applications, generally accepted as 1 ppb for the respective compounds. Working this close to the minimum limits tends to produce poorer precision values as observed below. The DAI minimum detectable limits are unacceptable for

*New electrolytic conductivity detectors are now available for the purge and trap method which makes this method more sensitive by a factor of 100 in the case of most VCOs.

bromoform and are only marginally acceptable for chloroform and chlorodibromomethane.

NTSU/LLE Parameters

Solvent section.--Pentane is used as the organic extraction solvent for several reasons. The Fisher electrolytic grade commercial pentane is usually pure enough to use as received. It is volatile enough to separate easily from the chloroform chromatographic peak, the first peak of analytical interest. It has a low electron capture response producing little or no solvent front. It is highly insoluble in water. And, it has a very favorable distribution coefficient versus water for the analytes of interest.

As noted earlier, Grob (13) first developed a liquid-liquid extraction procedure using pentane as a solvent. His system uses 200 uL of pentane to extract 900 mL of water. While this procedure seems to work reasonably well in his laboratory, it certainly requires a highly-skilled technician with much experience in the technique to achieve reproducible results. The Grob procedure also takes more personhours since it requires manual shaking of the extraction vessel for maximum efficiency. Moreover, a loss of extraction efficiency for more volatile components is reported. This problem might be attributed to

volatilization of such analytes due to the headspace present in the extraction apparatus (13).

Junk (15) also selected pentane as a solvent for essentially the same reasons cited above. For part of his work, a flame ionization detector was used which required more polar chromatographic columns for greater separation of the solvent front from the chloroform peak. This requirement was also observed in this work when using a GC/MS system for analysis.

Mieure (16) used methylcyclohexane as a solvent. Although this solvent has a boiling point of 101°C, it reportedly separated adequately from the analyte peaks. In this work, solvent interferences were observed with such solvents as hexane (b.p. 69°C) for our chromatographic system. Therefore, higher boiling solvents were not used.

Extraction apparatus.--The extraction apparatus used in the NTSU/LLE procedure is the only closed extraction system having no headspace in contact with the pentane/water matrix. The three other extraction systems cited above do have a headspace in contact with their respective extraction solvents. In each case a trend can be recognized for water/pentane ratios of 10:1 or greater. This trend is characterized by an increase in the extraction efficiency with an increase in analyte boiling points. Such a trend could be explained by decreased

volatilization tendencies for higher boiling materials. It is significant to note that in the NTSU/LLE system no such trend is observed (Table IX). Indeed, it is acknowledged

TABLE IX

EXTRACTION EFFICIENCY OF VHOs BY THE NTSU PENTANE LLE METHOD

Compound	Extraction Efficiency (%)
$CHCl_3$	62
$1,2\text{-}C_2H_4Cl_2$	41
CCl_4	87
$CHBrCl_2$	69
$CHBr_2Cl$	72
$CHBr_3$	66

by Junk (15) and others (17) that sample collection must be conducted in such a way as to avoid a headspace in the sampling container. It may also be true that such a requirement is important during sample extraction. Another advantage of the NTSU/LLE system is that emulsion problems seem to be eliminated due to the relatively docile nature of the shaking process. Even wastewater samples can usually be analyzed by this technique. This is not always the case with the more conventional extraction procedures where intractable emulsion formation may be a major problem. Extraction systems similar to that of Grob (13) showed a distinct tendency to form emulsions when tried in this laboratory.

Salt effects.--The recovery data for the three parallel ionic strength experiments are shown in Table X. Experiments 1 and 2 simulate the reasonable matrix limits in terms of ionic strength which might be expected to occur in the environment. The approximate NaCl concentrations for the respective experiments range from virtually 0 to 5.88 mg/L. Although the slightest general increase in recovery efficiency might be observable with the drastic increase in ionic strength, it is clear that all of the corresponding measurements are well within the precision of the analytical method. If one continues to increase the ionic strength to the saturation point as suggested by Mieure (16) for maximum recovery efficiency, the recovery efficiencies can indeed be significantly increased. However, the error caused by even this drastic matrix change results in an average error in accuracy of approximately 25 percent, a generally acceptable precision for environmental analyses at the parts-per-billion level.

An interesting exception to the general trends discussed above is the behavior of carbon tetrachloride, CCl_4. While other compounds exhibit an increase in extraction efficiency with increasing ionic strength, carbon tetrachloride exhibits the opposite trend. At this time no explanation can be offered for this observation.

TABLE X

RECOVERY OF VOLATILE ORGANOHALIDES BY THE NTSU/LLE METHOD

Compound	Concentration, µg/L	Average Percent Recovery (Range)		
		Experiment 1	Experiment 2	Experiment 3
$CHCl_2$	50	63.0 (2.3)	63.3 (0)	77.0 (1.9)
$C_2H_4Cl_2$	45,000	43.4 (0.8)	43.6 (0.1)	68.0 (0.1)
CCl_4	2.5	93.9 (0.6)	90.5 (4.0)	72.5 (2.6)
$CHCl_2Br$	10	55.8 (0.5)	56.5 (2.6)	65.1 (3.0)
$CHClBr_2$	15	77.2 (0)	78.3 (1.8)	89.4 (0.3)
$CHBr_3$	75	79.1 (0.6)	81.2 (2.0)	88.9 (1.8)
NaCl, Molarity		0	0.1	Saturated

Shaking time.--Standard samples for the evaluation of shaking time on extraction efficiency were prepared by adding VHOs to organic free water and extracting for varying lengths of time. Times of 2, 5, 10, 20, and 30 minutes were used. The resulting analyses indicated that equilibrium had been achieved within two minutes. Integrals for all the peaks in the sample were within the limits of precision of the technique relative to peak integrals of samples shaking for longer time periods. A shaking time of 25 minutes was arbitrarily selected because heavily-polluted samples might take longer to equilibrate and because such a long shaking time is not the limiting factor in the analysis when a multiple port shaker is used.

Extractant/water ratios.--It is clear that the extract/water ratio will determine the extraction efficiency. Junk (15) discusses this subject, citing the well-known equation

$$E = \frac{100D}{D + V_w/V_o} .$$

Here, E is the percent of the VHO extracted; V_w and V_o are the volumes of water and organic solvent, respectively. D is the distribution coefficient, the relative solubility of the VHO in water versus organic solvent. Looking at

published data, Junk (15) shows data yielding D values in pentane of 40 to 53, while Mieure's data gives D values from 49 to 114. On the other hand, distribution coefficients calculated from the data of Grob (13) have values of 1000 or greater, although chloroform was not analyzed. In describing this extraction system, Grob alludes to the difficulty in achieving these remarkable and dubiously high values of D, indicating that careful techniques are required.

With the exception of Grob's data, LLE extraction efficiencies observed in this laboratory and by other workers show that increasing water/solvent ratios lead to decreasing extraction efficiencies, thus placing a practical limit on the concentration factor which can be achieved.

Matrix effects.--Table XI shows a comparison of the analytical techniques when applied to Denton, Texas tapwater samples. Clearly, in this situation the precision of the LLE method is better than that for the Bellar procedure (no precision values for DAI are available).

Most important is the discrepancy in the results obtained by the DAI method as compared to the other two methods, particularly for chloroform and bromodichloromethane. The DAI values are seen to be much higher than corresponding values for the other techniques. Nicholson

TABLE XI

ANALYSIS OF VHOs IN DENTON, TEXAS TAPWATER

Method	µg/l Halogen, as Cl*			
	$CHCl_3$	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
NTSU/LLE	27.3±0.3	25.7±0.3	19.4±0.4	4.42±0.08
Modified Bellar	29.3±2.2	32.5±1.8	25.4±1.0	n.d.
Direct Aqueous Injection	71.5	47.1	29.5	n.d.

*Duplicative assays for each sample.

(9) observed a similar trend with his DAI procedure and attributed the higher values to haloform formation in the injector port of the gas chromatography. Apparently, the heat and/or catalytic activity of the surfaces of the port (175°C) is (are) somehow involved in the decomposition of chlorinated haloform precursors which increase the apparent haloform concentration. This is the primary objection to the method as an instantaneous VHO monitoring technique. These anomalous effects are not observed for the NTSU/LLE procedure because the chloroform precursors apparently are not extracted into the pentane layer, and the effects are not observed with the Bellar procedure because the precursors apparently are not purged from the water sample.

Thus, these latter two methods more accurately reflect the instantaneous concentrations of the halogenated species.

Procedure.--It is difficult to compare quantitatively the procedural advantages which one technique has over another. However, analysis time is one parameter that is of importance and can be accurately determined. Table XII shows a comparison of time of analysis for various numbers of samples. Clearly, the LLE method has a distinct time advantage over the Bellar procedure. The importance of this in a high sample volume survey program has been indicated above.

TABLE XII

TIME TO COMPLETE MULTIPLE VHO ANALYSES BY NTSU/LLE AND MODIFIED BELLAR METHODS

Number of Sample Set*	Time for Complete Analysis	
	NTSU/LLE	Bellar
1	1.6	3
2	2.5	4.5
4	4	6
8	6	13
16	10	25

*Duplicate assays for each sample.

The NTSU/LLE method has two other advantages over the Bellar procedure. Firstly, considerable special equipment is required for the Bellar process. The Bellar technique

requires a special concentration apparatus which can either be purchased commercially for about $3,000, or it can be built in-house, perhaps requiring several months of development time. At least some modifications are required in the plumbing of a commercial chromatograph, and conventional chromatography via syringe injection is sometimes impossible while the Bellar apparatus is in place. Thus, the system is considerably less flexible than might be desired. Finally, an electrolytic conductivity detector is almost universally used in the Bellar procedure (although other specialized detectors might potentially be used). For most laboratories, this means an additional $3,000 investment for the detector along with the accompanying installation problems.

The extraction/concentration procedure of the LLE method is carried out in the sample bottle, thereby eliminating the need for cleaning of extraction equipment. Once extracted, the sample is immediately ready for chromatographic analysis. The LLE procedure uses a conventional electron capture gas chromatograph in the configuration supplied by the manufacturer; thus, any laboratory equipped for pesticide analysis already has the necessary analytical instrumentation.

The other major procedural advantage of the LLE procedure relates to the technical expertise required of

the analyst. The simplicity of the LLE procedure has resulted in competent analyses being performed by the least-trained technicians in our laboratory. The Bellar method, on the other hand, has required highly-skilled analysts in our laboratory who have had enough experience with this specific technique to understand the idiosyncrasies of the system. Generally, the Bellar method requires more sample handling, more hardware manipulation, and leaves more room for "cockpit" errors.

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CHAPTER IV

LIMITED MASS SEARCH COMPUTER PROGRAM

Sir Joseph John Thomson's book, Rays of Positive Electricity and Their Application to Chemical Analysis (1), is a summary of several investigators' research efforts performed at the Cavendish Laboratory during the years 1906 through 1913. It is generally cited as the introduction of the original principles which describe the parabolic behavior of positively charged molecular ions in a potential field. These principles are still the basis of modern mass spectrometry.

Thomson's original techniques were crude. Only ionic fragments such as CO^+ (m/e = 28) and Cl^+ (m/e = 35) could be resolved. However, he was well aware of the potential of this newly discovered phenomenon, as were many other investigators who read the original account. Within six years, Aston (2) had published a description of his instrumentation which had achieved unit resolution for the fragments CH^+, CH_2^+, CH_3^+, and CH_4^+. He used this same instrumentation to determine that atomic species of non-integral atomic mass were, in fact, mixtures of isotopes having different but integral atomic masses (3).

Although the potential importance of mass spectrometry for qualitative analysis was recognized during those early years, the mechanics of the instrumentation proved to be awkward and troublesome. By 1960, there were still relatively few mass spectrometers being used for organic chemical analysis (4). During the next several years, however, mass spectrometry began to assume its rightful place in the analytical chemistry laboratory. By 1967, a dozen books and thousands of scientific articles had been published on the subject (5).

The technique of gas chromatography combined with mass spectrometry followed a similar pattern of development. It was introduced as early as 1957 (6), but it was not until Biemann (7) described the first fully computerized Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS) in 1968 that the technique began to realize its full potential. Their paper showed examples of how computerized data acquisition was important in processing the GC/MS data from complex, extracted samples which might have 25 to 100 peaks in the resulting gas chromatogram.

Today, gas chromatography has advanced to the point where many hundred organic compounds can be separated in a single chromatographic run (8). Processing the mass spectrographic data of such a run is still tedious, even with the most sophisticated computer facilities. To assist

in such data processing, specialized computer programs have been developed to simplify the data processing and/or to extract grossly obscured relevant information.

One such computer program has received various names in the literature: limited mass search, extracted ion current profile, mass chromatography, and selective ion chromatography. This is a post-analysis manipulation technique applied to GC/MS data subsequent to its acquisition and storage. The technique is used to identify the retention times of specific compounds or classes of compounds with a total ionization chromatogram. The computer program extracts the ion current intensities from each spectrum in the total ionization chromatogram at a specific mass which is characteristic of a compound or class of compounds. These intensities are then plotted as relative ion current intensity versus spectrum number. The limited mass search can then be compared to the total ionization chromatogram to determine which peak(s) is (are) a particular compound or class of compounds. Such as example is shown in Figure 23. The top chromatogram is a total ionization chromatogram of a water extract. The bottom chromatogram is a limited mass search at m/e 149. Almost all phthalate esters have a characteristic base peak at an m/e of 149. The phthalate esters are now conveniently marked, and each specific ester can be identified

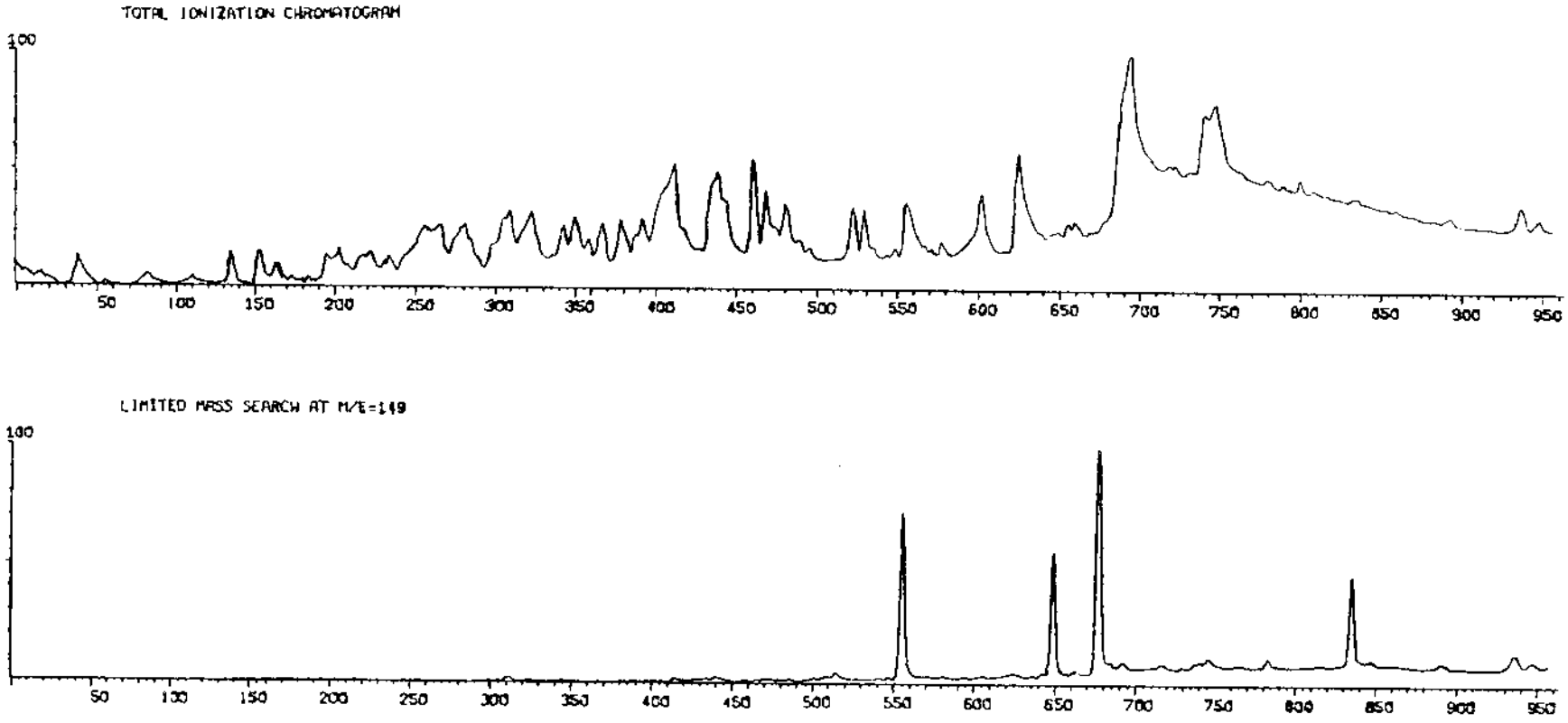

Fig. 23--Total ionization chromatogram (above) and limited mass search for phthalates (below).

by the fragmentation pattern produced at the masses above 149. Thus, comparison of the chromatograms facilitates the location and identification of the phthalate esters.

This technique has become common during the past several years. Recent literature cites examples of its application to determine phthalate esters (9), polynuclear aromatic hydrocarbons (10), mononuclear aryl hydrocarbons (11), and many others. Another important application of this technique has recently been reported to determine the location of chlorinated organics in water extracts (12). The ion with m/e of 35 was used. The mass is specific for chlorine. It is unlikely that any other elemental combination with an m/e of 35 would form. Unfortunately, not all chlorinated compounds produce this fragment (i.e., some chloroaromatics). Figure 24 shows an example of such an application. Chromatogram 2A is the total ionization chromatogram for a superchlorinated wastewater extract; chromatogram 2B shows the limited mass search at m/e of 35. The peaks shown in the limited mass search chromatogram show a high correlation with the presence of chlorinated organics in the total ionization chromatogram.

Other methods are also useful in detecting chlorinated compounds in gas chromatographic effluents. Glaze (13) used the Coulson electrolytic conductivity detector to determine chlorinated compounds in superchlorinated

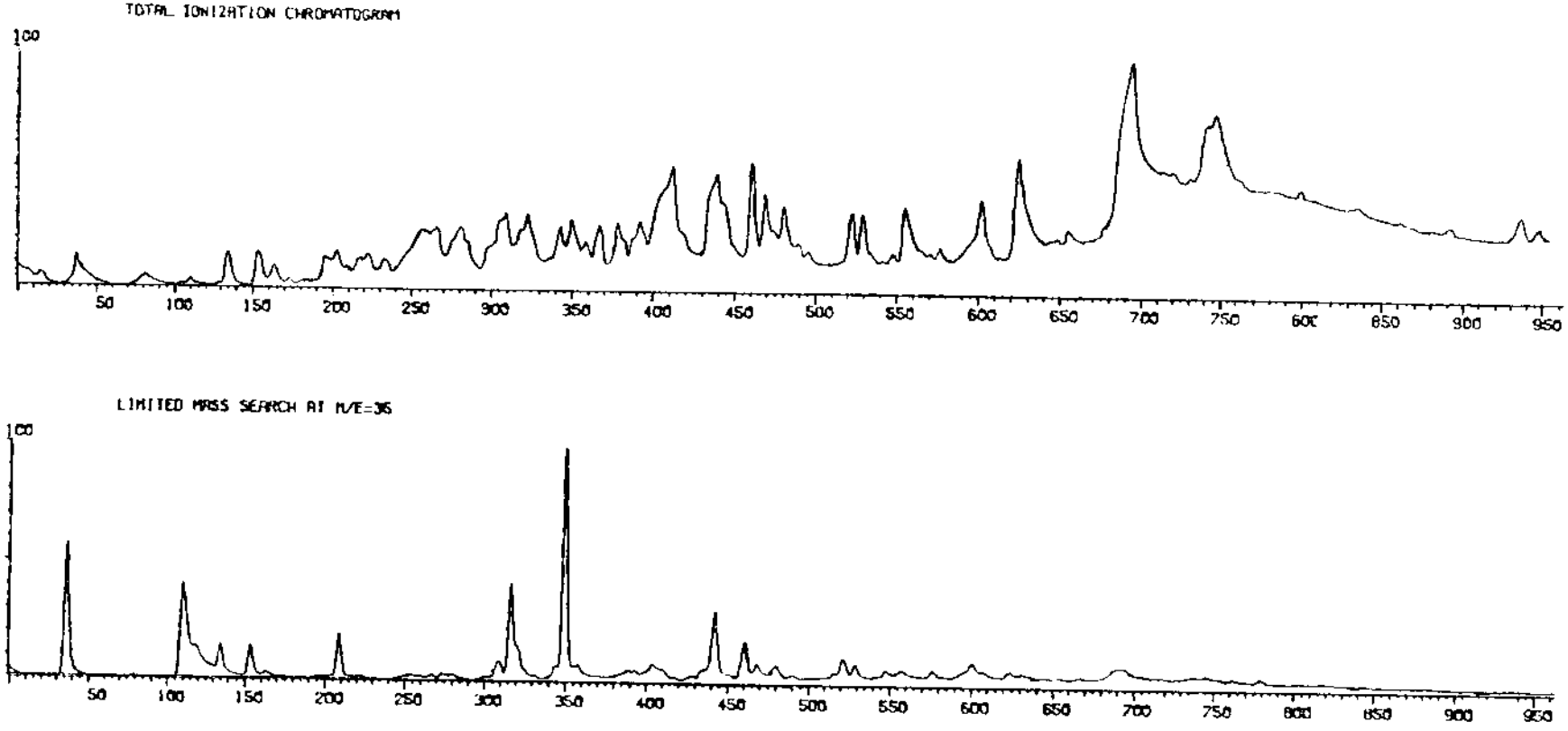

Fig. 24--Total ionization chromatogram (above) and limited mass search for chlorinated organics (below).

wastewater extracts. Giger (14) used an electron capture detector to indicate the presence of newly-formed chlorinated organics in chlorinated lakewater versus raw lakewater. Both of these detectors suffer to some extent from a tendency to respond to interferences such as sulfur-containing compounds and from unfavorable reactions to temperature programming in gas chromatography. Both specialized detectors also lack the ability to distinguish the number of chlorines which a chlorinated compound possesses, or to provide molecular structure information on the components of the chromatogram.

This chapter describes a new GC/MS/DS computer program which manipulates acquired and stored data to produce a limited cluster search. The resulting limited cluster search chromatogram indicates the peaks in a total ionization chromatogram which possess a specific number of chlorines and/or bromines. The program is similar to limited mass search programs in that it extracts specific information from each and every mass spectrum in a total ionization chromatogram. This information can then be plotted on a relative basis versus spectrum number for comparison with the total ionization chromatogram. Peaks appearing in the limited cluster search chromatogram have a high probability of containing a given number of chlorine and/or bromine atoms.

As Aston (3) recognized in 1920, chlorine contains a mixture of isotopes with masses, respectively, of 35 and 37 which occur naturally in a ratio of approximately 3 to 1 (^{35}Cl to ^{37}Cl). This is reflected in the mass spectra of such compounds. An ion possessing a chlorine atom will produce two peaks at masses X and X + 2 corresponding to the respective milecular weights of the ions with the Cl and Cl atoms. The ratio of the X to X + 2 peaks will be approximately 3 to 1. An ion possessing more than one chlorine atom will produce a cluster of peaks. The number of peaks in the cluster will be n + 1, where n is the number of chlorine atoms. The intensities of each peak in the cluster can be calculated by expanding the simple binomial expression $(3 + 1)^n$. Tables have been published (15) which show the relative ion intensities of the peaks in clusters for varying numbers of chlorine atoms.

Bromine is also a mixture of isotopes with masses of 79 and 81, respectively. The naturally occurring ratio for these masses is approximately 1:1. Tables for the clusters of fragments containing multiple bromine atoms are calculated in an analogous manner to chlorine clusters and have been published (15).

Ion fragments containing mixtures of bromine and chlorine atoms also can be calculated, and the resulting tables have been published (15).

The limited cluster search program searches a predetermined range of masses for the appropriate isotopic cluster. An important characteristic of this program is that it is not mass specific, that is, the recognition of a chlorinated or brominated compound does not require that the isotope cluster occur at specific masses in the mass spectrum. This means that a compound can possess a wide variety of additional functional moieties and still be recognized as containing chlorine and/or bromine. And, an absolute minimum of information is required to identify a chlorinated or brominated compound.

Many sophisticated computer programs have been written to perform mass spectral interpretation. They can be divided into three categories: (1) file research; (2) learning machine; and (3) artificial intelligence.

The file research computer programs (16) comprise the simplest approach whereby the unknown spectrum is compared against every spectrum in the reference library. The closest fits are then singled out based on predetermined criteria which indicate the library spectra that most closely resemble the unknown spectrum.

Learning machine programs (17) are often used to determine if an unknown compound is a member of a specific class of compounds. Two average training spectra are usually calculated based on what is called a training set

of known library spectra. One average training spectrum represents the average of the library spectra of compounds belonging to the specific class. The other average training spectrum is an average of the library spectra of compounds not belonging to the specific class. The determination is made by comparing the unknown spectrum with the two average training spectra. Unfortunately, this technique requires that the common characteristics of the specific class occur at the same masses for all spectra in the class. Otherwise, the distinguishing information tends to be averaged out of the average training spectrum of the compounds belonging to the specific class.

Artificial intelligence programs (18) interpret spectra in an analogous fashion to human interpretation. Fragmentation rules as previously observed and used by the spectroscopist are preprogrammed into the computer. The computer then tries to apply these rules to the unknown spectrum to determine the structure.

Although all of the above computerized spectral interpretation techniques have enjoyed varying degrees of success, none of them lend themselves well to interpreting raw GC/MS data, and none of them will identify specific isotopic halogen clusters regardless of mass.

Two papers have been published recently which describe computer programs that can identify chlorinated and/or

brominated isotopic clusters regardless of mass. McLaffery has extended his probability-based matching program (19) for this purpose. His goal is to identify the number of chlorines and/or bromines in a compound from the ratios in the molecular ion cluster. The program starts at the highest mass of the mass spectrum and works backward until it recognizes the molecular ion cluster. Then it compares that cluster to 36 theoretical isotope clusters. The theoretical isotope cluster which most closely resembles the molecular ion cluster should indicate the number of chlorines and/or bromines in the compound. His computer program in its present state is designed to be applied to individual spectra of relatively high quality. For GC/MS data, the appropriate background spectrum should be subtracted from the spectrum of interest before it is subjected to computer analysis. And, since there is no quantitative measure of the ion clusters, the program could not be easily adapted to produce a chromatographic profile showing relative peak intensities.

Regnier (20) has published the description of a computer program which does produce a chromatographic profile of the chlorinated and/or brominated compounds in a GC/MS data set. However, his goal was to use the relative heights for corresponding peaks in the different profile as a new identification technique. The relationship

between these peak heights tends to be specific for a particular compound. It should be noted that the goal of the limited cluster search computer program described in this chapter is to improve the ability of the analyst to find mass spectra of chlorinated and/or brominated compounds produced from the GC/MS analysis of matrices. Regnier has never reported the application of his computer program to such a sample, for such a purpose. In fact, the examples he uses in his report would not adequately test the ability of his program to process data in a complicated matrix which contains many interfering non-chlorinated compounds. The most complex samples which they analyzed were polychlorinated biphenyl mixtures. Although these samples produce a complex chromatogram, the individual peaks are closely related analogues of each other. This means that the fragmentation process for the different analogues will be very similar, and the spectra of overlapping GC peaks will tend to reinforce the isotopic clusters as opposed to interfering with them.

Experimental

Sample Analysis

All samples were analyzed on a Finnigan 3200 Gas Chromatograph/Mass Spectrometer System (Finnigan Instruments Corporation, Sunnyvale, California). During data

acquisition the GC/MS system was under the control of a Finnigan 6100 Data System. At the heart of the 6100 system is the Computer Automation Industries (Sunnyvale, California) 16 bit minicomputer with 8K of memory. The system acquired sequential mass spectral scans of the GC effluent once every four seconds. The data can then be recalled from disk storage and plotted as intensity (ordinate) versus scan number (abscissa). This plot, called the total ionization chromatogram, is analogous to the strip chart recording of the conventional gas chromatogram where the detector response (ordinate) is plotted against elapsed time (abscissa).

Two samples were run for demonstration of the new computer program. The first sample, HALSTI, was an artificial mixture of halogenated compounds and nonhalogenated normal alkanes. The names and sources of the compounds are listed in Table XIII. The sample was prepared by adding

TABLE XIII

NAMES AND SOURCES OF COMPOUNDS IN STANDARD MIXTURE

Compound	Source
Bromoform	Fisher, Certified Grade
N-Dodecane	Fisher, Certified Grade
1,3-Dichlorobenzene	Mallinckrodt, 98%
1,2,4-Trichlorobenzene	J. T. Baker, Practical Grade
1,3-Dibromobenzene	Fisher, Practical Grade
Hexachlorobutadiene	MCB, Practical Grade
N-Tetradecane	Fisher, Reagent Grade

approximately 250 microliters of each compound to 2 milliliters of acetone. Of this mixture, 0.5 microliter aliquots were then injected into the GC/MS for analysis. This sample was used to study the decision parameters in the computer program.

The second sample, CALCLI, was an XAD-2 extract of California Purifaxed wastewater as described in Chapter II. The ether eluant was concentrated to approximately 100 microliters, and a 2.5 microliter aliquot of that concentrate was injected into the GC/MS system. Only a portion of this total ionization chromatogram (scans 290 through 510) was processed by the computer program. The first spectrum of this data was selected prior to the dichlorobenzene peaks which were known to be present. The last spectrum was arbitrarily selected so that enough data would be processed to accurately reflect the ability of the program to extract important information. The entire RGC was not processed because of the computer central processing unit time limitations. The evaluation of each spectrum required about 0.75 minutes of computer time. Thus, for the limited data selected, each complete computer run took almost 2.5 hours.

The GC/MS data was transferred to Finnigan magnetic tape cassettes for long-term storage and transportation to

the computer system described below for the actual computer processing.

Computer Program

The limited cluster search computer program was originally written in BASIC computer language on the North Texas State University Hewlett-Packard 200 timeshare system. This system could not access the Finnigan GC/MS data directly, but program debugging could be affected by manually inputting masses and intensities for single spectra.

Once the program was debugged, it was transferred to a more powerful Finnigan 6100 computer system located at the University of Texas Health Science Center, Houston, Texas. This system possessed the Finnigan BASIC interpretor which required a total of 16K of CPU core. The system could execute the BASIC program and directly access the previously acquired GC/MS data. The program is shown in Appendix C.

Computer Hardware

The program is initiated by a pushbutton on the front panel of the computer system which activates the BASIC interpretor. Then the program instruction statements are ready to be entered manually via teletype or to be read in from magnetic tape storage. The GC/MS data must be stored on disk because spectra can only be retrieved from disk.

GC/MS data which has been previously stored on magnetic tape must be read onto the disk prior to program execution. Tabular limited cluster search data is output after each spectrum is processed. Once all the spectra have been processed, a command can be entered which returns the system to the assembler-controlled mode deactivating the BASIC interpretor. This process automatically transfers any computed chromatogram or mass spectrum onto the front panel display. Using the assembler, the limited cluster search data can be manipulated and plotted as though it were data which had been acquired in a conventional manner directly from the mass spectrometer.

Results and Discussion

Figure 25 shows a program flowchart which highlights the important features of the limited cluster search program. Each of these features is discussed in the sections below.

Calculation of Isotope Cluster

Figure 26 shows the typical computer/programmer dialogue and data output of the program. The program parameters which are underlined are input by the programmer in response to computer queries, and the tabular data are output below. These data include the mass data output and the spectral data output.

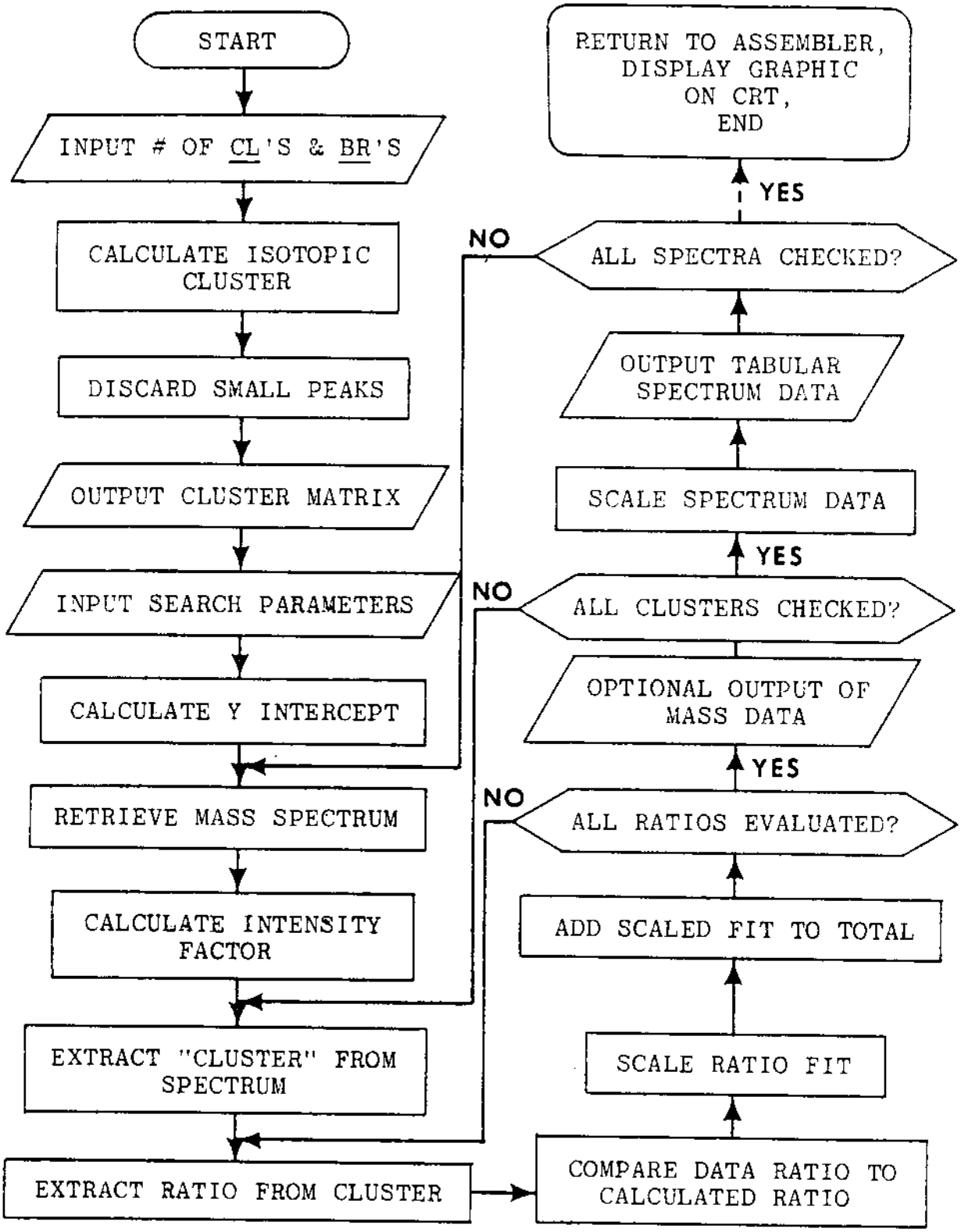

Fig. 25--Flowchart of limited cluster search algorithm

```
INPUT CL's THEN BR's
?2
?2

CL = 2  BR = 2
ISOTOPIC CLUSTER LISTING
A (1) = 100
A (2) = 64.7954
A (3) = 10.4961

INPUT LOWEST AND HIGHEST MASSES THEN-
FIRST AND LAST SPECTRA TO BE SEARCHED
?35
?160
?93
?93
BASELINE NOISE FILTER PER CENT
?7
INPUT PRECISION ESTIMATE
?2
INPUT VARIATION ESTIMATE
?-25

MASS= 35        CUMULATIVE FIT  =  0
MASS= 39        CUMULATIVE FIT  =  0.429949
MASS= 41        CUMULATIVE FIT  =  0.859898
MASS= 46        CUMULATIVE FIT  =  1.77292
MASS= 48        CUMULATIVE FIT  =  2.68595
MASS= 53        CUMULATIVE FIT  =  3.08933
MASS= 55        CUMULATIVE FIT  =  3.49272
MASS= 69        CUMULATIVE FIT  =  4.04368
MASS= 70        CUMULATIVE FIT  =  4.89866
MASS= 71        CUMULATIVE FIT  =  6.64601
MASS= 72        CUMULATIVE FIT  =  7.95617
MASS= 73        CUMULATIVE FIT  =  9.70351
MASS= 107       CUMULATIVE FIT  =  12.1219
MASS= 109       CUMULATIVE FIT  =  14.5402
MASS= 111       CUMULATIVE FIT  =  16.9585
MASS= 142       CUMULATIVE FIT  =  21.9585
MASS= 143       CUMULATIVE FIT  =  22.3255
MASS= 144       CUMULATIVE FIT  =  27.3255
MASS= 145       CUMULATIVE FIT  =  27.6925
MASS= 146       CUMULATIVE FIT  =  37.6925
MASS= 147       CUMULATIVE FIT  =  38.4265
SPECTRUM  = 93    CUMULATIVE FIT = 38.4265

    WEIGHTED FIT = 17746.9
```

Fig. 26--Computer program/operator dialogue

The program begins by requesting the number of chlorine and bromine atoms for which the data will be searched. A total of 20 atoms in any combination can be input. Then the program calculates the relative peak heights for the cluster and outputs them as percentages with the base peak of the cluster being assigned 100 percent.

