

COMPARISON OF THE EXTRACTION PROCEDURE TOXICITY  
TEST (EP) AND THE TOXICITY CHARACTERISTIC  
LEACHING PROCEDURE (TCLP) FOR THE ANALYSIS OF  
TRACE ORGANIC COMPOUNDS IN LAND APPLIED  
MUNICIPAL WASTEWATER SLUDGES

by

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(ABSTRACT)

The current Environmental Protection Agency (EPA) method utilized for analysis of trace organic chemicals and heavy metals leached from solid waste is the Extraction Procedure (EP) Toxicity Test. Because of various operational problems and limitations of the EP, the EPA has developed and plans to implement the Toxicity Characteristic Leaching Procedure (TCLP), which is an expanded version of the EP capable of analyzing more organic components, in particular volatile organic chemicals.

The purpose of this research was to investigate and compare the ability of the EP and TCLP test procedures to quantitatively recover added surrogate standards (1,2-dibromoethane, bromoform, 1-chlorooctane, fusarex, heptachlor, and DDT) and also qualitatively identify and evaluate unknown trace organic chemicals in domestic wastewater sludges. In order to meet the research objectives established, three small (approximately 1 MGD or less) municipal wastewater treatment plants that land applied their sludges were analyzed.

Recoveries of surrogate standards were low and highly variable for both tests. There was essentially no statistically significant difference between the TCLP and EP tests with respect to recovery of semi- and non-volatile sludge surrogate standards which were added to the wastewater sludges. The mean recovery of the volatile surrogate standards by the TCLP was slightly better than by the EP. Wastewater treatment plant exhibited a more statistically significant impact on recovery of the individual sludge surrogates than did test, i.e. TCLP and EP. Because no distinct relationship could be established between certain physical/chemical characteristics (vapor pressure, solubility, Henry's Law Constant,  $K_{ow}$ ,  $K_{oc}$ , and boiling point) of the surrogates and recovery at a particular wastewater treatment plant, it was hypothesized that the type of sludge was potentially an important criteria for recovery of various compounds.

Only a few unknown organic compounds (dichlorodimethoxybenzene, dimethylpentanol, 4-methylphenol, and tetramethylbutylphenol) were identified by GC/MS, though they were not found in all replicates or by both tests. No additional pesticides were detected in any of the sludges analyzed.

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## **I. INTRODUCTION**

### **A. Background**

A variety of wastewater sludge management techniques are currently practiced today including: land application, incineration and ocean disposal. The most widely utilized management option is land application which provides a low cost means of disposal (EPA, 1983). According to the Virginia Water Control Board nearly half of the sewage sludge from the State's publicly owned treatment facilities is land applied (Sawyer, 1989). Recently, public opposition to land application of sludge has increased in Virginia. Concern has arisen over the content and fate of potentially toxic organic and inorganic compounds in these land applied wastewater sludges. Commonwealth citizens are worried that unknown toxic substances in sludge may contaminate food crops, groundwater, and surface water, and therefore may endanger public health (Sawyer, 1989). In order to assess possible adverse health effects from organic and inorganic contaminants, analysis protocols and monitoring programs have been implemented.

The current method utilized for analysis of trace organic chemicals and heavy metals leached from solid waste is the Extraction Procedure (EP) Toxicity Test (EPA, 1986a). The EP test was originally conceived by the United States Environmental Protection Agency (EPA) in an effort to characterize hazardous waste components and is currently the required method for determination of toxic substances under the Resource Conservation and Recovery Act (RCRA), (Knocke, 1989). EP is a

laboratory test designed to simulate leaching of components from waste disposed in a sanitary landfill. Because of various operational problems and limitations of the EP, the EPA decided to investigate alternative testing procedures and increase the number of compounds analyzed. By 1981, the EPA began a research program to develop the Toxicity Characteristic Leaching Procedure (TCLP), (Kimmell, 1987). The TCLP is an expanded version of the EP capable of addressing more organic components in solid wastes including volatile compounds. The EPA is now considering requiring land waste disposers to comply with the new, more stringent TCLP. Although both tests were designed to mimic leaching of solid wastes by rainwater and both tests utilize a weak acid solution to extract metals and organics from solid samples, the TCLP was designed to optimize recovery of volatile organic compounds and requires specialized equipment.

The Virginia State Bureau of Wastewater Engineering is concerned that the added expense and difficulty of the TCLP may not be warranted for all sludge land application situations. In particular, the State questions the value of the TCLP for small (less than 1 MGD) plants with few or no industrial inputs. Currently there is a lack of data available comparing these two test procedures, EP and TCLP, as well as a lack of data concerning the presence of trace organic chemicals in municipal sludges.

## B. Research Objectives

The purpose of this research was to further the understanding of the extraction ability of both the EP and TCLP procedures, and to categorize the trace organic constituents in domestic sewage.

Specifically, this research focuses on these objectives:

1. Compare the EP and TCLP tests for their ability to analyze numbers, types and concentrations of trace organic chemicals in municipal sludge from wastewater treatment facilities that land apply, focusing on a list of organic compounds that are proposed to be regulated.
2. Evaluate the EP and TCLP procedures for their ability to detect trace organic chemicals known to be in sludge.
3. Identify unknown trace organic chemicals in these sludges.

## C. Experimental Design

In order to meet the research objectives established, three small municipal wastewater treatment plants which met the following criteria were selected: aerobically digested sludge; municipal inputs only; no addition of stabilizing polymers; and disposal by land application.

To test the ability of the TCLP to extract compounds in wastewater sludges, this test was compared to the regulated EP. The TCLP involves two procedures: a non-volatile analysis which is similar to the EP procedure for extracting metals, pesticides and semi-volatiles; and a volatile analysis capable of extracting volatile compounds as well as

pesticides and semi-volatiles. To optimize time and effort in the laboratory the TCLP volatile analysis was selected since this avenue does not discriminate against non-volatile compounds and the pH of the extracting fluid is closest to the EP extraction solvent.

Triplicate sludge samples and one water blank were analyzed by both tests for each of the three site. Due to equipment limitations only four samples per day could be processed. To eliminate statistical bias a sample analysis was designed so that EP samples, TCLP samples, and blank water samples were analyzed in a random fashion. Consequently, the samples were not processed in the same order for every site. Matched pairs of two EP and two TCLP samples were run one day and the remaining samples or blanks analyzed on alternating days. These arrangements were made to add validity to the results and reduce any statistical bias.

On the alternate days - between the test procedures - samples were extracted with methylene chloride to concentrate the organic constituents. The liquid/liquid extraction and subsequent concentration of the methylene chloride was performed in accordance with EPA Method 625 (EPA, 1982).

Following methylene chloride concentration, samples were analyzed by capillary gas chromatography (GC) which maximized sensitivity and chromatographic resolution. Detection of compounds by Flame Ionization Detection (FID), a universal detection system, allowed quantification of nanogram amounts. Selected samples were then analyzed by gas

chromatography/mass spectroscopy (GC/MS) to generate characteristic spectral data from which the identity of unknown trace organic compounds could be deduced.

To assess the extractability and recovery of specific organic compounds by the two methods, surrogate standards of known concentrations were added. These standards allowed assessment of the performance of both the TCLP volatiles analysis method as well as the EP organics analysis procedure. Volatile and non-volatile internal sludge standards were chosen because they could potentially be extracted by both procedures, they were not expected to be in municipal sludge waste, and they behaved similarly to pollutants which the State was interested in assessing. The compounds selected were a series of halogenated hydrocarbons which possessed various physical/chemical properties. For example, vapor pressure values ranged over seven orders of magnitude and Henry's Law Constants extended five orders of magnitude. Also these compounds were relatively stable; extensive biodegradation was not expected so that recovery was not likely to be influenced by loss due to sludge microbial activity. Finally, a range of retention times throughout the chromatographic analysis was necessary to avoid possible overlapping peaks and to ensure good quantitative data.

#### **D. Statistical Analysis**

To statistically compare the numbers and types of organics detected by the EP and TCLP tests for their ability to quantitatively

recover targeted compounds a Blocked Factorial Analysis of Variance (ANOVA) design was utilized. Statistical analyses were performed using the SYSTAT/SYGRAPH software from Systat, Inc. on a Compaq 386/20 computer. Specific statistical comparisons made were:

1. Compare the recovery of the sludge surrogates detected by each test within each site, (i.e. did test influence recovery?).
2. Compare the recovery of the sludge surrogates detected by each test between the sites, (i.e. did site influence the recovery?).

Other comparisons made as part of the ANOVA on the sludge surrogates included the interaction of test and site on recovery. The recovery of each compound in the blank reagent water was compared to the recovery in the triplicate sludge samples using a pooled t-Test. Lastly, recovery was correlated to the percent solids in the sludges and some physical/chemical properties associated with each surrogates using a multiple regression analysis in order to determine what factors affected the recovery variability.

The data gathered during this research and the subsequent statistical analysis evaluated the effectiveness of the TCLP and EP procedures for measuring trace organics. The results are intended to assist the Virginia Bureau of Wastewater Engineering in assessing the validity of requiring the potentially expensive and difficult TCLP test for small municipal waste sludge applicators.

## II. LITERATURE REVIEW

### A. Sludge Waste Management

#### 1. Techniques

Effective disposal of sludges produced from wastewater treatment facilities is a continually growing management problem. The quantity of municipal sludge produced annually has almost doubled since 1972, when the Clean Water Act imposed uniform minimum treatment requirements for municipal wastewater (EPA, 1984). Annually this country produces approximately 6.5 million dry tons of sludge and this amount is expected to double again by the year 2000 (EPA, 1983). Disposal options are based on the treatment processes ability to effectively reduce the influent wastewater characteristics. Currently, sludge disposal alternatives include: land application, distribution and marketing, landfilling, incineration and ocean disposal (EPA, 1984).

Land application, defined as the spreading of sludge on or just below the surface of the land, is the most widely employed sludge use option (EPA, 1984). Important sludge constituents which influence land application are nutrient content, presence of pathogenic bacteria, heavy metals concentration, and to a lesser extent volatile solids or the organic fraction of the suspended solids and toxic organic chemicals (EPA, 1985). There are primarily four types of land use options - agricultural application, forest soils utilization, soil conditioning and land reclamation (EPA, 1983). Approximately 25% of the Nation's



sludge is land applied and nearly 40% of the sludge produced by small treatment plants with less than 1 million gallons per day (MGD) production is land applied primarily to agricultural acreage (EPA, 1984). Agricultural application of waste sludge provides an inexpensive fertilizer substitute as well as an effective soil improvement agent (EPA, 1983).

Limitations exist as to the type of sludge management option used, but land application still remains a viable, cost effective means of sludge disposal.

## 2. Fate of Organics

With any waste disposal option employed there are associated health risks involved. Sludges tend to concentrate materials and most sludges contain heavy metals and a variety of organic compounds (Dacre, 1980). Toxic organic compounds linked to cancer such as polynuclear aromatic compounds and organohalogen pesticides have been shown to occur in municipal sludges (Dacre, 1980), although, domestic sewage does not contain significant mutagenic activity (Hopke et al., 1980). In other words, toxic compounds may be found in domestic sludge but at concentrations which do not exhibit mutagenic effects. Awareness as to the fate of many toxic compounds has increased attempts to understand and control environmental pollutants (Suffet, 1975).

Many pathways exist within complicated food webs from which compounds can translocate from soil and water eventually reaching man

(Curtis, 1983). One aspect of transport for a variety of compounds is the solid-water interface (Tinsley, 1979). Adsorption and subsequent desorption from solid colloids, such as sludge, can influence the fate of many highly toxic organic compounds. The main factors influencing the adsorption and desorption of organics are the physical and chemical properties of both the compound and solid substrate (Browman and Chesters, 1975). Bond strength, cation saturation, surface area, pH, temperature, and moisture content are all interrelated features which determine the relative adsorption/desorption mechanisms (Browman and Chesters, 1975).

One of the most important mechanisms of mass transport for toxic compounds is through leaching (Tinsley, 1979). Leaching involves the movement of a chemical across the soil-water interface and is related to the relative solubility of the chemical into the water matrix (Tinsley, 1979). Dynamic interactions between the source and the host water body can influence the introduction of pollutants into the water environment (Rumer, 1975). The leaching activity of compounds from the solid portion of sludge and subsequent movement into water supplies has led to serious questions concerning the safety and validity of land application (Sawyer, 1989). Consequently, it is important to determine compounds that may leach from solid substrate or predict the tendency for which a compound could leach and potentially contaminate surface and ground water supplies.

### 3. Testing

Management practices and regulatory requirements associated with waste disposal have increased (Jackson *et al.*, 1984) because of the rising number of sites in which leachate has contaminated underlying aquifers (Reinhard and Goodman, 1984). The concern over pollutant impacts within the environment has led to development of standardized leaching tests (Jackson *et al.*, 1984). These tests were intended to simulate naturally occurring leaching processes to further aid in the identification and quantification of potentially hazardous compounds. Performance evaluations from leaching tests can aid regulatory agencies in assessing the compatibility of various wastes for codisposal, adequacy of leachate collection, and predicting the impact of waste leachate on water resources (Jackson *et al.*, 1984).

The Resource Conservation and Recovery Act (RCRA) of 1976 provided a new directive to solid waste disposal (Knocke, 1989). The primary goals of RCRA were 1) to protect human health and the environment from potentially hazardous substances in disposed waste, 2) conserve energy and natural resources, 3) reduce the generation of waste, and 4) ensure wastes are managed in an environmentally sound manner (Knocke, 1989). Currently, domestic sewage is not included in RCRA regulations, although this could change in the near future due to increased public opposition. The EPA is considering restricting municipal land sludge application practices, and requiring detailed inorganic and organic analysis of municipal sludges (Flynn, 1989). Furthermore, under the Clean Water Act

Amendments of 1987, EPA is required to identify toxic pollutants, establish permissible concentrations for each pollutant, and specify acceptable management practices for regulated pollutants (Sawyer, 1989).

## **B. Extraction Procedure Toxicity Test (EP)**

### **1. Background**

In the continued efforts by the EPA to identify and characterize hazardous wastes the EP was developed. "The Extraction Procedure Toxicity Test (EP) was intended to be a first order approximation of the leaching action of compounds generated in an actively decomposing sanitary landfill" (Kimmell and Friedman, 1986). The test was originally designed to model the leaching of metals from substrate, mimicking the natural leaching process due to acid rain (Mason and Carlile, 1986). The EP simulated the effects of the waste on the environment and also helped determine to what extent toxic waste could leach into surrounding water bodies by both underground and surface supplies (McCarthy, 1988).

The EP uses a weak acid solution ( $\text{pH } 5.0 \pm 0.2$ ) to leach components from waste. The resulting extract from the EP test procedure was to be analyzed for 8 metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium and silver), two herbicides (2,4-D and 2,4,5-T silvex), and 4 pesticides (endrin, lindane, methoxychlor, and toxaphene) for which National Interim Primary Drinking Water standards had been previously established for these chemicals (Francis *et al.*, 1986). When

analyzing for metals the EP extract is subjected to atomic adsorption (AA) whereas when analyzing for herbicides and pesticides the organic constituents are partitioned into an organic solvent such as methylene chloride, concentrated and subjected to gas chromatograph (GC).