The program uses two constants, 3.08664 for chlorine and 1.02041 for bromine, which represent the natural abundances for ^{35}Cl relative to ^{37}Cl and ^{79}Br relative to ^{81}Br, respectively. These constants produce isotope peak percentages which are in agreement with the U.S. Environmental Protection Agency mass spectral tables (21) to two decimal places. Either constant can be changed by altering the corresponding equality instruction statement in the program.

Isotope peaks which have an intensity less than 7 percent relative to the base peak of the cluster are discarded. This is done in an effort to avoid possible mismatches based on the possibility of not finding peaks of relatively low intensity.

Search Parameters

The following are input consecutively in response to computer queries: first and last masses; first and last spectra; baseline noise, percent; precision estimate;

variation estimate. The first and last masses define the spread of masses to be examined in each spectrum. The same masses must be examined for all spectra in a given run, but not all masses which were acquired in a GC/MS run must be examined. The first mass selected was usually the mass of the smallest probable fragment for a given cluster. Thus, for a two-chlorine search, the smallest probable fragment was $(CCl_2)^+$ at an m/e of 82.

The baseline noise parameter eliminated some computer calculations of trivial data. This was done by not comparing a data cluster to the calculated cluster if the intensity of the base peak for that data cluster was below the baseline noise percent parameter relative to the base peak of the partial spectrum as defined by the first and last mass search spectrum. A baseline noise percentage of 7 percent was empirically selected for all the data shown below.

The precision and variation estimation parameters are involved in the decision process of determining whether a data cluster is that of a chlorine- and/or bromine-containing fragment. That process is described below.

Decision Process

A chart describing the flow of the GC/MS data as it is processed by the limited cluster search computer program is

shown in Figure 27. Once the search parameters have been input, the program retrieves the first spectrum to be examined from the data file. Then, the first data cluster to be examined is extracted from that spectrum beginning at the first mass search parameter. The total number of peaks in the data cluster is equal to the total number of isotope peaks in the calculated cluster.

The comparison of the calculated cluster with the data cluster is a three step process. First, the difference between the two clusters, the Z-value, is calculated. Then, the Z-value is scaled to produce the cumulative fit. The scaling process accomplishes two objectives. It introduces two independent parameters into the calculations which allows the Z-value to be empirically optimized. And, it allows the establishment of a directly proportional relationship between the data and the numerical description of that data, the cumulative fit.

Once the cumulative fit has been calculated, other necessary factors are applied to produce the weighted fit. This is the actual value that is plotted against the spectrum numbers in the LCS chromatogram.

Z-value.--The Z-value is the absolute numerical difference between the ratio of the peak heights of two adjacent peaks in the data cluster versus two corresponding peaks in the calculated cluster. It is formulated as:

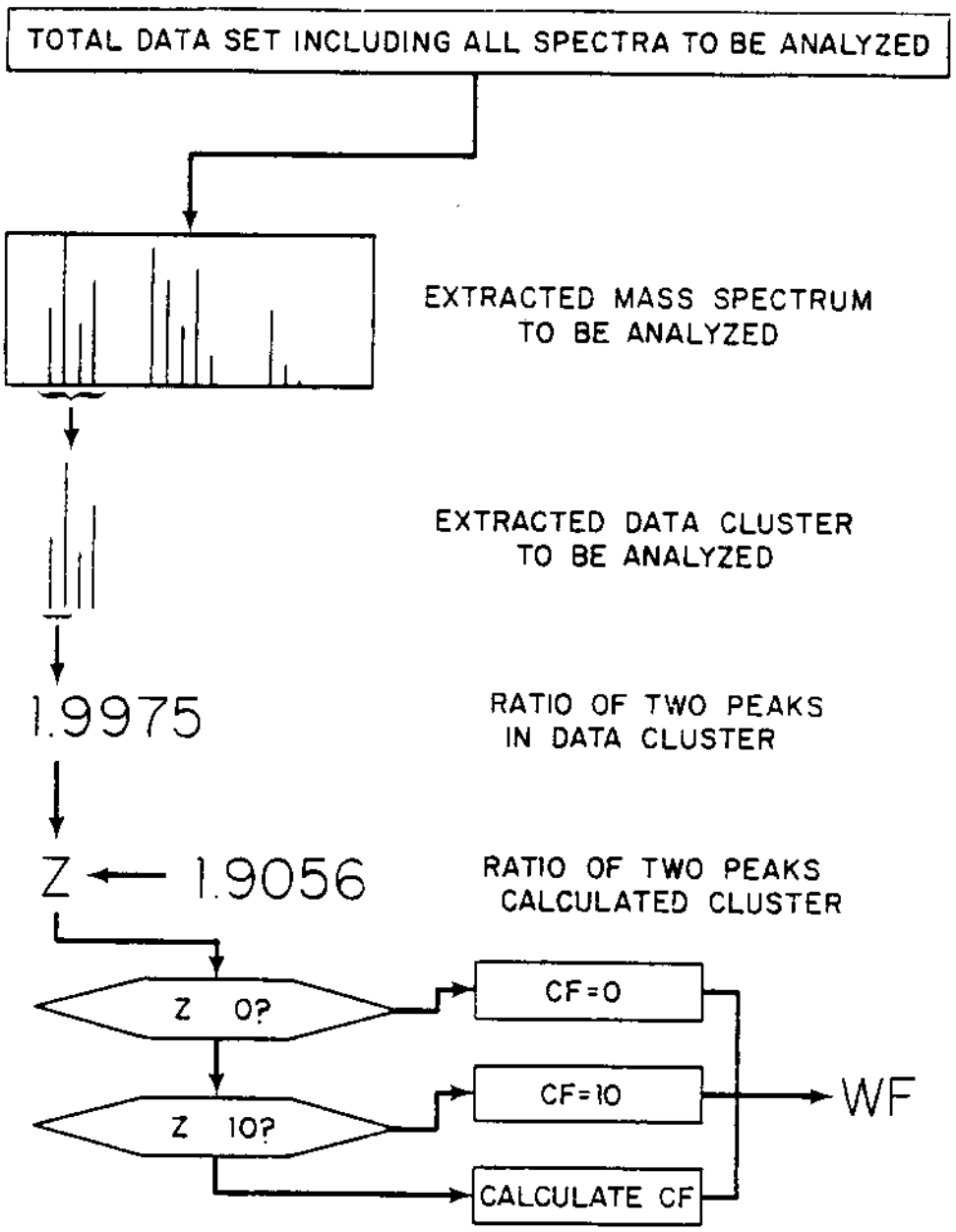

Fig. 27--Schematic diagram of the GC/MS data reduction process.

$$Z = |C_X/C_{X+2} - D_X/D_{X+2}|$$

where C is the ion intensity of a peak in the calculated cluster at mass X or X+2, respectively, and D is the ion intensity of a peak in the data cluster at mass X or X+2, respectively. As the relative data cluster peak heights approach the relative peak heights of the calculated cluster, the Z-value approaches zero indicating a high probability that the data cluster contains the same number of chlorines and/or bromines as the calculated cluster. Note that this formula compares the peak heights of only two adjacent peaks at a time. Therefore, n-1 Z-values will be generated for each total cluster examination where n is the number of peaks in the cluster. If the calculated cluster were derived from two chlorine atoms, for example, the cluster would contain three isotope peaks, and two Z-values would be produced. This is important in analyzing raw data as shown below.

An example of the relationship between the Z-value and a data peak ratio is shown in Figure 28. This example refers to the first Z-value generated for a dichlorinated isotopic cluster. In such a calculated cluster, the relative peak heights of the X and X+2 peaks are 100 percent and 64.7954 percent, respectively. The X-axis in Figure 28 shows the percent deviation of the X+2 peak in the data cluster from that perfect relative peak height as defined

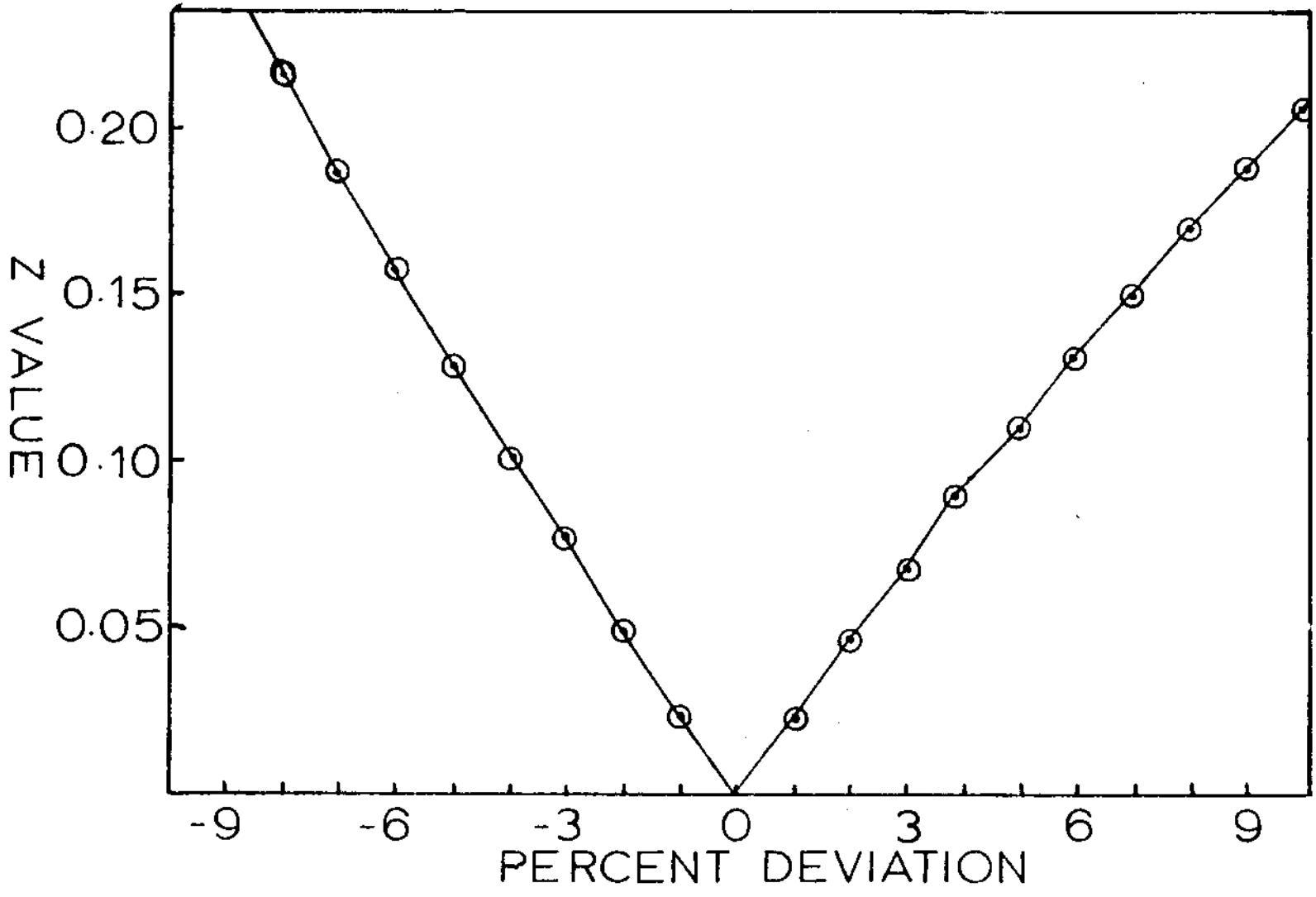

Fig. 28--Relationship between the Z-value and the ratio of the two mass spectral peaks.

in the calculated cluster (64.7964 percent). This can be calculated as

$$Z = 100.0/64.7954 - 100/(65.7954 \pm \% \text{ deviation}) .$$

Thus, if the mass spectrometer recorded the D_{X+2} peak in the data cluster with a relative intensity of 62.7954 percent, the percent deviation would be -2.0, and the corresponding Z-value would be 0.049.

Cumulative Fit.--The scaling procedure which converts the Z-value to the cumulative fit is itself a three step process as indicated in Figure 27. Initially, the cumulative fit is calculated according to the formula

$$CF = VZ + C$$

where CF is the cumulative fit, V is the variation estimate parameter, and C is a dependent variable which is a function of both the precision estimate and the variation estimate parameters. As indicated in Figure 29, the cumulative fit has a range of 0.0 to 10.0. The 10.0 cumulative fit value indicates a perfect fit between the data cluster and the calculated cluster. Note that this value corresponds to some Z-value which is always greater than zero and is defined by the precision estimate as described below. The 0.0 cumulative fit value indicates the fit between the data cluster ratio and the calculated cluster ratio are so poor that there is virtually no probability

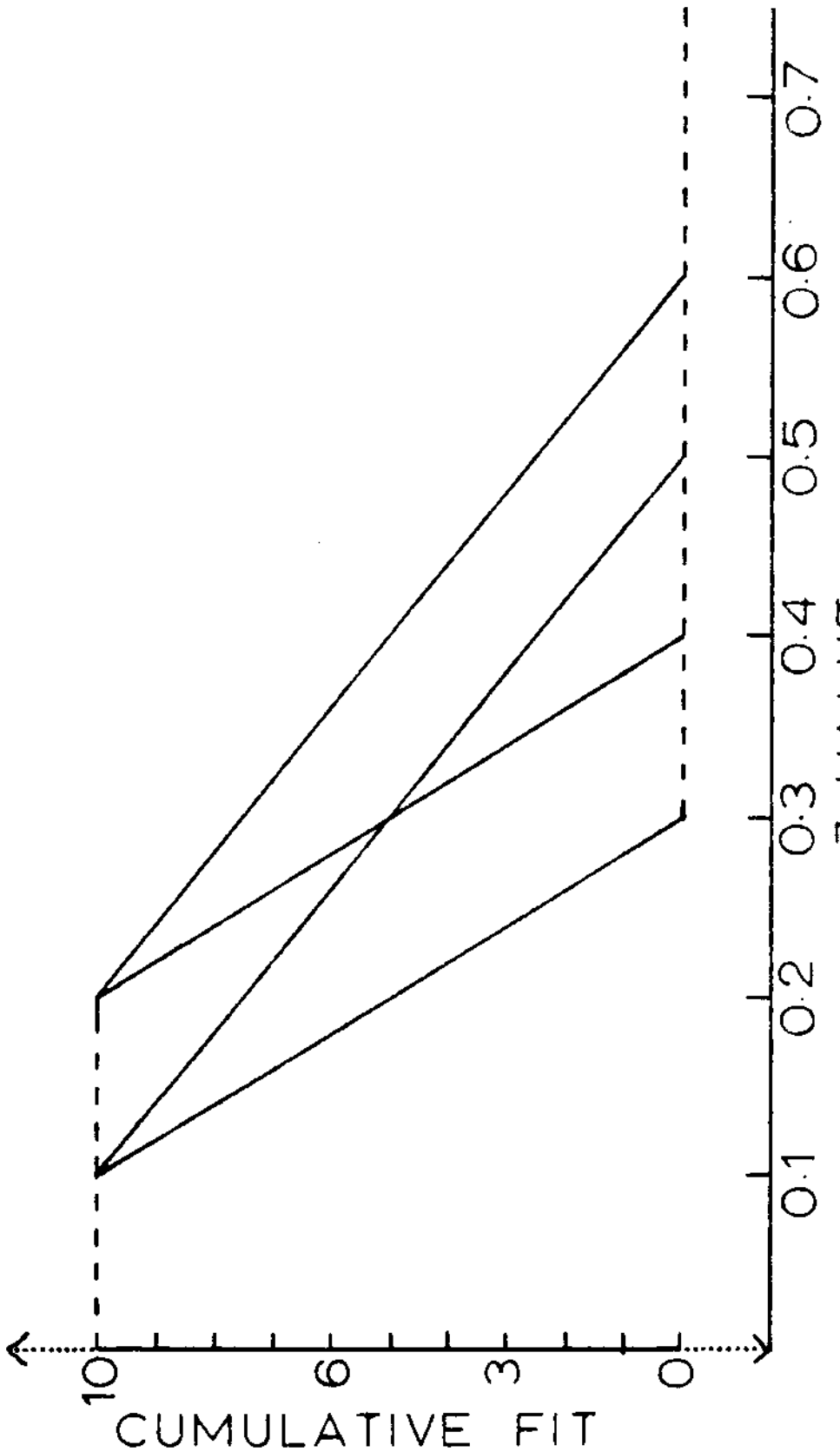

Fig. 29--Relationship between the cumulative fit and the Z-value

that the data cluster could represent an ion fragment which contains the proper number of chlorines and/or bromines. Fits can be worse than this and generate negative cumulative fits. However, since the probability of a fit can be no worse than zero, the lowest rational cumulative fit value is 0.0, and the negative values are adjust to that value.

The precision estimate parameter.--The precision estitime parameter reflects the spread of values (precision) which the mass spectrometer produces when the same species is analyzed repeatedly. This spread, resulting from natural instrumental variability, can be greater than ±10 percent (19).

Within this spread no reliable distinction can be made between a match and a mismatch. Therefore, the precision estimate defines the maximum Z-value below which improvements in fits cannot be distinguished. Cumulative fit values which are greater than the 10.0 perfect fit are automatically reset to the perfect fit value.

The variation estimate parameter.--The variation estimate parameter adjusts for the other primary contributions to the variation of the relative data peak heights from the theoretical values. This deviation has several sources. They all result in the unequal spurious

contribution of ion intensity to peaks in the data cluster. These unequal contributions cause distortions in the Z-values, and consequently in the cumulative fits. Instrument background and chromatographic column bleed are primary sources of this effect. Contributions from non-halogen atoms can also cause distortions. Atoms such as oxygen, silicon, sulfur, and even hydrogen can contribute to the distortion of X+2 peak heights due to significant contributions of the X+1 and X+2 isotopes of these atoms. This effect is more pronounced in fragments which occur at higher m/e values. Therefore, a provision was made in the program which allows for a partial fit that indicates some, though less than certain, probability that the data cluster contains the appropriate number of chlorines and/or bromines. The partial fit region of Figure 29 shows the line which relates the cumulative fits partial fits to the corresponding Z-values. Note that the variation estimate parameter controls that relationship since it is the slope of that line. As the variation estimate parameter becomes a larger negative number, the decision process approaches a yes/no system. In such a system, the decision depends only on the value of the precision estimate; below this value a perfect fit is indicated, and above this value a perfect miss, no probability of a fit, is indicated. Such a system has a high risk of misinterpreting data which

happens to fall close to the decision boundary. Examples of such data will be seen later.

Both the precision estimate and the variation estimate parameters were empirically optimized using the HALSTI data set. The optimum combination was then used to process the CALCLI data set.

Other Scaling Factors

Three other scaling factors are required in this program including the halogen number factor, the cluster intensity factor, and the spectral intensity factor.

The halogen number factor.--For each complete cluster analysis, n-1 comulative fits are generated where n is the number of peaks in the calculated cluster. Since the total cumulative fit for a perfect match between the calculated cluster and the data cluster has been defined as 10.0, the cumulative fit for each ratio within a given cluster must be divided by (n-1), the halogen number factor, in order that each cumulative fit contributes the appropriate fractional amount to the total cumulative fit for the cluster. If a calculated cluster contains three peaks, as it would in a limited cluster search for two chlorines, two cumulative fits would be generated for each cluster analysis. Therefore, each cumulative fit must contribute 5.0, 10.0/(3-1), to the total cumulative fit for the cluster. This

effect is important in comparing two different limited cluster searches of the same data set. Using this factor, a perfect fit of a limited cluster search for two chlorines would generate the same cumulative fit as would a perfect fit for three chlorines. This is indicated in Figure 30 which shows raw spectra (no background subtracted) from the HALSTI data set. The dichlorobenzene spectrum was searched for ion fragments containing two chlorines. A perfect fit for one dichlorinated ion cluster was detected as indicated by the cumulative fit of 10.0. The trichlorobenzene spectrum was searched for ion fragments containing three chlorines. The cumulative fit of 9.6 indicates a partial fit which is almost equal to one trichlorinated ion fragment. The 0.4 unit error in the cumulative fit is due to the recorded ion intensity of the X+2 peak in the data cluster which begins at m/e 180 (the molecular ion cluster). The relative value for the peak was 92.8 percent versus 97.2 percent for the corresponding peak in the calculated cluster. This -4.4 percent deviation in the relative peak height causes the first two Z-values for the cluster to be outside the precision limits of a perfect fit. Therefore, the cumulative fits for those Z-values will be determined in the partial fit sector of the decision process, and the values of those cumulative fits will be less than the perfect fit of 3.3333, 10.0 (4-1). Note that if the decision

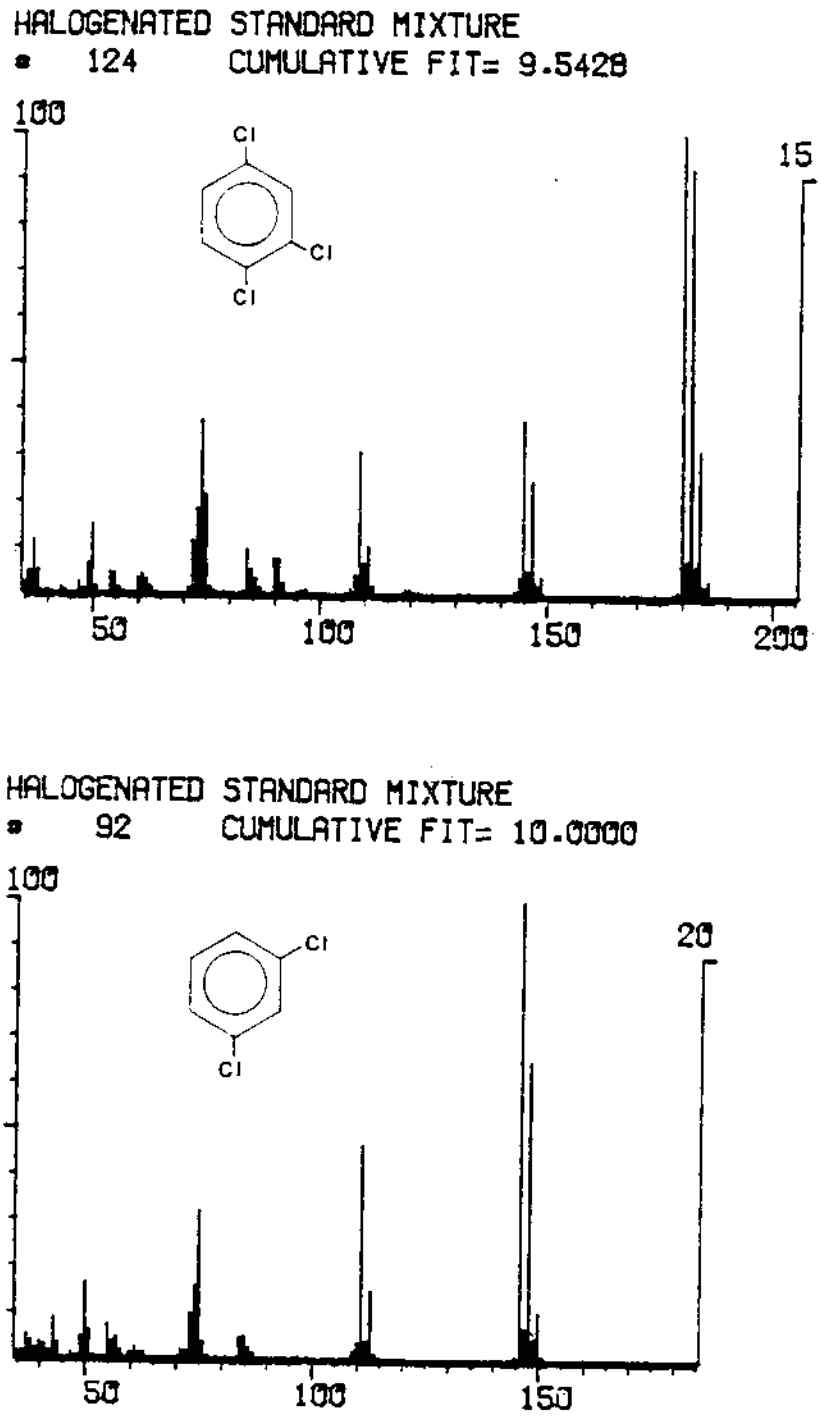

Fig. 30--Cumulative fit values for trichlorobenzene and dichlorobenzene.

process had been a yes/no system, the total cumulative fit for the cluster would have been only 3.3333 because the first two cumulative fits would have been zero.

The cluster intensity factor.--Because of the ability of chlorine and bromine to stabilize a positive charge, ion fragments containing these atoms tend to produce mass spectral clusters with high relative intensities. To take advantage of this observation, the cluster intensity factor was developed. This factor is simply the base peak of the data cluster divided by the base peak of the partial mass spectrum as defined by the first and lass mass input parameters. All newly generated cumulative fits are multiplied by this factor before they are added to the total cumulative fit. This de-emphasizes good fits for clusters containing relatively small peaks. Such clusters often do not contain halogen atoms at all, but rather contain noise-like inconsequential data which coincidentally happen to resemble the calculated cluster. The factor tends to emphasize a good fit for a cluster containing relatively high intensity peaks which is often an accurate indication that the ion fragment does indeed contain the proper number of chlorine and/or bromine atoms. The trichlorobenzene spectrum shown in Figure 30 contains a data cluster which is generated by a dichlorinated ion fragment beginning at m/e 145, $(m-35)^+$. When the spectrum was

searched for two chlorines, a perfect fit was observed beginning at m/e 145, however the base peak of that cluster was only about 38 percent relative to the base peak of the partial spectrum at m/e 180. Therefore, the total cumulative fit was 3.8, 10.0 times 0.38.

The spectral intensity factor.--The mass spectrometer scans the GC effluent once every four seconds. A compound requires about 20 to 40 seconds to elute from the column. Thus, about five to ten scans are made of that analyte as it passes into the mass spectrometer. Although all of these spectra are practically identical, the total ionization chromatogram of that analyte peak has roughly a Gaussian shape. This is because the total ionization chromatogram reflects the absolute intensity of the ion fragments in the mass spectrum as opposed to the relative intensities of the ions. The absolute intensities are proportional to the instantaneous concentration of the analyte in the spectrometer as the scan is being made. The limited cluster search program, however, is a function of the relative ion intensities. Therefore, the cumulative fits of all the spectra acquired during the elution of a GC peak tend to have the same value regardless of the absolute intensity of the ion fragments and the limited cluster search analyte peak shape tends to be rectangular in shape rather than Gaussian.

To achieve the desired Gaussian peak shape, the total cumulative fit for the limited cluster search of the spectrum is multiplied by the spectral intensity factor. This factor is simply 0.01 times the total ion current for the partial spectrum as defined by the first and last mass input parameters. The 0.01 multiplicative factor was selected so that the product of the cumulative fit times the spectral intensity factor will be abouve the same order of magnitude as the total ionization chromatogram. This is important to the computer internally in plotting the limited cluster search data. The product of the cumulative fit times the spectral intensity factor is called the weighted fit. The weighted fit is the actual value which is plotted along the ordinate axis in the limited cluster search chromatogram.

Figure 31 shows the relationship between the total ionization chromatogram, the cumulative fit, and the weighted fit which is the limited cluster search chromatogram. The data set is being searched for dichlorinated compounds. The total ionization chromatogram indicates all of the compounds which eluted from the GC-column including chlorinated and nonchlorinated compounds alike. The limited cluster search chromatogram indicates only those peaks which contain dichlorinated ion fragments. Note the square shape of the cumulative fit chromatographic

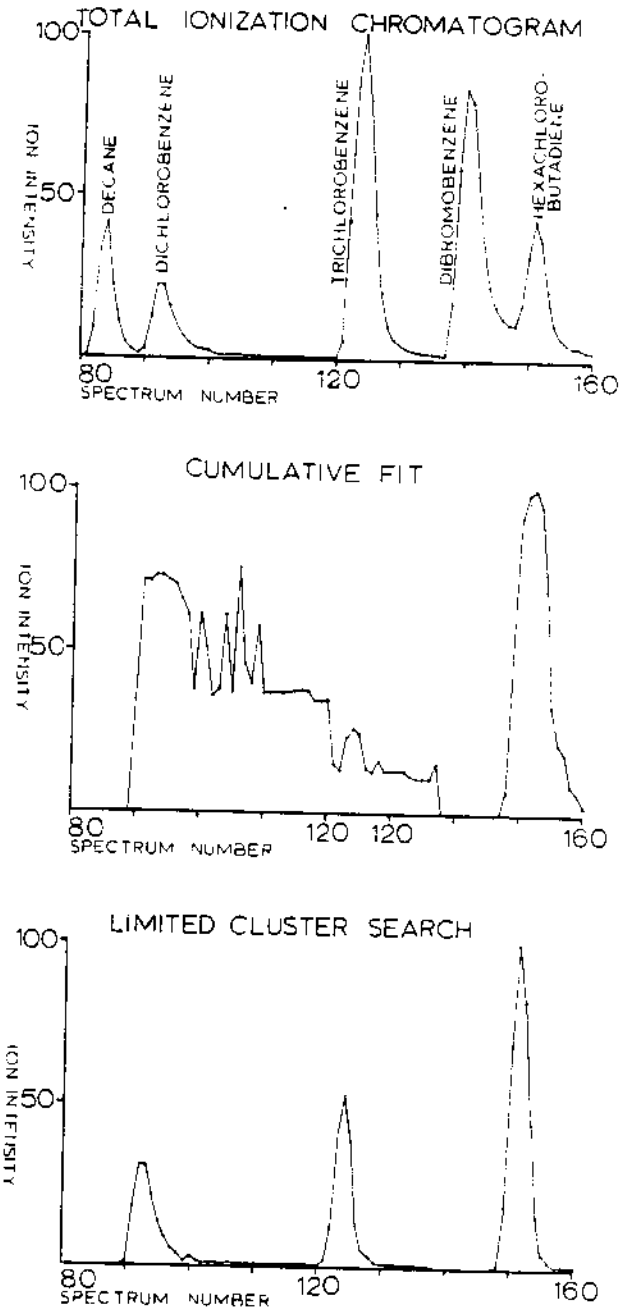

Fig. 31--Relationship between the total ionization chromatogram, the cumulative fit, and the weighted fit (limited cluster search).

peak of the dichlorobenzene peak (spectrum numbers 89 through 99). This is also observed to some extent for the trichlorobenzene peak (spectrum numbers 122 through 127) and the hexachlorobutadiene peak (spectrum numbers 147 through 157).

The noise in the cumulative fit chromatogram between spectrum numbers 100 and 120 is caused by traces of dichlorobenzene which are adsorbed to the ion source housing of the mass spectrometer. As it desorbs, the dichlorobenzene spectrum of low absolute intensity is produced. However, since no other compound elutes at that time, and since the instrument background and chromatographic column bleed are both low, the weak dichlorobenzene spectrum still accounts for the most significant ions in the scans. Therefore, the cumulative fit had a high value because the ion intensities were close to the detection limit of the instrument. When this factor is multiplied by the spectral intensity factor, the resulting weighted fit is quite low as observed in spectrum numbers 100 through 120. This same phenomenon is also observed between spectrum numbers 130 through 138. Note that when the nonchlorinated analyte, n-tetradecane, begins to elute from the chromatographic column at spectrum number 137, the residual adsorbed trichlorobenzene becomes insignificant and the cumulative fit drops to 0. Thus, although the spectral intensity factor

is high, the limited cluster search response is zero because the cumulative fit is zero.

Empirical Optimization of the Search Parameters Using the HALSTI Data Set

A preliminary study of the relationship between the precision estimate parameter and the variation estimate parameter was made in an effort to select starting values for the subsequent empirical optimization study. Spectra from the apices of two GC peaks in the HALSTI data set were used for the preliminary study. The peaks were bromoform, spectrum number 46, and dichlorobenzene, spectrum number 92. Spectra of the raw data (no background subtracted) are shown in Figure 32. Both spectra were subjected to a series of limited cluster searches for dichlorinated ion fragments. The bromoform spectrum shows a dibrominated ion fragment, $(M-Br)^+$, of high relative intensity whose data cluster begins at m/e 171. The X+2 and X+4 peaks of this cluster have a similar relative height relationship as that of the X and X+2 peaks in the calculated cluster. Because of this, bromoform can show a partial fit for the dichlorinated limited cluster search at m/e 173. The value of the cumulative fit will depend on the values of the precision estimate and variation estimate parameters. Such a mismatch, as indicated by a bromoform peak in the limited cluster search chromatogram, should be considered

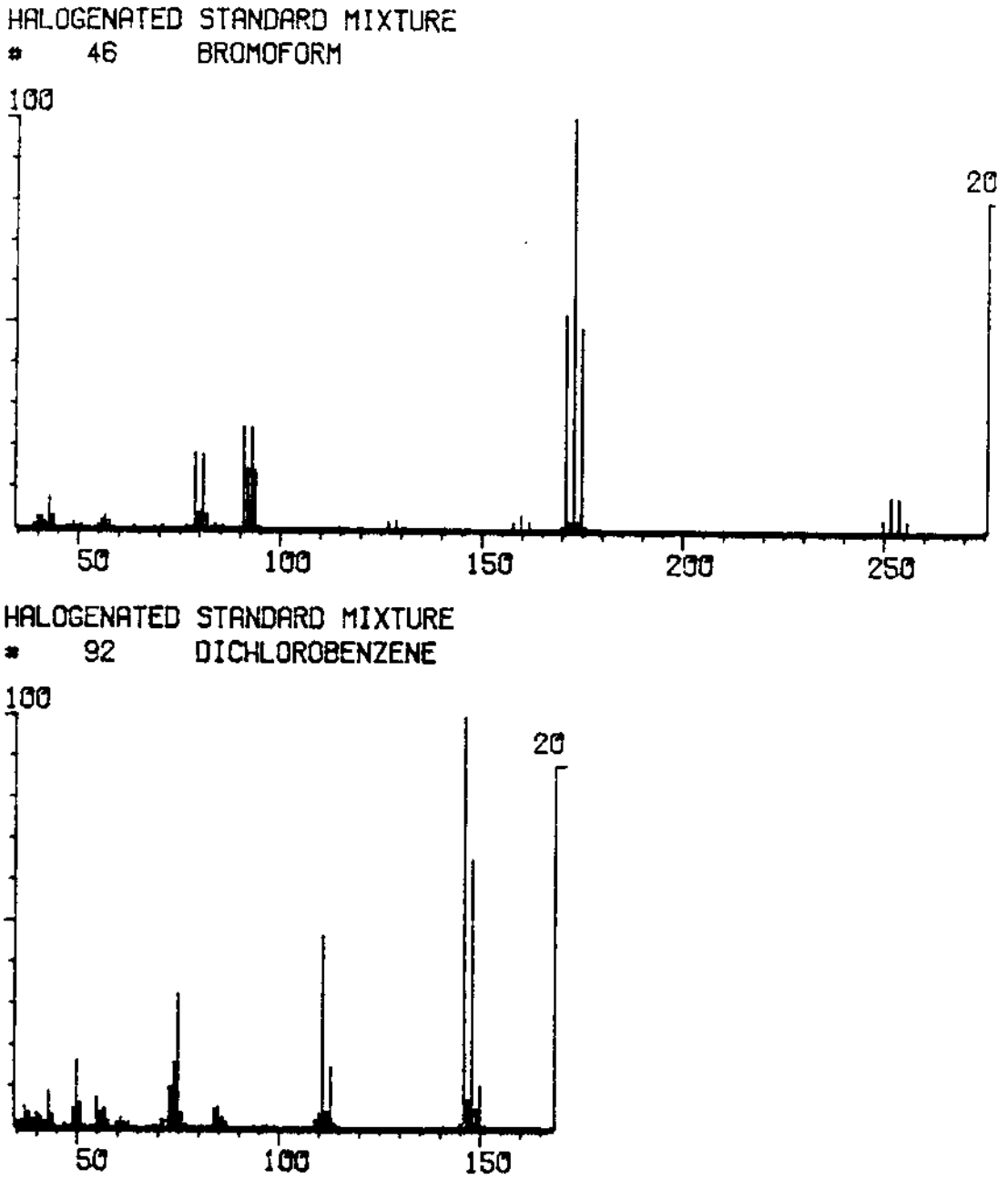

Fig. 32--Bromoform and dichlorobenzene mass spectra used in the study of the relationship between the precision and variation estimate parameters.

an interference. The dichlorobenzene mass spectrum shows the expected intense dichlorinated data cluster beginning at m/e 146, the M^+ cluster.

Figure 33 shows the data from this preliminary study. The study comprised three series of comparative limited cluster searches. Each graph shows the weighted fit versus the precision estimate. A single variation estimate parameter is used in each graph. In all three cases, for low values of the precision estimate parameter where the fit requirements are rigorous, the bromoform spectrum shows a weighted fit of zero. This indicates zero probability of the spectrum containing a dichlorinated data cluster. The dichlorobenzene spectrum shows a constant positive weighted fit indicating a perfect match. As the precision input parameter is increased, the fit requirements are less rigorous, and the computer program begins to indicate incorrectly some probability that the bromoform spectrum contains a dichlorinated data cluster. As the value of the precision estimate parameter is increased further, the value of the weighted fit for the dichlorobenzene spectrum also begins to increase due to the interfering mismatch of the data cluster beginning at m/e 111, an isotopic cluster produced by a monochlorinated ion fragment.

Comparison of the three graphs shows the effect of the variation estimate parameter on the decision process.

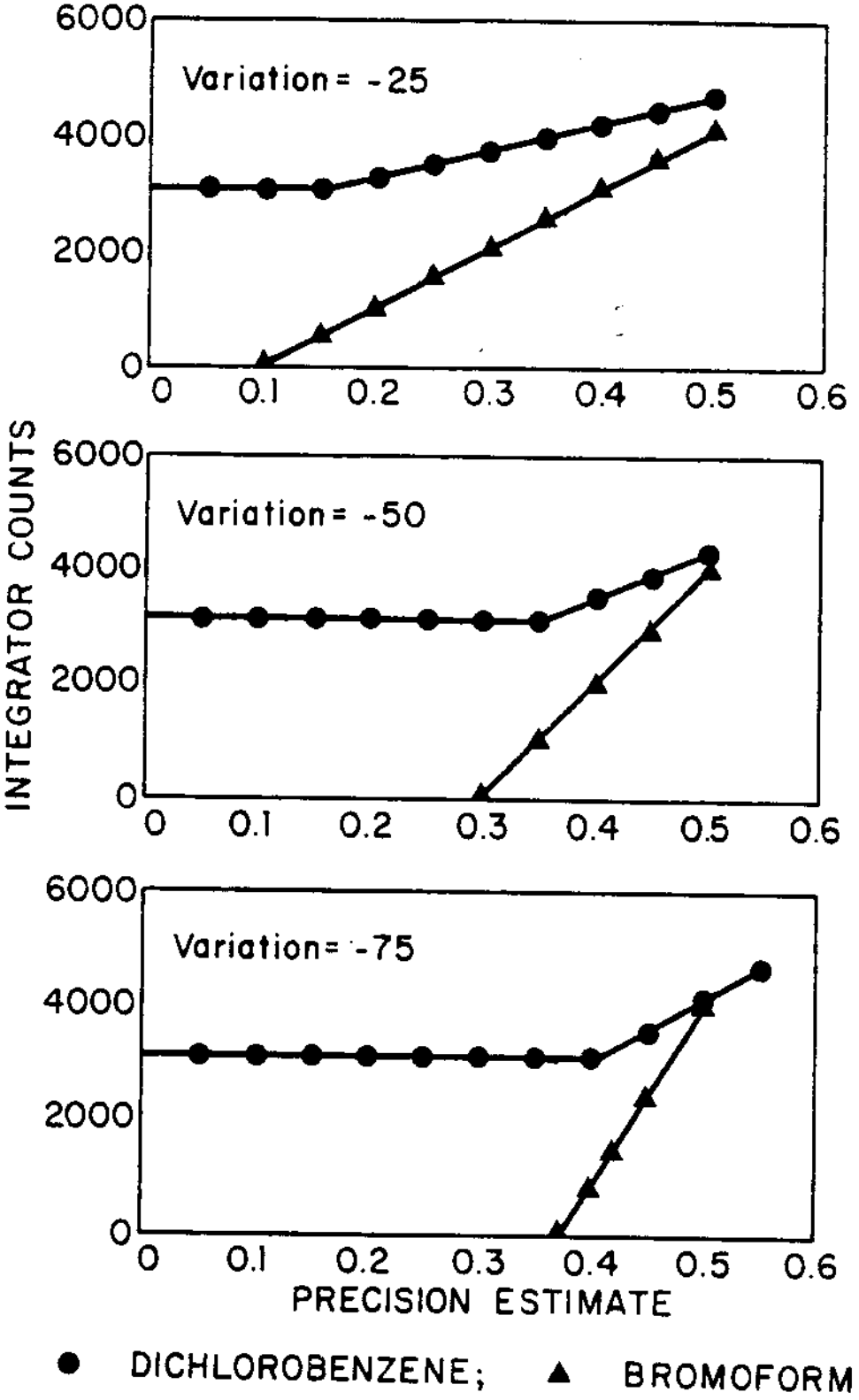

Fig. 33--Weighted fit versus the precision estimate for three variation estimate values.

With a variation estimate parameter value of -25, the precision estimate parameter must be set at a low value (less than 0.01) in order to avoid possible mismatches for the bromoform spectrum. However, for higher precision estimate parameter values at this variation estimate parameter value, the effect of the mismatch is diminished because the system is generally less sensitive to mismatches as indicated by the increasing bromoform interference as indicated by the increasing integrator count value. With a variation estimate parameter of -75, the system is extremely sensitive to mismatches, as indicated by the steep slope of the increasing bromoform interference, but the latitude of the precision parameter before a mismatch is detected is much greater. The graph showing the data with a variation estimate parameter value of -50 appears to indicate a good compromise between sensitivity and precision estimate latitude. This value was therefore selected as the initial variation estimate parameter. It was compared to the value of -25 in an effort to avoid the extreme sensitivity observed with the high variation estimate parameter value.

The initial precision estimate parameters were selected based on a second preliminary study which was an investigation of the precision of the mass spectrometer. A series of ten 100 nanogram injections of dichlorobenzene

were made. The percent deviation of the relative height of the $(M+2)^+$ ion at m/e 148 was compared against the 64.7954 percent relative height of the X+2 peak in the calculated cluster. The data values ranged from 62.11 percent to 65.69 percent corresponding to deviations of -2.69 percent and 0.89 percent, respectively. The Z-values for these deviations were 0.067 and 0.021 (note that both positive and negative percent deviations produce positive Z-values). Since this sample was analyzed under ideal conditions, the minimum Z-value selected for use as the initial precision estimate parameter was 0.1, approximately twice the average of the Z-value deviations observed in the preliminary study. A value of 0.2, twice the minimum value, was used for comparison.

Figure 34 shows the total ionization chromatogram and the limited cluster search for the entire HALSTI data set. The four possible combinations of the two precision estimate parameters and the two variation estimate parameters were used. Chromatograms 34-B and 34-C show the limited cluster searches using a variation estimate parameter of -25. No interference is observed in either chromatogram from the normal alkanes in the data set. Some interference is observed from the dibrominate compounds demonstrating the lack of adequate discrimination ability associated with the variation estimate parameter value. However, the

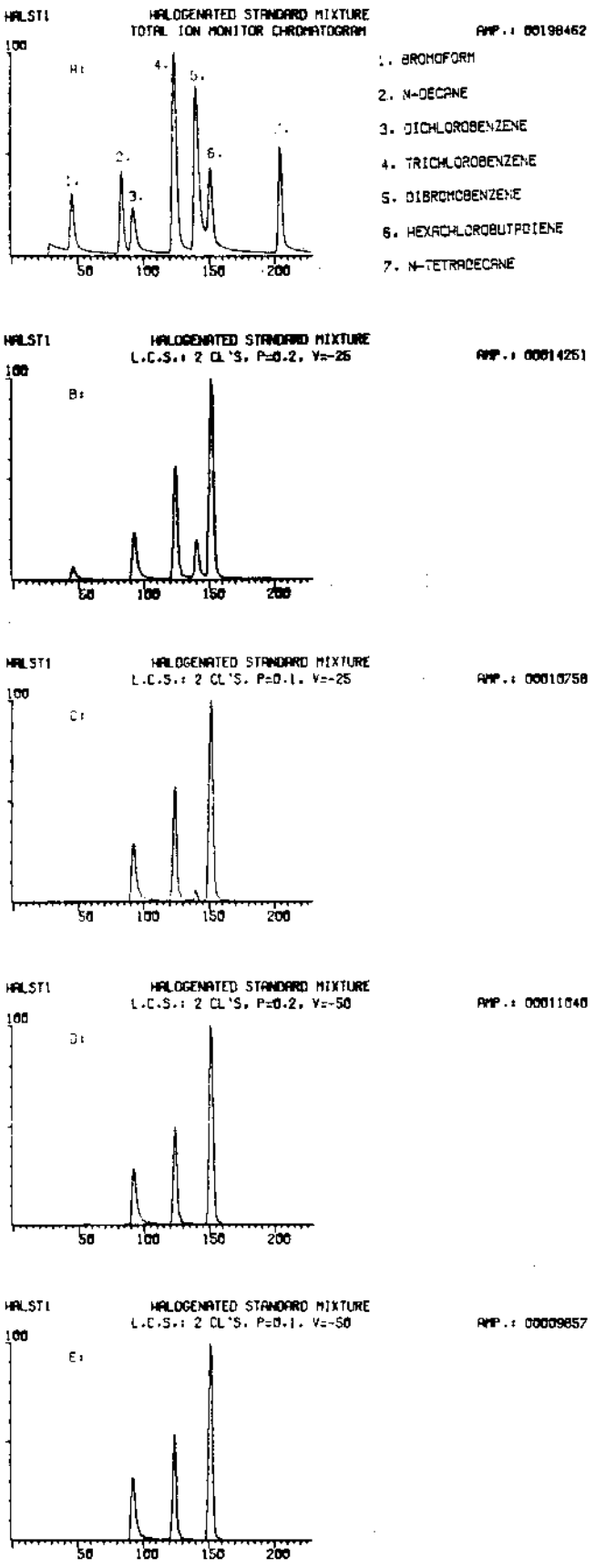

Fig. 34--Total ionization chromatogram and limited cluster searches for the HALST1 data set.

decreased peak heights of the interfering analytes relative to the height of the peaks which contain dichlorinated data clusters indicate the decreased sensitivity of the system to the interferences.

Chromatograms 34-D and 34-E show the limited cluster searches using a variation estimate parameter of -50. In these chromatograms, no interference is observed from the normal alkanes, and the interference from the dibrominated compounds is also eliminated. Although the two chromatograms appear to be identical, subtle differences do exist as indicated by the differences in the amplitude values. These values are the weighted fits of the apical spectra of the tallest analyte peak in the chromatogram, in this case hexachlorobutadiene. Figure 35 shows the raw spectrum, and Table XIV shows the cumulative fit data for that spectrum. The cumulative fits for m/e's 82, 94, 106, and 118 represent the proper recognition of clusters formed by dichlorinated ion fragments. The cumulative fit for m/e 143 is actually a mismatch of the X+2, X+4, and X+6 peaks in a trichlorinated data cluster which begins at m/e 141. The cumulative fit for m/e 155 is a mismatch of the X+4, X+6, and X+8 peaks in the data cluster generated from a pentachlorinated ion fragment beginning at m/e 153. The cumulative fits at m/e 225 and 227 are mismatches of various combinations of peaks from a data cluster of

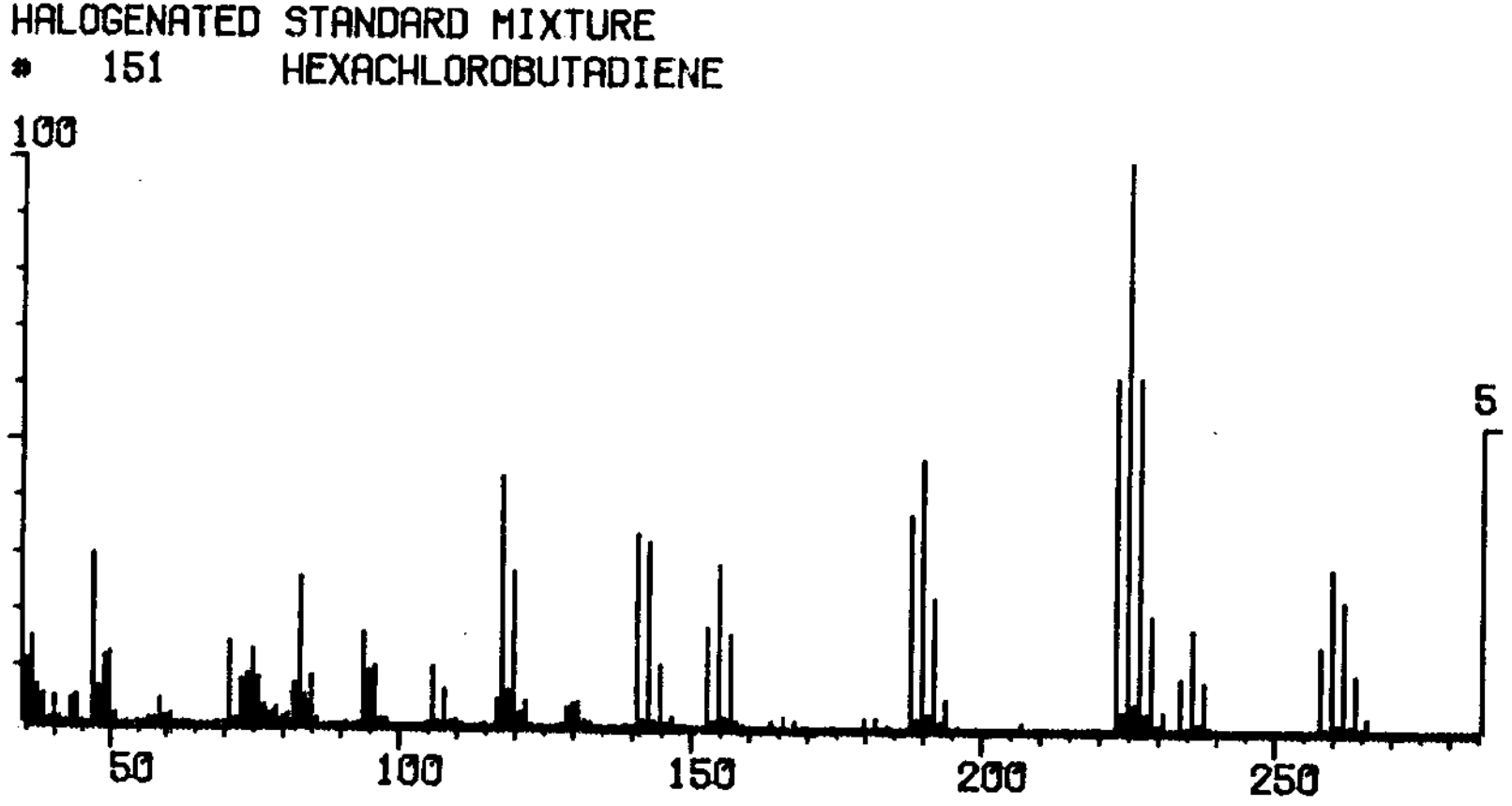

Fig. 35--Mass spectrum of hexachlorobutadiene (no background subtraction)

TABLE XIV

CUMULATIVE FACTORS FOR HEXACHLOROBUTADIENE USING PRECISION ESTIMATE PARAMETERS (PEP) OF 0.1 AND 0.2

Mass	Cumulative Factor Using PEP = 0.1	Cumulative Factor Using PEP = 0.2
82	0.28	0.38
94	1.11	1.21
106	1.64	1.73
118	6.06	6.13
143	*	6.79
155	6.80	8.23
225	11.80	13.23
227	14.60	16.35

*Cumulative factor was zero and therefore did not print.

pentachlorinated ion fragment beginning at m/e 223. Note that the total cumulative fits for the clusters which are produced from dichlorinated ion fragments are approximately the same for the two different precision estimates, 6.13 versus 6.04. However, the higher cumulative fit for the 0.2 precision estimate parameter indicates that it will exhibit a higher sensitivity to mismatches than will the 0.1 value. Therefore, values of 0.1 for the precision estimate and -50 for the variation estimate were selected as optimum values for the precision process. These values were then used for the analysis of the CALCLI data set.

Analysis of Complex Data Using the CALCLI Data Set

The CALCLI data set was produced from the GC/MS analysis of a water sample collected in Ventura, California. Digestor sludge produced at that treatment plant was purifaxed (22) subjected to an oxidative treatment process in which extremely high (greater than 1,000 ppm) doses of chlorine are used. A sample of the purifaxed supernatant was collected, chilled, and shipped to Denton, Texas for analysis in this laboratory. Previous analyses of purifaxed wastewaters from various sources all showed large numbers of chlorinated compounds to be present in the GC/MS chromatograms.

The computerized analysis of the CALCLI data set was hindered by the poor quality of the raw spectra. This was partly due to the complexity of the sample matrix and partly due to a basic shortcoming of the Finnigan 6100 data system. The system acquires data for each mass using a single, fixed integration time period which must be long enough (four to eight milliseconds) to allow reasonable precision when measuring a peak of low absolute intensity. The fixed time period limits the dynamic range of the mass spectral peak intensities which the spectrometer can record before reaching a saturation point. This in turn limits the range of compound concentrations which will produce

accurate representative spectra. The concentrations of compounds in the CALCLI sample cover a range of at least four orders of magnitude. This clearly exceeds the dynamic range of the data system.

One way to get usable spectra for all the compounds in such a sample is to make several GC/MS runs of the same sample at different dilution strengths. Mass spectra of compounds of high concentrations can be selected from the GC/MS run of the diluted sample; mass spectra of the trace components can be produced from the GC/MS run of the sample after further concentration. Another alternative is to concentrate the sample until spectra for the smallest GC peaks are interpretable, and then select spectra from the sides of the GC peaks whose apical spectra contain saturated mass spectral peaks. Thus, the analyst can adjust for the saturation problem of the larger GC peaks by the proper saturation problem of the larger GC peaks by the proper selection of the representative mass spectrum. In situations where the quantity of sample is limited, the latter procedure is preferable, and this was the procedure which was used to produce the CALCLI data set.

Unfortunately, the gross distortion of some mass spectra due to saturated mass spectral peaks can cause problems for a computerized data analysis system which is forced to analyze all spectra as though each were produced

within the dynamic range of the instrument. Nevertheless, the data was analyzed using the limited cluster search computer program to search for ion fragments containing two, three, and four chlorines. For all runs, the precision estimate parameter was 0.1, and the variation estimate parameter was -50. The resulting chromatograms shown in Figure 36 are displayed in two columns. At the top of both columns are identical total ionization chromatograms for the CALCLI data set. Below the total ionization chromatograms are the limited cluster searches for the two, three, and four chlorine isotopes. The set of limited cluster searches in the left column is normalized to the tallest peak in each respective limited cluster search chromatogram. The limited cluster searches in the column on the right are all normalized to the tallest peak in the limited cluster search for two chlorines. Note that the amplitude values are all identical. Since the computer program is designed to produce cumulative fits of equal value for any isotope cluster whose base peaks have equal relative peak heights, the comparison shown in the right column gives an indication of the relative quantity of the particular chlorine cluster. However, this is only an indication of the trends which occur. The comparison is not exactly quantitative because the three limited cluster searches use different partial spectra as defined by

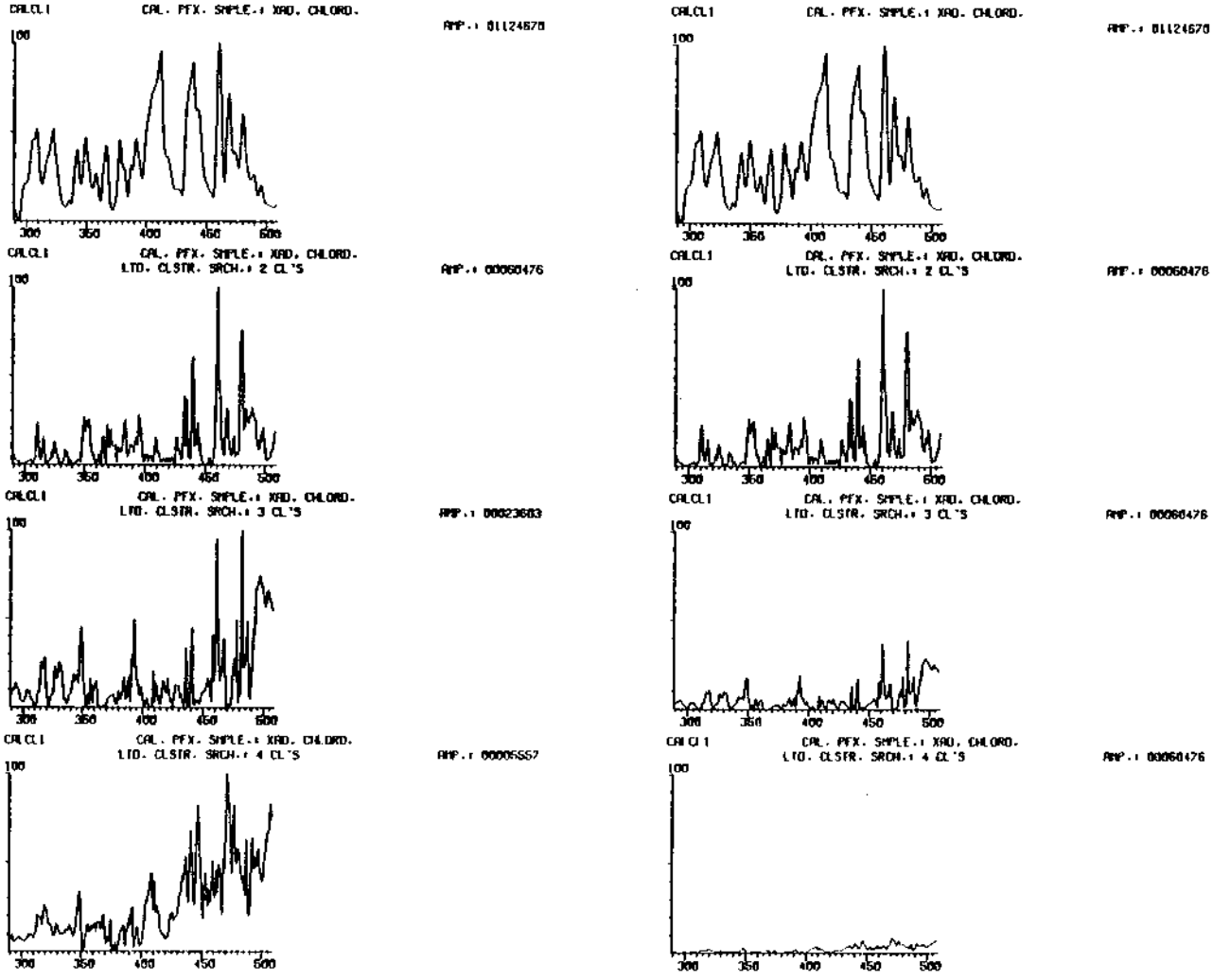

Fig. 36--Total ionization chromatogram and limited cluster searches for the CALCL1 data set.

different first mass input parameters. However, the trends do correctly indicate that clusters representing the higher numbers of chlorines occur with progressively lower intensity.

Table XV shows the results of a detailed analysis of CALCLI limited cluster searches. All of the mass spectra which were processed by the limited cluster search computer program are listed in the column on the far right. The next column shows the total ionization chromatogram intensity for each spectrum expressed as a percentage of the tallest GC peak in the total ionization chromatogram. Also indicated in this column are the locations of all the peaks and shoulders in the total ionization chromatogram. This allows the comparison of the positions of the total ionization chromatogram peaks with the positions of the limited cluster search peaks. Note that many of the limited cluster search peaks do not occur at total ionization chromatogram peak maxima. Such peaks are extremely difficult to find when the total ionization chromatogram is the only guide. The rest of the table is a coded analysis of the apical spectra in the three limited cluster searches. The data for all the spectra from a respective limited cluster search are listed in five columns. The column on the left indicates the weighted fit, or GC peak height, for that partial spectrum expressed as a percent of the weighted

TABLE XV

ANALYSIS OF MASS SPECTRAL DATA IN GC/MS DATA SET "CALCLI"

Spec. No.	TIC, %-Type	2 Chlorines					3 Chlorines					4 Chlorines				
		LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec
290	5.8															
291	4.1															
292	1.6															
293	0															
294	0.4						14.0	42.0	E		1					
295	5.6															
296	14.9															
297	18.4															
298	20.6-S															
299	21.1															
300	21.6															
301	22.5															
302	25.5															
303	32.8						10.2	16.6	E		5					
304	41.6															
305	45.6-P															
306	45.3						9.7	11.9	E		4					
307	46.0															
308	49.2															

TABLE XV--Continued

Spec. No.	TIC, %-Type	2 Chlorines					3 Chlorines					4 Chlorines				
		LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec
309	52.0-P															
310	44.8															
311	32.5	24.2	13.02	A-146-100	1	34										
312	25.3															
313	21.0															
314	20.3															
315	23.9															
316	28.2	15.3	5.99	A-83-100 A-111-20		95	26.2	19.1	C-191-24		6					
317	32.8-S															
318	35.7															
319	37.2						28.5	26.4	E		4	10.9	12.5	C-191-41		2
320	40.2															
321	44.6															
322	49.5															
323	51.6-P	7.5	2.89	A-146-16	1	92										
324	41.2															
325	35.2	12.8	7.07	A-146-12	1	38										
326	30.4															
327	24.4						23.6	30.53	E		3					

TABLE XV--Continued

Spec. No.	TIC, %-Type	2 Chlorines					3 Chlorines					4 Chlorines				
		LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec
328	19.2															
329	14.1															
330	11.0															
331	9.4						25.8	51.95	E		1					
332	8.1															
333	7.5															
334	7.8	8.4	10.09	C-105-40		15										
335	10.1															
336	11.7-P															
337	10.1															
338	9.0															
339	14.3															
340	22.7															
341	30.8															
342	38.1															
343	40.3-P						18.8	30.21	E		2					
344	32.1															
345	23.9															
346	20.0						18.4	29.43	E		3					

TABLE XV--Continued

Spec. No.	TIC, %-Type	2 Chlorines					3 Chlorines					4 Chlorines				
		LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec
347	21.9															
348	32.4															
349	45.9						43.6	10.75	A-117-100	(3)	34	33.9	13.09	A-165-100		3
350	46.8-P	26.9	5.92	A-83-100 A-111-26 A-123-27	(3) (3) (3)	100										
351	38.9															
352	33.8-S															
353	28.7															
354	21.4	25.9	12.64	D-83-56		27										
355	17.7															
356	17.8															
357	20.7						16.6	10.27	B-140-100		17					
358	26.8															
359	26.9-P															
360	21.1															
361	14.7															
362	11.0						15.2	19.51	F(2)-140-100		4					
363	12.4															
364	24.7															

TABLE XV--Continued

Spec. No.	TIC, %-Type	2 Chlorines					3 Chlorines					4 Chlorines				
		LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec
365	32.1															
366	37.2	15.8	4.07	E		89										
367	42.4-P															
368	36.9															
369	22.4	22.4	9.60	E		32										
370	11.1															
371	7.1															
372	5.9	19.7	13.27	E		22										
373	6.2															
374	9.1															
375	12.3															
376	18.0															
377	35.4															
378	45.5-P															
379	42.4															
380	32.6															
381	28.9															
382	30.1-P															
383	24.9															

TABLE XV--Continued

Spec. No.	TIC, %-Type	2 Chlorines					3 Chlorines					4 Chlorines				
		LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec
384	16.4	25.5	14.11	E		18										
385	13.3						17.2	13.79	E		9					
386	21.7															
387	30.9															
388	31.5-P															
389	28.6						17.6	7.40	E		17					
390	34.5															
391	45.0															
392	46.3-P															
393	40.0						49.5	15.34	A-180-22	(4)	15	25.0	5.79	F(2)-162-29		
394	36.1															
395	30.3	28.3	8.69	E		49										
396	24.6															
397	23.8															
398	30.9															
399	42.6															
400	50.2															
401	55.5-S															
402	59.7															

TABLE XV--Continued

Spec. No.	TIC, %-Type	2 Chlorines					3 Chlorines					4 Chlorines				
		LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec
403	64.2															
404	69.1															
405	72.3															
406	73.6-S															
407	75.4															
408	77.3															
409	80.1	16.0	2.92	E		100	20.8	5.00	E		100	44.2	28.71	E		2
410	86.5															
411	92.3						14.0	2.81	E		100					
412	95.8-P															
413	72.2															
414	50.9															
415	41.1															
416	36.4															
417	36.3-S						15.2	4.38	E		100					
418	35.8															
419	33.7															
420	28.8															
421	25.1						16.7	5.66	E		100					

TABLE XV--Continued

Spec. No.	TIC, %-Type	2 Chlorines					3 Chlorines					4 Chlorines				
		LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec
422	21.3															
423	18.6															
424	17.6															
425	18.0															
426	18.2-P															
427	18.0	15.4	5.49				12.8	5.11	E		100					
428	17.3															
429	15.7						12.9	5.42	E		100					
430	13.7															
431	20.4															
432	43.6															
433	61.1-S	38.7	6.38	E		100										
434	68.6															
435	73.9	36.7	5.34	E		100										
436	77.8						33.9	5.47	E		100					
437	81.5											53.3	25.10	E		3
438	85.7															
439	89.1-P															
440	71.3	60.9	8.32	B-83-84		100										

TABLE XV--Continued

Spec. No.	TIC, %-Type	2 Chlorines					3 Chlorines					4 Chlorines				
		LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec
441	61.7						45.2	8.87	E		100	68.2	29.80	E		3
442	62.2															
443	63.3-P															
444	59.4	11.0	3.33	B-83-62		100										
445	51.1															
446	41.3															
447	32.0											82.6	40.21	E		3
448	26.1															
449	23.6															
450	22.3															
451	20.2															
452	18.1															
453	16.9															
454	16.2															
455	14.2															
456	13.3															
457	19.7															
458	44.3						41.1	9.61	E		33	32.1	8.33	E		8
459	81.8															

TABLE XV--Continued

Spec. No.	TIC, %-Type	2 Chlorines					3 Chlorines					4 Chlorines				
		LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec
460	100.0-P	100.0	10.01	C-105-58		100										
461	96.9						95.3	12.71	E		54			F(3)-1		
462	78.8															
463	49.6															
464	31.1															
465	21.6															
466	28.3															
467	53.2						38.2	6.90	A-196-14	(5)	59					
468	71.6-P	31.9	4.06	E		100										
469	71.8															
470	57.8															
471	44.1											100.0	34.47	F(3)-196-100	(5)	3
472	37.7															
473	37.5															
474	38.8-P	16.7	3.78	E		100										
475	36.3															
476	31.4						28.0	8.76	E		33					
477	29.3											82.6	32.92	E		2
478	36.7						49.5	11.43	E		39					

TABLE XV--Continued

Spec. No.	TIC, %-Type	2 Chlorines					3 Chlorines					4 Chlorines				
		LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec
479	52.3															
480	60.7-P	76.1	10.92	D-91-100		100										
481	56.3															
482	45.2						100.0	22.62	E		26					
483	36.0															
484	30.2	31.8	8.19	E		100										
485	26.2															
486	23.6															
487	23.1						49.2	16.07	E		14	63.4	21.88	E		3
488	24.6															
489	27.0-P	32.5	8.11	E		100										
490	25.8															
491	20.8															
492	15.7											64.4	23.00	E		4
493	14.1															
494	16.7															
495	20.4-P															
496	19.8	16.9	5.31	E		70										
497	15.4						74.6	28.78	E		10					

TABLE XV--Continued

Spec. No.	TIC, %-Type	2 Chlorines					3 Chlorines					4 Chlorines				
		LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec	LCS, %	Cum Fac	Type-m/e-%	Cmpd	BP,% Spec
498	12.2															
499	10.5															
500	9.7															
501	9.2															
502	9.0															
503	8.5															
504	8.5						66.1	27.17	E		18					
505	8.3															
506	7.9															
507	8.1											83.0	27.98	E		4
508	9.2															
509	0.0															

fit for the tallest peak in the chromatogram. The next column shows the cumulative fit for that spectrum. The center column indicates the occurrences of the appropriate isotope cluster. If a cluster is present, the first mass of the cluster and its relative base peak intensity are also listed. The next column indicates the compound identifications when possible. The last column on the right shows the total spectrum peak height for the base peak of the partial spectrum expressed as a percentage of the base peak of the total spectrum. Often, a partial spectrum does not include the base peak of the total parent spectrum. In such cases, the computer will define a new base peak for the partial spectrum. The partial spectrum base peak is only a fraction of the height of the base peak of the total spectrum. An example of this process is shown in Figure 37. The total spectrum shown at the top has a base peak of m/e 43. The partial spectrum used in the limited cluster search for two chlorines does not include that peak. Therefore, a new peak at m/e 117 was assigned as the base peak which is only 27 percent of the height of the base peak in the total spectrum. This effect has a significant influence on the accuracy of the limited cluster search program as described below.