The EPA intended to develop a second model for metals since many metal species generally behave differently in the ground water environment. Since the model had not been fully developed, however, the EPA decided to retain the present EP Toxicity characteristic levels for the elemental toxicants (EPA, 1986a). The EPA believes that the EP was, and still is, adequate for identifying metal contaminants in wastes that have the potential to leach, although they do concede the need for a more comprehensive analysis with respect to organics (EPA, 1980).

## 2. EP Analysis Variability

Besides the need for a more complete analysis of toxic compounds including volatile organics, many operational aspects of the EP test procedure have been questioned by researchers and test operators. These inherent problems have been shown to add unnecessary variability to the EP test and seriously question its ability to identify and monitor toxic compounds (Kimmell, 1987).

The EP analysis consists of three basic steps: separation, pH adjustment and agitation. One problem existing within the EP protocol is the initial liquid/solid separation. The initial liquid/solid separation technique currently involves 0.45 micron pressure filtration

(Kimmell and Friedman, 1986). Often, oily and paint type wastes which frequently migrate to ground waters tend to clog the 0.45 micron filter even if considerable (75 psi) is applied (EPA, 1986c).

"This problem is serious since materials which do not pass the 0.45  $\mu\text{m}$  filter are treated as solids even if they physically appear to be a liquid. It is important for the liquid/solid separation to treat, as liquids, those materials which can behave as liquids in the environment. However, it is important to recognize that some materials such as some paints and some oily waste (while they have some liquid properties) will generally behave as solids in the environment (i.e. will not migrate in total)." (EPA, 1986c)

In order to simulate the *in situ* leaching process that could occur in an impounded solid waste site, the EP utilizes a 0.5 N acetic acid solution for pH adjustment (EPA, 1986a). The final pH of the waste solution is to remain at  $5.0 \pm 0.2$  pH units (EPA, 1986a). Continual pH monitoring is required during the course of the extraction.

"The EP procedure involves continual pH adjustment or titration. The procedure calls for periodic pH adjustments if necessary at 15 minute intervals for up to 6 hours or more. This is very tedious, time consuming and expensive and is also the single most important element in the EP protocol contributing to variability." (EPA, 1986c).

Finally, there is concern that the EP does not accurately define the agitation technique. The EPA defines an acceptable extractor as one which will impart sufficient agitation to the mixture to not only prevent stratification of the sample and extraction fluid but also to insure that all sample surfaces are continuously brought into contact with well mixed extraction fluid. The exact agitation technique is never stated. A variety of laboratory agitation equipment exists which

will provide agitation such as magnetic stirring apparatus, paddle stirrers and shaker tables. However, testing facilities using different agitation equipment can add unnecessary variation because the specific agitation technique is not clearly defined (EPA, 1986c).

In summary, the EP test analyzes toxic compounds which can leach from solid matrices. The EP testing procedure was originally designed for solid wastes, but the method, once formulated, was also applied to waste water sludges. Variability existing within the EP protocol raises questions of its ability to accurately monitor solid waste disposal and also questions its use as a sludge testing protocol.

## C. Toxicity Characteristic Leaching Procedure (TCLP)

### 1. Background

Awareness of the need to enhance the analytical capabilities of the EP prompted the EPA to consider a new testing approach.

"As a result of the EPA's efforts to expand the capabilities of the Extraction Procedure leaching test to address organic components, including volatiles, and also to address some of its operational problems, a new leaching test, known as the Toxicity Characteristic Leaching Procedure (TCLP) has been developed" (Kimmell, 1987).

The TCLP was published in the Federal Register on January 14, 1986 as part of the Land Disposal Restriction Rules (Blackburn, *et al.*, 1987) and the test is proposed as an expanded hazardous waste characteristic test under the Resource Conservation and Recovery Act (Kimmell, 1987).

The EPA began development of the TCLP in 1981, through an agreement with the U.S. Department of Energy's Oak Ridge National Laboratory (ORNL), (Kimmell, 1987). Closely related experiments using the sanitary waste codisposal model, a model which simulates the activities of a domestically designed landfill that may have had industrial inputs, which was used to develop the EP was also used to develop the TCLP (EPA, 1980). After finalizing the model assumptions, i.e. sanitary waste codisposal, ORNL developed the actual TCLP protocol. The TCLP has been proposed for determination of 53 analytes which are presented along with their regulatory concentrations in Table II.1.

The TCLP test procedure is broken into two categories, volatiles and non-volatiles. TCLP analysis of non-volatile components which includes: metals, inorganics, semi-volatiles, and pesticides, is performed much like the EP in a conventional bottle extractor (Blackburn *et al.*, 1989). The only major difference is the use of a buffered pH fluid instead of the 0.5 N acetic acid solution, thereby eliminating the six hour pH adjustment period of the EP. In contrast, the TCLP analysis for volatile compounds incorporates the use of a specially designed zero head-space extractor (ZHE) to minimize loss of volatile compounds (EPA, 1986d). Originally the ZHE was intended to analyze all wastes but due to the ZHE volume limitations, the EPA decided to use the ZHE only for analysis of volatile constituents (Kimmell, 1987).

Several management model alternatives including sanitary landfill codisposal, codisposal with hazardous waste and segregated management



Table II.1. Proposed TCLP Contaminants and  
Regulatory Levels

Contaminant	Regulatory Level mg/l
Acrylonitrile	5.0
Benzene	0.07
Carbon disulfide	14.4
Carbon tetrachloride	0.07
Chlorobenzene	1.4
Chloroform	0.07
1,2-Dichloroethane	0.04
1,1-Dichloroethylene	0.1
Isobutanol	25
Methylene chloride	8.6
Methylethyl ketone	7.2
1,1,1,2-Tetrachloroethane	10.0
1,1,2,2-Tetrachloroethane	1.3
Tetrachloroethylene	0.1
Toluene	14.4
1,1,1-Trichloroethane	25
1,1,2-Trichloroethane	1.2
Trichloroethylene	0.07
Vinyl chloride	0.05
o-Cresol	10.0
m-Cresol	10.0
p-Cresol	10.0
Pentachlorophenol	3.6
Phenol	14.4
2,3,4,6-Tetrachlorophenol	1.5
2,4,5-Trichlorophenol	5.8
2,4,6-Trichlorophenol	0.30
Bis(2-chloroethyl)ether	0.05
1,2-Dichlorobenzene	4.3
1,4-Dichlorobenzene	10.8
2,4-Dinitrotoluene	0.13
Hexachlorobenzene	0.13
Hexachlorobutadiene	0.72
Hexachloroethane	4.3
Nitrobenzene	0.13
Pyridine	5.0

(continued)

EPA, 1986(c)

Table II.1 Proposed TCLP Contaminants and  
Regulatory Levels continued:

Contaminant	Regulatory Level mg/l
Chlordane	0.03
Endrin	0.003
Heptachlor	0.001
Heptachlor epoxide	0.001
Lindane	0.06
Methoxychlor	1.4
Toxaphene	0.07
2,4-D	1.4
2,4,5-TP (Silvex)	0.14
Arsenic	5.0
Barium	100
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

EPA, 1986(c)

were considered in developing the TCLP (EPA, 1986b). "The sanitary landfill codisposal model was selected because the concern that potentially hazardous waste, if not brought under control by the RCRA hazardous waste system, may be sent to sanitary landfills and result in a high degree of leaching, has not changed." (EPA, 1986b). The EPA believes that the likelihood of wastes disposed in hazardous or industrial landfill facilities causing ground water contamination is much lower than if placed in a sanitary landfill which lacks forms of secondary protection (EPA, 1980)

## **2. TCLP Analysis Improvements**

During development of the TCLP in 1981, the EPA investigated specific design parameters including: reducing the pH variability associated with the continual pH adjustments required in the EP, increasing liquid/solid separation, decreasing the loss of volatile organic compounds (VOC's), increasing test precision and sensitivity, as well as trying to decrease cost of capital investment, operation and maintenance (Kimmell, 1987). Three specific improvements achieved are outlined in detail below.

In an effort to solve the EP continual pH adjustment problem, which adds variability especially during metals analysis, a predefined leaching medium was proposed (EPA, 1986c). "Using a buffer system eliminates the problem of pH adjustment since this medium does not require such adjustment during extraction." (EPA, 1986b). Two buffered

leaching mediums or "extraction fluids" were developed and which fluid to use depends on the type of waste to be analyzed. Extraction fluid #1, 5.7 mL glacial acetic acid plus 64.3 mL of 1.0 N sodium hydroxide to a final volume of 1 L with a pH of  $4.93 \pm 0.05$ , is used when volatiles are involved, whereas extraction fluid #2, 5.7 mL glacial acetic acid diluted to 1 L with a pH of  $2.88 \pm 0.05$ , is used when analyzing for metals and non-volatiles. Specific rules governing the type of extraction fluid to use are outlined in the Federal Register Volume 51 Number 114 pages 21651-21682, June 1986. (During this research extraction fluid #1 was used in all cases).

The second improvement concerned the separation of liquid from the solid fractions. A larger, more porous filter was incorporated into TCLP compared to EP. "After investigating several options, EPA opted for the continued use of pressure filtration but changed the filter medium to a 0.6-0.8 micron glass fiber filter" (Kimmell, 1987). Using a glass fiber filter also reduced the possibility of adsorption of analytes to the filter (EPA, 1986b). In both the EP and TCLP, phase separation of materials that tend to clog the filter such as paints and oily wastes still pose serious problems (EPA, 1986d). Though "use of these filters decreases filtration time, improve the precision of the method and is believed to provide adequate differentiation between those materials that behave as liquids in the environment and those that behave as solids." (Energy Resources Co., 1985).

A third and important improvement of the TCLP was that it could (or should) analyze for volatile organic chemicals. Since the loss of volatile compounds can occur during both the liquid/solid separation and the actual extraction procedure, development of the zero head-space extractor device was incorporated into the testing protocol (Kimmell, 1987). This device is shown in Figure II.1. "The ZHE is capable of conducting the initial liquid/solid separation, agitation, as well as final extract filtration with only minimal loss of volatiles." (EPA, 1986b). Although these ZHE vessels add considerable cost to the procedure, they are only required for analysis of volatile components (Kimmell, 1987).

In addition to the three major improvements a number of subordinate improvements were added to the TCLP in order to increase the overall precision of the method (EPA, 1986b). One notable improvement is an extremely rigorous test protocol with specific agitation guidelines. The EP protocol defines what is considered acceptable agitation, but it fails to specifically describe the agitation means. This lack of specificity in agitation conditions led to a major source of variability (Brown et al., 1983). "The TCLP protocol eliminates this source of variability by specifying a single means of agitation (i.e. rotary or tumbler), and a fixed agitation rate ( $30 \pm 2$  rpm)." (EPA, 1986b). Rotary agitation was selected because of its ability to reproduce contact between the liquid and solid (EPA, 1986c). Rotary agitators approved by the EPA are equipped for both ZHE and bottle

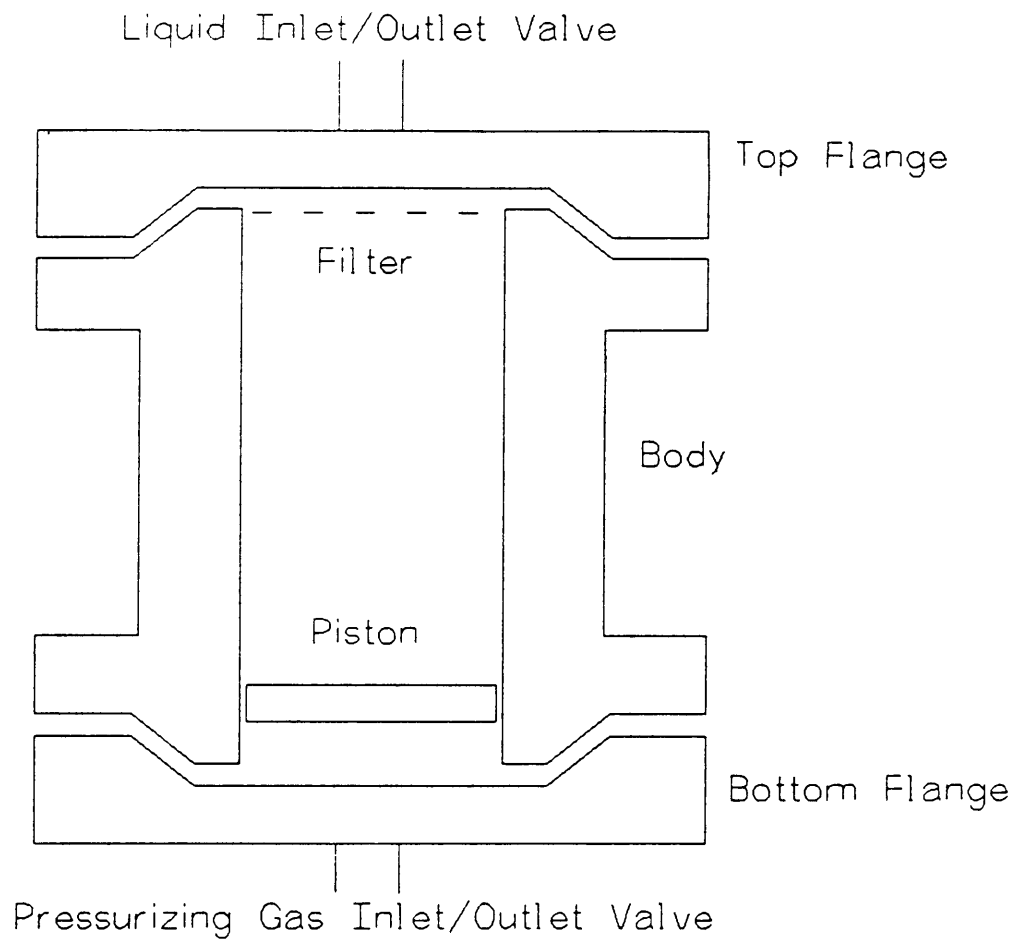


Figure II.1 ZHE - Zero Head Space Extractor

extractors (Analytical Laboratories, Warrington, PA). The EPA recognized that using the rotary shaker would require some laboratories to purchase additional equipment, but has proposed the rotary shaker as the only means of agitation (EPA, 1986b).

Ongoing efforts to further improve the TCLP are currently focused on possible modifications of the test protocol with respect to "problem matrices". Problem matrices, notably oily wastes which clog filters, and solids which require size reduction, pose potential variations in test precision and accuracy (Marsden, 1988). Test methods become more precise, accurate, sensitive and rugged as additional data is gathered and technological advances are made (Kimmell, 1987). Protocol refinements as experience is gained will provide further improvements of the TCLP test procedure.