It is difficult to assess accurately the interpretive ability of the limited cluster search computer program

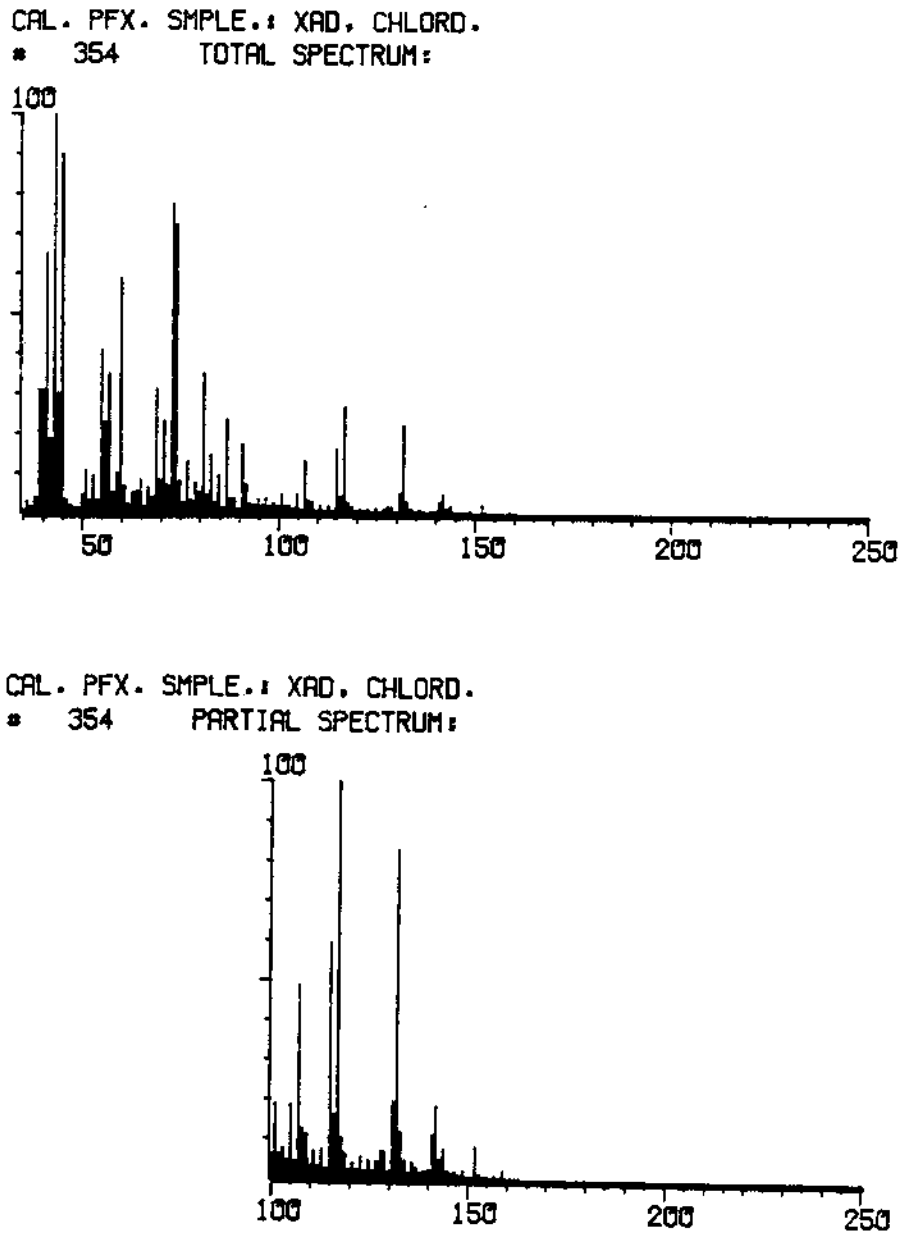

Fig. 37--Relationship between the base peak of a total mass spectrum and a partial mass spectrum.

because there are no guaranteed right answers which can serve as a reference. As shown in Figure 34, the program performs excellently for relatively clean, uncomplex samples. For the CALCLI data set, the matrix is so complex that almost every raw spectrum contains gross interferences from overlapping compound peaks. During the manual interpretation of these data, even the most careful selection and subtraction of background spectra usually did not totally eliminate the interferences. An example of this problem is shown in Figure 38. The top spectrum shows the raw data of the dichlorobenzene spectrum buried under interferences from overlapping compound peaks. Careful selection and subtraction of the appropriate background spectrum produced the center spectrum. The bottom reference spectrum (23) indicates that the CALCLI background-subtracted spectrum still shows the presence of interferences even though an identification can be made on the basis of the chlorine isotope clusters at m/e 146, the $(M)^+$ ion, and m/e 111, the $(M-Cl)^+$ ion. Therefore, some spectra at chromatographic peak apices could contain the proper cluster which might be recognized by the computer program, but might not be easily visible to the analyst doing manual interpretation.

Two methods were used to evaluate the accuracy of the computer program. The first method compares the number of

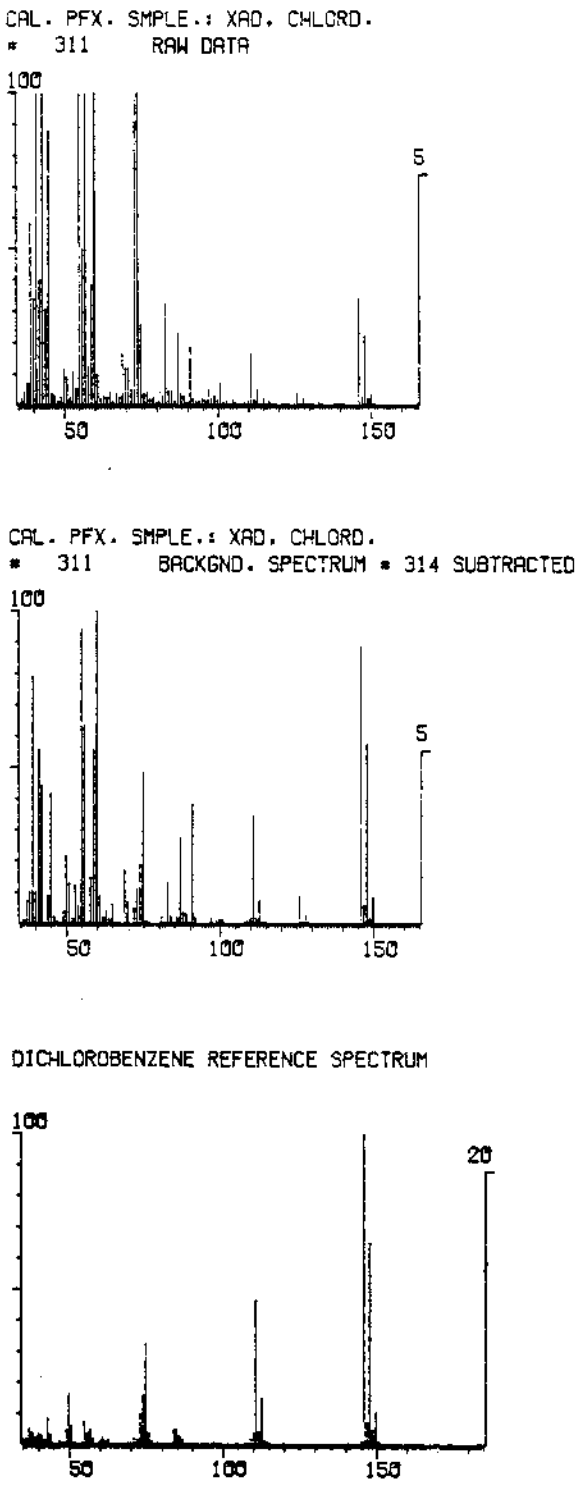

Fig. 38--Example of background interference in a dichlorobenzene mass spectrum.

chlorine-containing spectra obtained from manual data interpretation versus the number of chlorine containing spectra found with the aid of the limited cluster search chromatograms.

Table XVI shows the results of evaluation method I.

TABLE XVI

EVALUATION OF THE LIMITED CLUSTER SEARCH PROGRAM ACCURACY: NUMBER OF CHLORINE-CONTAINING SPECTRA IDENTIFIED USING MANUAL AND COMPUTER-ASSISTED INTERPRETATIONS

	Number of Chlorine Atoms		
	2	3	4
Manual Interpretation	6	3	1
Computer-Assisted Interpretation	11	6	5
Percent Improvement	83	100	500

Compounds Identified:

1. Dichlorobenzene isomer
2. Tetrachloroacetone
3. Dichlorobenzene isomer
4. Pentrachloroacetone
5. Dichlorophenol
6. Trichlorobenzene
7. Trichlorophenol

Data interpretation assisted by the use of the limited cluster search chromatograms increased the number of chlorine-containing spectra observed for every chlorine combination. The spectra which were derived from both methods of interpretation lead to the identification of

the same seven compounds listed at the bottom of Table XVI. However, the additional partial spectra obtained with the assistance of the limited cluster search chromatograms may be valuable in the future as more chlorinated organic compounds are identified in samples from other sources. Such subsequent identifications sometimes lead to the recognition of compound identities from the partially obscured spectra of the previous runs.

The second method of evaluation compares the number of limited cluster search apical spectra which were observed to contain the appropriate isotope cluster versus the total number of limited cluster search peaks for each combination of chlorine atoms tested. While the first method is an important measure of the usefulness of the limited cluster search program to the analyst, the second method more accurately reflects the state-of-the-art of the computer program itself. This evaluation method may be less reliable because of the lack of known correct answers as discussed above. The results are shown in Table XVII. The table indicates that only a minority of the significant peaks in all three chromatograms did, in fact, contain the appropriate chlorine cluster.

At least three factors contribute to the low percentage of correct identifications in the limited cluster searches. First, the precision and variation input

TABLE XVII

EVALUATION OF THE LIMITED CLUSTER SEARCH PROGRAM ACCURACY: FRACTION OF CHLORINE-CONTAINING SPECTRA CORRECTLY IDENTIFIED

	Number of Chlorine Atoms		
	2	3	4
Spectra Correctly Identified	11	6	5
Total Spectra Identified	25	32	13
Percent Correctly Identified	44	19	38

parameters, which were derived using a data set of ideal quality, allowed too much latitude in the decision process for the complex data set. Apparently, the empirical optimization process must be performed using a data set of similar quality to the data of interest. This means that there is probably no universal set of input parameters which can be used for all data. Hopefully, a few sets of input parameters will prove adequate for data sets of different quality, and the optimization process will not have to be performed for every data set of interest.

Secondly, the CALCLI data set analysis made visible two significant weaknesses in the program. The selection of a new base peak by the computer for partial spectra implies a scaling up of the higher molecular weight mass spectral peaks. If a base peak of a partial spectrum is only 33 percent of the height of the base peak in the total

spectrum, the partial spectrum is scaled up by a factor of three when the new base peak of the partial spectrum is assigned a relative height of 100 percent. This is illustrated in Figure 37 which shows spectrum number 354 from the CALCLI data set and was discussed above. The new base peak used for the partial spectrum only 27 percent of the base peak of the total spectrum implying a scaling factor of almost four. The data in Table XV indicates that the majority (53 percent) of the apical spectra which did not contain the appropriate chlorine clusters had base peaks which were less than 8 percent of the base peak in the total spectrum. Thus, in at least some of those cases, the computer program was probably trying to analyze nothing more than baseline noise. Therefore, some additional factor will probably have to be added to the limited cluster search program which relates the base peak of the partial spectrum to the base peak of the total spectrum. The factor could then be used as cutoff limit similar to baseline noise factor, or it could be applied as a scaling factor in a similar manner to the cluster and spectral intensity factors.

A third problem was also recognized as a result of exercising the limited cluster search program with the CALCLI data set. The small peaks at the background noise level of the instrument possess random intensities. It is

not unusual for the many combinations of background peaks occasionally to produce a peak ratio which closely matches the ratio of interest in a calculated cluster. This chance occurrence will, of course, generate a large partial cumulative fit. In complicated matrices, background peaks can have enough absolute intensity to offset the cancellation effect of the spectral intensity factor. Thus, the combination of the occurrence of the matching of the background peak ratio with the calculated cluster peak ratio and the high intensity of the background noise can result in the formation of spurious peaks in the limited cluster search chromatogram. Therefore, a mechanism is needed which recognizes and compensates for a high background noise level.

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APPENDIX A

MASS SPECTRA OF CHLORINATED ORGANIC COMPOUNDS FROM THE SUPERCHLORINATION OF MUNICIPAL WASTEWATER

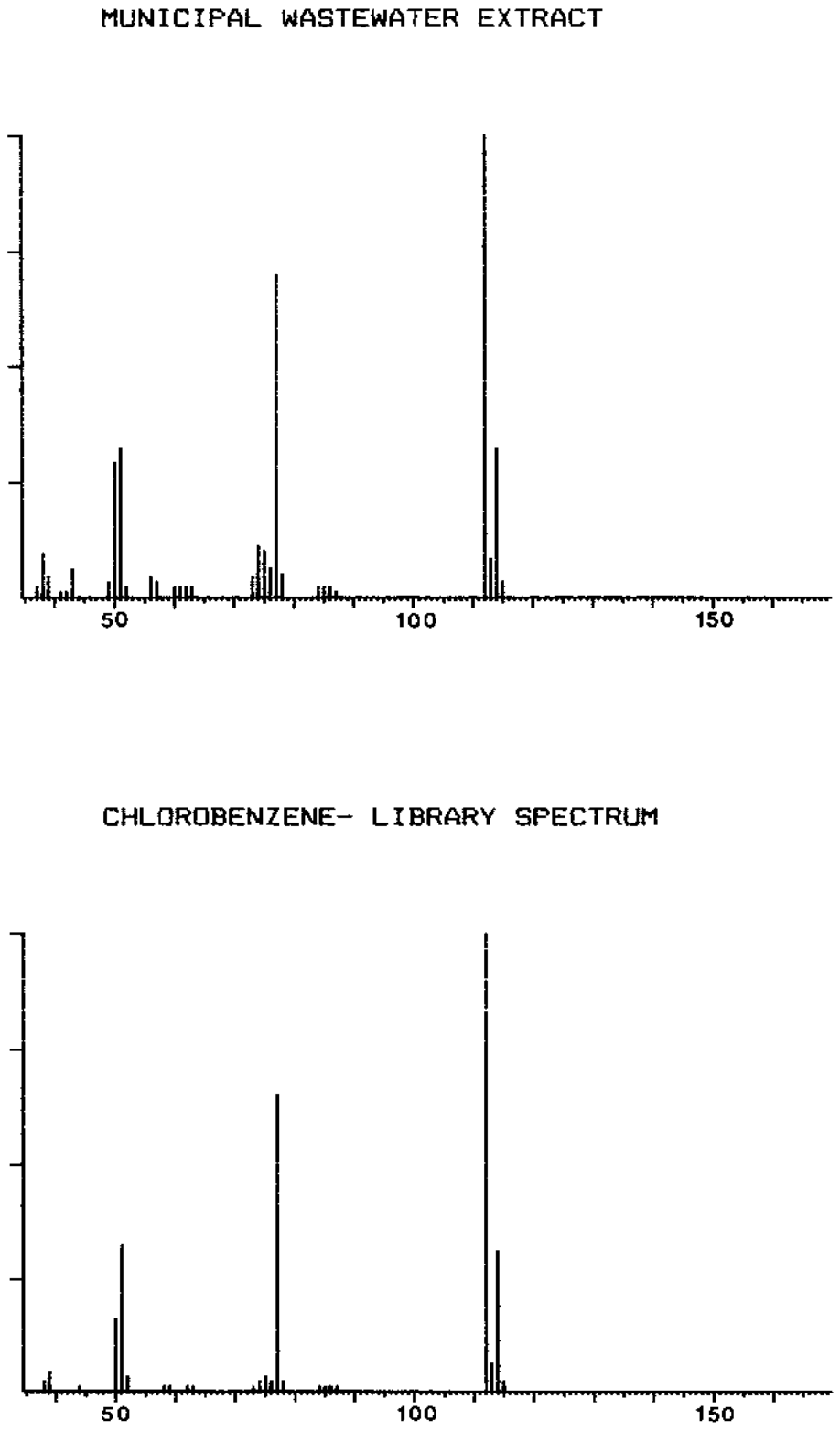


Fig. A-1--Chlorobenzene identification and library reference spectrum.

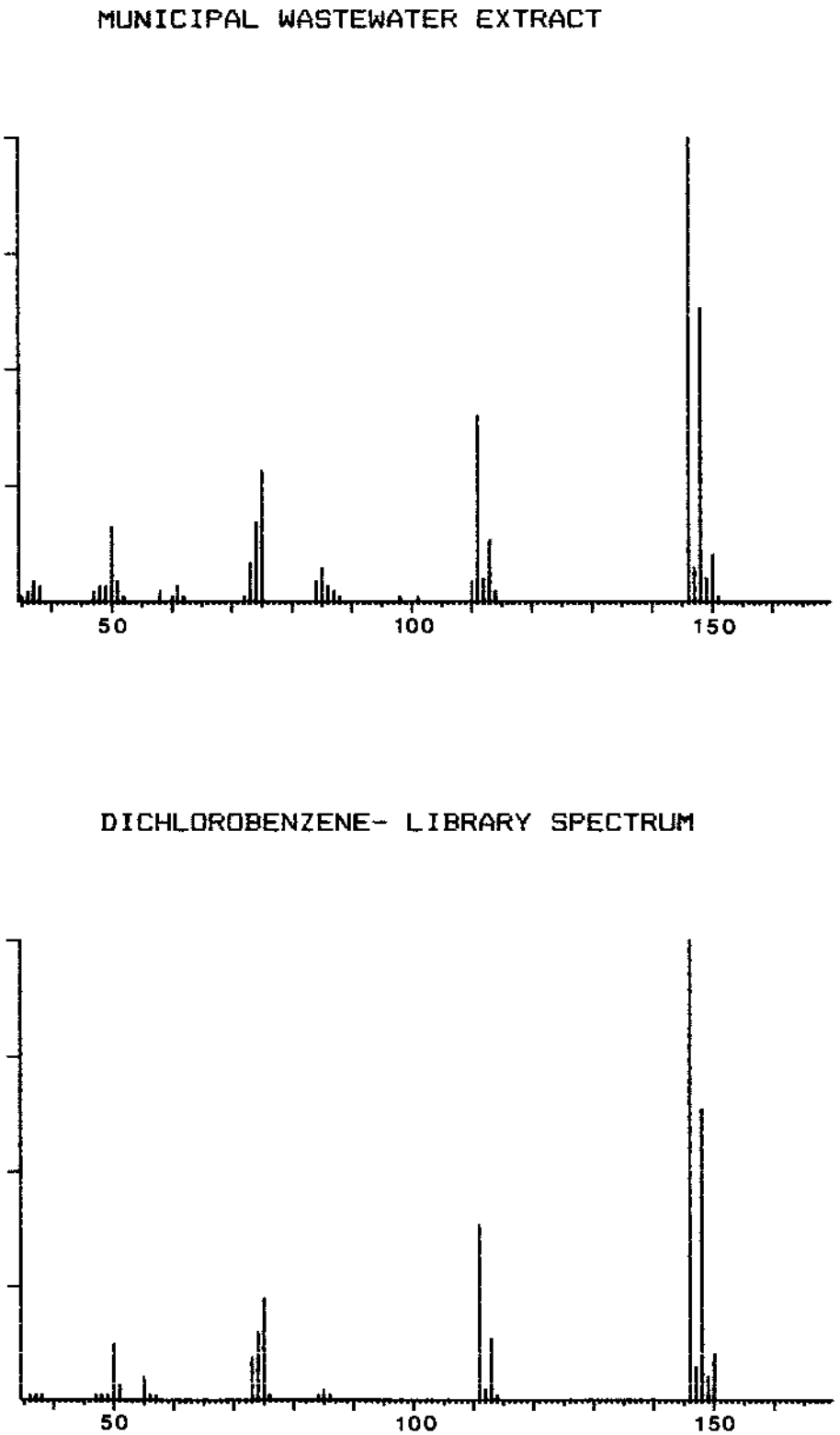


Fig. A-2--Dichlorobenzene identification and library reference spectrum.

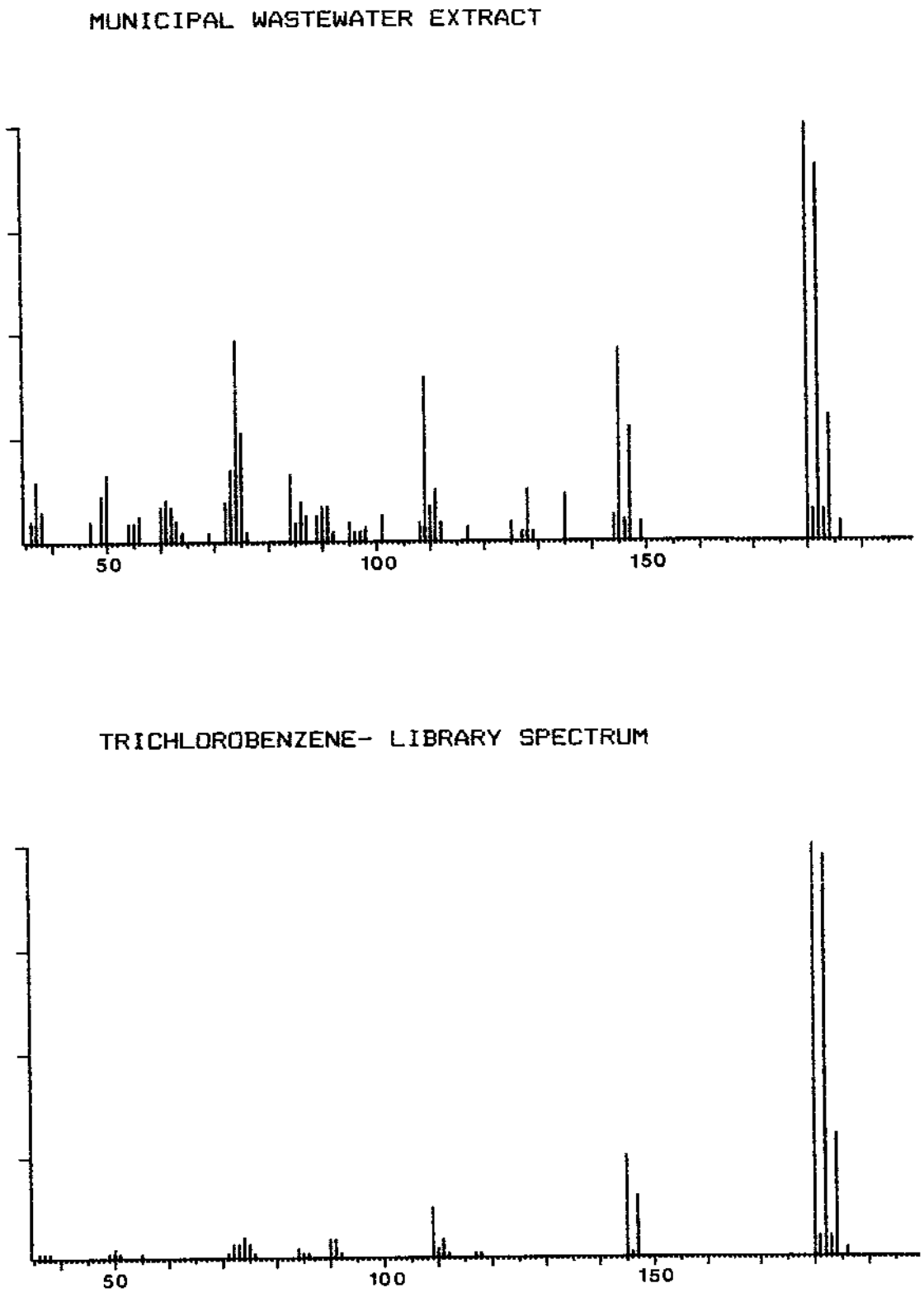


Fig. A-3--Trichlorobenzene identification and library reference spectrum.

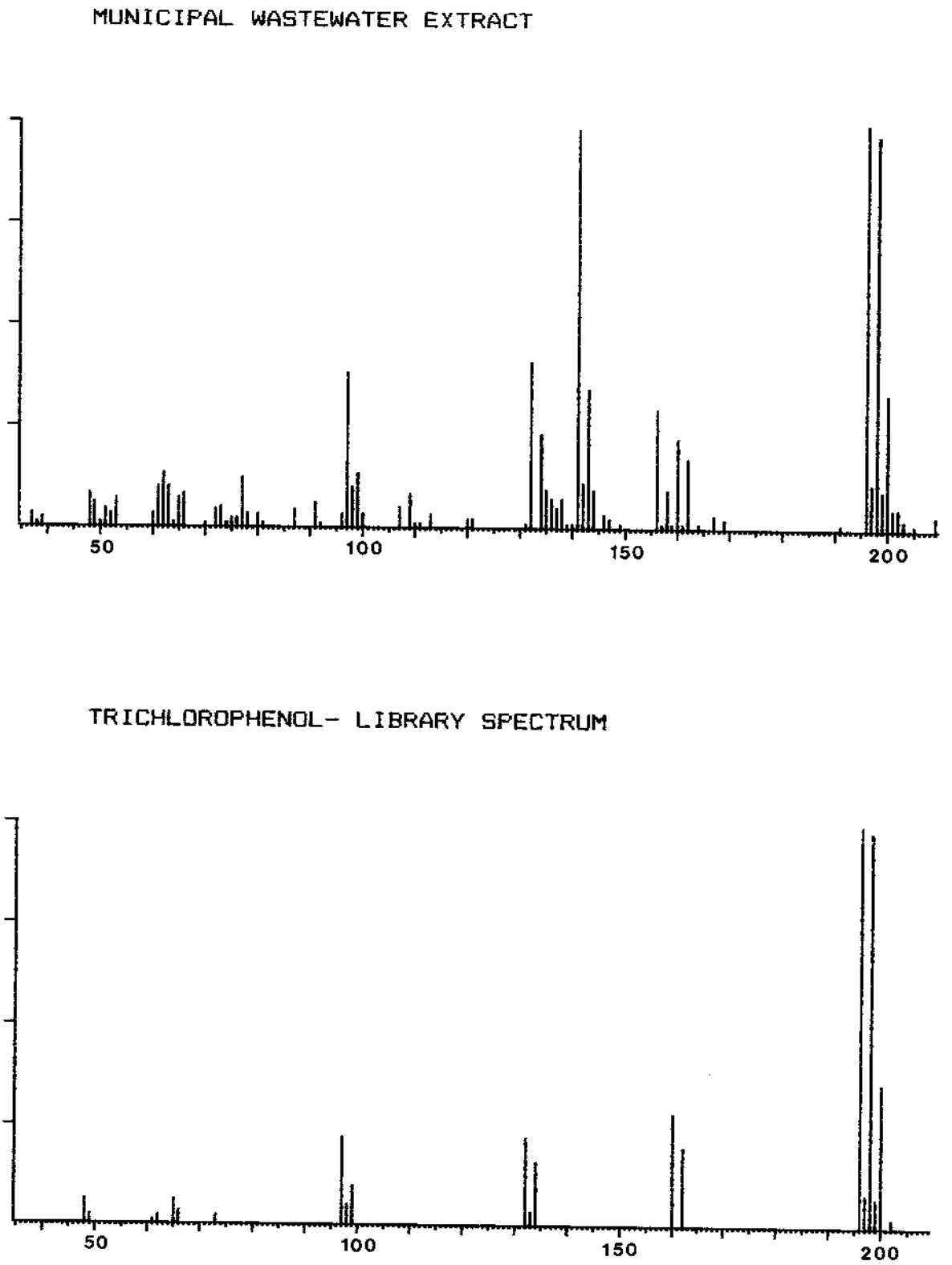


Fig. A-4--Trichlorophenol identification and library reference spectrum.

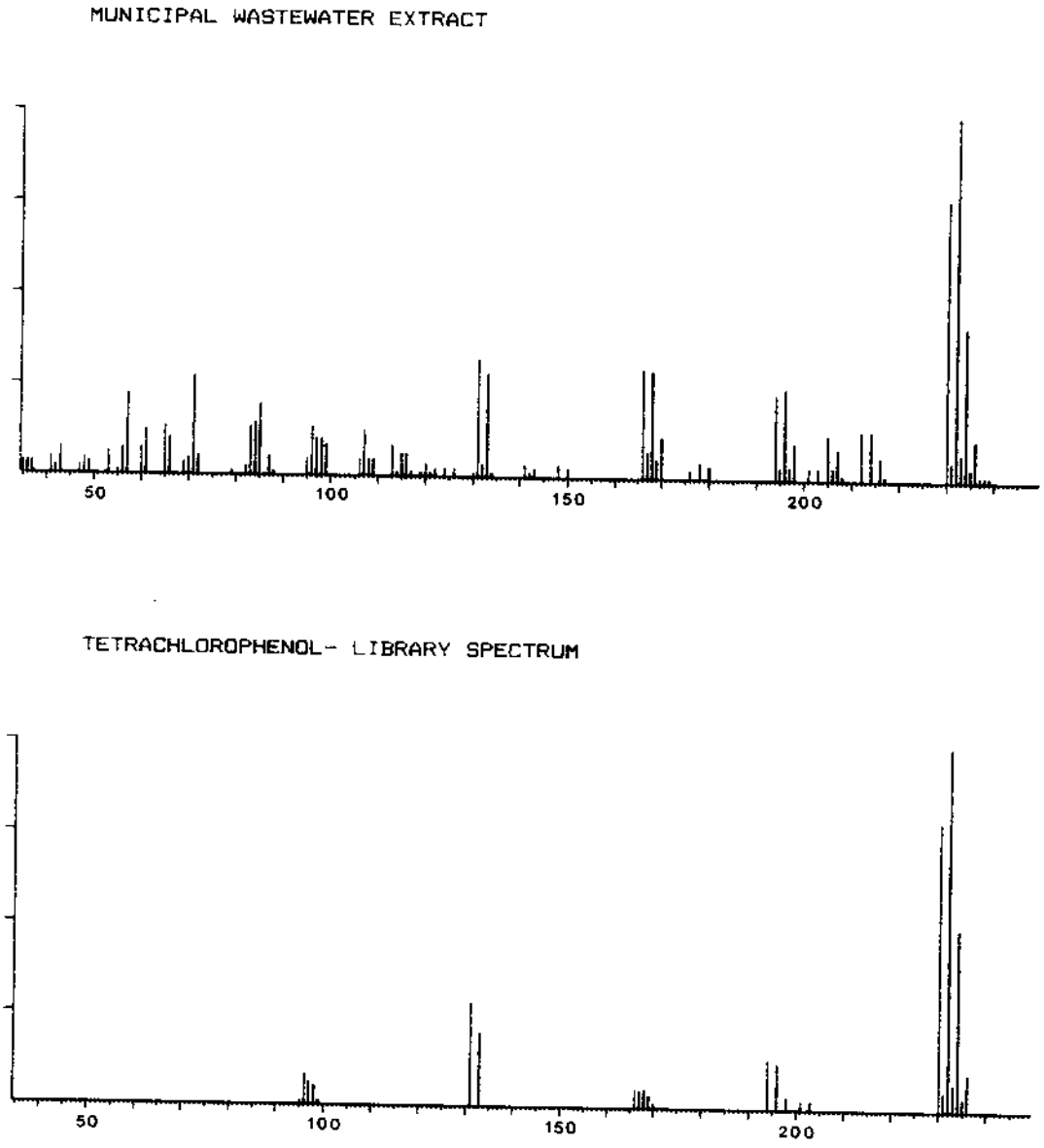


Fig. A-5--Tetrachlorophenol identification and library reference spectrum.

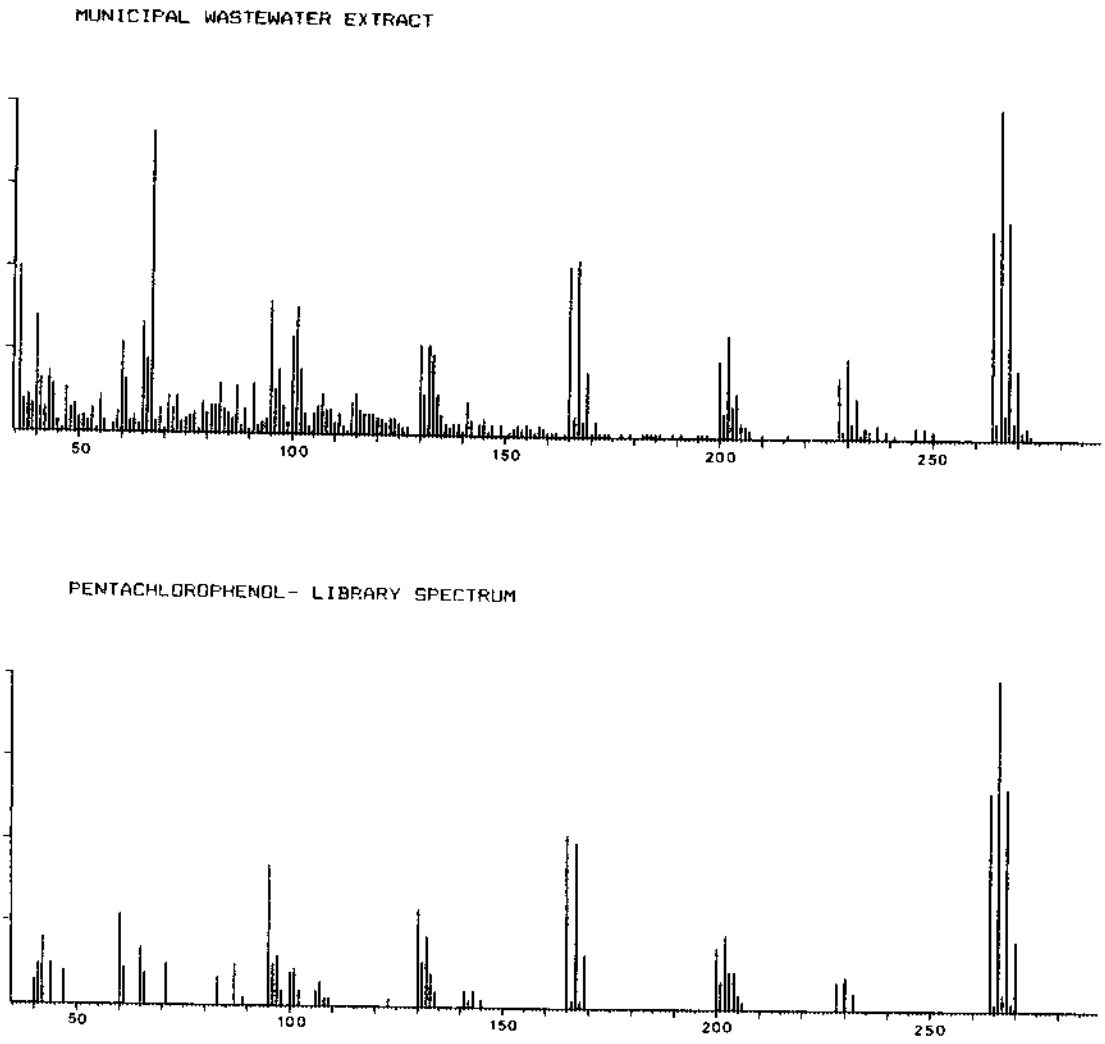


Fig. A-6--Pentachlorophenol identification and library reference spectrum.

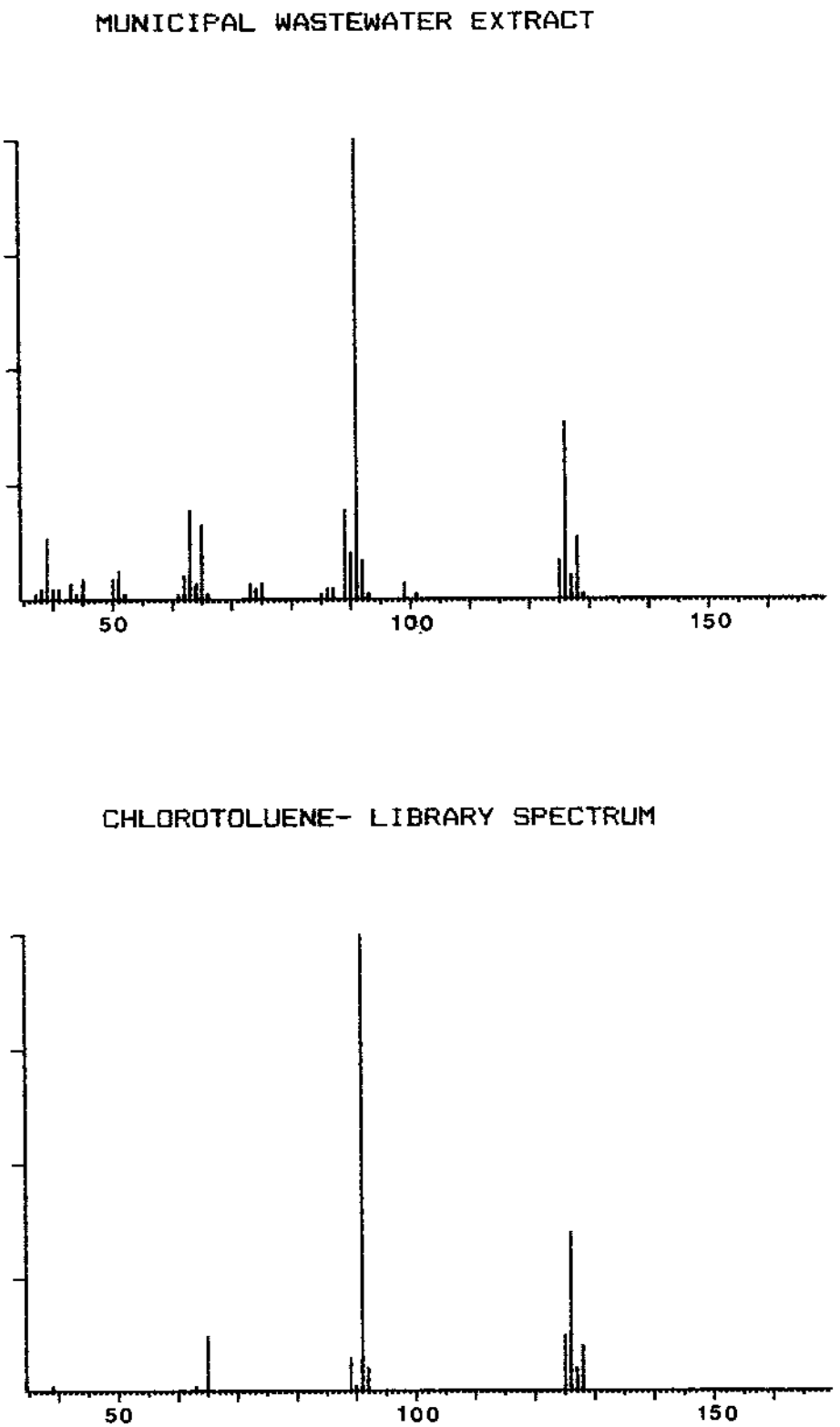


Fig. A-7--Chlorotoluene identification and library reference spectrum.

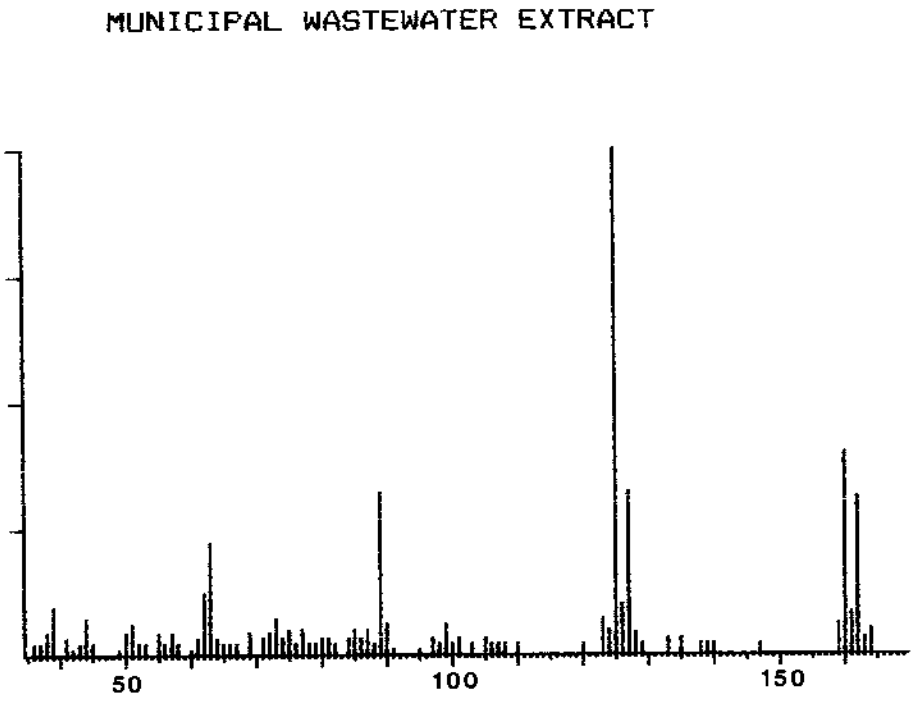


Fig. A-8--Dichlorotoluene identification and library reference spectrum.

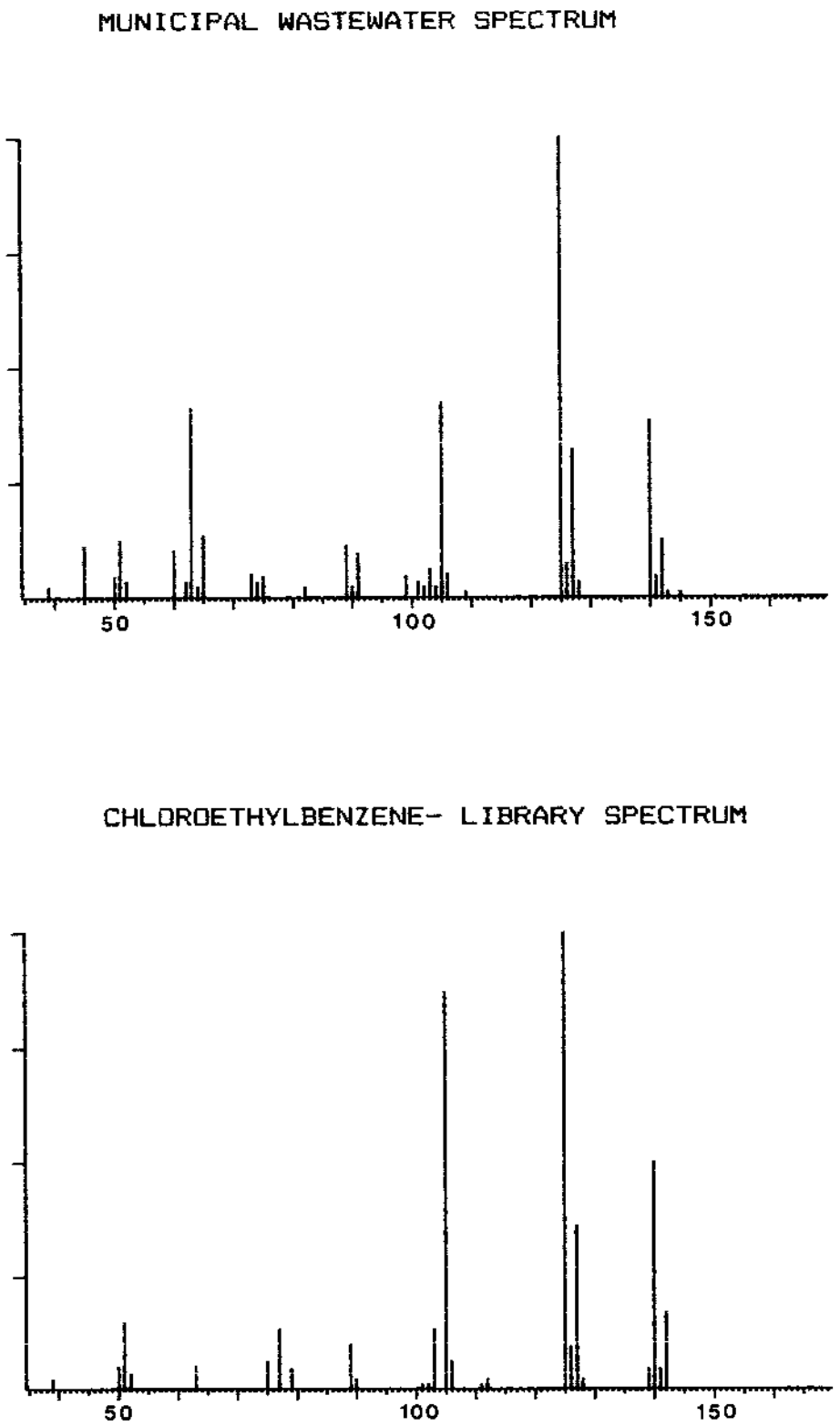


Fig. A-9--Chloroethylbenzene identification and library reference spectrum.

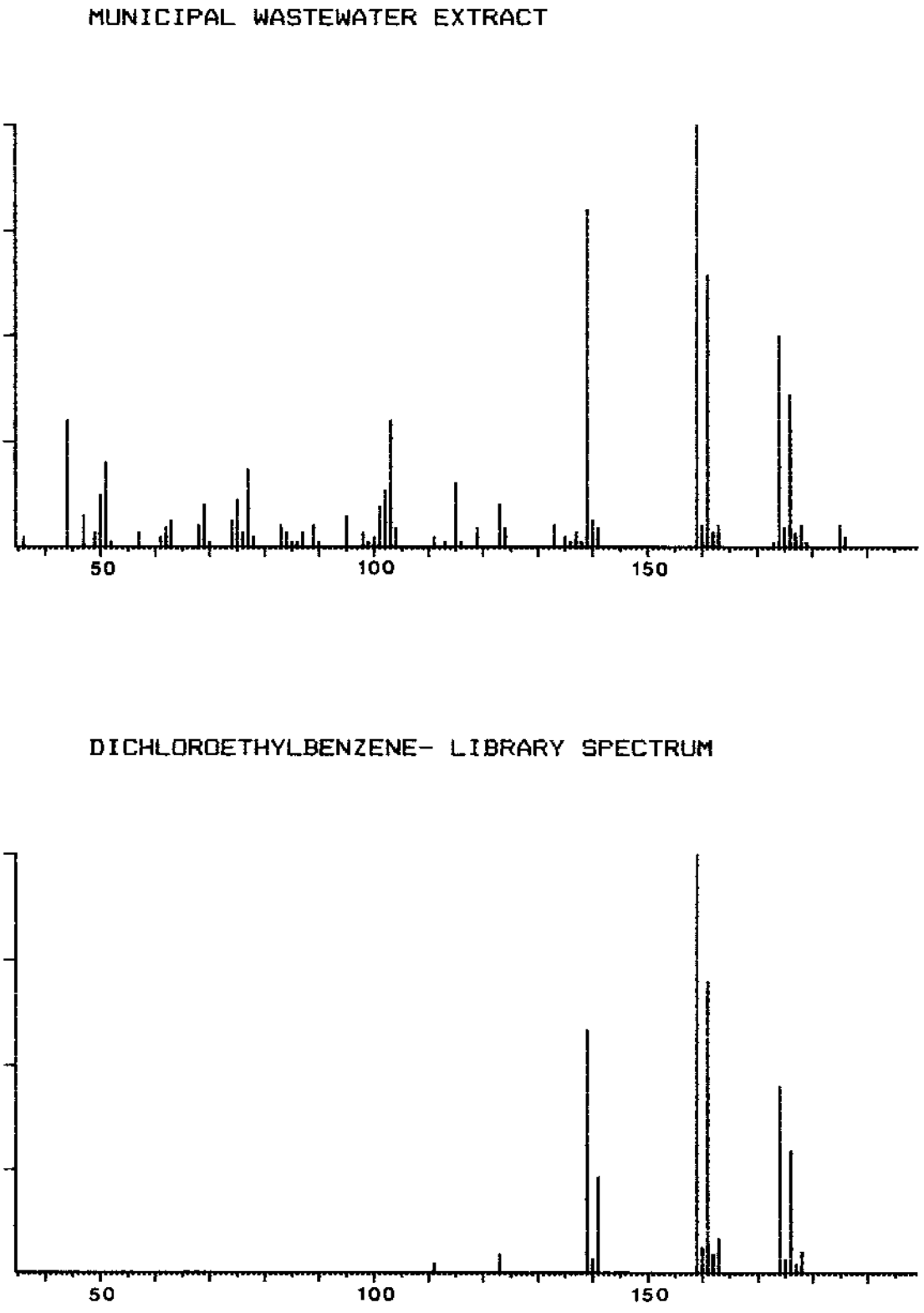


Fig. A-10--Dichloroethylbenzene identification and library reference spectrum.

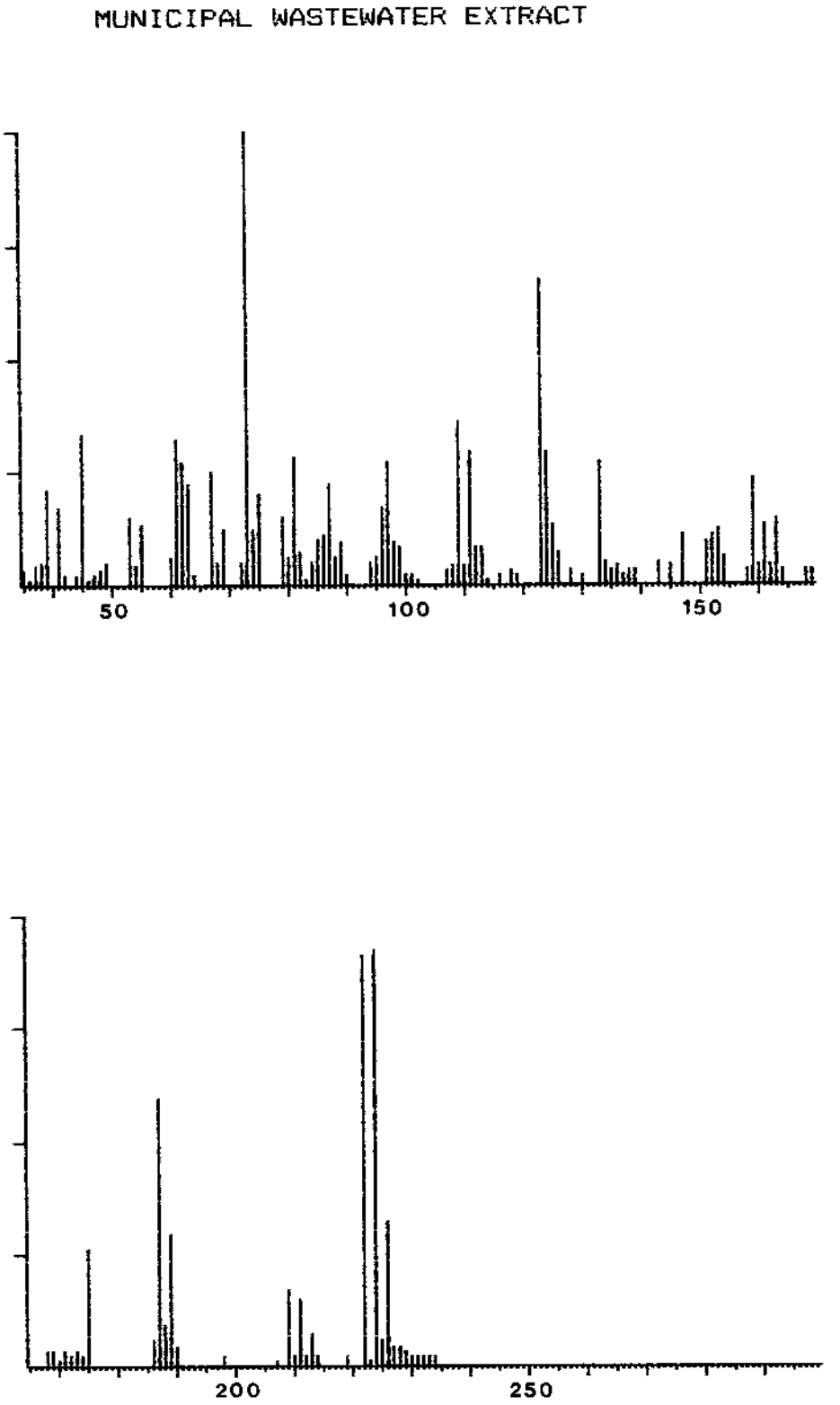


Fig. A-11--γ-chloropropyl-dichlorobenzene identification (no library reference spectrum available).

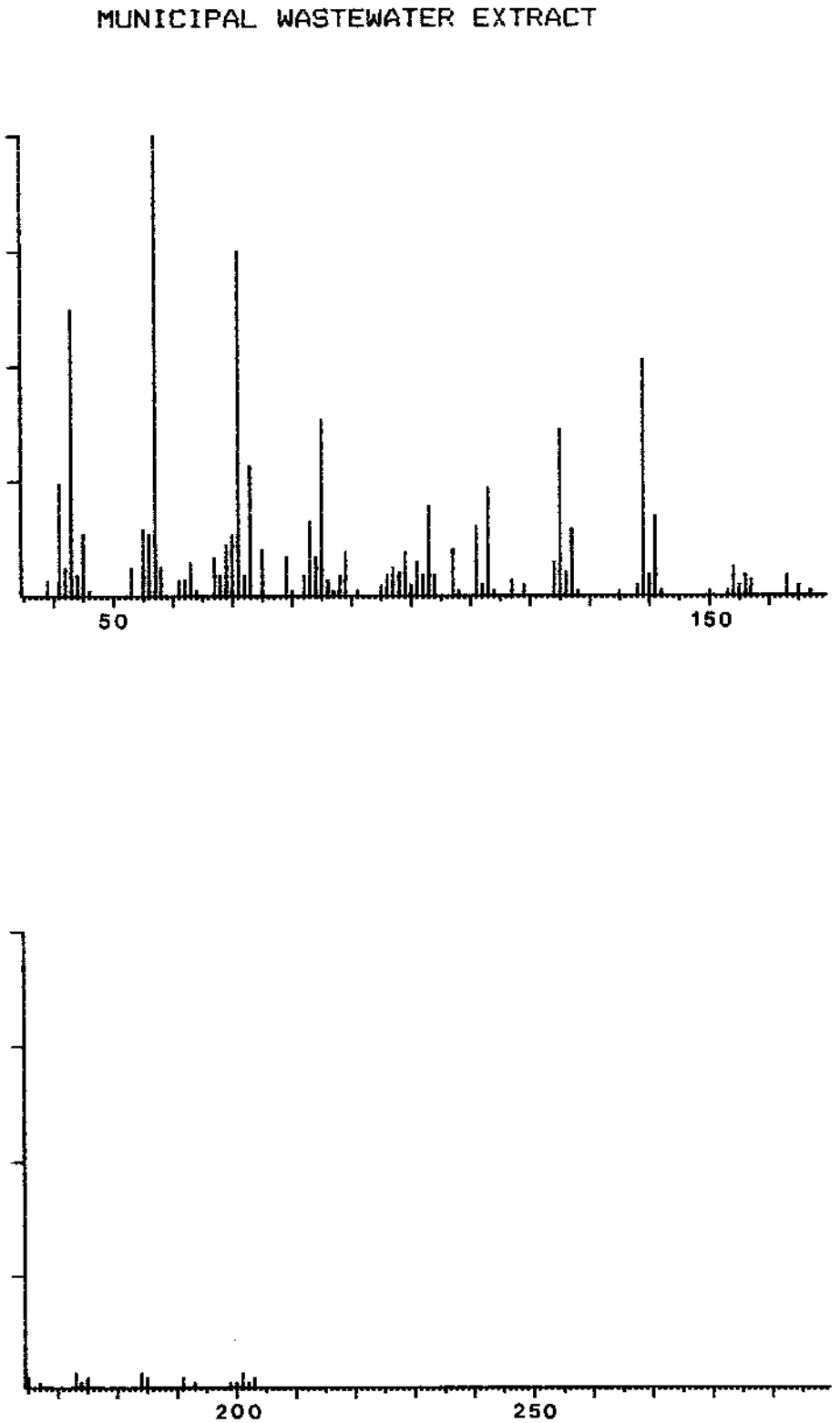


Fig. A-12--α-chloropropylbenzene identification (no library reference spectrum available).

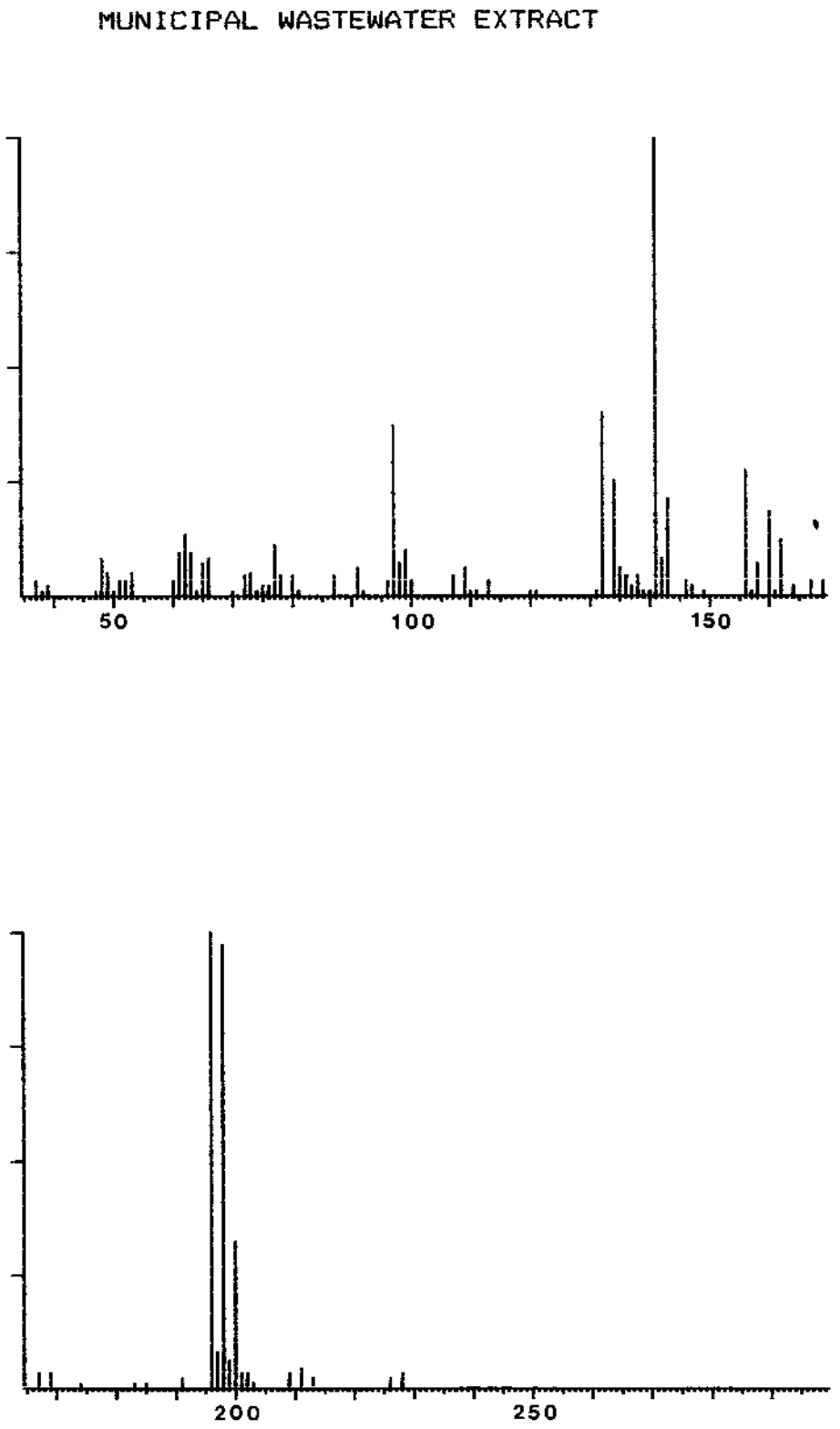


Fig. A-13--Chloroethylphenol identification (no reference spectrum available).

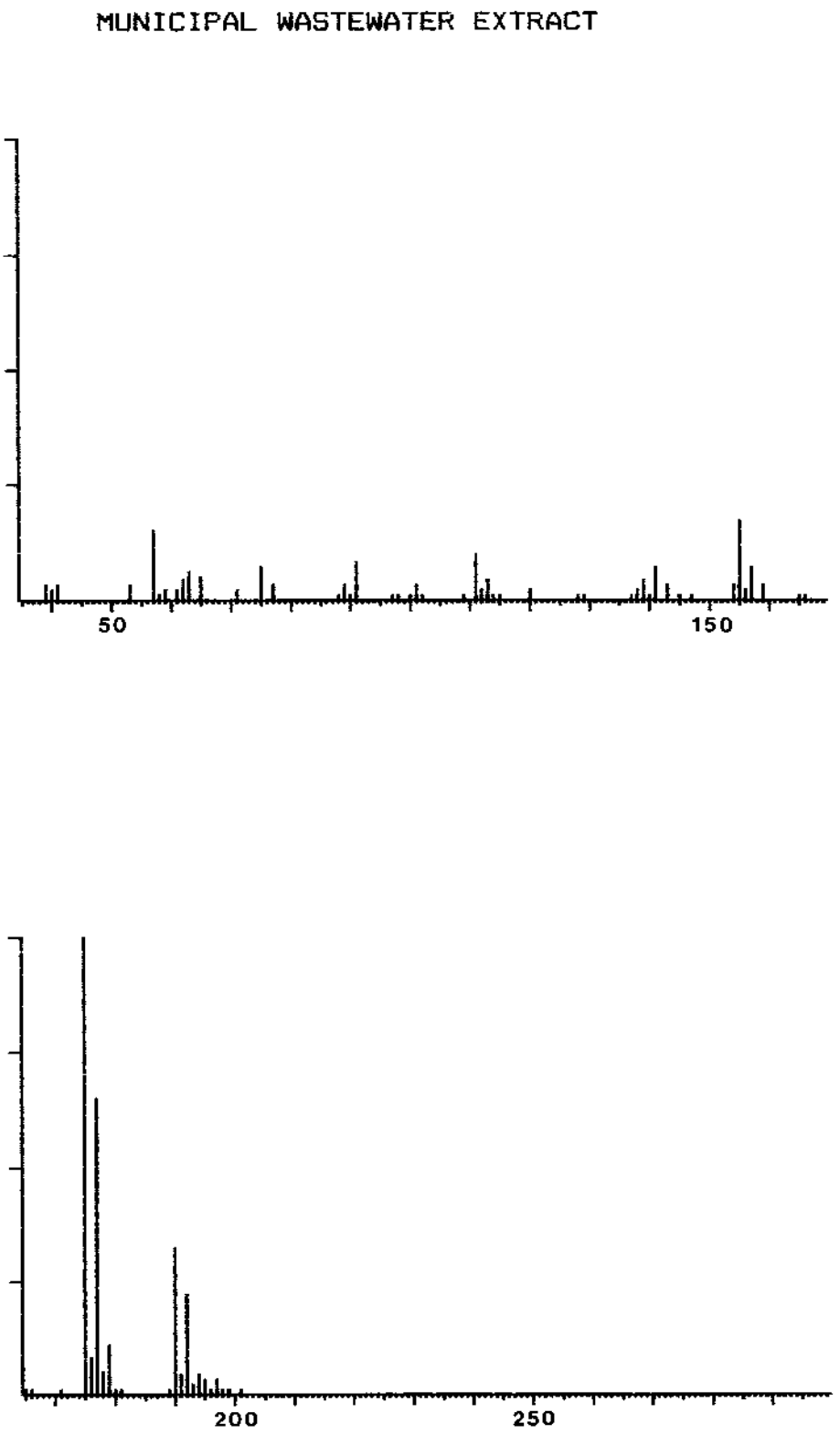


Fig. A-14--Dichloroethylphenol identification (no library reference spectrum available).

MUNICIPAL WASTEWATER EXTRACT

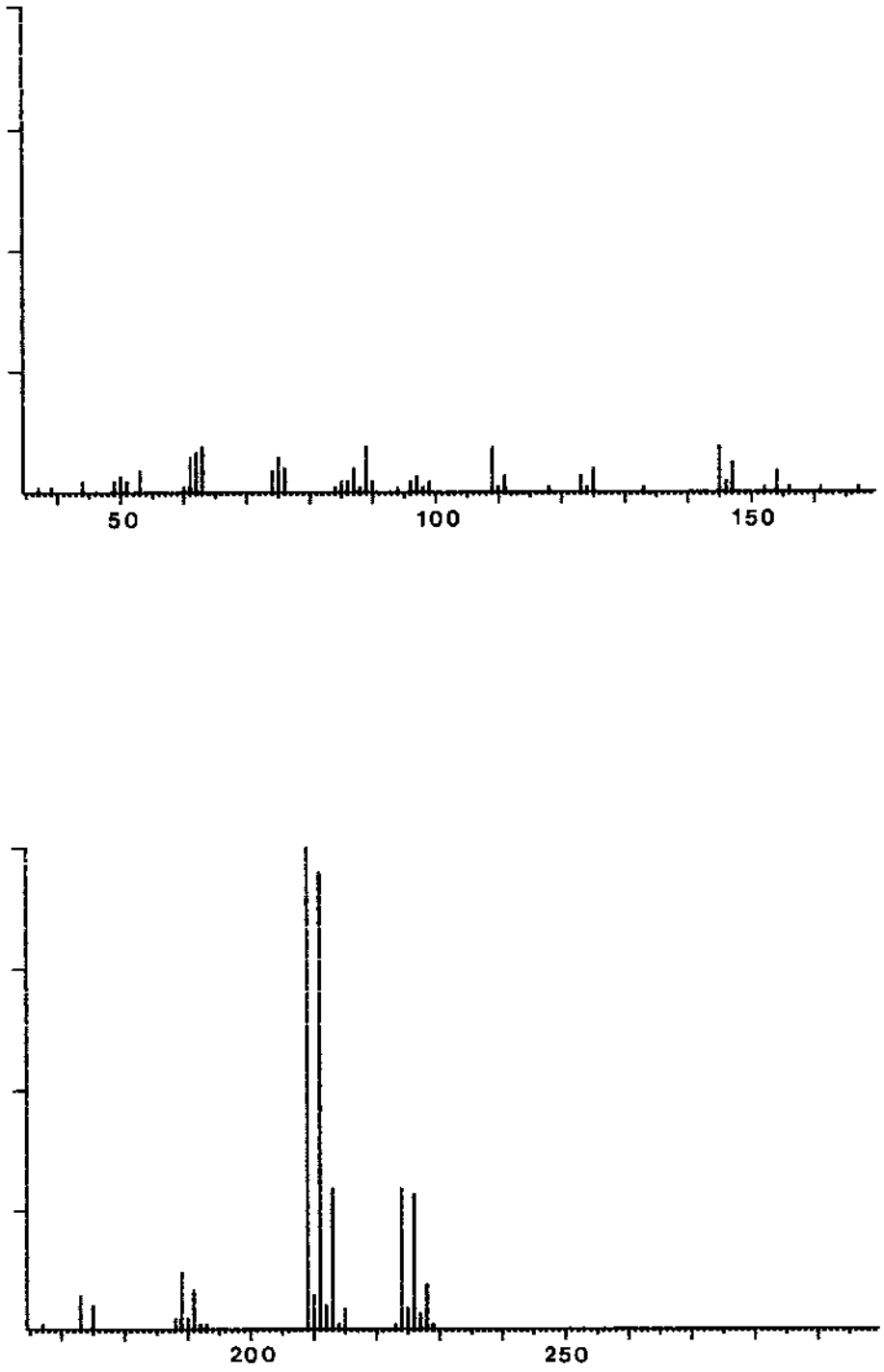


Fig. A-15--Trichloroethylphenol identification (no library reference spectrum available).

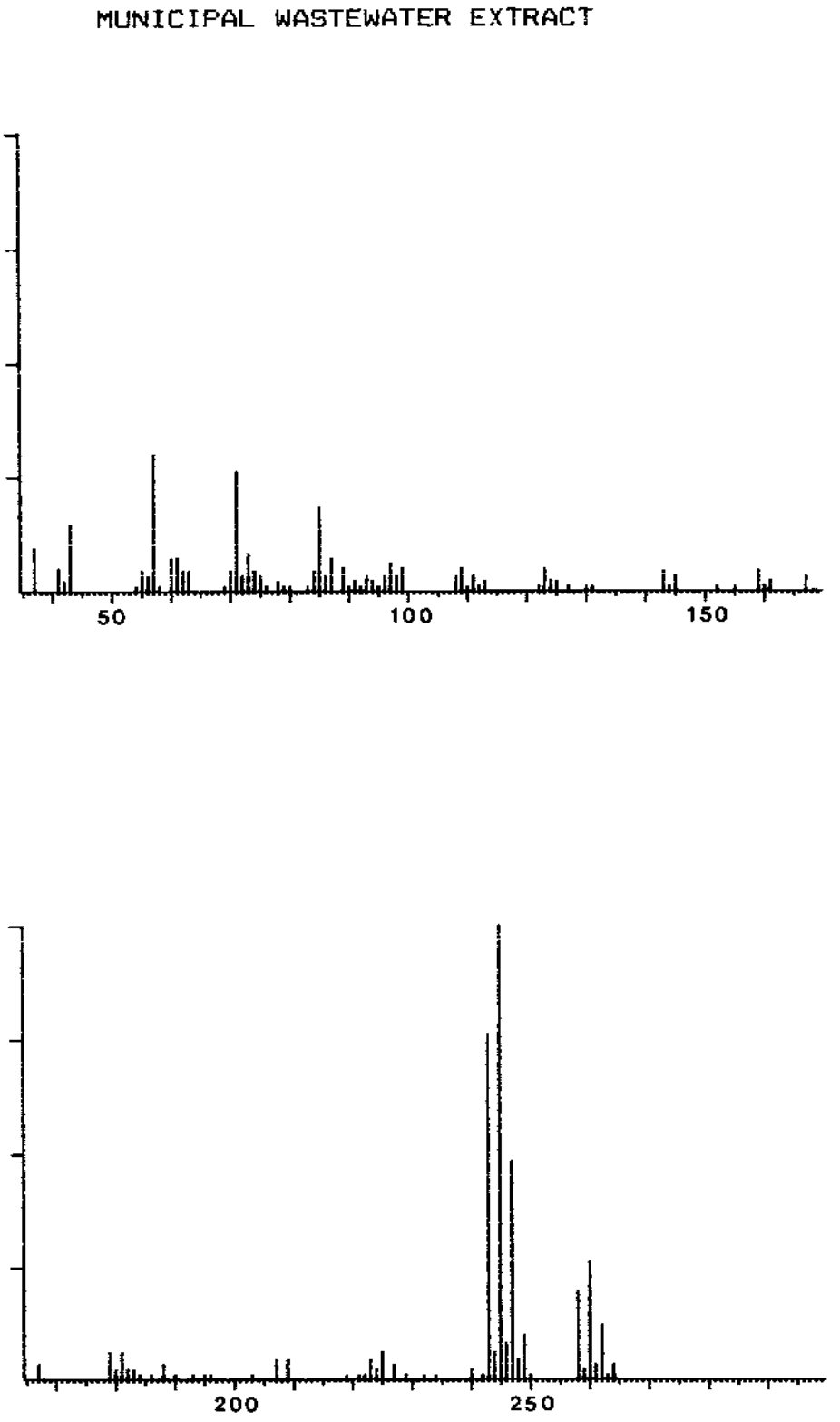
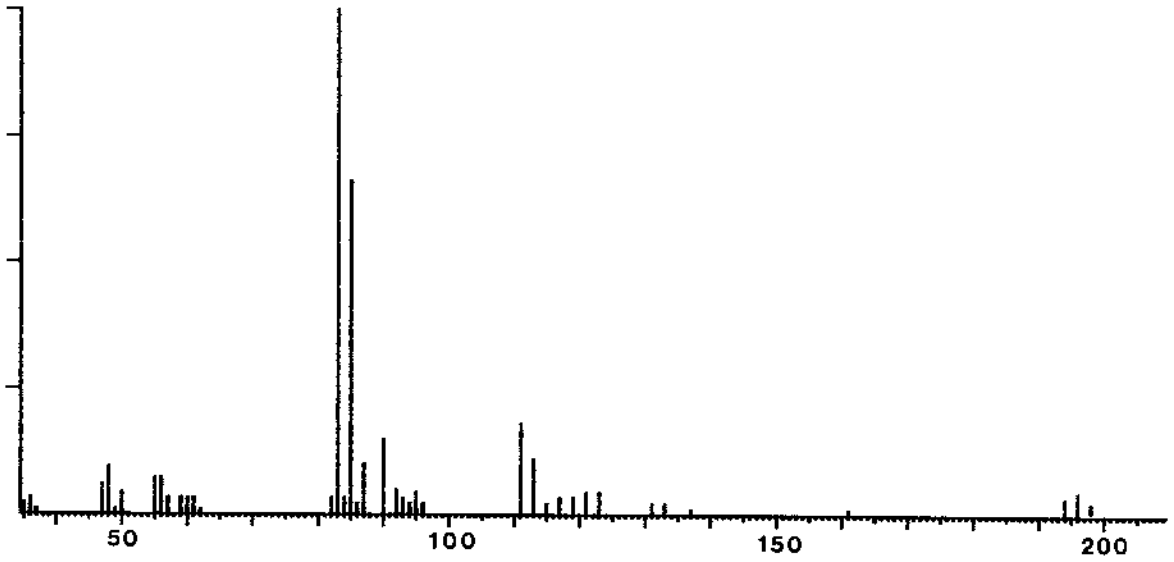


Fig. A-16--Tetrachloroethylphenol identification (no library reference spectrum available).