### 3. TCLP Reported Precision and Accuracy Values

In an effort to improve the EP procedure and expand the applicability of the protocol to larger numbers of toxins that could potentially leach from an unsecured landfill, the EPA proposed the TCLP in the Federal Register in 1986 (Blackburn *et al.*, 1987). To assess the ability of the new procedure (i.e. TCLP), the Office of Research and Development within the EPA commissioned S-CUBED Laboratories LaJolla, California (referenced under Blackburn *et al.*, 1987) to conduct an interlaboratory precision study for the determination of metals, pesticides, base/neutral and acid extractable organic compounds, and

volatile compounds, many of which are listed in Table II.1. Twenty-three laboratories took part in the study, although not all labs participated in determination of all analytes. Laboratories were supplied with spiked sludge samples from three different matrices: an ammonia lime still bottom, an American Petroleum Institute separator sludge, and a fossil fuel fly ash, and were then required to perform the TCLP test on some samples and the TCLP with ZHE on samples containing volatile components.

S-CUBED reported that there was no significant difference between labs, at a 95% confidence interval, for the recovery of semi- and non-volatile compounds. For semivolatile compounds the percent standard deviation or the relative standard deviation (RSD, standard deviation divided by the mean) ranged between 12 and 305 percent, and for non-volatile pesticides the RSD ranged between 69 and 278 percent. Further examination of the data revealed that 36% and 91% of the reported RSD values were above 100% for semi-volatiles and pesticides, respectively. These results indicate that the recoveries were highly varied and a majority of the reported standard deviations, particularly in the case of pesticides, were extremely diverse.

"For pesticides, the results suggest that there were no significant differences between the samples. It is felt that samples with larger amounts of pesticides would have yielded comparable results to those for the semivolatile organic compounds." (Blackburn *et al.*, 1987). This statement by S-CUBED leaves one to question both their



insight as to the concentrations of pesticides expected from codisposed sanitary landfill leachate for which the test was originally designed, and the ability of the TCLP to detect small amounts. Typically there is a directly proportional effect such that higher initial starting concentrations yield higher final recoveries which is true for almost all analytical methods. So naturally one would expect better recoveries and most likely more comparable results with increased initial concentrations. Also in a final report by S-CUBED (referenced under Taylor and Shurtleff, 1986) they demonstrate that the starting concentration of volatile compounds affected the final recovery. In that report for a reagent water sample with added acrylonitrile the mean percent recovery from five samples and the corresponding percent RSD values were as follows: 100 and 2.7 for 1ppm spike level; 89 and 8.4 for 200ppb spike level; and lastly 77 and 4.5 at 20 ppb spike level. It is clear from these reported recovery values that percent recoveries decrease with decreasing initial concentrations of the same compound in the same matrix.

S-CUBED also reported that there was no statistically significant difference between labs, at a 95% confidence limit, for the recovery of volatile compounds with the use of the ZHE. S-CUBED reported a (1-p) value of 0.939845 (i.e. p-value = 0.060155). Although this p-value is not inside the legal limits of a strict adherence to a 95% confidence interval (p-value <0.05), it does fall within the gray area that would normally be considered somewhat statistically significant or at least

require further investigation.

Previous studies by the Department of Energy, and the Electric Power Research Institute (EPRI), Palo Alto, California, in 1981 and 1986 concluded from round-robin evaluations that "the interlaboratory analysis variability was the major source of variation" when comparing the recoveries of the EP to that of the TCLP for all types of compounds (Mason, 1986). They attribute this variation to a number of factors including staff experience and source of analytical standards. EPRI states that in general the tests performed equally with respect to metals but that the TCLP appeared to be influenced more by the analytical laboratory than did the EP. In closing, EPRI concluded that the main advantage of the TCLP was in the use of a pH buffering solution instead of the time consuming continual pH monitoring associated with the EP, and that the tests did not perform much differently.

Finally, in a collaborative summary by Newcomer from Wilson Laboratories, Blackburn from S-CUBED, and Hansen from the EPA, of all the studies designed to evaluate the TCLP method presented at the EPA Symposium on Solid Waste Testing and Quality Assurance in 1987, they concluded:

"From strictly an analytical application, the TCLP provides a workable method which performs equally well or better than the EP procedure. With practice and good laboratory skills, the extraction procedure can become routine. As stated earlier, difficulties in achieving sample homogeneity and in collecting representative samples from waste sources, may imply that a single TCLP analysis of a waste could provide misleading information.

The TCLP was designed to provide reproducible extraction results, not to determine total constituents of a waste. It is likely that some waste constituents may give highly variable results which are matrix dependent and unpredictable. In general, TCLP performance appears to satisfy regulatory needs." (Newcomer *et al.*, 1987)

In response to these findings it is this author's opinion that:

1. Any laboratory procedure can become routine with experience, it is just a question of how much experience.
2. If difficulties are encountered in sample collection and that single samples give misleading information, then maybe the TCLP is not the ideal procedure for analysis of sludge, since sludge is a complex mixture and can vary from treatment plant to treatment plant. And if single samples give misleading information and multiple samples would be needed, the enormous cost associated with multiple sample analysis may defeat the purpose of requiring this testing procedure.
3. The TCLP was designed to produce reproducible results, as well as be able to discern a more complete analysis of waste constituents.
4. More research is needed to determine exactly what matrices give unpredictable results and ways to overcome these procedural problems, especially if the TCLP is to become the EPA required test method for sludge disposal.

### III. METHODS AND MATERIALS

#### A. Site Selection

This research project focused on the ability of the EP and TCLP tests to extract and evaluate organic pollutants. Small municipal waste treatment plants with less than 1 MGD that land apply sludge were chosen to be sampled. Sludges from these small municipal plants were hypothesized not to be severely contaminated with toxic or regulated organic pollutants, and therefore, the added expense of the TCLP procedure is possibly unwarranted. The following three sites met the necessary waste treatment, land application and geographic criteria and were selected for this project.

Christiansburg Municipal Waste Treatment Plant Christiansburg, VA was the first site chosen. This site was sampled twice, once in September, and then again in November of 1989, and designated Christiansburg #1, and Christiansburg #2, respectively. The sludge undergoes aerobic digestion for 15-20 days, and then is either land applied directly as a sprayed liquid or placed in drying beds for thickening and then land applied. Only the liquified sprayed sludge was selected for analysis in this research, since stabilizing polymers were added to the sludge prior to drying and may have interfered with the analytical research procedures.

The next site selected was the Fishersville Waste Treatment Plant, Staunton, VA. Fishersville also aerobically digested their sludge and land applied the sludge as a liquid. Fishersville was chosen due to its similarity to the Christiansburg facility as well as its geographic location. This site was sampled in early October of 1989.

The last site sampled in late October, 1989 was Honaker Municipal Waste Treatment Plant, Honaker, VA. Honaker aerobically digested it's sludge but then thickened the sludge in drying beds for a total processing time of approximately three months. Honaker was selected since land application of dried sludge constitutes a major portion of land applied sludges in Virginia. No stabilizing polymers or chemical additives were incorporated prior to spreading. Honaker also allowed the opportunity to perform both EP and TCLP tests on a solid sample, for which the tests were originally designed and thus allowed comparison to the liquid sludge results.

#### **B. Research Chemicals and Materials**

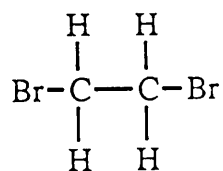
To minimize introduction of laboratory contaminants into the sludge samples, all reagents and standards utilized were the most chemically purified substances available. Reagent water was distilled prior to filtration in a Milli-Q Reagent Water System (Millford, MA) consisting of Super C Carbon, two Ion-Ex, and Organex-Q cartridges in series.

Glassware was cleaned for a minimum of four hours by immersion in a chromic acid bath prepared from chromerge and sulfuric acid from Fisher Scientific (Fairlawn, NJ), rinsed three times with Milli-Q water, and allowed to stand dry. All other non-glass tubing, fittings, stoppers and centrifuge tubes were teflon obtained from Cole-Parmer (Chicago, IL). Tedlar bags with TCLP adaptation fittings were purchased from Scott Specialty Gas (Plumstead, PA).

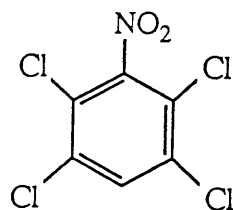
The following A.C.S. certified grade reagents were purchased from Fisher Scientific (Fairlawn, IL): glacial acetic acid, sodium hydroxide, sulfuric acid, and bromoform. Solvents - methylene chloride, methanol, and acetone - were from Burdick and Jackson (Muskegon, MI).

Whatman #1 and #4 qualitative filters, 0.7 micron glass fiber filters and magnesium sulfate purchased from Fisher Scientific (Fairlawn, IL) were Soxhlet extracted for six hours with methylene chloride prior to use.

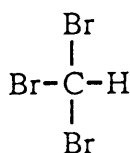
Purified standards purchased from Chem Service (West Chester, PA) included the sludge surrogates, illustrated in Figure III.1: p,p-DDT (99%), heptachlor (99%), dibromoethane - EDB - (99+%), 1-chlorooctane (99%) and fusarex - tetrachloronitrobenzene - (97%); the acid surrogate standard mix for EPA Method 625: 2-fluorophenol, phenol-d<sub>5</sub>, and 2,4,6-tribromophenol; and the base/neutral surrogate standard mix for EPA Method 625: nitrobenzene-d<sub>5</sub>, p-terphenyl-d<sub>14</sub> and 2-fluorobiphenyl. The secondary internal standard, 2-fluoronaphthalene was obtained from Supelco (Bellefonte, PA).



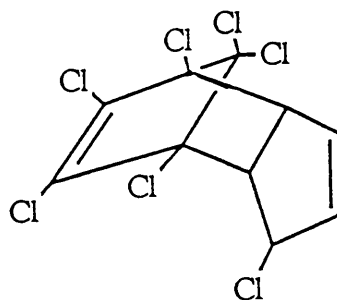
1,2-Dibromoethane  
(EDB)



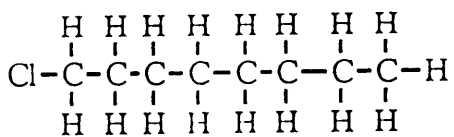
1,2,4,5-tetrachloro-3-nitro-benzene  
(Fusarex)



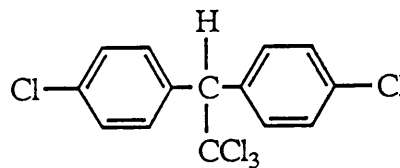
Bromoform



Heptachlor



1-Chlorooctane



DDT-p,p'

Figure III.1 Sludge Surrogates: Chemical Structures

A DB-5, Durabond, fused silica capillary chromatographic column was purchased from J&W Scientific (Folsom, CA). The capillary column had a 1.0 micron film of 5% phenyl and 95% methylsilicone, and was 30 m long with a 0.32 mm internal diameter.

### C. Chemical Stock Solutions and Reagents

All solutions were prepared in glass containers with glass stoppers or teflon liners and stored at 4°C. Volumetric flasks, pipettes and syringes were used for liquid stock solutions. Dry compounds were weighed on a Mettler balance able to weigh to a tenth of a milligram.

Extraction fluid #1 used as the TCLP reagent was prepared by adding 5.7 mL glacial acetic acids to 500 mL Milli-Q water then adding 64.3 mL of 1.0 N sodium hydroxide and diluting to a final volume of 1.0 L. Final pH of the fluid is  $4.93 \pm 0.05$ .

A 0.5 N acetic acid solution was prepared and used for pH adjusting in the EP procedure.

EPA Method 625 pH reagents were prepared in accordance with the Environmental Monitoring and Support Laboratory Manual, EPA 1982. For 10 N sodium hydroxide, 40 g sodium hydroxide was dissolved in reagent water and diluted to 100 mL. A 50 percent or 1+1 sulfuric acid solution was prepared by adding 50 mL of sulfuric acid ( $H_2SO_4$ ) to 50 mL of reagent water.



The sludge surrogate stock mix for Christiansburg #1 contained bromoform, 1-chlorooctane and fusarex (tetrachloronitrobenzene), at a concentration of 0.5 mg/mL methanol. For Fishersville and Honaker, the sludge surrogate stock solution of 0.5 mg/mL contained p,p-DDT, dibromoethane (EDB), heptachlor and fusarex. A 0.5 mg/mL stock surrogate solution of bromoform, fusarex, p,p-DDT, heptachlor, EDB and chlorooctane was added to Christiansburg #2. A final concentration of 250  $\mu\text{g}/100\text{ g}$  sludge was used for all additions of sludge surrogates.

The acid mix (fluorophenol, phenol and tribromophenol) and base/neutral mix (nitrobenzene, p-terphenyl, and fluorobiphenyl) surrogate solutions used in EPA Method 625 had a concentration of 100 mg/mL methanol.

Fluoronaphthalene, a secondary standard added after sample concentration but prior to GC injection, was added so that a final concentration of 10  $\mu\text{g}$  per sample was obtained regardless of sample size.

A reagent water blank, for quality control, was analyzed for each site. Sludge surrogates, acid surrogates and base/neutral surrogates were added to reagent Milli-Q water at the same concentration used for the sludge samples; the blank was stored at 4°C.

#### **D. Sample Collection and Handling**

Sludge samples were collected in head space free glass stoppered bottles thus decreasing atmospheric interactions and increasing the

probability of maintaining volatile components within the sample. Sample bottles were kept on ice during transport to laboratory.

Sludge surrogates were quantitatively added for a final concentration of 2.5 mg/L sludge, or 2.5 mg/kg sludge in the case of Honaker, and shaken repeatedly before usage. Separate bottles were maintained for each replicate. One bottle containing no standards was used specifically for initial TCLP solids determinations and to analyze for the presence of surrogates, prior to addition, at each site. All samples were stored at 4°C.

EPA regulations governing sample storage and analysis were followed which required sample concentration completion in 7 days and final analysis by 30 days.

#### **E. TCLP Apparatus and Equipment**

Manually pressurized zero-head space extraction vessels (ZHE) were purchased from Analytical Testing and Consulting Services, Inc. (Warrington, PA). Pressure is applied to a mechanically activated piston by means of a torque wrench. Each ZHE had an internal volume of 550 mL and came equipped to accommodate a 90 mm, 0.7 micron glass fiber filter. Also the inlet/outlet valve located on the top plate had a side part attachment for a 1 L Tedlar collection bag. Tedlar is a DuPont product mixture of mylar to decrease diffusivity and teflon for inertness.

The shaker device capable of rotating the extraction vessels end-over-end at  $30 \pm 2$  revolutions per minute (rpm) was also purchased from Analytical Testing. Additional mounted attachments on the rotary shaker permitted adaptation for EP containers. Mounts, EP vessels and hardware purchased allowed simultaneous agitation of both EP and TCLP vessels.

#### F. TCLP Preliminary Determinations

A complete experimental explanation of the TCLP procedure is provided in Federal Register Volume 51, Number 216, pages 40642-40653, November 1986. The following procedure describes the analysis of volatile components in a liquid matrix without particle reduction which was the method applied in this research. A flow diagram of the TCLP procedure utilized is included in Appendix A.