MUNICIPAL WASTEWATER EXTRACT



TETRACHLOROACETONE- LIBRARY SPECTRUM

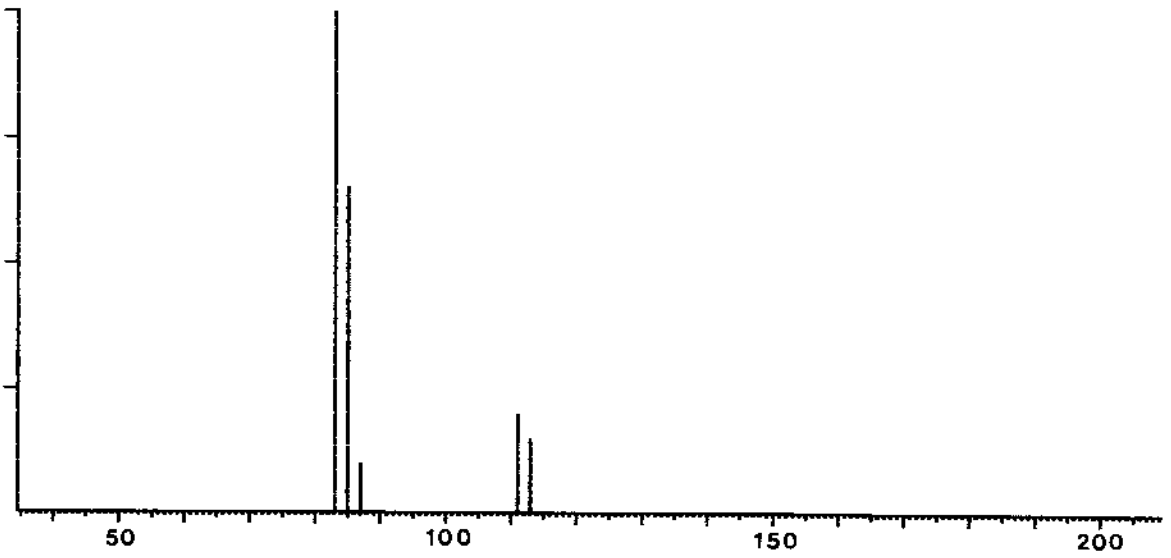


Fig. A-17--Tetrachloroacetone identification and library reference spectrum.

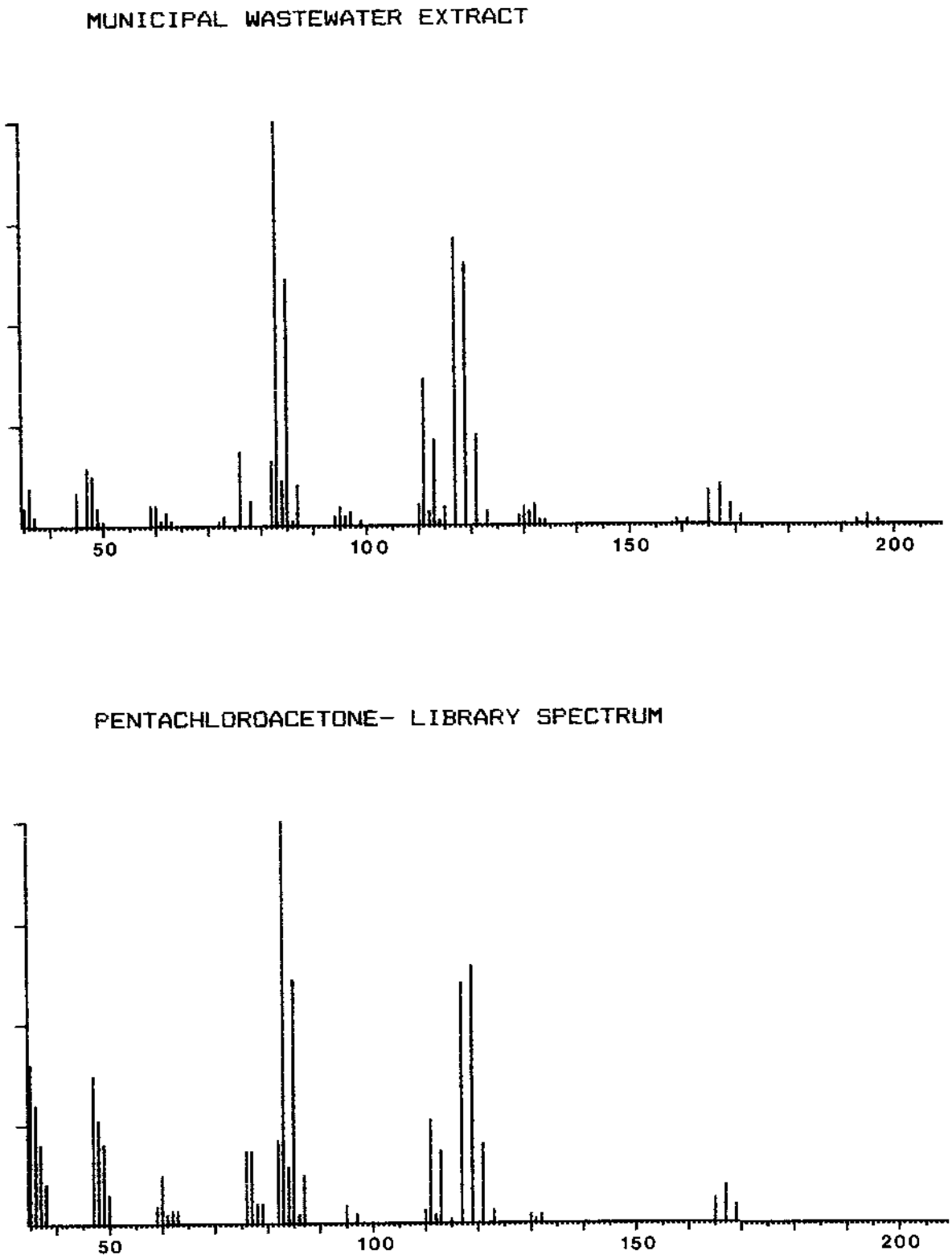


Fig. A-18--Pentachloroacetone identification and library reference spectrum.

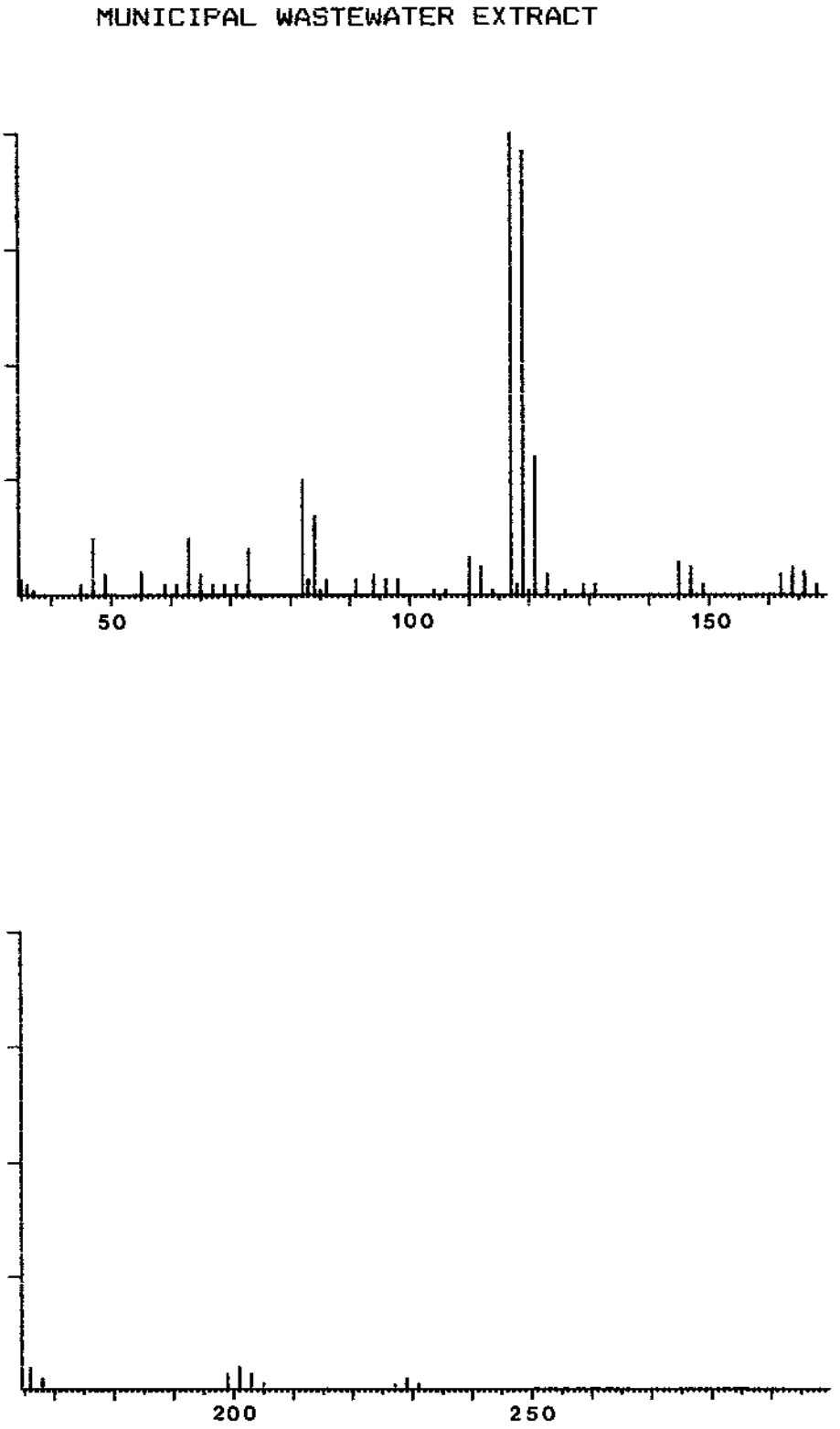


Fig. A-19--Hexachloroacetone identification (no library reference spectrum available).

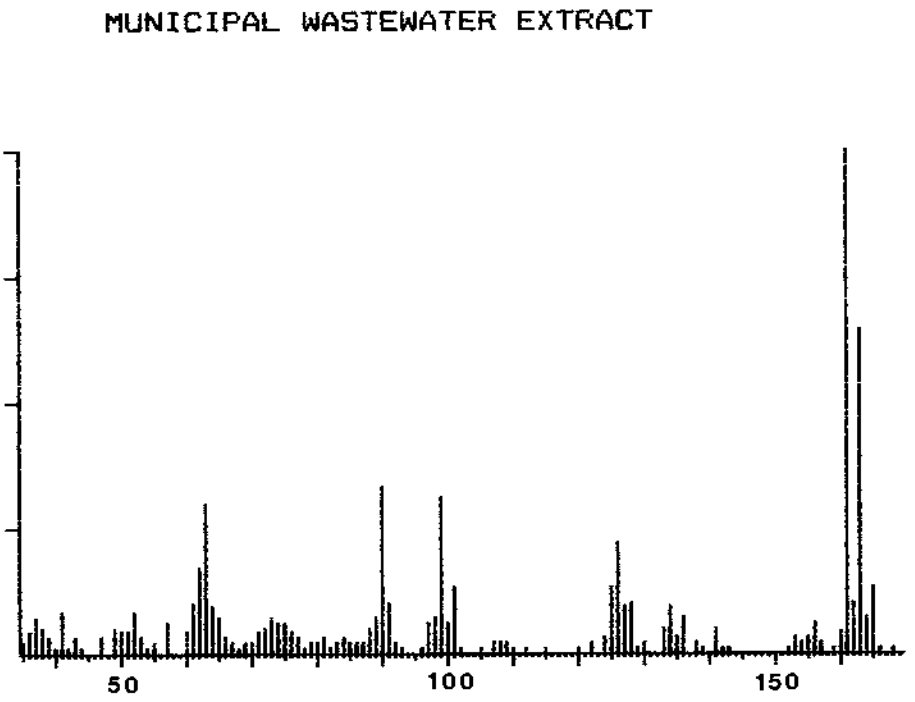


Fig. A-20--Dichlorobenzamine identification (no library reference spectrum available).

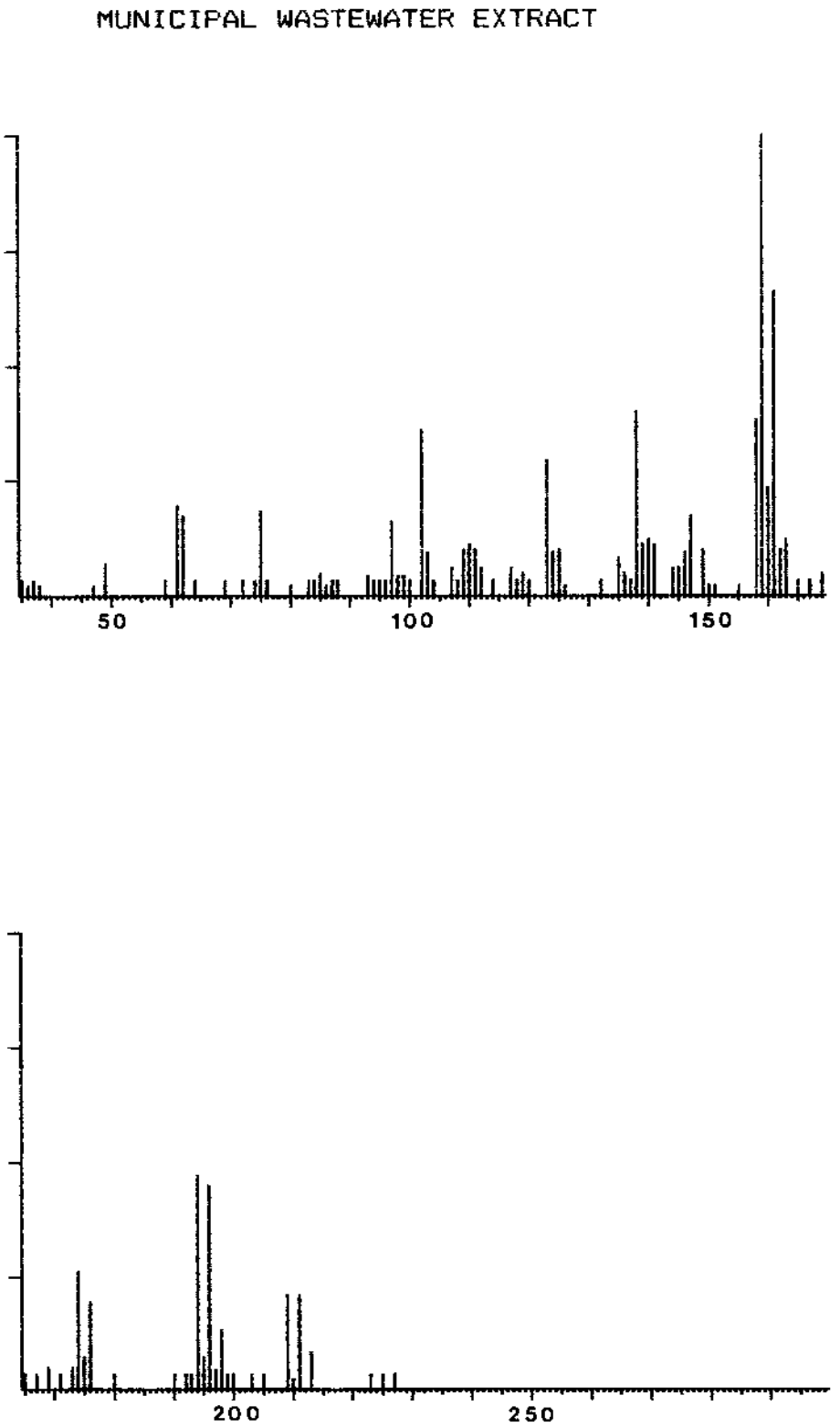
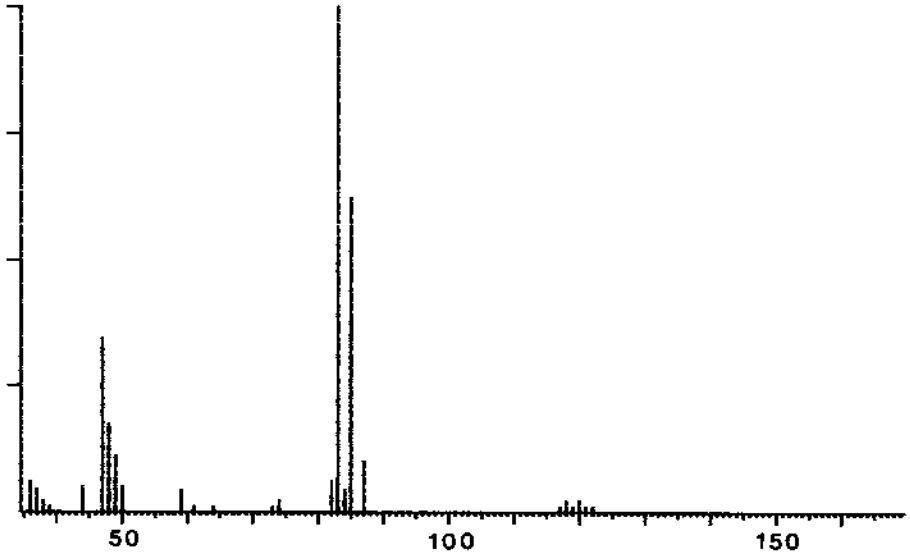


Fig. A-21--Trichloro-N-methylbenzamine identification (no library reference spectrum available).

MUNICIPAL WASTEWATER EXTRACT



CHLOROFORM- LIBRARY SPECTRUM

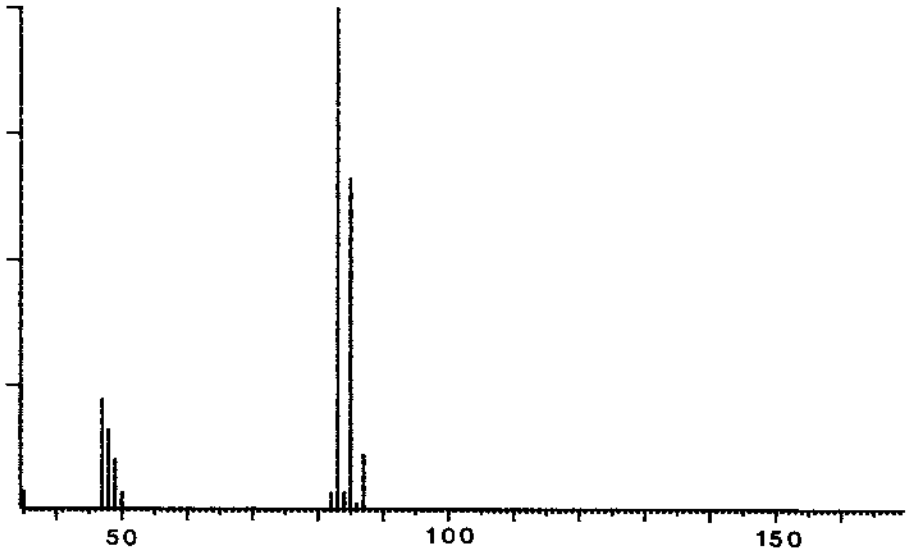


Fig. A-22--Chloroform identification and library reference spectrum.

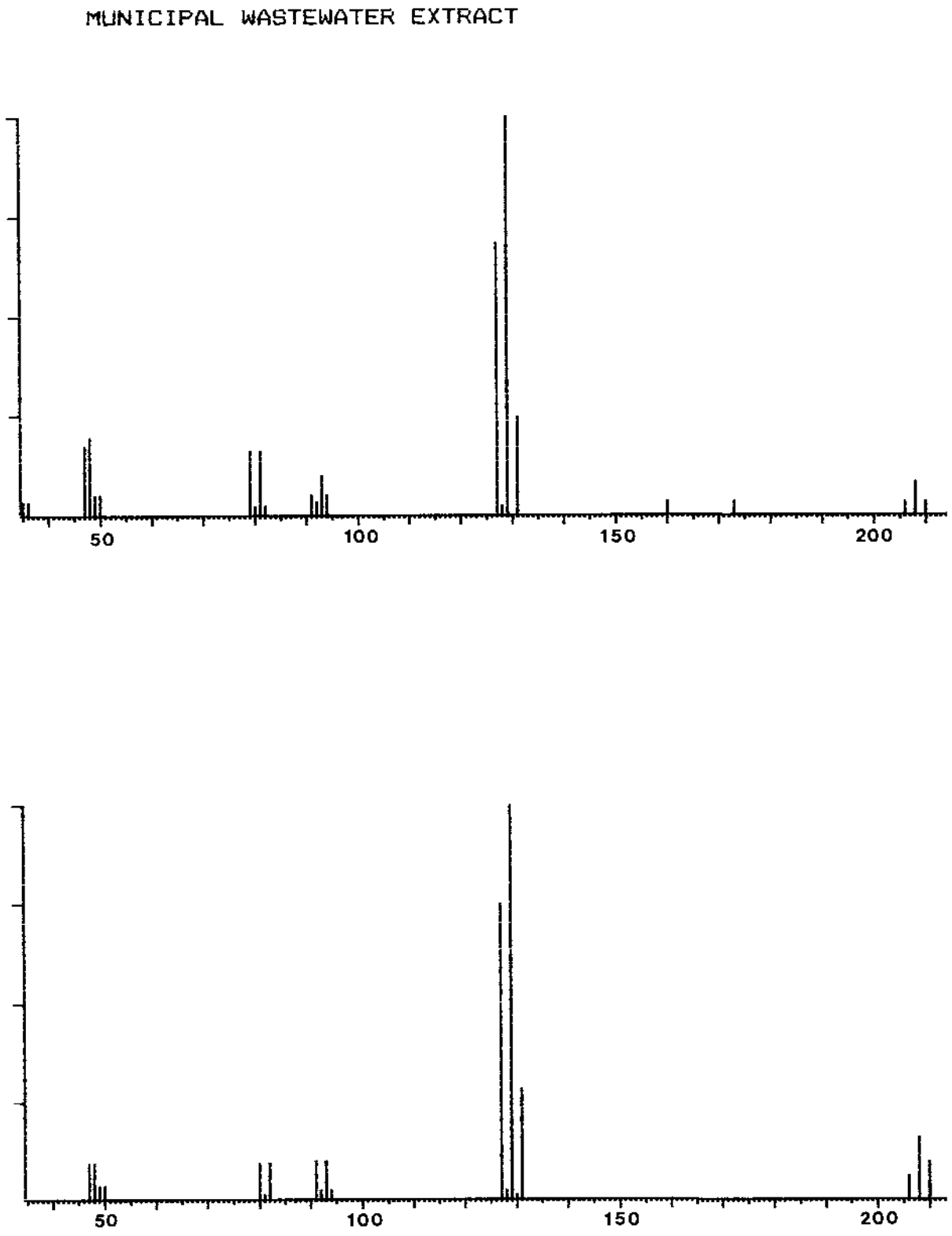


Fig. A-23--Dibromochloromethane identification and library reference spectrum.

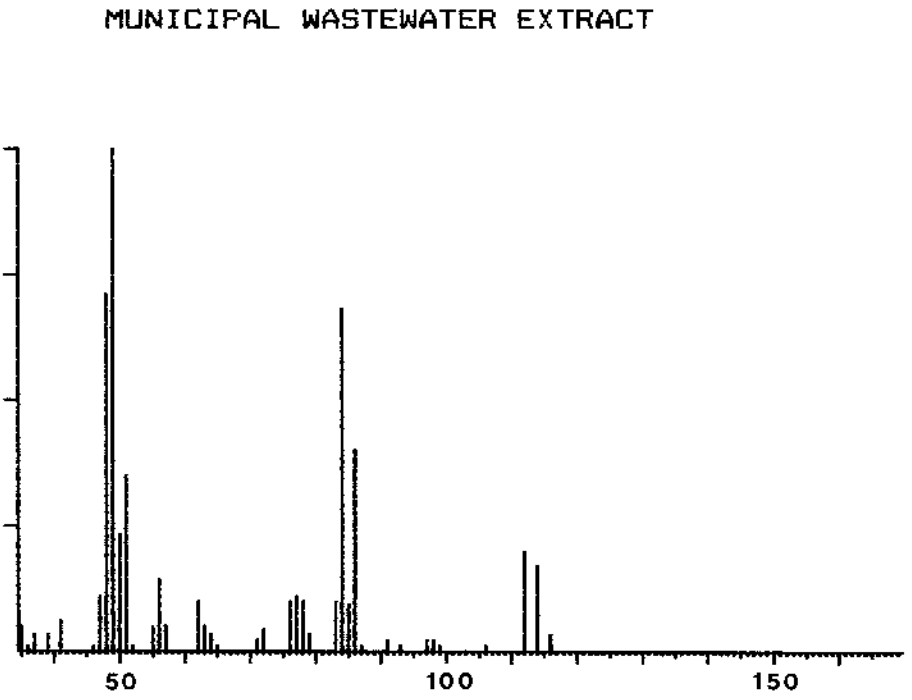


Fig. A-24--Dichloroacetaldehyde identification (no library reference spectrum available).

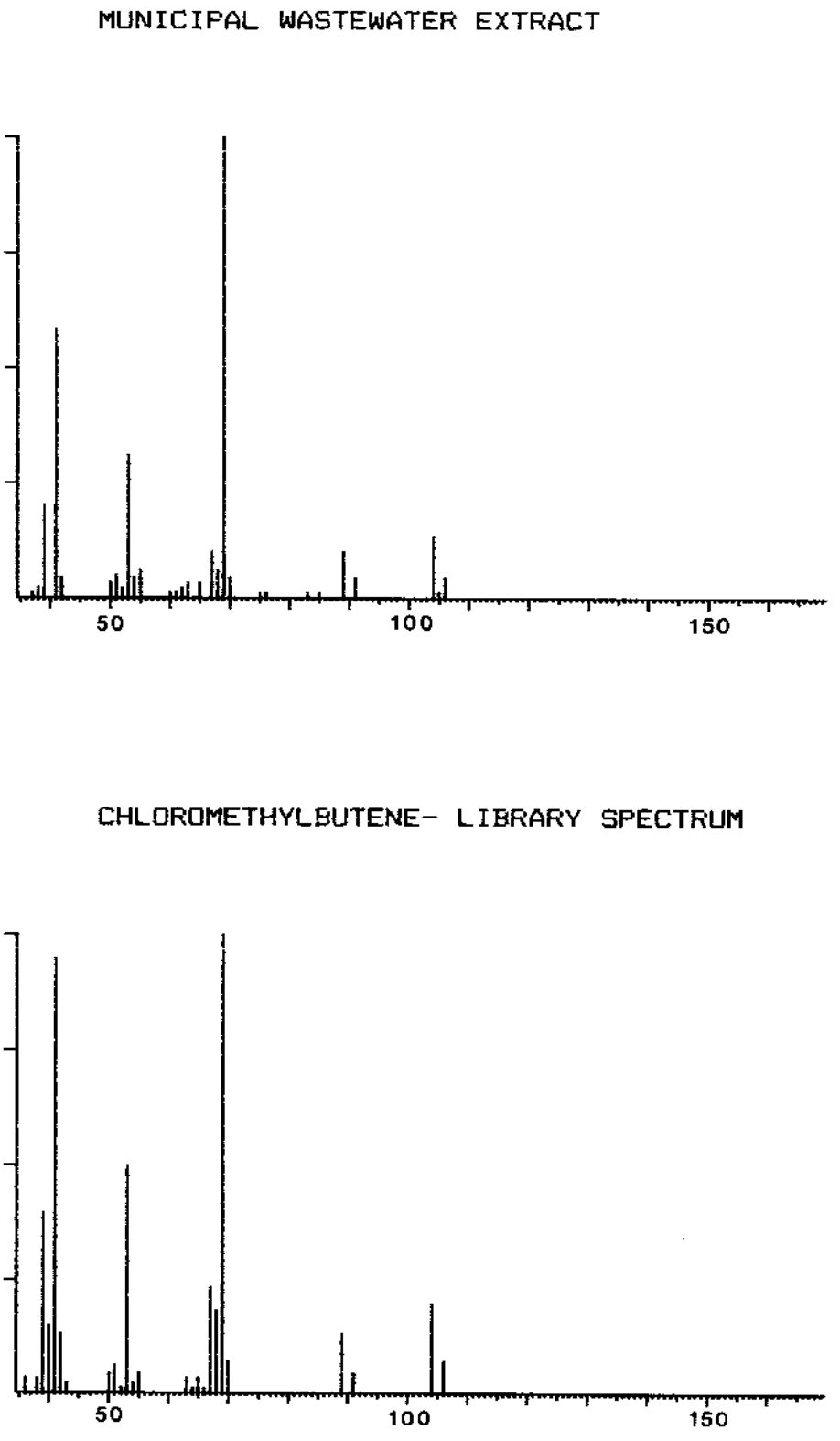


Fig. A-25--Chloromethylbutene identification and library reference spectrum.

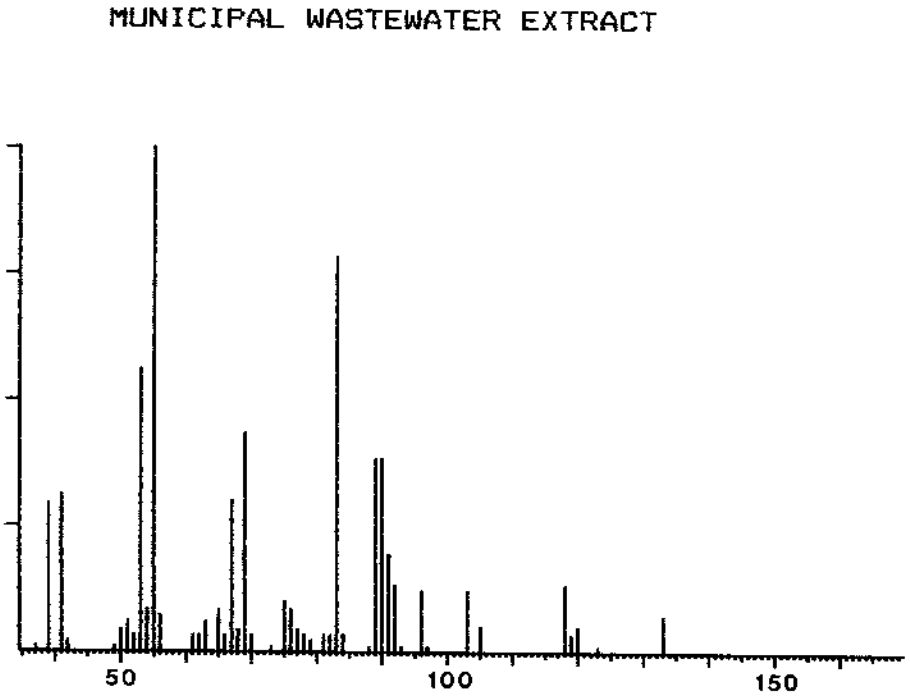


Fig. A-26--Chloro-1-hexene identification (no library reference spectrum available).

MUNICIPAL WASTEWATER EXTRACT

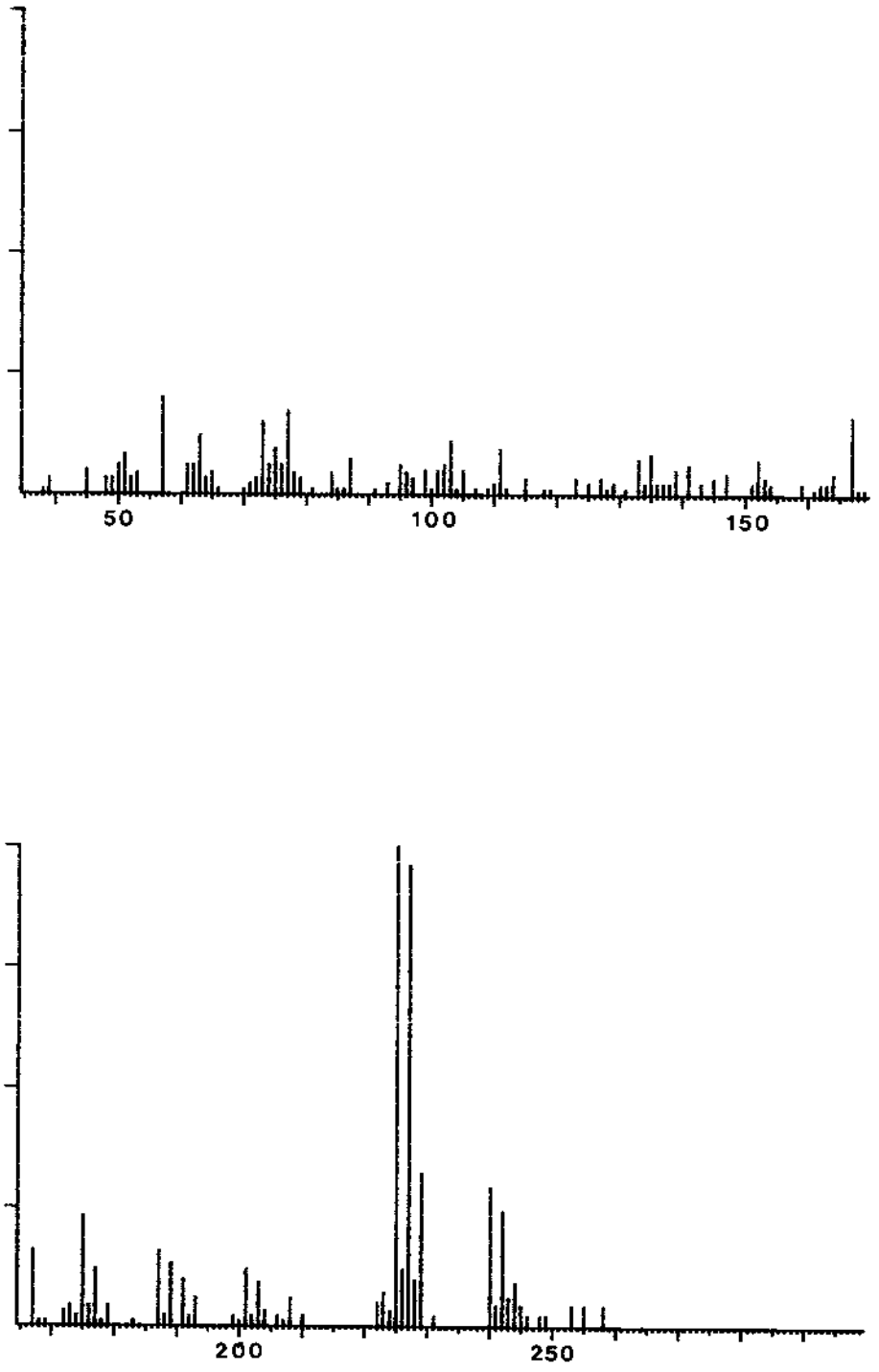


Fig. A-27--Trichlorodihydroxybenzene identification (no library reference spectrum available).