A percent dry solids determination was performed to ascertain if the liquid had an insignificant amount of solid material for the TCLP analysis. A 10 g representative sample was filtered onto a Whatman #1 filter. The filter cake was dried for 1 hour at  $100^{\circ}\text{C}$  and weighed until two sequential weights yielded the same value within  $\pm 1\%$  of each other. If the percent dry solid portion was less than 0.5% the sample was considered homogeneous, it becomes the TCLP extract, and would be analyzed directly for organic chemicals. Samples having greater than 0.5% dry solids continued through the entire TCLP procedure.

A percent solids (solids remaining after filtration) determination was performed to find the weight of sample to charge the ZHE. Due to

the limited volume capacity of the extraction vessel and the need to add extraction fluid equal to twenty times the solid weight, a maximum size of 25 g solids could be accommodated. A 100 g subsample of sludge was placed into the ZHE body and the ZHE piston adjusted to minimize air space. Support screens and a glass fiber filter were placed in a flange and secured under the top plate which housed the inlet/outlet valve. The threaded shaft was turned, driving the piston upward until resistance was felt, while a weighed container was positioned under the opened valve to catch the free liquid expelled from the ZHE. As directed by the manufacturer, a torque wrench was used to apply 48 inch pounds (in-lbs) of torque for 10 minutes.

Following the 10 minutes of applied pressure, the weight of the free liquid was measured and the percent of solids left inside the ZHE body calculated. The amount of sample required for TCLP evaluations was then calculated by the equation:

$$\text{ZHE charge weight} = (25/\text{percent filterable solids}) * 100$$

Some wastes such as oily wastes and some paints will obviously contained material that appears to be a liquid. But even after applying pressure filtration of the material will not filter. In this case, the material within the filtration device is defined as a solid and carried through the TCLP extraction as a solid (EPA, 1986b).

### G. TCLP Procedure

The sample size determined from the solids procedure was quantitatively transferred into a clean ZHE extractor. Slurries were not permitted to stand so that there was no phase separation. A glass fiber filter and the support screens were secured under the top plate and all fittings tightened. The ZHE was charged with a sample and the device was not opened until the final extract (of the solids) had been collected.

An evacuated pre-weighed Tedlar bag was attached to the inlet/outlet valve after the initial airspace was vented from the ZHE. As previously described in the percent solids determination, torque pressure was applied for 10 minutes to the piston rod after resistance from hand turning was felt. Any free liquid from the sample was collected into the Tedlar bag. After completion of the required pressure and time, the inlet valve was closed, the Tedlar bag removed, sealed, weighed, and stored at 4°C. After determination of the solids remaining in the ZHE and amount of Extraction Fluid #1, equal to twenty times the weight of solids, was added.

Addition of extraction fluid was conducted in such a manner as to minimize air exposure to the sample. A pre-flushed hose was attached from the extraction fluid reservoir to the inlet valve. Upon opening the valve, the piston was rotated downward, drawing in the required dosage of fluid. The valve was closed and the ZHE rotated two to three times. Five to ten psi was applied to the piston and any head space

slowly bled from the body. A final 5-10 psi were applied to the piston prior to end-over-end rotation for  $18 \pm 2$  hours at  $30 \pm 2$  rpm.

After the required rotation period, pressure inside the ZHE was checked by quickly opening and closing the inlet/outlet valve and noting the escape of gas. If a burst of gas was not heard, the sample was discarded and the above procedure repeated with a fresh sample.

The liquid portion of the solid extract was filtered out of the ZHE by repressurizing the piston and collecting the fluid into the Tedlar bag containing the initial liquid phase. The solids were discarded. The liquid collected in all steps was considered the TCLP extract. Further analysis of the TCLP extract is outlined in EPA Method 625, liquid/liquid extraction.

#### **H. EP Apparatus**

Glass jars with teflon liners and attachments for the rotary shaker were purchased from Analytical Testing and Consulting, Inc. (Warrington, PA). The jars served as the extraction vessels and the rotary shaker as the agitation device.

#### **I. EP Procedure**

A complete outline of the EP procedure is provided in the Code of Federal Register Volume 40 Part 261, July 1986, and a schematic of this method is included in Appendix A.

A representative minimum 100 g sludge sample was required for testing purposes. To insure proper liquid/solid phase separation, the sample was centrifuged for 15 minutes at 2000 rpm which represents approximately a 500 g-force. The supernatant was filtered through a Whatman #1 qualitative filter, collected and stored in a glass stoppered flask at 4°C. The pellet and any solids caught on the filter were weighed and transferred into the extraction vessel. Reagent water equal to sixteen times the weight of the pellet was also added to the extraction jar.

After an initial agitation period the pH of the solution was adjusted to  $5.0 \pm 0.2$  by addition of 0.5 N acetic acid. The pH was monitored and adjusted accordingly for six hours at various time intervals during continual agitation. However, in no event did the aggregate amount of acid added to the solution exceed 4 mL of acid per g solid. The mixture was agitated for 24 hours end-over-end at  $30 \pm 2$  rpm's. If at the end of the 24 hour extraction period the pH was not below 5.2, the pH was further adjusted for an additional 4 hours at 1 hour intervals.

The solid portion was again separated from the liquid phase by centrifugation. The supernatant filtered and combined with the previous filtrate while the pellet was discarded. A final volume adjustment with reagent water was made prior to further analysis.

Volume adjustment was made by the following equation:

$$V = 20 (W) - 16 (W) - A$$

V = volume reagent water needed  
W = weight of solids  
A = mL of 0.5 N acetic acid added

The liquids resulting from initial filtration, solids extraction and volume adjustment were combined and analyzed by EPA Method 625 liquid/liquid extraction.

#### J. EPA Method 625

This method covers the determination of a number of organic compounds that are partitioned into an organic solvent and which are amenable to gas chromatography (GC) and gas chromatography/mass spectroscopy (GC/MS) analysis. A graphic outline of this procedure is incorporated in Appendix A. The non-polar solvent, methylene chloride, was utilized to serially extract non-polar to semi-polar organic chemicals from the polar water matrix.

During this procedure each sample was separated into two fractions, a base/neutral and an acid fraction by varying the pH of the sample and extracting with methylene chloride at each pH. At pH values greater than 11, all organic base compounds should be in their unionized form, and therefore, organic bases and neutrals could be extracted from the aqueous solution. Ionized organic acids at high pH values were not extracted until they were forced into the unionized form at pH values below 2.

Acid and base/neutral spiking standards were added to a final



concentration of 100  $\mu\text{g/L}$  sample. These primary GC standards were added for both quality control and to aid in percent recovery determinations.

The sample to be extracted, usually a one liter sample, was added to a two liter separatory funnel. Volumes of the primary surrogate spikes were adjusted and added to the sample. A 10 N sodium hydroxide solution was used to adjust the pH above 11. Sixty mL of methylene chloride for each liter of sample were added to the funnel, shaken, the phases allowed to separate, and the organic phase collected. This extraction procedure was repeated three times for each sample at pH above 11.

The pH was readjusted below 2 using 1+1  $\text{H}_2\text{SO}_4$ . Again the samples were serially extracted three times with 60 mL aliquots of methylene chloride per liter of sample. The organic phase was collected into a new collection flask for the acid fraction.

When emulsions occurred during phase separation, the emulsed layer was placed in a centrifuge tube and spun for 2 minutes at 2000 rpm's. Following centrifugation, the organic layer was pipetted into the collection flask, the water phase recombined into the separatory funnel and any emulsion not disrupted discarded.

Since water is roughly five percent soluble in methylene chloride and incompatible with normal GC analysis, the samples had to be "dried". Anhydrous magnesium sulfate was used to adsorb the water and then removed by filtration through a Whatman #1 filter. The flask and filter paper were rinsed with a few mL of methylene chloride to insure a complete quantitative transfer.

## K. Concentration

EPA Method 625 recommends sample concentration via Kuderna-Danish (K-D) concentrators. K-D concentrators consist of a 10 mL receiving flask attached to a 500 mL evaporating flask which is connected to a three ball Snyder column. The sample plus boiling chips were added to the K-D which was partially immersed in a 60-65°C water bath. The organics extracted into methylene chloride with boiling points greater than 40°C, the boiling point of methylene chloride, were concentrated into a small volume of the solvent.

K-D concentration was utilized only for Christiansburg #1. After further analysis of the concentrated samples, contamination between acid and base/neutral fractions was found. It was established that the cross-contamination arose from inadequate rinsing and cleaning of the elaborate K-D glassware between samples.

To eliminate cross contamination and still achieve adequate sample concentration, each methylene chloride sample was placed in a beaker and evaporated to 0.5 mL in the hood under ambient conditions. Although this method deviated from the EPA protocol, it should be stressed that blanks were maintained for every site, evaporation was at a lower temperature and gentler, therefore not driving volatiles off and finally cross-contamination was not observed with this method. It should also be noted that laboratories which routinely run EPA method 625 would not allow samples to evaporate due to the length of time each sample required.

#### L. GC and GC/MS Analysis

Capillary column gas chromatography (GC) was utilized as the analysis for trace organics since it maximized sensitivity and chromatographic resolution. A Hewlett-Packard (Avondale, PA) 5890 capillary gas chromatograph with flame ionization (FID) and electron capture (ECD) detectors. A GC temperature program consistent with EPA Method 625 recommendations was used in this project. The injector temperature was set at 225°C and the FID sustained at 320°C. The temperature program was as follows: 40°C hold for 3 minutes, ramp 8°C/minute to 300°C, hold 4.5 minutes, for a total run time of 40 minutes. The program was run with a split injection of 10:1, and utilized helium as the carrier gas flow equal to 1.8 mL/min and a linear velocity of approximately 37 cm/sec. The temperature program gave excellent peak separation.

Following sample concentration and addition of 10 µg the internal standard, fluoronaphthalene, 1 µL of each sample was injected onto the column. Flame ionization detection was employed for all samples, whereas, electron capture detection was utilized as a quality control step to insure detection of halogenated compounds.

GC/MS analysis as utilized to generate characteristic spectral data from which the identity of unknown trace organic compounds could be deduced. From the total 16 sample 8 EP and 8 TCLP (1 blank and 3 sludge replicate acid extracts for each test and 1 blank and 3 sludge replicate

base/neutral extracts for each test) obtained for each site, only the "best" acid and base/neutral set for each test were chosen for GC/MS analysis. The "best" replicate represented the sample which included all peaks found in the other chromatograms as well as any additional peaks detected. A set of blank samples (i.e. TCLP acid and base/neutral and EP acid and base/neutral) was selected for GC/MS analysis to minimize duplication and expense. The best replicate and blank sample chromatograms for the Fishersville Treatment Plant are presented in Appendix B.

Due to the complex nature of the mass spectroscopic instrumentation, the GC/MS analysis was performed by MS operator Kim Harich on a Hewlett-Packard (Avondale, PA) 5790 gas chromatograph interfaced with a VG-Micromass model 7070E double focusing mass spectrometer equipped with a VG-Datasystem 11-250 (VG Instruments, Manchester, England) in the Biochemistry Department at Virginia Polytechnic Institute and State University. To insure duplication of results from the original GC to the GC/MS, the same column and temperature program were used. Confirmation of the identity of trace organics detected in the GC/MS analysis was based on library matching of spectra using a National Bureau of Standards (NBS) library which has approximately 38,000 entries, by manual interpretation of mass spectral data, and by comparison of unknowns to spectra of purified standards. Mass spectra of the various unknown compounds identified are presented in Appendix C.

Quantitative analysis of the targeted compounds (i.e. sludge surrogates, trace organic compounds in sludge samples, and contaminants) was made by GC-FID. Response factors or Relative Weight Responses (RWR's) for the trace organics detected were determined in the laboratory under the same conditions used to chromatograph the sample extracts. Purified chemicals were purchased from Chem Service and 100:10, 10:10, and 1:10 dilutions of selected chemicals to fluoronaphthalene, respectively, were prepared. These dilutions were chosen because initial observations indicated detection of 1-100 nanogram quantities of the trace organics.

Each dilution was injected seven times. RWR's were calculated with the following equation:

$$\text{RWR} = \frac{\text{Peak Area Compound/Peak Area Internal Standard}}{(\text{mg Internal Standard/mg Compound})} *$$

The RWR for each compound for each injection was calculated and all RWR's averaged for a mean overall RWR per compound. The RWR was used to calculate the actual quantity detected in each sample by the formula:

$$\text{RR/RWR} * 10 \text{ mg Fluoronaphthalene} = \text{mg Compound}$$

Where RR = Peak Area Compound per sample/Peak Area Fluoronaphthalene per extracted sludge sample and the 10 mg fluoronaphthalene was the original quantity added to each sample prior to injection.

The response factors enabled the calculation of the quantity detected or the final concentration in each sample. Since the initial concentration of the sludge surrogates and primary standards was known a

percent recovery could be calculated. Only a final amount in the methylene chloride extract of the trace organics could be calculated; therefore the initial concentration in the sludge could only be postulated.

#### **M. Source of Contamination**

An investigation to evaluate the introduction of contaminants into sludge samples from laboratory procedures was undertaken. Two experiments were performed to discern if the impurities arose from the Milli-Q water or if they came from the acid and base solutions used to pH the extract during EPA Method 625. The first test involved liquid/liquid extraction with methylene chloride on a 1 L Milli-Q water sample without altering the pH, while the second analysis utilized 1 L Milli-Q water also but the sample was pH adjusted and broken into the normal acid and base/neutral fractions. All samples were concentrated and analyzed using the identical GC conditions implemented for the sludge samples.

## **IV. RESULTS**

### **A. Preliminary Results**

General site characteristic data were gathered and are summarized in Table IV.1. Yearly averages for flow, pH, and BOD effluent are presented, as well as the sludge processing scheme, time for processing, and the percent of sludge solids existing during land application. The average percent dry suspended solids, of four trials, ascertained during site sampling trips is presented in Table IV.2.

The average sludge sample size used for each test by site is also listed in Table IV.2. A 100 g sample was used for the EP analysis for all sites, where as the TCLP sample size was based on the preliminary filterable percent solids determination. Reagent blank samples for the corresponding testing procedure were the same volumes as the sludge samples used.

Initial extraction and analysis of each sludge sample indicated that the six sludge surrogates were not present in any of the four sludge samples at detectable concentrations. The gas chromatography analysis was performed by both FID and ECD to insure determination of trace quantities of the halogenated surrogates.

### **B. Sludge Surrogate**

The mean percent recovery and standard deviation for each surrogate with respect to test are shown in Table IV.3. Percent

Table IV.1. Site Characteristics Data: Yearly Averages

PARAMETER	SITE		
	Christiansburg	Fishersville	Honaker
Flow (MGD)	1.0	1.44	0.07
pH	7.9	7.0	7.3
Temp (°F)	42	44	48
BOD eff (mg/l)	10	3.6	6
D0 eff (mg/l)	8.3	7.5	8.0
Sludge Processing	Aerobic Digestion	Aerobic Digestion	Aerobic dgst. & Drying Beds
Process Time	15-20 day	27-35 day	3 month
% Dry Solids	1.4	0.9	70



Table IV.2. Percent Dry Solids and Average Sample Size

SITE	% Dry Solids *	% Solids (ZHE)	TCLP Sample (gram)	EP Sample (gram)
Christiansburg #1	1.67	32	80	100
Christiansburg #2	0.90	64	40	100
Fishersville	0.86	8	330	100
Honaker	25.20	99	25	100

\* Mean of 4 Trials

Table IV.3. Sludge Surrogates: Percent Recovery

SURROGATE	SOURCE	PERCENT RECOVERY			
		TCLP Sludge	EP Sludge	TCLP Control	EP Control
EDB	mean	18.7	10.3	26.3	21.0
	st.dev.	21.4	13.0	22.5	13.2
Bromoform	mean	33.4	21.8	22.0	10.9
	st.dev.	16.1	24.7	10.6	4.6
1-Chlorooctane	mean	1.1	1.7	1.8	13.5
	st.dev.	0.7	3.8	2.1	19.1
Fusarex	mean	2.0	1.3	17.6	27.4
	st.dev.	1.9	1.0	10.7	20.0
Heptachlor	mean	0.1	0.1	7.8	22.6
	st.dev.	0.1	0.3	9.0	23.9
DDT	mean	1.0	0.3	5.2	19.6
	st.dev.	2.6	0.6	4.3	27.8

recoveries are based on a starting concentration of 250  $\mu\text{g}$  standard/100 g sludge. Recoveries are listed by triplicate sludge samples and reagent water blanks (the four blanks, one each from the four sampling trips were averaged).

Pooled t-test values, Table IV.4, which tested the significance of the recovery of the surrogates in the blank reagent water to the recoveries in the triplicate sludge samples are presented by test. The significance of the probability value (p-value) was established using a 95% confidence interval in which a p-value less than 0.05 was considered statistically significant, a p-value greater than 0.10 was not statistically significant, and a p-value between 0.05-0.10 was judged slightly significant.

The Analysis of Variance (ANOVA) results presented in Table IV.5 represent the percent recovery of the six sludge surrogates from triplicate sludge samples at the four sampling sites. Full ANOVA tables are presented in Appendix D. So as not to skew the ANOVA results, percent recovery data for the blank water samples were not included. The ANOVA analysis also used a 95% confidence level.

In an effort to explain some of the variability associated with the mean recovery values across the sludge surrogates, a number of physical and chemical parameters for each sludge surrogate, Tables IV.6 and IV.7, were investigated. Vapor pressure, the equilibrium relationship of a pure compound into the gaseous phase; aqueous solubility, the saturation concentration of a solute in a known solvent;

Table IV.4. Pooled t-Test: Percent Recovery  
Blank Reagent Water to Triplicate Sludge Samples

Compound	TCLP p-value	Sign.*	EP p-value	Sign.*
EDB	0.611	N	0.243	N
Bromoform	0.399	N	0.575	N
1-Chlorooctane	0.459	N	0.141	N
Fusarex	0.000	Y	0.000	Y
Heptachlor	0.016	Y	0.010	Y
DDT	0.069	S	0.042	Y

\* Significance

Y = yes statistical significant, p-value < 0.05

N = no statistical significance, p-value > 0.10

S = slight statistical significance, 0.10 > p-value > 0.05

Table IV.5. ANOVA Results: Percent Recovery

COMPOUND	SOURCE	p-value	#Significance
EDB	Test	0.064	S
	Site	0.000	Y
	Test*Site	0.160	N
Bromoform	Test	0.318	N
	Site	0.073	S
	Test*site	0.768	N
1-Chlorooctane	Test	0.719	N
	Site	0.203	N
	Test*Site	0.441	N
Fusarex	Test	0.130	N
	Site	0.032	Y
	Test*Site	0.009	Y
Heptachlor	Test	0.561	N
	Site	0.034	Y
	Test*Site	0.398	N
DDT	Test	0.413	N
	Site	0.588	N
	Test*Site	0.331	N

# Y = yes statistical significance, p-value <0.05  
 N = no statistical significance, p-value >0.10  
 S = slight statistical significance, 0.10 > p-value > 0.05

Table IV.6. Physical Properties: Sludge Surrogates

SLUDGE STANDARDS	Molecular Weight (gram)	BP °C	MP °C
EDB	187.9	131	9.97
Bromoform	252.8	149	6-7
1-Chlorooctane	148.4	182	-57.8
Fusarex	260.9	304	99-100
Heptachlor	373.5	NA	95-96
DDT	354.5	185	108

NA = not available

Values obtained from Verschueren, 1983; Lyman, 1982; EPA, 1979.

Table IV.7. Coefficients: Sludge Surrogates

SLUDGE STANDARD	log Vapor Pressure <sup>1</sup>	log Solubility <sup>2</sup>	log Henry <sup>3</sup>	log K <sub>ow</sub>	log K <sub>oc</sub>
EDB	1.146	0.634	-0.097	3.85	3.29
Bromoform	0.748	3.504	-3.237	2.30	1.71
1-Chlorooctane	-0.721	0.690	-2.119	3.79	3.26
Fusarex	-2.770	1.199	-4.444	3.24	2.98
Heptachlor	-3.523	-0.745	-3.086	4.41	4.04
DDT	-6.721	-2.488	-4.569	6.91	5.01

1. mm.Hg @ 25 °C  
 2. mg/l @ 25 °C  
 3. atm·m<sup>3</sup>/mol  
 Values obtained from Verschuieren, 1983; Lyman, 1982; EPA, 1979.

Henry's Law Constant, the relative diffusion into the gas phase from the aqueous state;  $K_{ow}$ , the octanol-water partitioning coefficient of a pure compound from the aqueous phase into an organic phase;  $K_{oc}$ , the adsorption constant of a chemical to the portion of carbon affiliated with a solid; (Tinsley, 1979), and boiling point were chosen.

Percent recovery versus the logarithm of the parameter of interest was plotted by test in a "jittered" mode, and are shown in Figures IV.1 through IV.6. Jittered plots were chosen so that any patterns within the data could be recognized and also to give a discriminate representation to an otherwise confusing diagram. The actual data points are slightly skewed so that underlying data points can be distinguished. The actual numerical axes values do not necessarily correspond to the data point although the values are nearly true.

A linear regression analysis relating percent recovery to the logarithm of the particular physical/chemical parameter was performed for TCLP and EP separately on non-jittered data. The proportion of the total variation in the y-axis that is explained or accounted for by the fitted regression is termed the coefficient of determination,  $r^2$ . The results of the regression for each parameter by test are shown in Table IV.8. Since these physical/chemical parameters are correlated, the coefficient of determination values are not additive.

Lastly, box plots, Figures IV.7 and IV.8, were generated so that a simple graphical representation of the variation for the sludge surrogates within each test could be perceived. The median is marked by