MUNICIPAL WASTEWATER EXTRACT

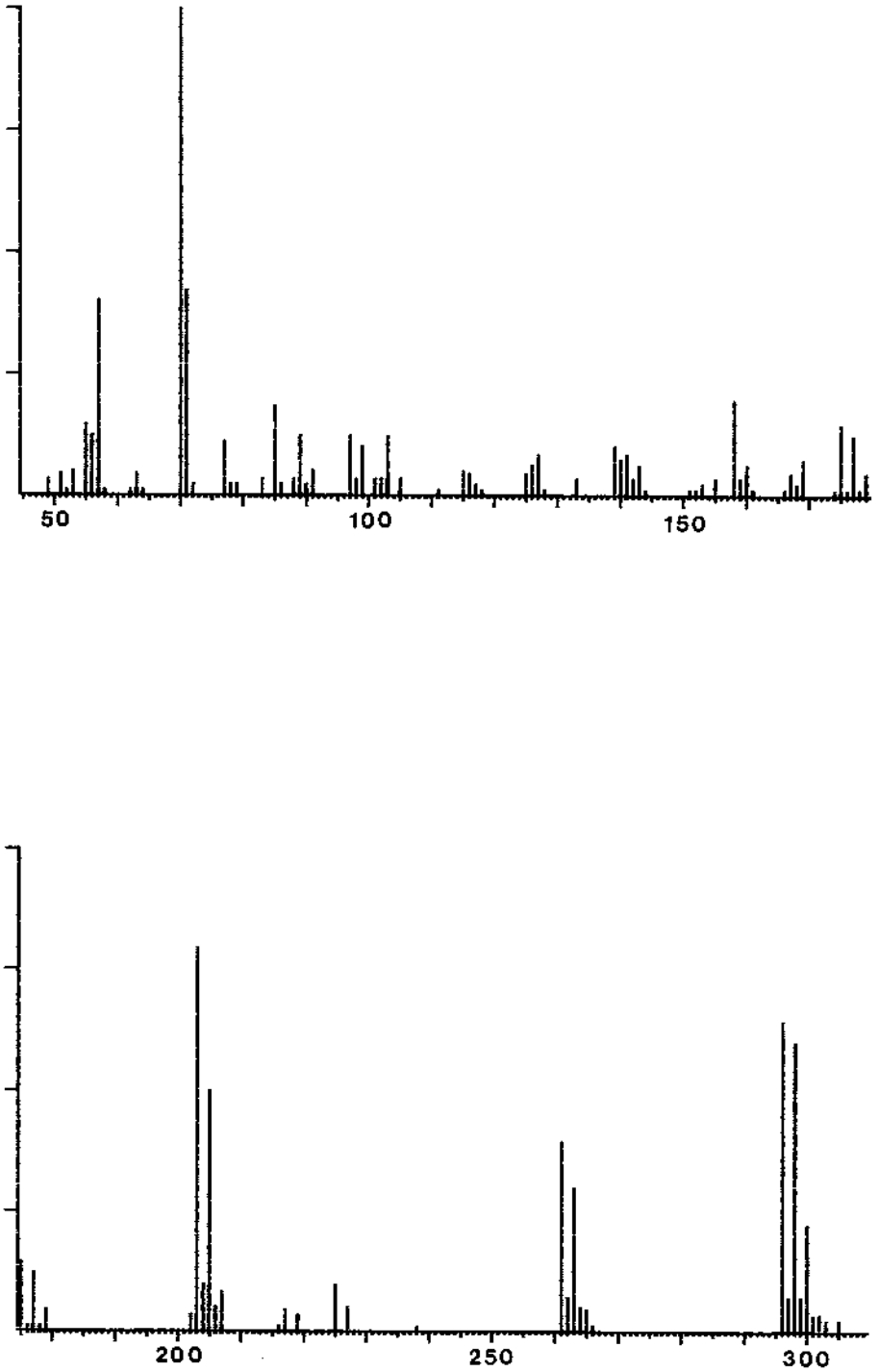


Fig. A-28--Chlorobis(chloromethyl)phenyldicarboxylate identification (no library reference spectrum available).

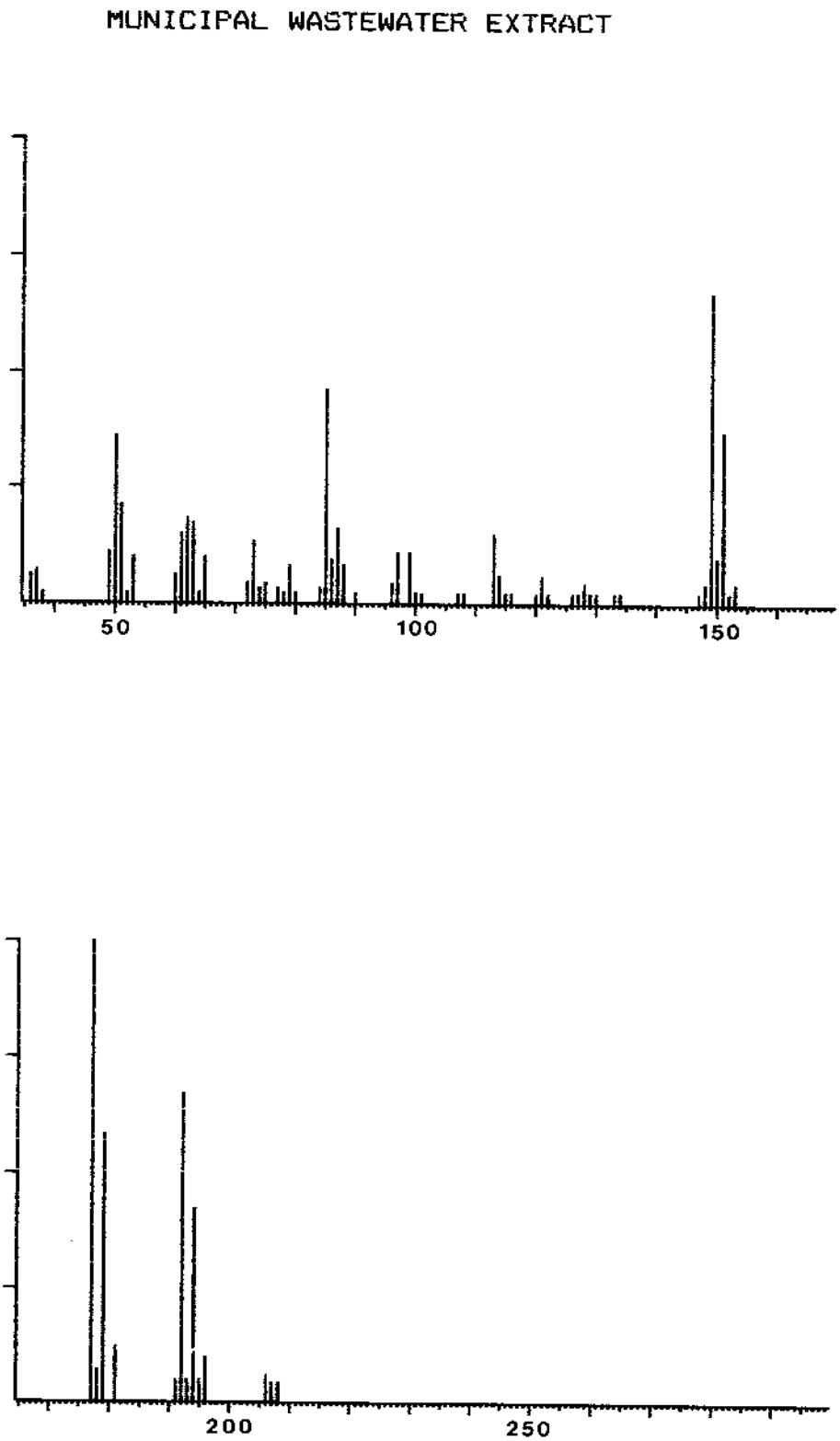


Fig. A-29--Dichlorodimethoxyphenol identification (no library reference spectrum available).

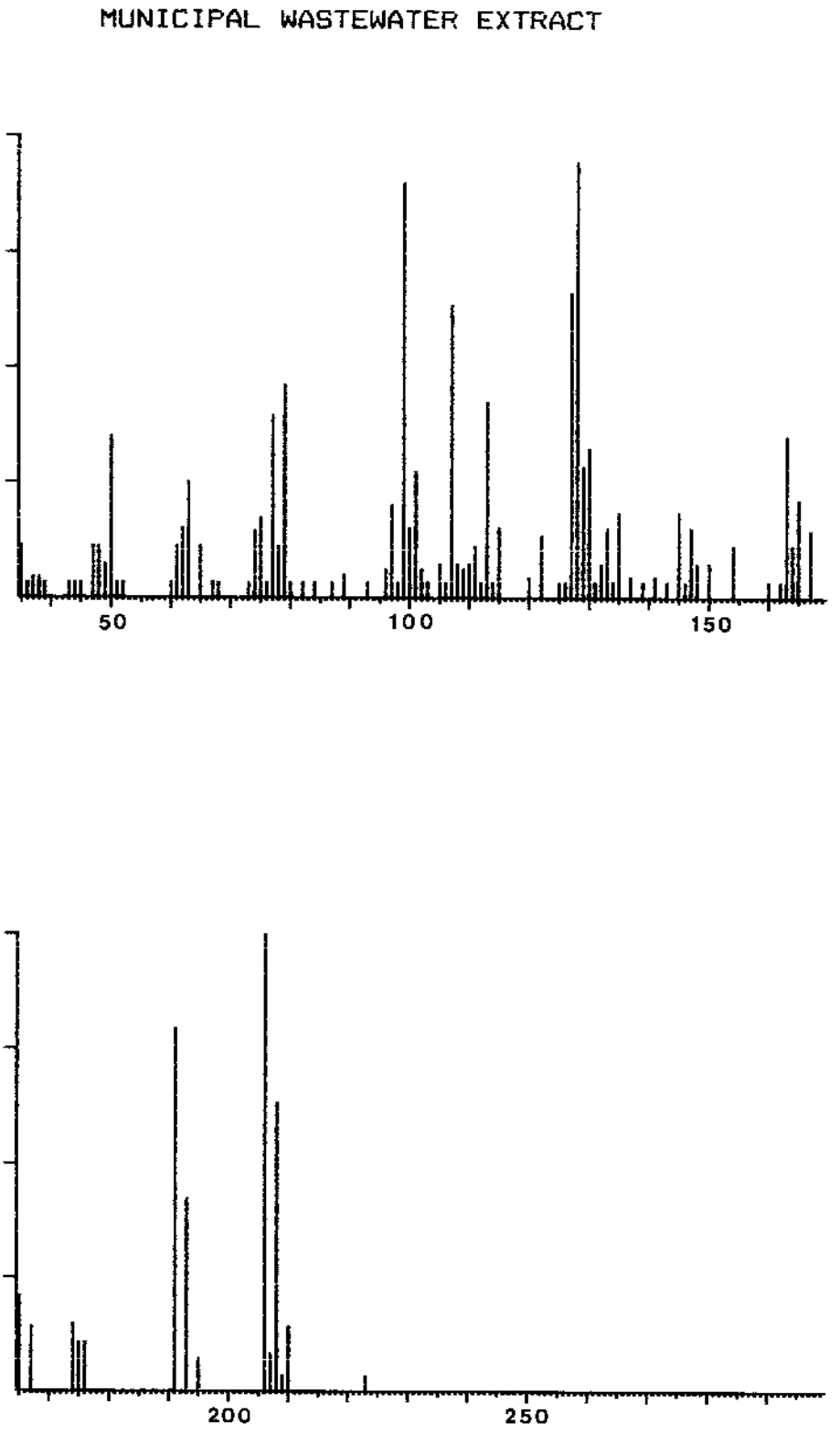


Fig. A-30--Dichlorodimethoxybenzene identification (no library spectrum available).

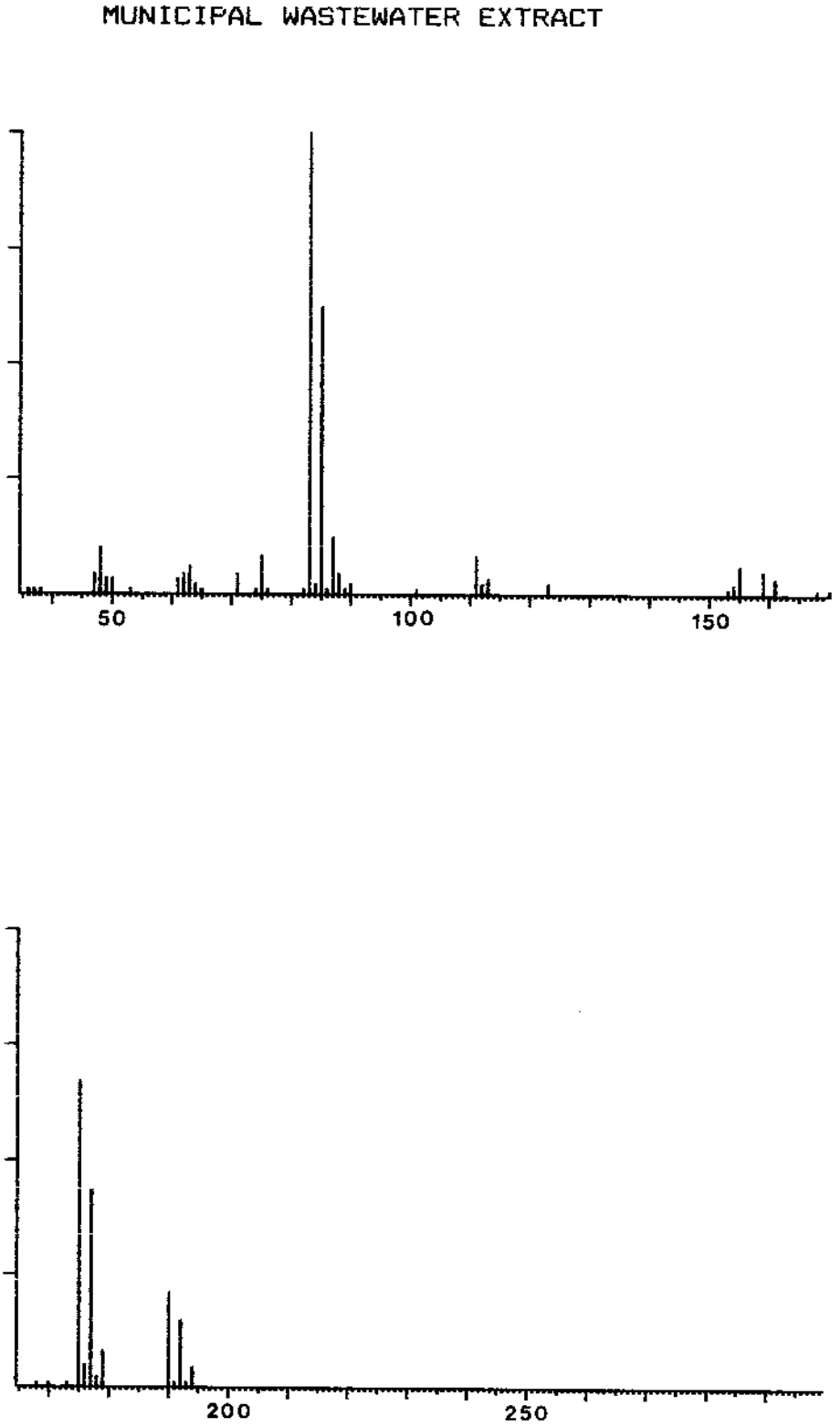
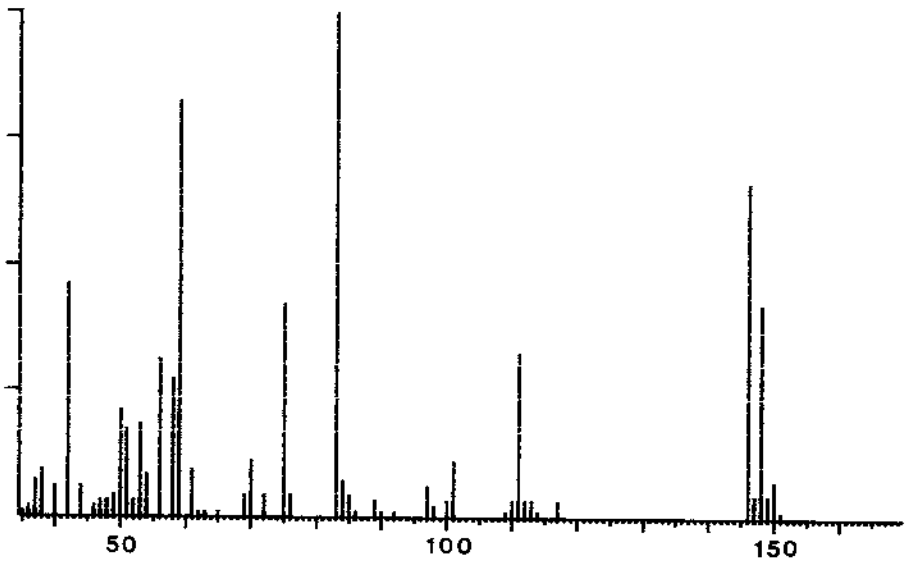


Fig. A-31--α,α-dichloromethoxytoluene identification (no library reference spectrum available).

APPENDIX B

MASS SPECTRA OF CHLORINATED ORGANIC COMPOUNDS FROM THE COMMERCIAL SUPERCHLORINATION OF MUNICIPAL WASTES

COMMERCIALLY SUPERCHLORINATED WASTEWATER



DICHLOROBENZENE- LIBRARY SPECTRUM

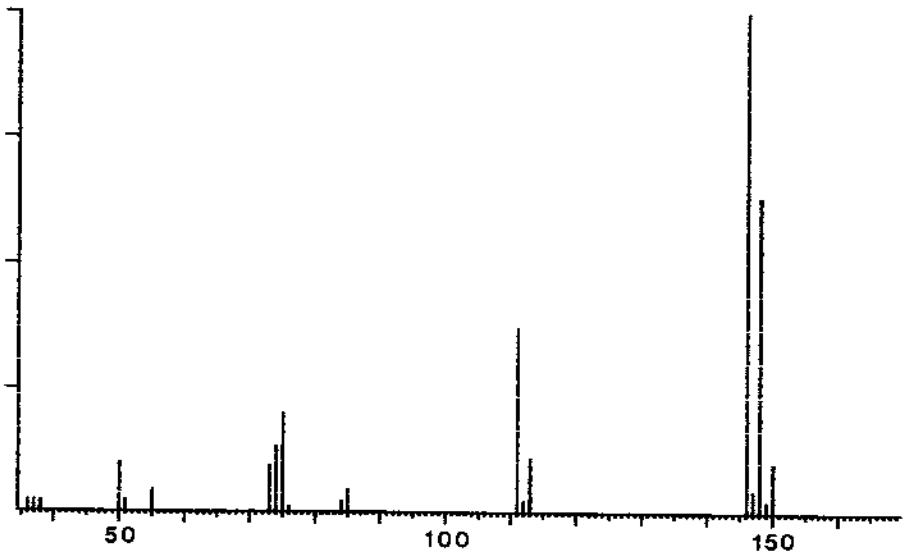
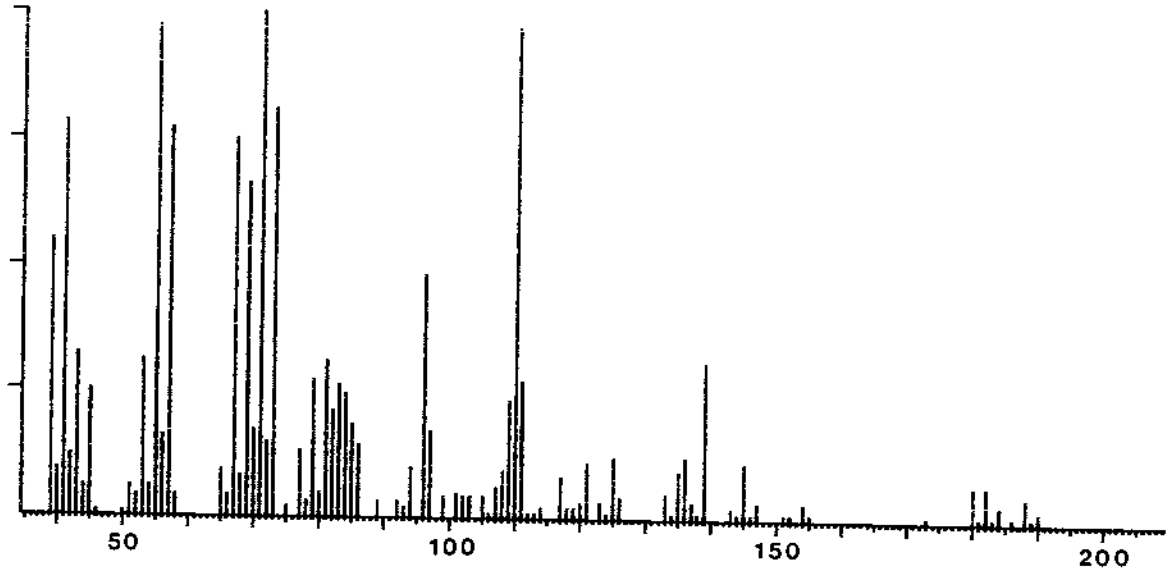


Fig. B-1--Dichlorobenzene identification and library reference spectrum.

COMMERCIALLY SUPERCHLORINATED WASTEWATER



TRICHLOROBENZENE- LIBRARY SPECTRUM

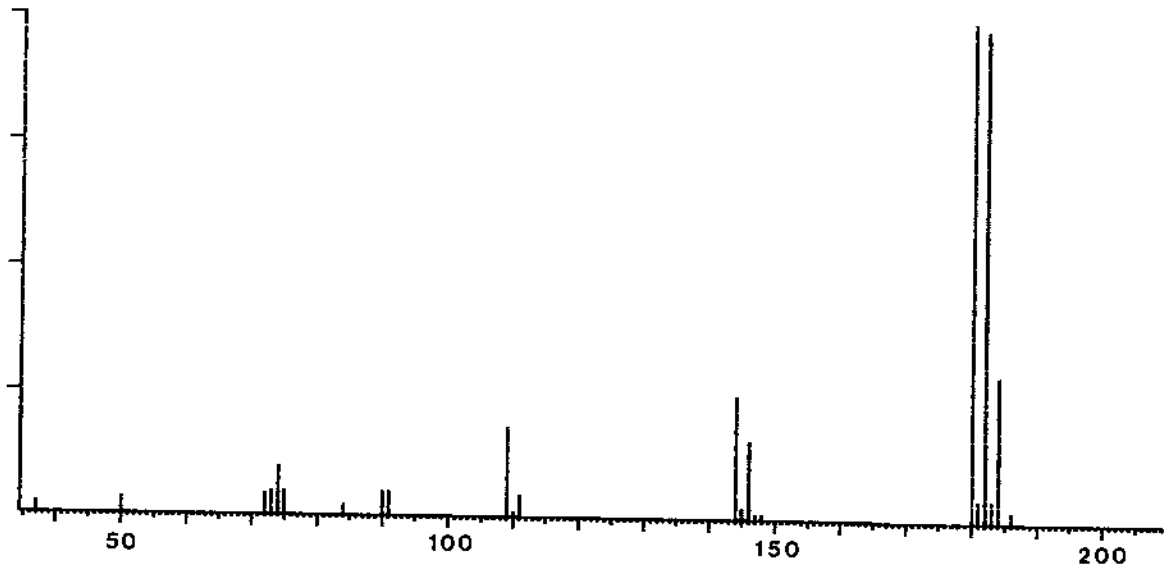


Fig. B-2--Trichlorobenzene identification and library reference spectrum.

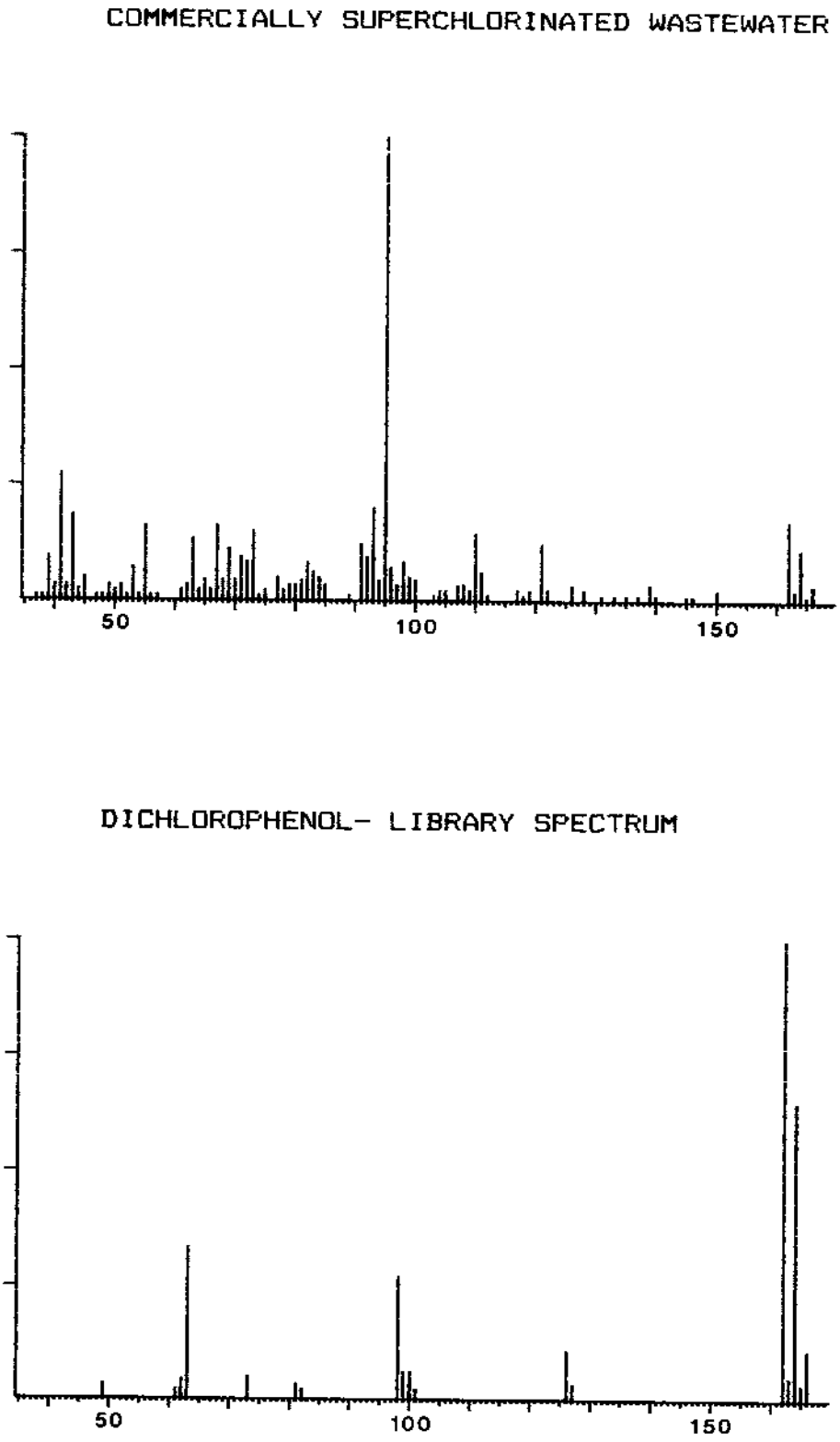


Fig. B-3--Dichlorophenol identification and library reference spectrum.

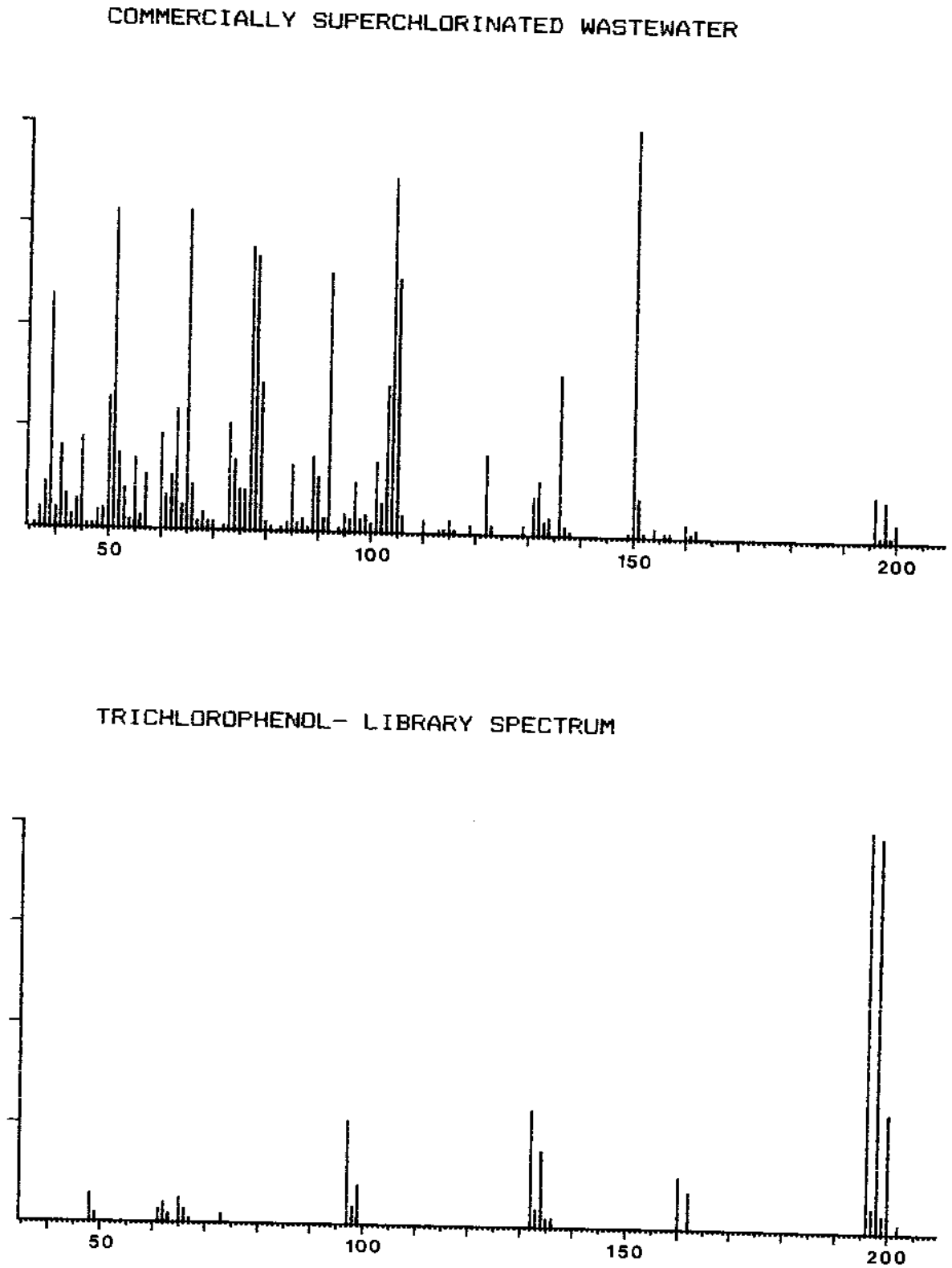
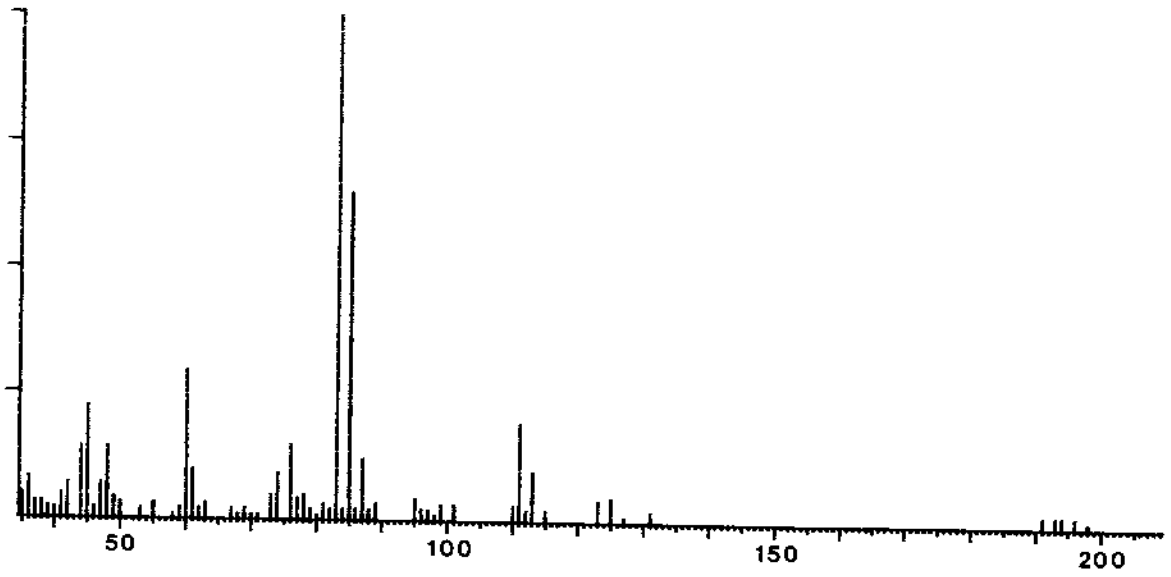


Fig. B-4--Trichlorophenol identification and library reference spectrum.

COMMERCIALLY SUPERCHLORINATED WASTEWATER



1,1,3,3-TETRACHLOROPROPANE- LIBRARY SPECTRUM

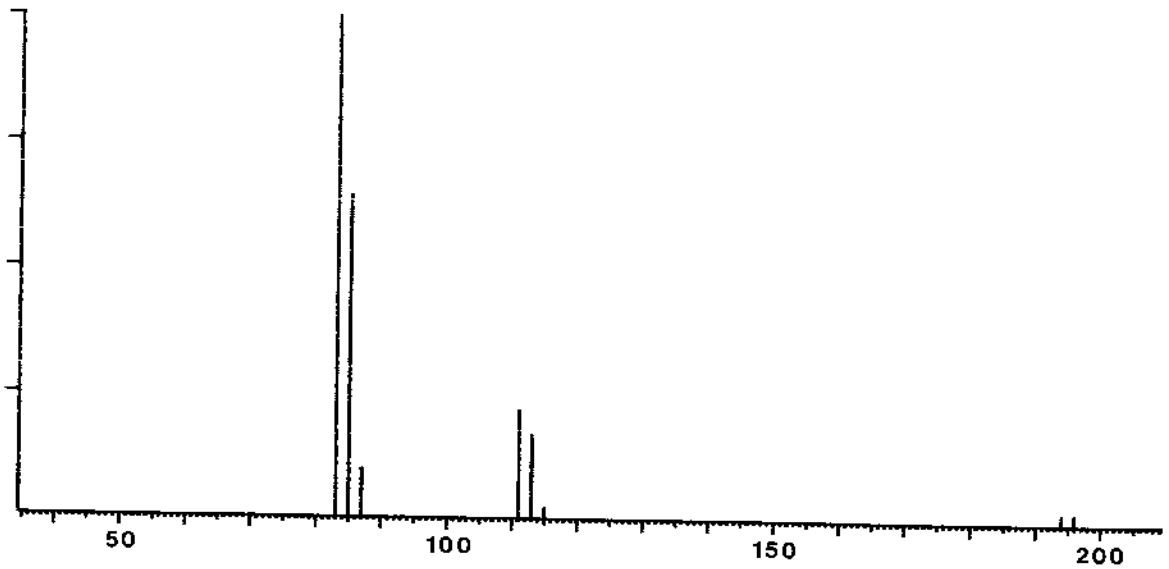


Fig. B-5--1,1,3,3-tetrachloropropanone identification and library reference spectrum.

COMMERCIALLY SUPERCHLORINATED WASTEWATER

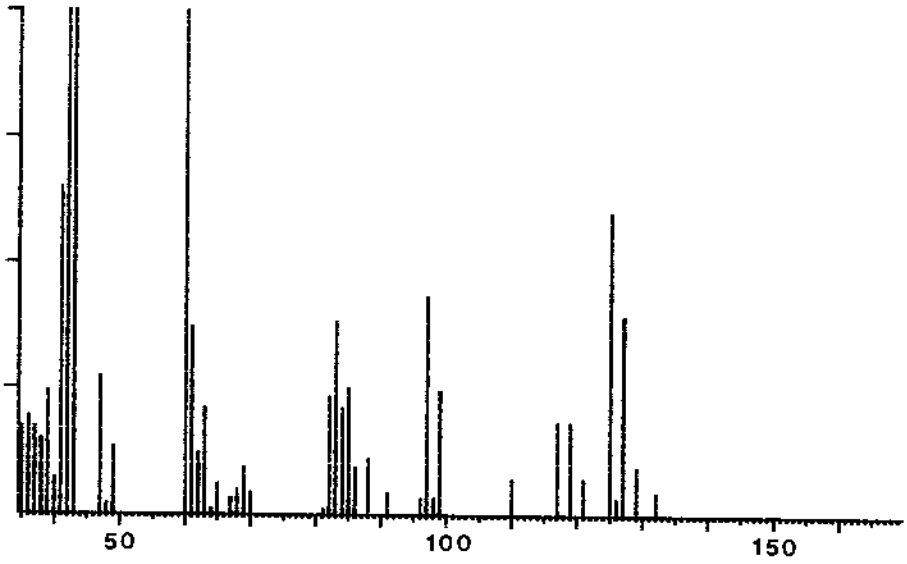


Fig. B-6--1,1,1,4,4-pentachloro-2-butanone identification (no library reference spectrum was available).