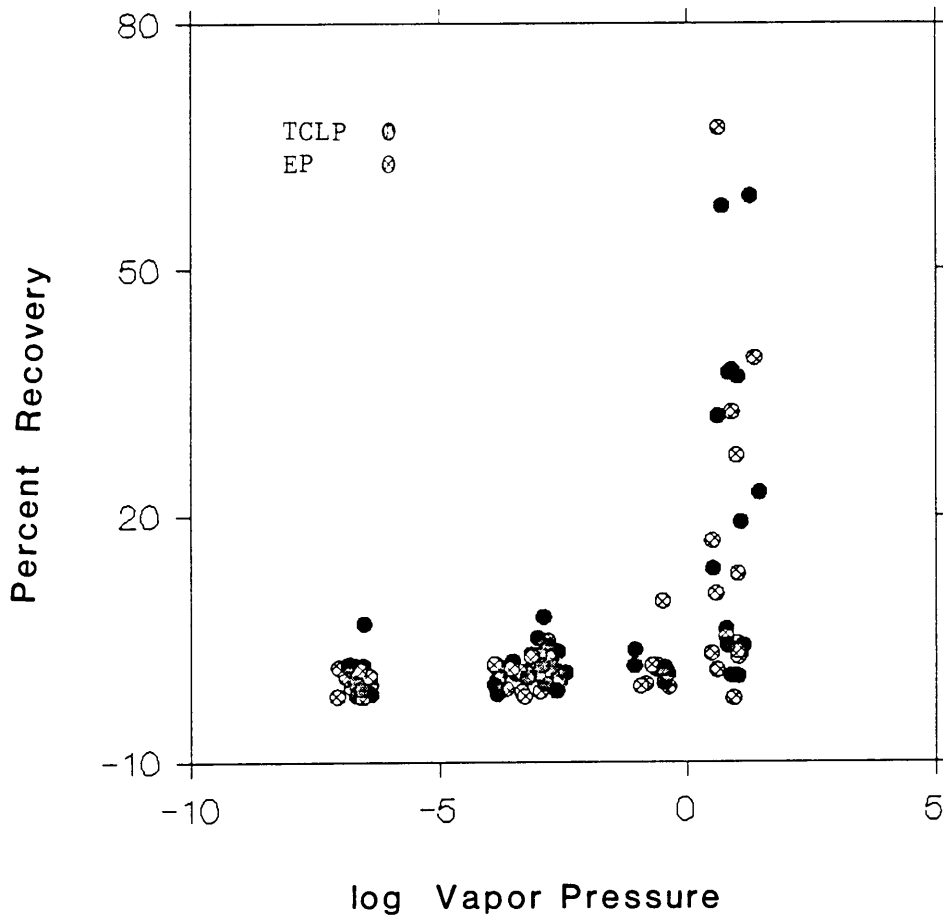


Figure IV.1 Jitter Plot - % Recovery vs. log Vapor Pressure

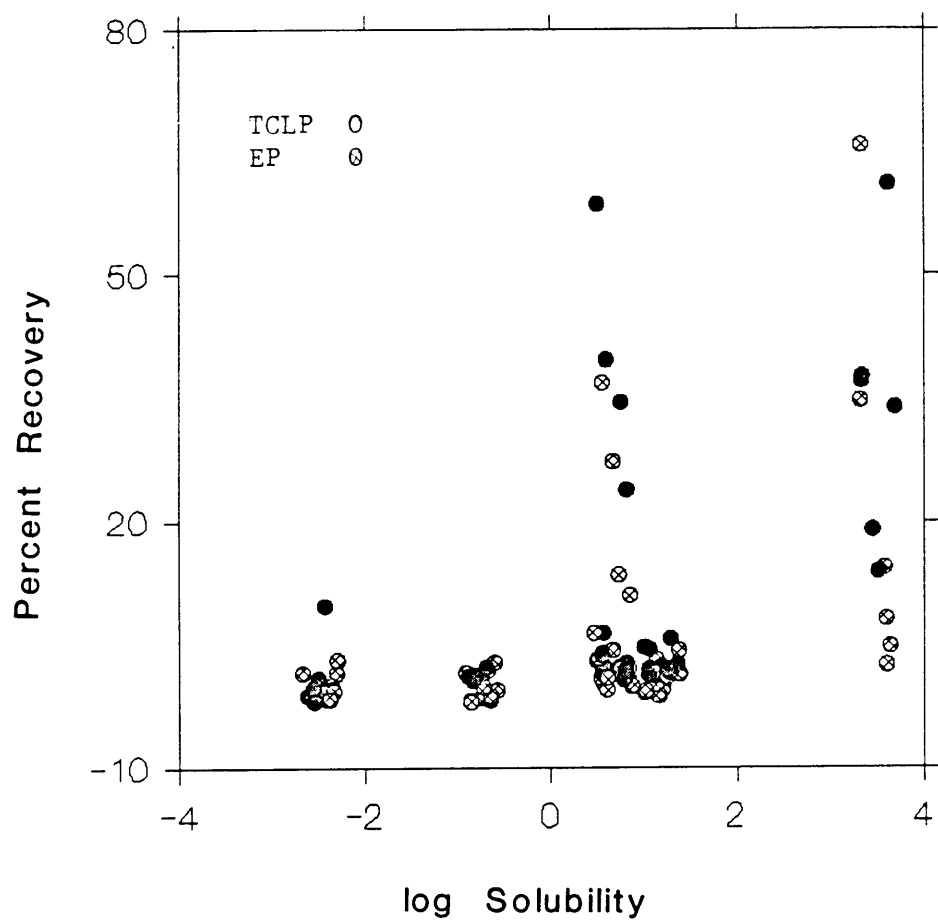


Figure IV.2 Jitter Plot - % Recovery vs. log Solubility

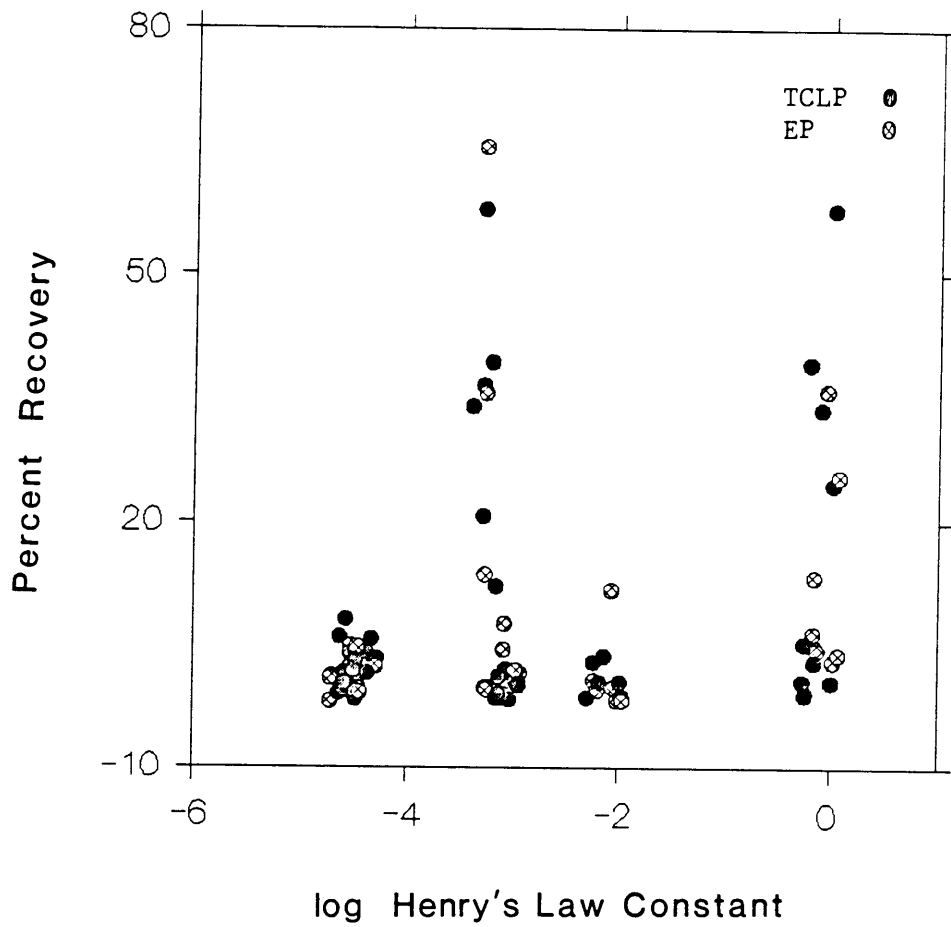


Figure IV.3 Jitter Plot - % Recovery vs. log Henry Law Constant

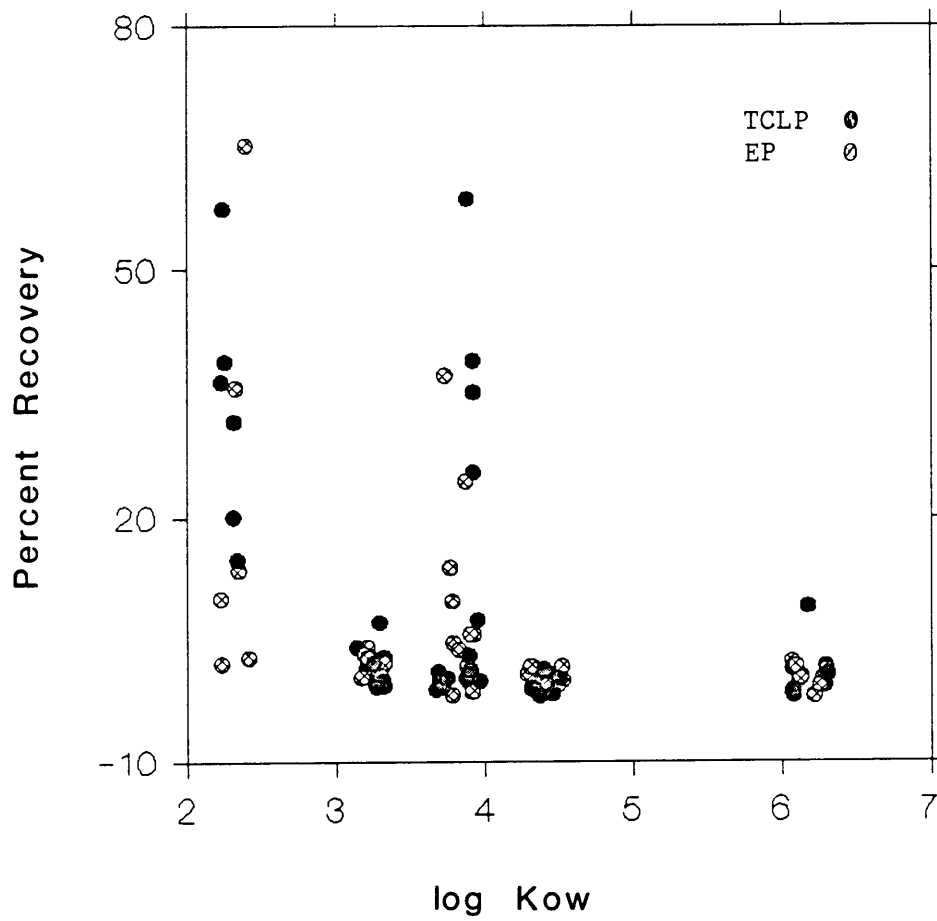


Figure IV.4 Jitter Plot - % Recovery vs. log Kow

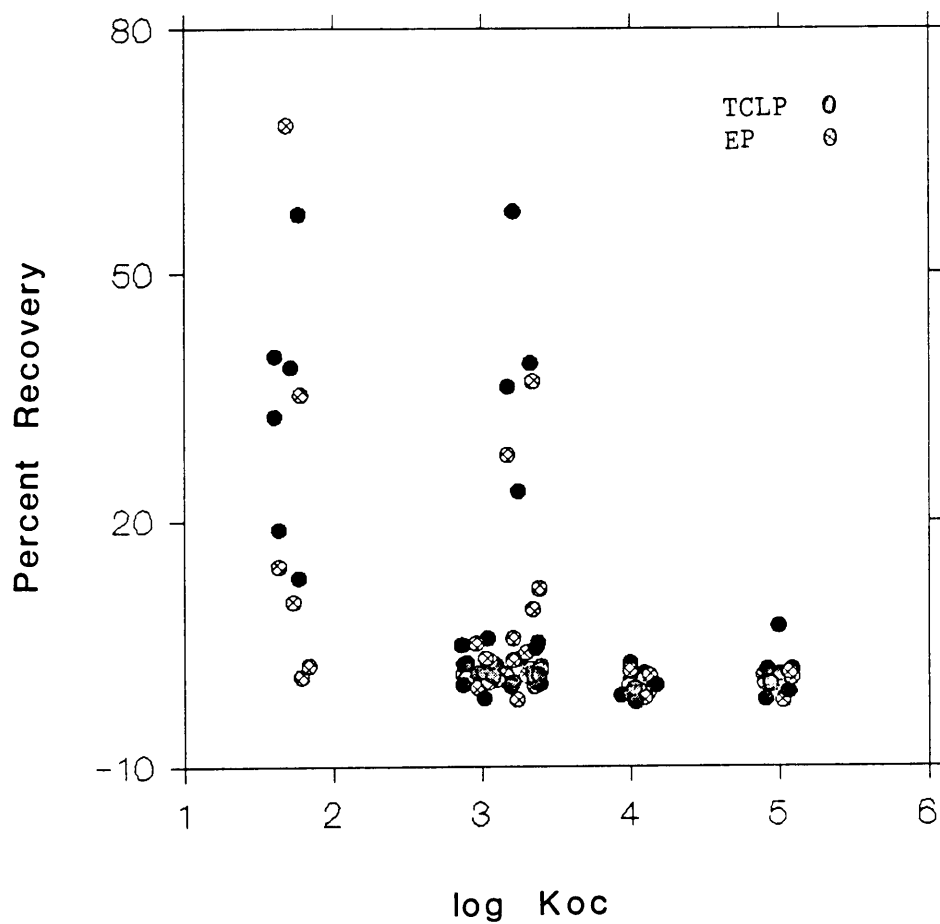


Figure IV.5 Jitter Plot - % Recovery vs. log Koc

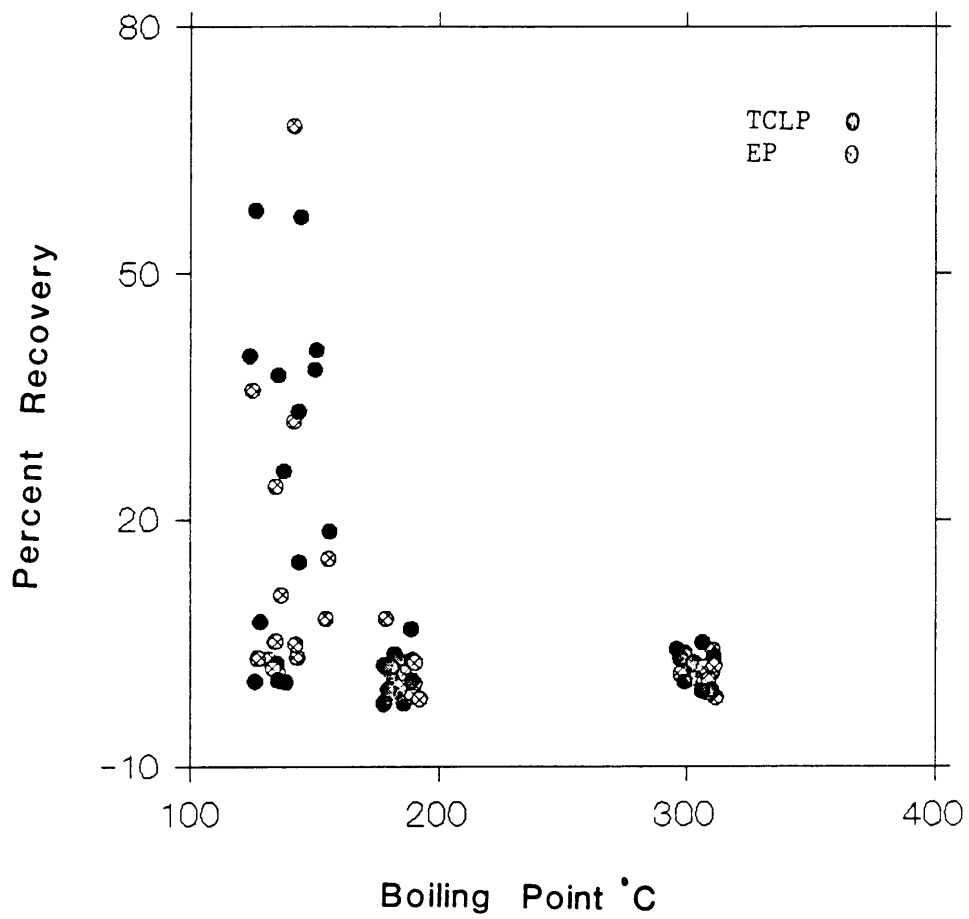


Figure IV.6 Jitter Plot - % recovery vs. Boiling Point

Table IV.8. Proportion of the Percent Recovery  
Explained by Various Parameters ( $r^2$  values)

PARAMETER	TCLP	EP
log Vapor Pressure	28.9	18.9
log Solubility	26.8	19.2
log Henry Constant	10.0	5.9
log $K_{ow}$	12.9	12.0
log $K_{oc}$	19.2	18.3
Boiling Point	13.5	11.3

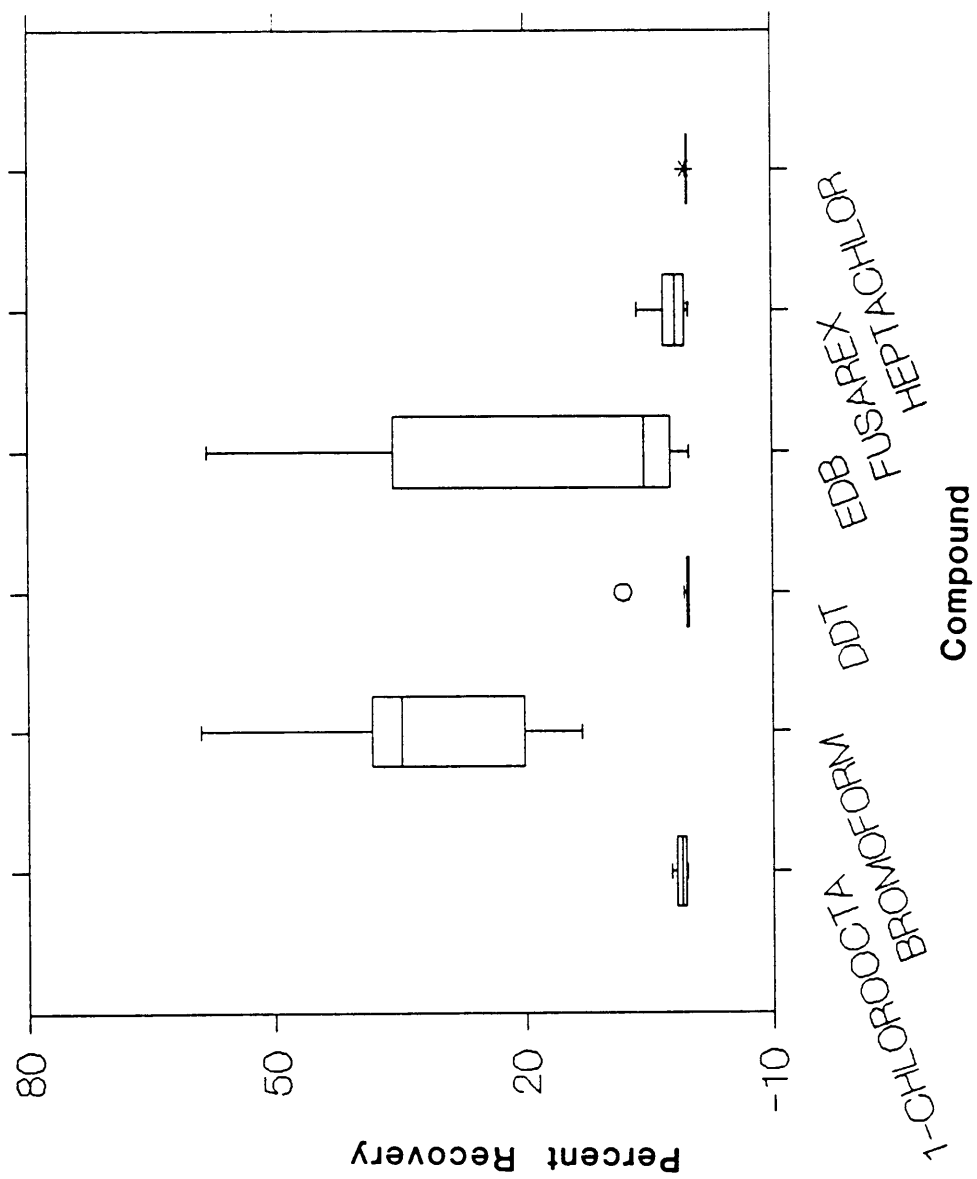


Figure IV.7 Box Plot - % Recovery vs. Compound (TCLP)



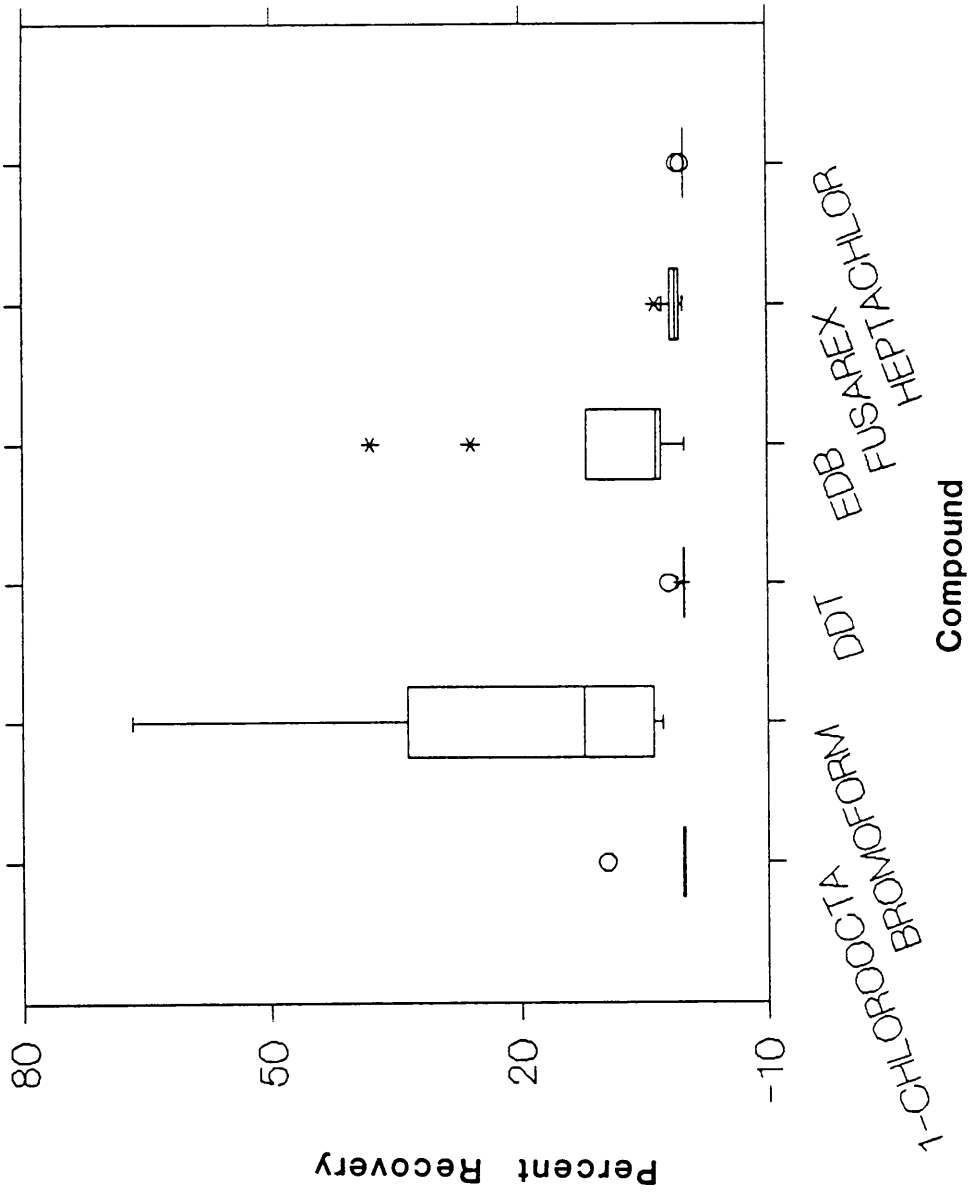


Figure IV.8 Box Plot - % Recovery vs. Compound (EP)

a vertical line within each box and splits the data in half. The upper and lower hinges split the remaining halves in half again. Values outside 1.5 times the interquartile or midrange are marked with astricks, while values outside 3 times the interquartile range are plotted with empty circles.