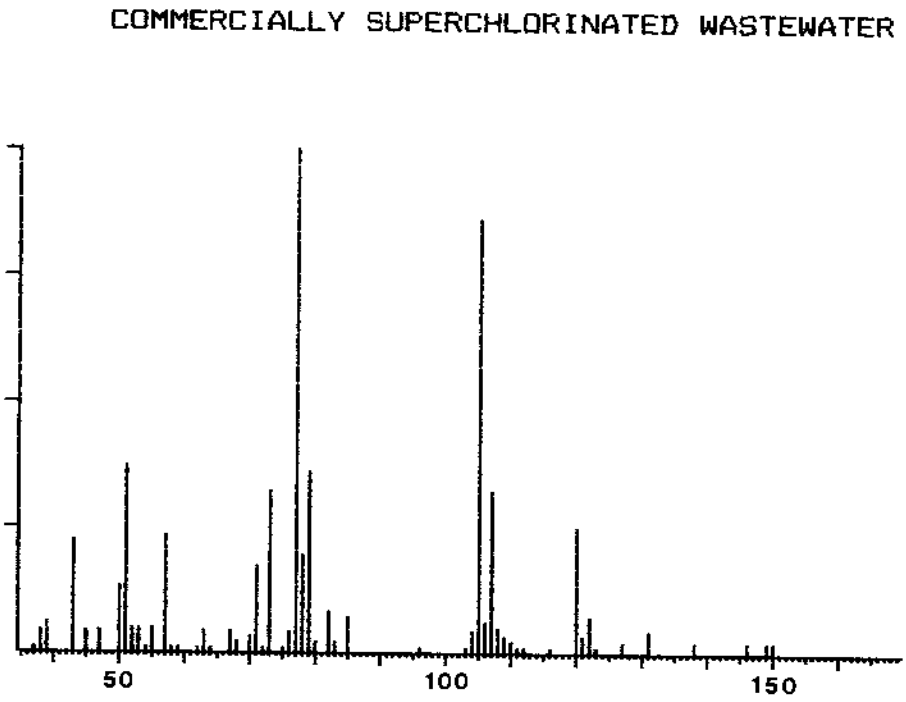


Fig. B-7--3-chloro-2-pentanone identification (no library reference spectrum was available).

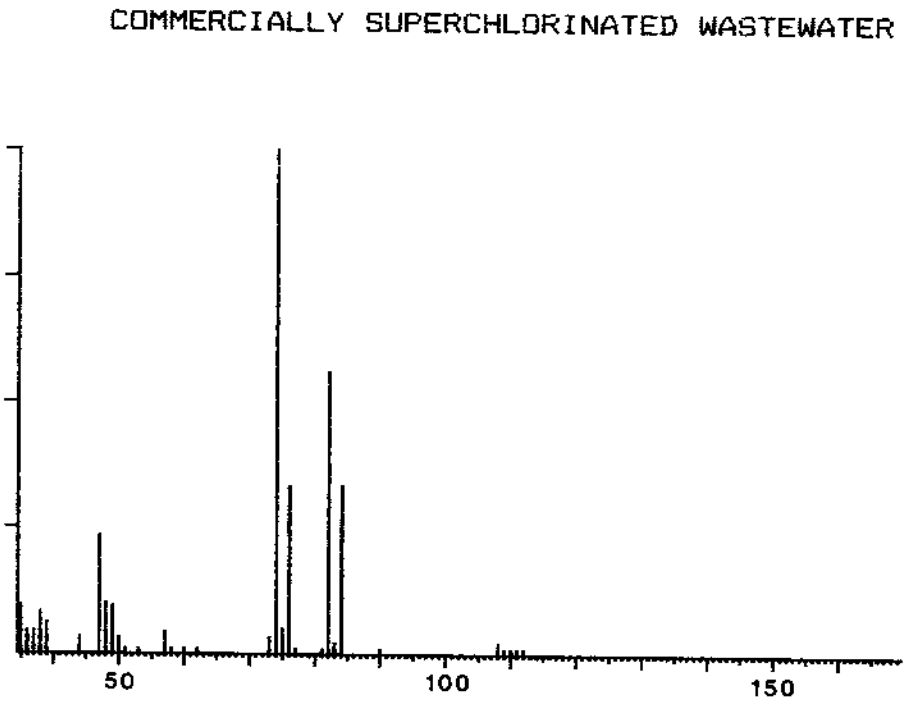


Fig. B-8--Dichloroacetonitrile identification (no library reference spectrum was available).

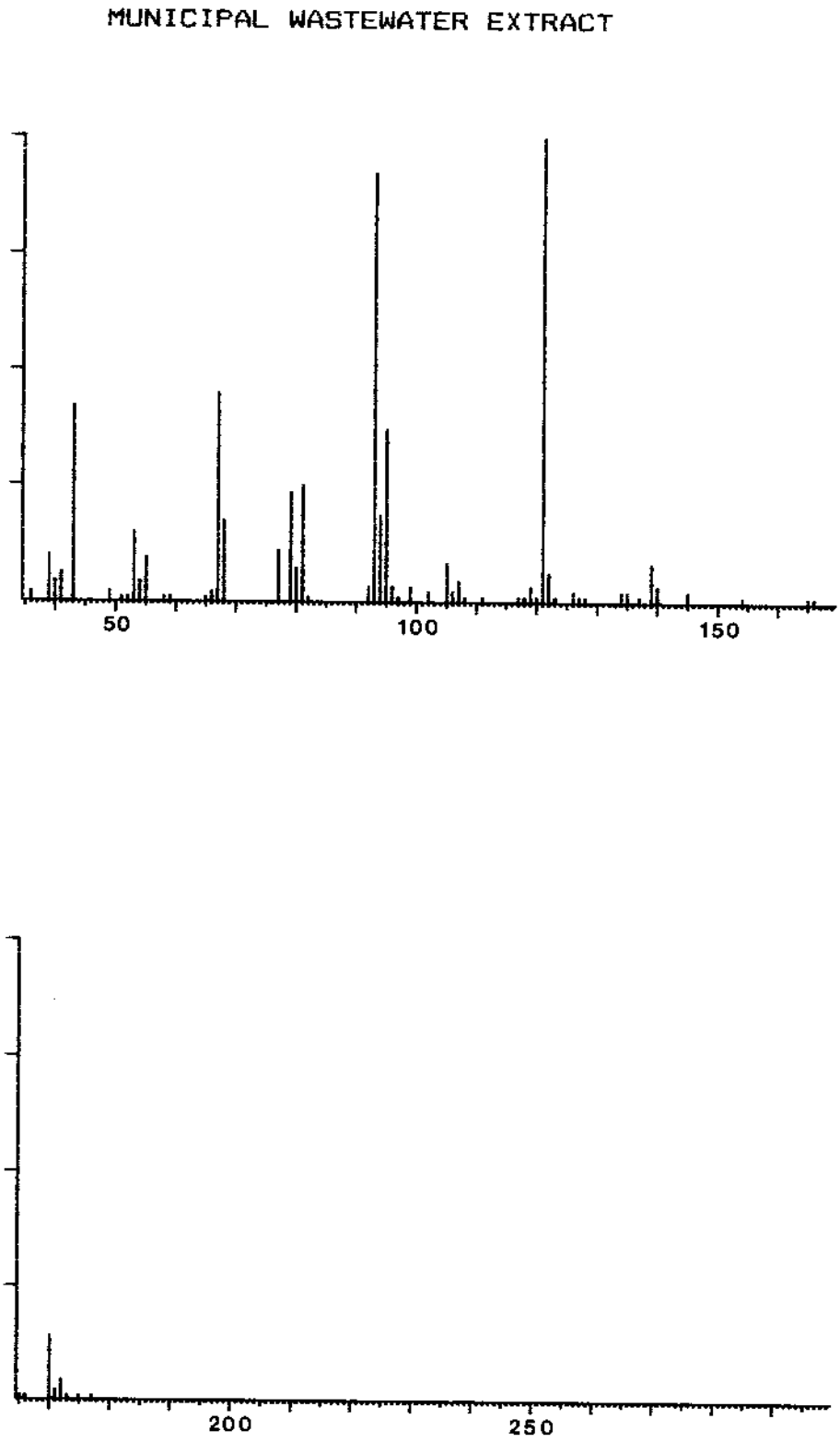


Fig. B-9--Phenyl chloroacetate identification (no library reference spectrum was available).

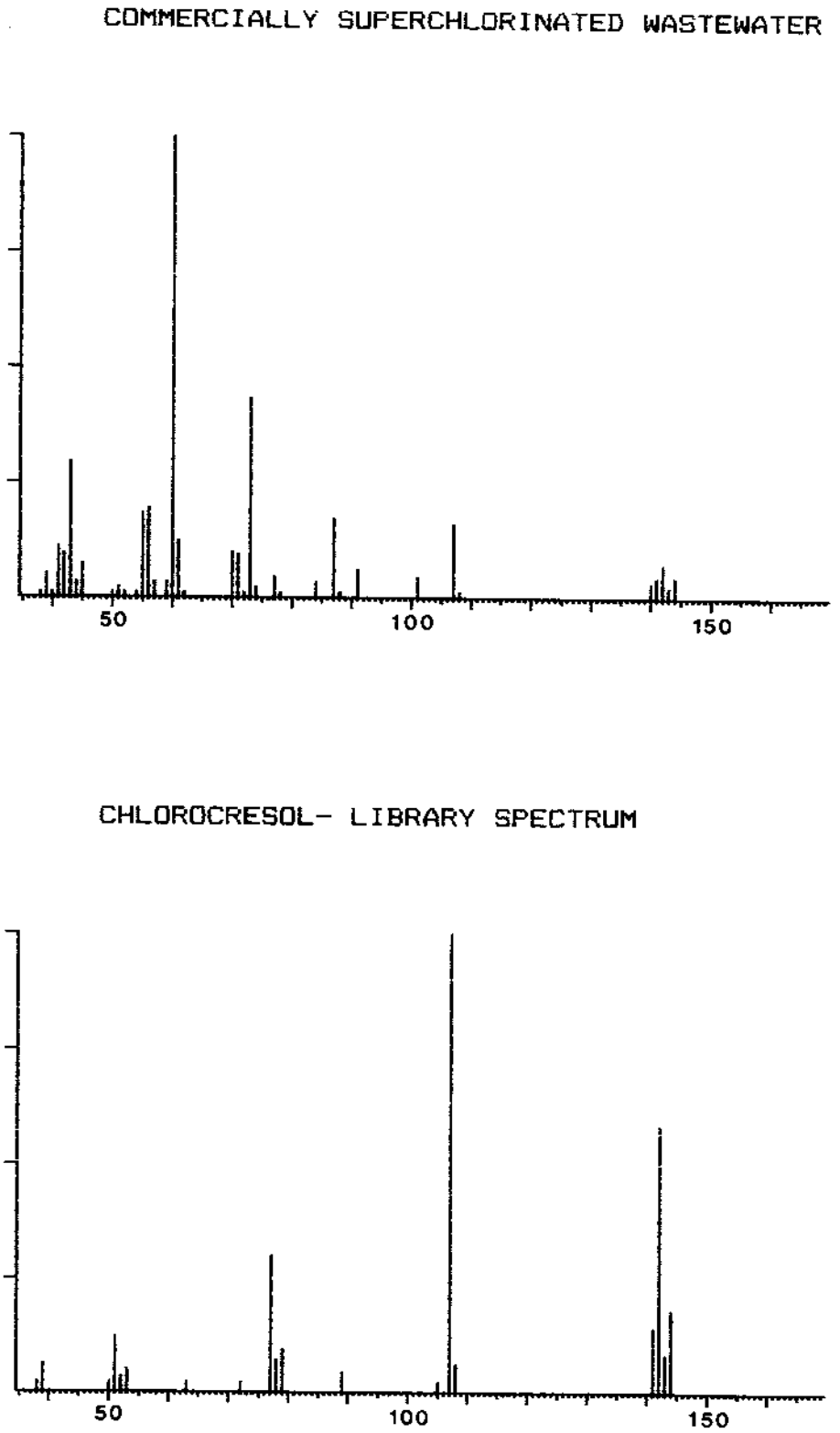


Fig. B-10--Chlorocresol identification and library reference spectrum.

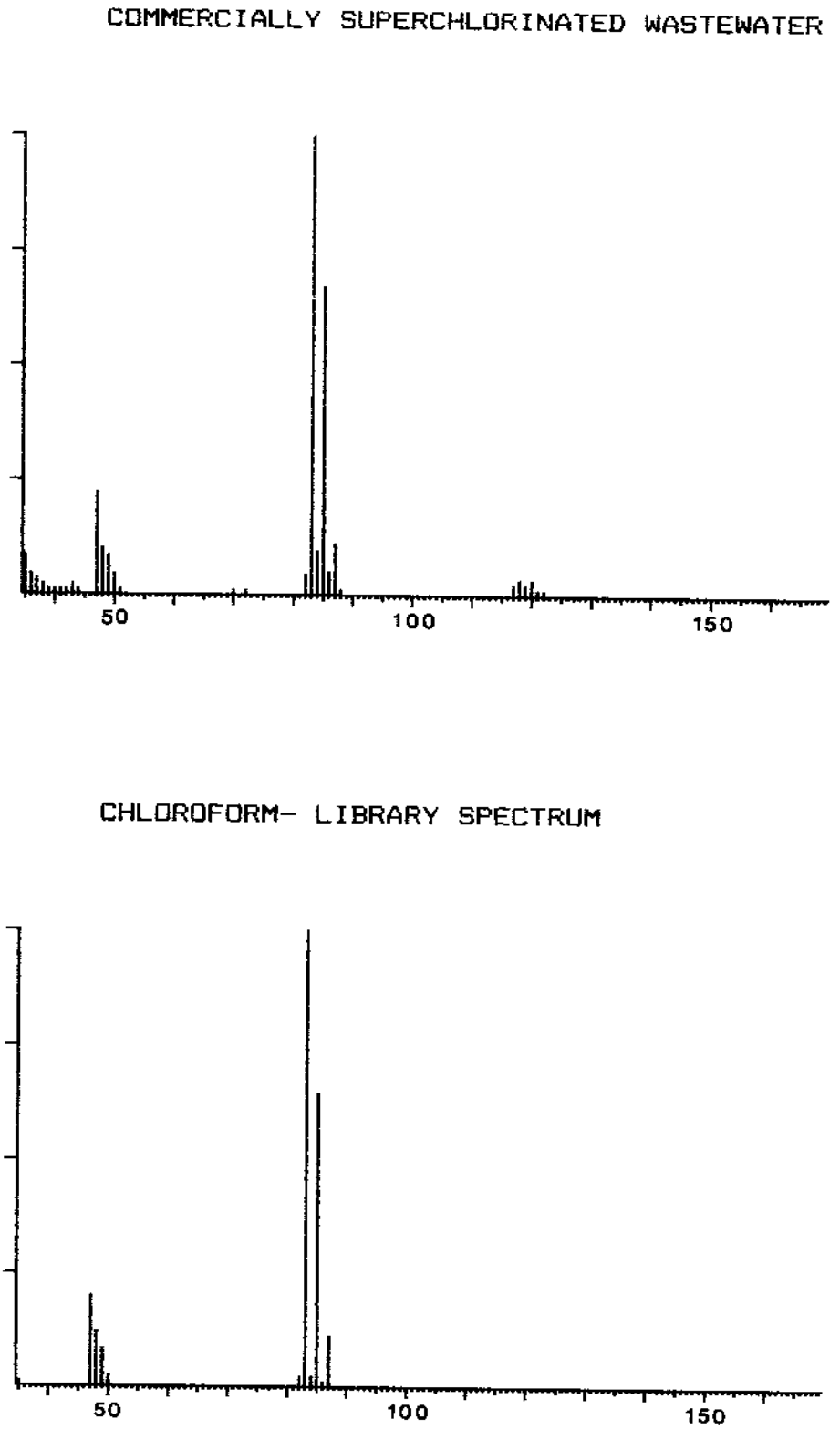


Fig. B-11--Chloroform identification and library reference spectrum.

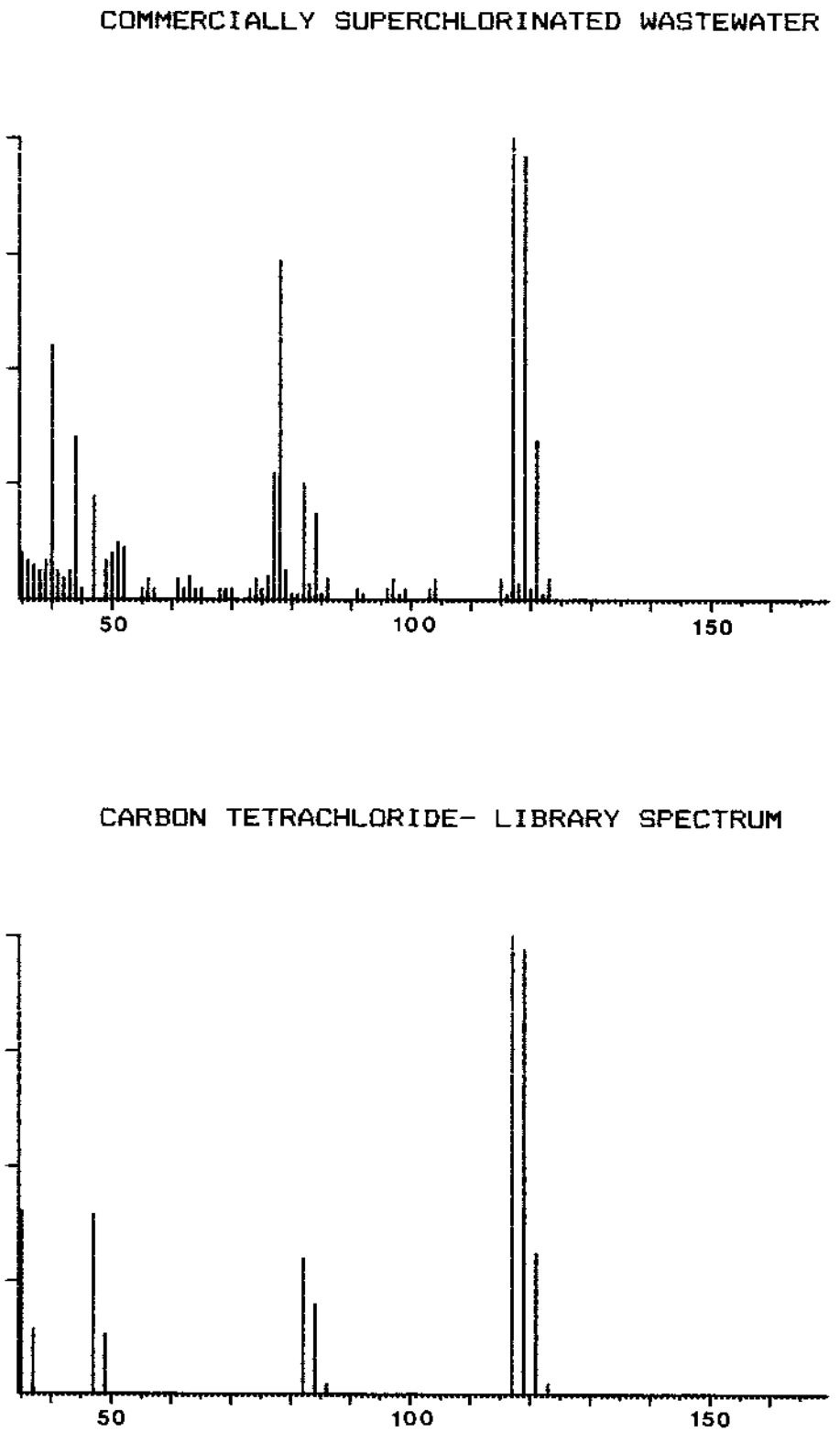
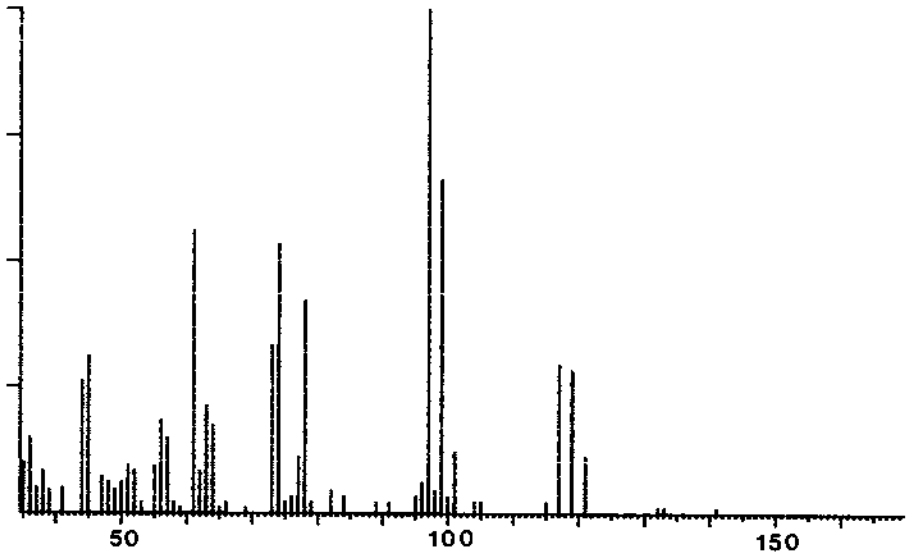


Fig. B-12--Carbon tetrachloride identification and library reference spectrum.

COMMERCIALLY SUPERCHLORINATED WASTEWATER



1,1,1-TRICHLOROETHANE- LIBRARY SPECTRUM

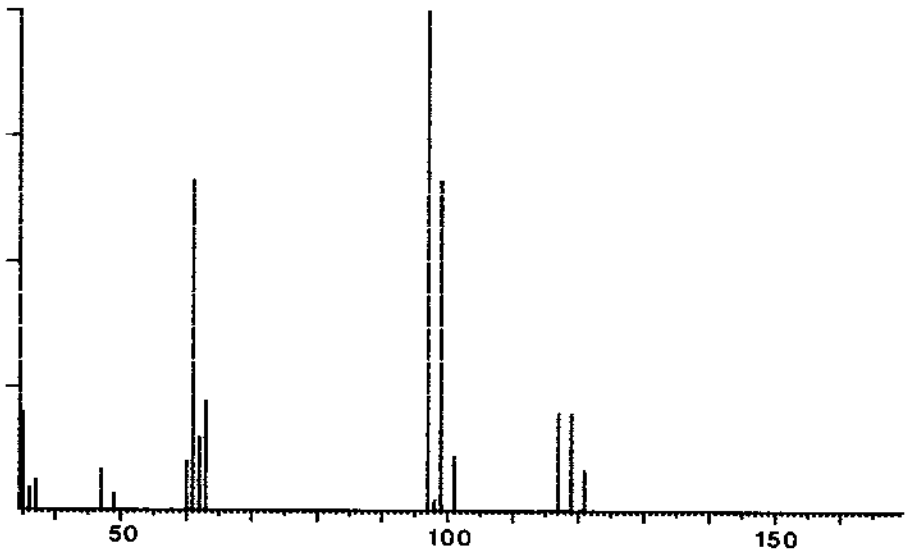


Fig. B-13--1,1,1-trichloroethane identification and library reference spectrum.

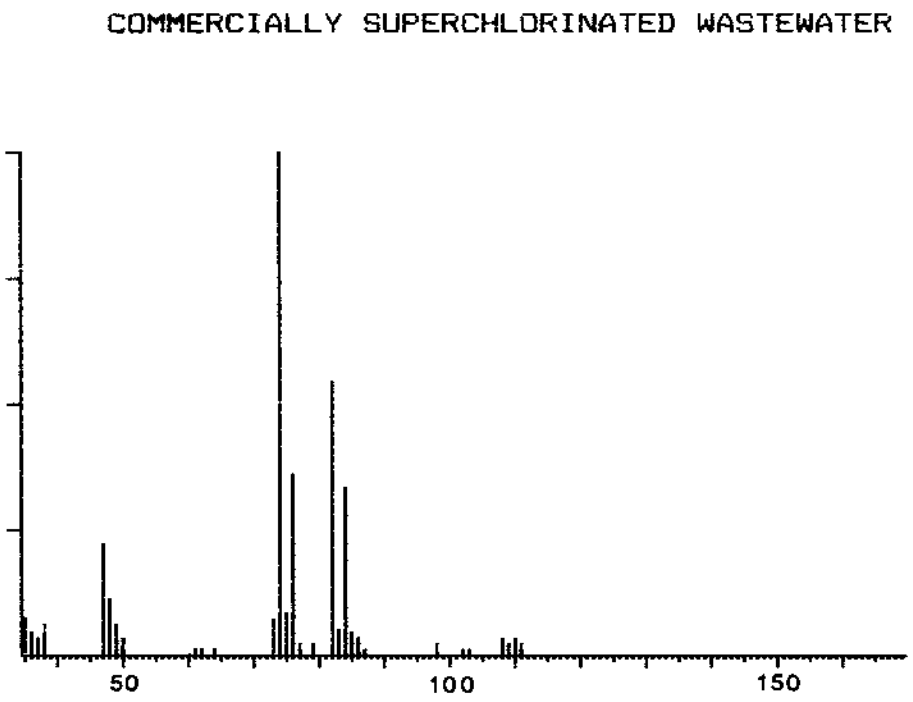
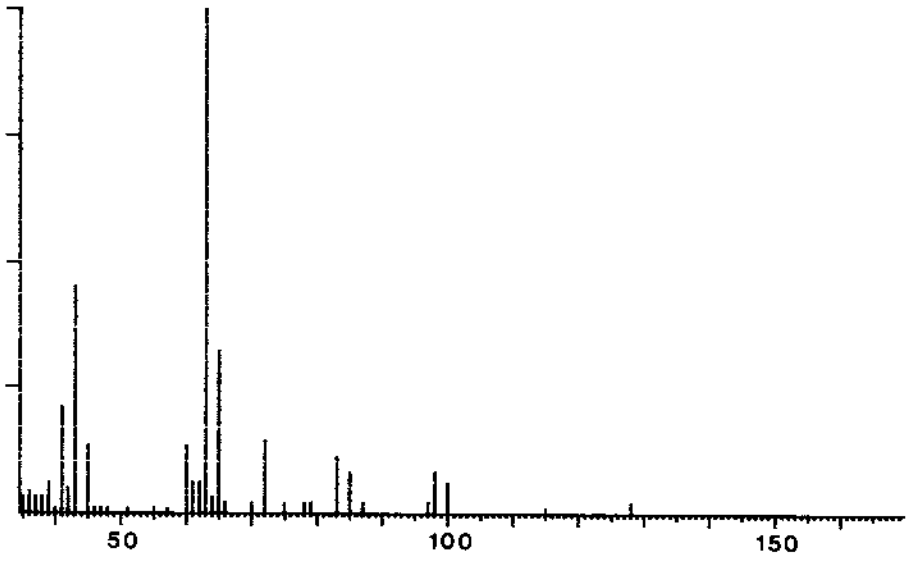


Fig. B-14--Dichloroacetaldehyde identification (no library reference spectrum was available).

COMMERCIALLY SUPERCHLORINATED WASTEWATER



1,1-DICHLOROETHANE- LIBRARY SPECTRUM

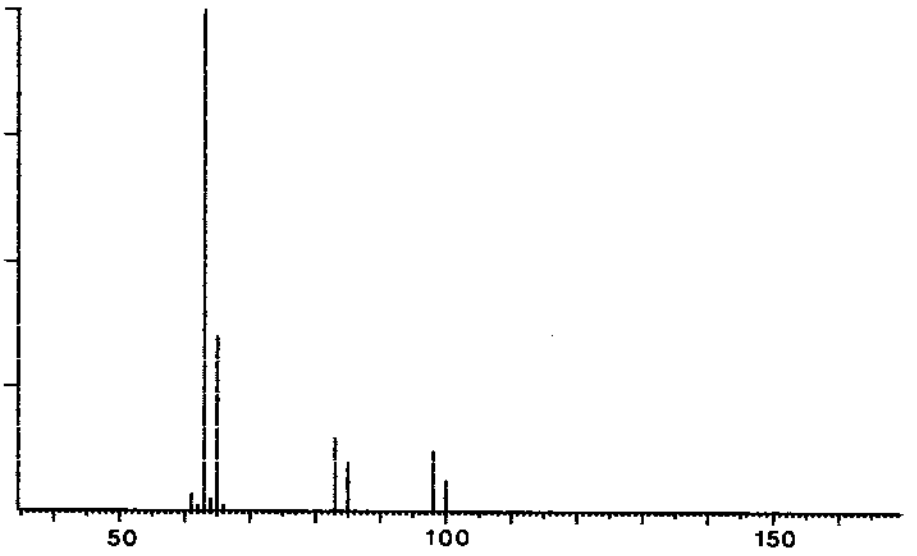


Fig. B-15--1,1-dichloroethane identification and library reference spectrum.

APPENDIX C

COMPUTER PROGRAM FOR THE ANALYSIS OF GC/MS RAW DATA FOR CHLORINATED ORGANIC COMPOUNDS

```
LIS
ISOFN2

10  DIM G[999],M[999]
20  REM FILES ******
30  DIM A[21],B[21]
40  DIM T$[50]
50  PRINT "INPUT NUMBER OF CHLORINES THEN NUMBER OF BROMINES"
60  INPUT N,L
70  LET T=-1
80  MAT A=ZER
90  MAT B=ZER
100  MAT G=ZER
110  MAT M=ZER
120  REM  **********CHLORINE CLUSTER**************************
130  IF N=0 THEN 250
140  LET R=3.08664
150  LET A[1]=R
160  LET A[2]=1
170  IF N=1 THEN 250
180  FOR W=2 TO N
190  FOR I=1 TO W
200  LET A[W-I+2]=A[W-I+2]*R+A[W-I+1]
210  NEXT I
220  LET A[1]=A[1]*R
230  NEXT W
240  REM  **********BROMINE CLUSTER**************************
250  IF L=0 THEN 430
260  LET X=L
270  LET R=1.02041
280  IF A[1]>0 THEN 330
290  LET A[1]=R
300  LET A[2]=1
310  LET X=L-1
320  IF L=1 THEN 430
330  FOR W=1 TO X
340  FOR I=1 TO 19
350  LET A[21-I]=A[20-I]
360  NEXT I
370  LET A[1]=0
380  FOR I=1 TO 19
390  LET A[I]=A[I+1]*R+A[I]
400  NEXT I
410  NEXT W
```

Fig. C-1--Limited cluster search compouter program

```
420  REM  ••••••••••BASE PEAK: ISOTOPIC CLUSTER••••••••••••••
430  LET W=A[1]
440  LET W1=1
450  FOR I=2 TO 20
460  IF A[I]<W THEN 490
470  LET W=A[I]
480  LET W1=I
490  NEXT I
500  REM  ••••••••••CLUSTER ADJUSTMENT-CHUNK SMALL PEAKS••••••
510  LET Q=0
520  FOR P=1 TO 20
530  IF A[P]>.07*W THEN 620
540  IF A[P]=0 THEN 640
550  FOR R=P TO 20
560  LET A[R]=A[R+1]
570  NEXT R
580  LET Q=Q+1
590  IF P>W THEN 610
600  LET W=W-1
610  LET P=P-1
620  NEXT P
630  REM  ••••••••••PRINT ISOTOPIC CLUSTER••••••••••••••••••
640  PRINT
650  PRINT
660  PRINT "CL=";N;"BR=";L
670  PRINT "ISOTOPIC CLUSTER LISTING:"
680  IF W=0 THEN 730
690  FOR I=1 TO 21
700  IF A[I]=0 THEN 720
710  PRINT "A(";I;")=";A[I]/W*100
720  NEXT I
730  PRINT
740  PRINT
750  LET N=N+L-Q
760  REM••••••••••• INPUT DATA ••••••••••••••••••••••••••••••••
770  PRINT "DATA  #"
780  INPUT I1
790  FOR I2=1 TO I1
800  READ T$,I3
810  FOR I4=1 TO I3
820  READ I5,M[I5]
830  NEXT I4
840  NEXT I2
```

Fig. C-1--Continued

```
850  REM  ♦♦♦♦♦♦♦♦♦♦INPUT SEARCH PARAMETERS♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦
860  REM
870  PRINT "INPUT LOWESR AND HIGHEST MASSES THEN"
880  PRINT "FIRST AND LAST SPECTRA TO BE SEARCHED"
890  INPUT L,H,C,F
900  REM  ♦♦♦♦♦♦♦♦♦♦INPUT DATA BASELINE NOISE FILTERING %♦♦♦
910  PRINT "BASELINE NOISE FILTERING, PERCENT:"
920  INPUT D
930  LET D=D/100
940  REM  ♦♦♦♦♦♦♦♦♦♦SPECTRUM SELECTION LOOP♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦
950  FOR I=C TO F
960  REM   DREAD,#1,I,M
970  REM  ♦♦♦♦♦♦♦♦♦♦ CALCULATE SPECTRUM INTENSITY FACTOR ♦♦♦♦
980  REM  ♦♦♦♦♦♦♦♦♦♦      AND BASE PEAK, SPECTRUM      ♦♦♦♦♦♦♦♦
990  LET R=0
1000  LET E=M[L]
1010  FOR J=L TO H
1020  LET E2=M[J]
1030  IF E>E2 THEN 1050
1040  LET E=E2
1050  LET R=R+E2
1060  NEXT J
1070  LET R=R♦.01
1080  LET G[I]=0
1090  REM  ♦♦♦♦♦♦♦♦♦♦CLUSTER SELECTION LOOP♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦
1100  FOR J=L TO H-2♦N
1110  REM  ♦♦♦♦♦♦♦♦♦♦COPY DATA CLUSTER INTO B MATRIX♦♦♦♦♦♦♦♦♦
1120  FOR P=1 TO N
1130  LET B[P]=M[J+(P-1)♦2]
1140  NEXT P
1150  REM  ♦♦♦♦♦♦♦♦♦♦ASSIGN CLUSTER HEIGHT SCALING FACTOR♦♦♦♦
1160  LET X=B[W1]/E
1170  REM  ♦♦♦♦♦♦♦♦♦♦ RATIO SELECTION LOOP ♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦♦
1180  FOR P=1 TO N-1
1190  REM  ♦♦♦♦♦♦♦♦♦♦DATA BASELINE NOISE FILTERING TEST♦♦♦♦♦♦
1200  IF B[P]<E THEN 1300
1210  IF B[P+1]<E THEN 1300
1220  REM  ♦♦♦♦♦♦♦♦♦♦DISQUAL. IF DATA RATIO TOO FAR OFF♦♦♦♦♦♦
1230  IF Z>2 THEN 1300
1240  REM  ♦♦♦♦♦♦♦♦♦♦PERFECT FIT INCL. RANDOM NOISE VAR.♦♦♦♦♦
1250  IF ABS(Y-Z)>.001 THEN 1290
1260  LET G[I]=G[I]+9♦X/(N-1)
1270  GOTO 1300
1280  REM  ♦♦♦♦♦♦♦♦♦♦CALCULATED FIT- LESS THAN PERFECT♦♦♦♦♦♦♦
1290  LET G[I]=G[I]+((LOG(ABS(Y-Z))/2.30259) ♦♦ 2)♦X/(N-1)
1300  NEXT P
```

Fig. C-1--Continued

```
1310  REM  ◆◆◆◆◆◆◆◆◆◆PRINT DATA ANALYSIS◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆◆
1320  IF G[I] <= T+.2 THEN 1340
1330  PRINT "MASS=";J;"CUMULATIVE FIT=";G[I]
1340  LET T=G[I]
1350  NEXT J
1360  LET T=G[I]
1370  LET G[I]=G[I]◆R
1380  PRINT "SPECTRUM#=";I;"CUMULATIVE FIT=";T;"WEIGHTED FIT=";G[I]
1390  LET T=-1
1400  NEXT I
1410  END
```

Fig. C-1--Continued

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