### C. Acid and Base/Neutral Standards

To assess compliance with quality control procedures, secondary base/neutral extractable and acid extractable secondary standards were added during EPA Method 625. The mean recovery and standard deviation for the triplicate wastewater samples and reagent water samples are presented in Tables IV.9 and IV.10. EPA reported wastewater percent recovery values for phenol and nitrobenzene are  $36 \pm 21$ , and  $82 \pm 54$ , respectively. Reported recoveries for reagent water are  $36 \pm 14$  for phenol and  $72 \pm 31$  for nitrobenzene.

### D. Detected Trace Organic Compounds

GC/MS identified of trace organic chemicals in the sludge samples were quantified relative to the internal standard fluoronaphthalene to yield a final concentration per sample. Only trace organic chemicals that were never identified in the blank water samples were considered to be actual pollutants. The range of concentrations detected for the four (4-methylphenol, dichlorodimethoxybenzene, dimethylpentanol, and tetramethylbutylphenol) quantified unknowns are listed in Table IV.11.

Table IV.9. Wastewater: Percent Recovery of Internal Standards

COMPOUND	SOURCE	TCLP	EP
<hr/> BASE/NEUTRAL EXTRACTABLE COMPOUNDS <hr/>			
Nitrobenzene-d <sub>5</sub>	mean	43.0	40.0
	st.dev.	17.7	21.6
2-Fluorobiphenyl	mean	31.0	27.8
	st.dev.	13.8	14.9
p-Terphenyl-d <sub>14</sub>	mean	16.1	8.5
	st.dev.	11.4	7.5
<hr/> ACID EXTRACTABLE COMPOUNDS <hr/>			
Phenol-d <sub>5</sub>	mean	31.7	27.4
	st.dev.	18.6	30.3
2-Fluorophenol	mean	32.5	27.9
	st.dev.	22.6	18.8
2,4,6-Tribromo-phenol	mean	28.2	26.6
	st.dev.	15.4	25.9

Reported Percent Recovery Values:  
 Nitrobenzene 82 ± 54.  
 Phenol 36 ± 21.  
 EPA, 1982.

Table IV.10. Reagent Water: Percent Recovery Internal Standards

COMPOUND	SOURCE	TCLP	EP
<hr/> BASE/NEUTRAL EXTRACTABLE COMPOUNDS <hr/>			
Nitrobenzene-d <sub>5</sub>	mean	38.4	52.1
	st.dev.	16.2	18.7
2-Fluorobiphenyl	mean	34.5	39.7
	st.dev.	11.2	16.8
p-Terphenyl-d <sub>14</sub>	mean	24.6	27.1
	st.dev.	14.1	19.8
<hr/> ACID EXTRACTABLE COMPOUNDS <hr/>			
Phenol-d <sub>5</sub>	mean	26.2	25.6
	st.dev.	14.4	12.0
2-Fluorophenol	mean	40.2	41.7
	st.dev.	24.3	20.8
2,4,6-Tribromo-phenol	mean	33.5	31.4
	st.dev.	24.2	26.5

Reported Percent Recovery Values:  
 Nitrobenzene 72 ± 31.  
 Phenol 36 ± 14.  
 EPA, 1982.

Table IV.11. Concentration of Trace Organic Chemicals\*\*

Compound	Test	Site	N	ug/sample* Range
4-Methylphenol	TCLP	F	2/3	0.26-0.34
	EP	F	2/3	0.18-0.86
	EP	H	1/3	0.42
Dichlorodimethoxy- benzene	TCLP	C#1	2/3	0.29-0.31
Dimethylpentanol	EP	F	1/3	0.15
Tetramethylbutyl- phenol	TCLP	C#2	3/3	0.34-0.63

\* Values not corrected for extraction losses.

\*\* Small chain organic acids identified in sludges but was not quantified

The compounds are arranged by test at the particular site they were identified. The number of times detected, N, equals the number out of 3 that the compound was found. These compounds were not arranged into acid and base/neutral fractions, therefore out of 3 indicates the three sludge samples per site per test.

An additional class of compounds were identified as true unknowns but were not quantified. Small chain organic acids, such as benzoic and hexanoic acids were identified in nearly all sludge samples. These compounds were not quantified because they were recognized as normal microbial degradation products.

#### **E. Contaminants**

Inherent contaminants found randomly through out samples, EP blanks, TCLP blanks, and Milli-Q blanks included benzaldehyde, benzonitrile, hydroxybenzaldehyde, and various phthalate esters. Only benzonitrile and benzaldehyde have been quantified and the results tabulated in Table IV.12. N or the number of times the contaminant was found, is sorted according to fraction and grouped out of 4, being the 3 triplicates plus the 1 blank.

Artifacts or compounds produced during sample preparation from reactions of constituents in or added to original samples (Dietrich et al. 1988), were produced during sample extraction and were detected. Commercial methylene chloride contains cyclohexene (which was detected in all sample extracts) as a preservative which will react to form

Table IV.12. Concentration of Contaminants

Site	Test	Fraction	BENZALDEHYDE		BENZONITRILE	
			N	ug/sample Range	N	ug/sample Range
Christiansburg #1	TCLP	A	3/4	0.99-1.48	0/4	---
	EP	A	0/4	---	0/4	---
	TCLP	B/N	4/4	0.17-5.7	3/4	0.13-0.48
	EP	B/N	1/4	0.16	1/4	0.09
Christiansburg #2	TCLP	A	2/4	2.28-4.15	0/4	---
	EP	A	1/4	4.65	0/4	---
	TCLP	B/N	4/4	1.77-4.97	2/4	0.59-1.65
	EP	B/N	4/4	2.31-9.33	4/4	0.22-0.73
Fishersville	TCLP	A	0/4	---	0/4	---
	EP	A	0/4	---	0/4	---
	TCLP	B/N	2/4	0.26-0.63	3/4	0.63-0.82
	EP	B/N	0/4	---	1/4	0.13
Honaker	TCLP	A	0/4	---	0/4	---
	EP	A	0/4	---	0/4	---
	TCLP	B/N	0/4	---	0/4	---
	EP	B/N	4/4	0.17-0.62	2/4	0.36-0.55

chlorinated and oxygenated cyclohexene artifacts depending on sample components.

Oxygenated artifacts, cyclohexenone and cyclohexenol, were detected in all blank reagent water samples and a few sludge samples. Whereas the chlorinated cyclohexene derivatives, chlorocyclohexanol and chlorocyclohexene, were only observed in the sludge samples. The various chlorine species contained in chlorinated drinking water can react with cyclohexene by a variety of mechanisms including addition, substitution, and free radical reactions to produce oxygenated and chlorinated cyclohexene artifacts (Dietrich *et al.*, 1988). The chlorinated cyclohexene derivatives detected in the sludge samples are believed to have originated from reactions during methylene chloride liquid/liquid extraction of samples and normal chlorination species that would be present in domestic treatment plants, therefore these compounds were not considered true sludge trace organic compounds.



## V. DISCUSSION

### A. Sludge Surrogates

The mean recovery and standard deviation associated with the percent recovery for each surrogate with respect to test are shown in Table IV.3. For the two volatile surrogates, EDB and bromoform, the TCLP to some degree extracted volatile compounds better than the EP when examining the mean recovery values. With regard to the semi-volatile 1-chlorooctane and the non-volatile pesticides, fusarex, heptachlor, and DDT, there seemed to be no statistical difference in mean test recovery for the sludge triplicates. Although in all cases the substantially sizable variations in recoveries makes it difficult to conclusively determine which compounds were extracted better. Also, in all situations both tests yielded low recovery values.

When comparing the mean recovery of each compound in the sludge to the recovery in the blank by test (see Table IV.3) a wide difference was evident. With the exception of bromoform, the mean recovery of the sludge surrogates was substantially higher in the blanks than in the sludge samples. To test this point statistically, a pooled t-test, an estimation of the variance that combines all the data points in a set to predict the variability was chosen to determine the significance of the recoveries from the blank reagent waters to that in the triplicate sludge samples. When surveying the pooled t-test results (see Table IV.4) at the 95% confidence level by test, the non-volatile compounds (fusarex, heptachlor, and DDT) exhibited statistical significance in

recovery from the spiked reagent water to the actual sludge sample. This was true for both tests. This does not seem to support the EPA's decision that the TCLP with ZHE volatile analysis is not as reliable as the EP for semi- and non-volatile compounds. These results may even suggest that both tests are relatively unreliable for semi- and non-volatile compounds, since the EP gave results similar to the TCLP in that both displayed significant difference from the blank recoveries to that in the sludge samples, and also the mean recovery values were low but comparable. These results also indicate that the sludge particles may influence the recovery of certain compounds and that a small percent of sludge solids had a marked effect on recovery.

It was originally hypothesized that the percent dry solids of the sludge was correlated to recovery, although when tested statistically by analyzing recovery as a function of solids there was found to be low or no correlation. The fact that no correlation was found may not be a weakness in the original assumption but more of a deficiency in the data. Since this correlation was not expected at the start of data collection, it was not deemed necessary to chose sites that had a wide range of dissimilar percentages of sludge solids. From Table IV.2, it is clear that three sites had very low solids (0.8% - 1.7%), whereas only one site (Honaker at 25.28% solids) had substantially more sludge solids. To properly assess the impact of the solids on recovery a greater diversity of sludge solids needs to be evaluated.

In addition to the % Dry Solids, Table IV.2 provides data on the ZHE solids determination. The ZHE solids determination was performed to determine the charge weight of the sample required. This determination was accomplished by placing a known amount of sludge inside the ZHE, applying pressure for 10 minutes at 50 psi, collecting the filtrate, and calculating the percent of solids left within the ZHE body. Any portion of the sample that was not filtered after 10 minutes was considered part of the solids even if it appeared to be liquid. From Table IV.2, the % Dry Solids for Christiansburg #2, 0.90, and Fishersville, 0.86, are essentially the same but the ZHE solids are extremely different (64% and 8%, respectively). The Fishersville sludge seemed to immediately clog the filter, and not allow any more liquid to pass. This occurrence may be due to decrease settling properties with longer sludge ages (Benfield and Randall, 1980), i.e. Christiansburg 15-20 days and Fishersville 27-35 days. With longer sludge ages there is a microbial population shift from the free swimmers and ciliates to the more dispersed filamentous bacteria which have very poor settling properties (Bisogni et al., 1971). It is believed that there was a microbial population difference in the Fishersville sludge, and it was this variation that contributed to the dissimilar ZHE solids determination.

At the 95% confidence interval (see Table IV.5) there was no significant difference between the TCLP and EP procedures for recovery of the sludge surrogates except in the case of EDB. The slight

significance assessment for EDB indicated that the test procedure had an effect on the percent recovery for some volatile compounds. Since the TCLP procedure utilized in this research was designed to extract volatiles to a greater extent than the EP, it seems reasonable that EDB was recovered better by the TCLP procedure. It could also be expected that bromoform, another volatile surrogate slightly less volatile than EDB, would behave similarly to EDB, but this was not the situation. This inconsistency implies that possibly factors other than volatility were involved in the recovery of compounds by each test.

Wastewater treatment plant, exhibited a more statistically significant impact on recovery than did test, i.e. TCLP and EP for sludge surrogates. Because no clear connection could be drawn between the type of compound (volatile vs. non-volatile) and the recovery at a particular site, the data suggests that the type of sludge was potentially an important criteria. Therefore, it is speculated that other factors such as bacterial/algal/protozoan population, organic content, sludge age, adsorption sites, pH, analysis temperature, etc., as well as the physical and chemical nature of the chemical surrogate are all potentially interrelated properties that influence recovery. Furthermore, these results indicated that all municipal sludges, even those meeting this studies requirements, may not be alike and should not be classified as such.

The non-volatile pesticide fusarex was the only compound for which the interaction between test and site showed any significance. This

indicated that both the test performed and the site had an impact on the recovery.

Though these results suggested there was little difference in recoveries by the two tests, it should be restated that recoveries for both tests were low and highly variable. In an effort to explain some of the variability in the mean values across the different sludge surrogates, various physical and chemical parameters relating to the sludge surrogate behavior in the solid/water matrix were investigated.

A linear regression analysis relating percent recovery to the particular physical/chemical parameter of interest was performed for TCLP and EP separately. The proportion or percent of the total variation in the y-axis that is explained or accounted for by the fitted regression is termed the coefficient of determination,  $r^2$ . The  $r^2$  values for each parameter are summarized by test in Table IV.9 and essentially these values translate into what percentage of the variation could be explained by that particular parameter. In the case of vapor pressure, the coefficient of determination explains 28.9% and 18.9% of the variability for percent recovery in the TCLP and EP procedures, respectively. Coefficient of determination values are not additive because they were developed as independent quantities; because the physical/chemical parameters are interrelated, the  $r^2$  values may overlap. When all six parameters - log vapor pressure, log solubility, log Henry Constant, log  $K_{ow}$ , log  $K_{oc}$ , and boiling point - were entered into a linear regression equation the  $r^2$  values explained 56.6% and

36.7% of the total variation for the TCLP and EP tests, respectively.

Box plots, Figures IV.7 and IV.8, were generated so that variations within the batched surrogate data could be realized by test. These plots demonstrate graphically the mean recoveries and related variability. For the semi- and non-volatile surrogates it is easy to observe the low recoveries for both tests. The only predominant contrast between the plots was the median recovery and related variability with respect to EDB. This difference merely restates the ANOVA results, that for EDB "test" made a somewhat statistical significance in recovery,  $p\text{-value} = 0.064$ .

#### **B. Acid and Base/Neutral Internal Standards**

Acid and base/neutral extractable compounds were added prior to the start of EPA Method 625 as a quality control technique. Although recovery ranges for only two (phenol and nitrobenzene) of the six compounds added could be found in the literature, there does not seem to be any indication of failure to comply with the EPA established QA guidelines. For both cases, wastewater and reagent water, after execution of the quality control equations in the EPA manual 1982, there was no deviations from the proposed quality standards. Lastly EPA Method 625 did not perform differently on either of the extracts, TCLP or EP, since the mean recoveries and standard deviations for the internal standards was not substantially different from one another.

### C. Trace Organic Compounds Identified in Sludge Samples

Chromatogram peaks identified by GC/MS were sorted as either an unknown or a contaminant, to be discussed in detail in the following section. The unknowns were then further segregated into quantifiable and nonquantifiable compounds because many peaks identified during GC/MS were not identifiable from the original the GC runs. An inconsistent injection volume, 1  $\mu\text{L}$  for GC and 10  $\mu\text{L}$  for GC/MS, was employed because mass spectroscopic instrumentation is notorious for being less sensitive. A 10  $\mu\text{L}$  GC/MS injection volume drastically intensified background noise and uncovered peaks which could not be found in the original FID chromatograms. In addition to nondetected peaks, some peaks coeluted, and therefore had overlapping spectra which never separated well enough to enable a suitable library match.

Other identified peaks which were not quantified included a number of organic acids, in particular: benzoic, hexanoic, propanoic, and butyric acids. These compounds are common microbial biodegradation byproducts and normal end products from hydrolysis of organic compounds (Grant and Long, 1981). Carboxylic acids including benzoic acid and alkanic acids with 4 or more carbons, have been identified in landfill leachates and account for approximately 18% (by mole fraction) of the organic segment (Boardman, 1989). Conversely, propanoic and butyric acids are conventional anaerobic degradation products (Grady and Lim, 1980). Propanoic acid is also believed to originate from the acetic acid used to pH adjust samples in the EP and in the extraction fluid

used during the TCLP. Organic acids are widely used compounds to control molds and some bacteria in food and cosmetics, and since the body metabolizes these organic acids readily their use is considered quite safe (Tortura et al., 1986).

Of all the peaks and spectra examined, only four true unknown compounds were identified and quantified. Table IV.11 lists the range of final concentration values calculated, test, site and number of times each compound was identified. Dichlorodimethoxybenzene, dimethylpentanol, tetramethylbutylphenol, and 4-methylphenol or p-cresol have been identified as constituents of gasoline exhaust from principally high octane and diesel exhaust (Verschueren, 1983). 4-Methylphenol has also been utilize in disinfectants and tetramethlybutylphenol as a surfactant (Merck, 1983).

The range of concentrations for the above mentioned four compounds detected in the final extracts was 0.15-0.86  $\mu\text{g}/\text{sample}$ . Considering that an average sludge sample tested was approximately 100 g, and the mean percent recovery for the six sludge surrogates from both tests was 7.7%, an estimated concentration in the original sludge sample can be postulated. After applying the average percent recovery to the final concentration range, the estimated concentration of the unknowns in the original sludge sample was 19-112 ppb.

The GC/MS data from the triplicate analyses of the four sludge samples were examined for the presence of other pesticides. No additional pesticides were identified in any of the sludge samples by either GC/FID or GC/ECD.



#### D. Contaminants

Based on GC/MS library identification from the reagent water blanks analyzed, and retention times from the same chromatograms, four compounds, benzaldehyde, benzonitrile, hydroxybenzaldehyde, and dibutyl phthalate were identified in all the extracted Milli-Q water samples. This indicated that the impurities were originating in either the Milli-Q water, since both the pH adjusted and non-pH adjusted samples contained these pollutants or they infiltrated samples during normal laboratory operations. Benzaldehyde and hydroxybenzaldehyde have been used as gasoline additives (Verschueren, 1983), whereas benzonitrile's use has traditionally been as a solvent (Merck, 1983). It is speculated that these benzene derivatives entered samples from either the solvent, methylene chloride, or reagent water. It is possible that the Milli-Q cartridges used to make extraction fluid and volume adjust samples introduced these contaminants. In contrast, phthalate esters, used as plasticizer/softeners in the production of plastics, are believed to have been introduced into samples through laboratory practices, even though no plastics were used, and glassware was chromic acid washed. Phthalates are ubiquitous compounds found throughout the laboratory environment.

To determine if inherent impurities could possibly interfere with detection of trace organics by the TCLP and EP tests, benzaldehyde and benzonitrile were quantified. Purified standards were purchased and response factors calculated. Table IV.12 lists the range of

concentrations calculated and N, the number of times identified by site, fraction, and test. Applying the same criteria to the contaminants as with the unknowns, a 7.7% average recovery of the surrogates from both tests, and assuming that on the average 2000 mL of reagent water was added to an EP sample and 500 mL of extraction fluid was added to a TCLP sample then the range of corrected concentrations across all sites for both compounds would be 3 - 108 ppb and 1-61 ppb for TCLP and EP, respectively.

Given that the concentration range for the unknowns was between 19 and 112 ppb, and that the contaminants are also within the same range, questions are raised to the ability of these tests to identify background impurities from true sludge constituents. Blank reagent water samples were run in order to discern contamination from true trace organics components. Even so, erroneous identification could be made because the contaminants were not always found in the blanks while at the same time they were identified in some of the triplicate samples. Additionally, presence of contaminant peaks could overlap GC peaks of true sludge components making detection/identification of sludge components difficult.

## VI. CONCLUSIONS AND SUMMARY

In summary the major findings of this research are as follows:

- Site (i.e. type of sludge from the individual waste treatment plants) had a significant effect on recovery.
- The volatile surrogate EDB was the only compound that displayed a slight significance in recovery with respect to test; the mean recovery for EDB was greater by TCLP than EP.
- There was essentially no difference between the TCLP and EP tests with respect to recovery of semi- and non-volatile compounds, although recovery was low for both tests.
- Both tests had highly variable results.
- Recovery variability was not shown to be correlated with the percent solids of the sludges
- Various physical/chemical parameters for the sludge surrogates explained only a small portion of the total variation.
- No additional pesticides were identified by GC/MS in any of the sludge samples.
- Base/neutral and acid internal standards recoveries did not deviate from EPA established Quality Assurance guidelines.
- Only a few trace organic compounds (4-methylphenol or p-cresol, dichlorodimethoxybenzene, dimethylpentanol, and tetramethylbutylphenol) were identified in the four sludge

samples; they appeared to be extracted in the ppb concentration range. Again, results were variable in that a single compound was not necessarily detected in all replicates.

- Laboratory procedures introduced contaminants to the sludge samples at approximately the same concentration range as the sludge trace organic compounds; contaminants and trace organic compounds quantified were approximately in the ppb concentration range.

Future research, needed to more comprehensively evaluate municipal wastewater sludges and the application of the TCLP and EP tests, includes:

- Investigation of specific sludge characteristics (e.g., age, solids content, microbiological populations) and their effect on the recovery of known compounds by the TCLP and EP tests
- Determination of which factors lead to such high variability within the TCLP test and within the EP test.
- Examination into which waste matrices are amenable to the TCLP procedure.
- Closer review of test protocol and required equipment in order to reduce the cost of the TCLP test procedure.

## VII. REFERENCES

Benfield, Larry D., and Randall, Clifford W., Biological Process Design for Wastewater Treatment, Prentice-Hall, Inc., Englewood Cliffs, NJ (1980).

Blackburn, W. B., Taylor, D. R., and Marsden, P. J., "Collaborative Study of the Toxicity Characteristic Leaching Procedure (TCLP)." Environmental Monitoring Systems Laboratory. Office of Research and Development. EPA/600/4-87/045, USEPA, Las Vegas, Nevada (1987).

Boardman, Gregory, Personal Communication (1989).

Browman, Michael G., and Chesters, Gordon, "The Solid-Water Interface: Transfer of Organic Pollutants Across the Solid-Water Interface." in Fate of Pollutants in the Air and Water Environments: Part 1, I.M. Suffet, ed., John Wiley and Sons, Inc., New York, N.Y., pp.49-105 (1977).

Brown, D. K., Francis, C. W., and Maskarinec, M., "Mobility of Organic Compounds from Hazardous Wastes." National Technical Information Service (NTIS), # PB83 163-956; Oak Ridge, TN. (1983).

Curtis, Helena, Biology, 4<sup>th</sup> Ed. Worth Publishers, New York, N.Y. (1983).

Dacre, Jack C., "Potential Health Hazards of Toxic Organic Residues in Sludge." in Sludge Health Risks of Land Application, G. Britton, B. L. Danron, G. T. Edds, and J. M. Davidson, eds., Ann Arbor Science, Ann Arbor, Michigan, pp. 85-102 (1980).

Dietrich, Andrea M., Christman, Russell F., and Durell, Gregory S., "Gas Chromatographic/Mass Spectrometric Identification of Chlorinated and Oxygenated Cyclohexene Artifacts Formed during the Analysis of Chlorinated Water Samples." Biomedical and Environmental Mass Spectrometry, 15, 453-458 (1988).

Energy Resources Company, "Filtration of Various Wastes Using Various Filter Media." USEPA 68-01-7075. Washington, D.C. (1985).

Environmental Protection Agency, "Water-Related Environmental Fate of 129 Priority Pollutants." EPA-440/4-79-029, Washington, DC. (1979).

Environmental Protection Agency, "Characteristic of Extraction Procedure Toxicity Test: Background Document." Section 261.24, National Technical Information Service (NTIS), #PB81 185-027, Washington, D.C. (1980).

Environmental Protection Agency, "Test Method: Base/Neutral and Acid-Method 625." Environmental and Monitoring and Support Laboratory, 559-092/0443, Cincinnati, Ohio (1982).

Environmental Protection Agency, "Process Design Manual: Land Application of Municipal Sludge." USEPA 625/1-83-016, Washington, D.C. (1983).

Environmental Protection Agency, "Environmental Regulations and Technology Use and Disposal of Municipal Wastewater Sludge." USEPA 625/10-84-003, Washington, D.C. (1984).

Environmental Protection Agency, "Composting of Municipal Wastewater Sludges." USEPA 625/4-85014, Washington, D.C. (1985).

Environmental Protection Agency, "EP Toxicity Test Procedures." Code of Federal Register, Vol. 40, part 261, Ch. 1, 386-393, Washington, D.C. (July 1, 1986a).

Environmental Protection Agency, "Toxicity Characteristic Leaching Procedure: Background Document." Subtitle C - Hazardous Waste Management Systems, Section 3001, Office of Solid Waste, Washington, D.C. (1986b).

Environmental Protection Agency, "Proposed Rules." Federal Register, Vol. 51, No. 114, 21651-21682, Washington, D.C. (June 1986c).

Environmental Protection Agency, "Toxicity Characteristic Leaching Procedure." Federal Register, Vol 51, No. 216, 40642-40653, Washington, D.C. (November 7, 1986d).

Flynn, Kevin C., "EPA Proposes New Sludge Regulations: The Sludge Dilemma." Water Pollution Control Federation's Operations Forum, 6, 15-16 (1989).

Francis, C. W., Maskarinec, P., and Goyert, J. C., "A Laboratory Extraction Methods to Simulate Codisposal of Solid Wastes in Municipal Waste Landfills." Hazardous and Industrial Solid Waste Testing: Fourth Symposium, American Society for Testing and Materials, Philadelphia, PA. (1986).

Grady, C. P. Leslie, and Lim, Henry C., Biological Wastewater Treatment Theory and Applications, Marcel and Dekker, Inc., New York, NY, pp. 847-870 (1980).

Grant, W. D., and Long, P. E., Tertiary Level Biology: Environmental Microbiology, John Wiley and Sons, New York, NY, pp. 97-126 (1981).

Hopke, D. K., Plewa, M. J., Stapleton, D. L., and Weaver, D. L., "Comparison of the Mutagenicity of Sewage Sludges." Environmental Science and Technology, 18, 909-916 (1984).

Jackson, D. R., Garrett, B. C., and Bishop, T. A., "Comparison of Batch and Column Methods for Assessing Leachability of Hazardous Waste." Environmental Science Technology, 18, 668-673 (1984).

Kimmell, Todd A., and Friedman, David, "Model Assumptions and Rationale Behind the Development of EP-III." Hazardous and Industrial Solid Waste Testing: Fourth Symposium, American Society for Testing and Materials, Philadelphia, PA. (1986).

Kimmell, Todd A., "Development, Evaluation, and Use of the Toxicity Characteristic Leaching Procedure (TCLP)." Chemical and Biological Characterization of Sludges, American Society for Testing and Material, Philadelphia, PA. (1987).

Knocke, William, Personal Communication (1989).

Lyman, Warren J., Reehl, W.F., and Rosenblatt, D.H., Handbook of Chemical Property Estimation Methods. McGraw-Hill, New York, N.Y. (1982).

Marsden, Paul J., "Modification of the TCLP for Problem Matrices." United States Environmental Protection Agency Symposium on Solid Waste Testing and Quality Assurance, American Public Works Association, Washington, D.C., pp. 1-8 (1988).

Mason, B. J., and Carlile, D. W., "Round-Robin Evaluation of Regulatory Extraction Methods for Solid Wastes." Environmental Physics and Chemistry Program EPRI EA-4740. Energy Analysis and Environmental Division, Washington, D.C. (1986).

McCarthy, Donald J., "A Comparison of the EP Toxicity Test to the TCLP." Analytical Techniques and Residuals Management Specialty Conference, Atlanta, GA. (1988).

Merck Index, 10th Ed., M. Witndholz, S. Budavari, R. F. Blumetti, and E. S. Otterbein eds., Merck and Company, Inc., Rahway, NJ (1983).

Newcomer, Lynn R., Blackburn, W. Burton, and Hansen, Gail A., "Performance of the Toxicity Characteristic Leaching Procedure." Third Annual United States Environmental Protection Agency Symposium on Solid Waste Testing and Quality Assurance, American Public Works Association, Washington, D.C., pp. 4.25-4.45 (1987).

Reinhard, Martin, and Goodman, Naomi L., "Occurrence and Distribution of Organic Chemicals in Two Landfill Leachate Plumes." Environmental Science and Technology, 18, 953-961 (1984).

Rumer, Ralph R., "Physical Processes for Pollutant Transport in the Water Environment." in Fate of Pollutants in the Air and Water Environments: Part 1, I.M. Suffet, ed., John Wiley and Sons, Inc., New York, N.Y., pp. 297-314 (1977).

Saywer, Cal. Personal Communication (1989).

Suffet, Irwin M., "Fate of Pollutants in the Air and Water Environments: A Frame of Reference." in Fate of Pollutants in the Air and Water Environments: Part 1, I.M. Suffet, ed., John Wiley and Sons, Inc., New York, N.Y., pp. 8-15 (1977).

Tinsley, Ian J., Chemical Concepts in Pollutant Behavior. John Wiley and Sons, Inc., New York, N.Y. (1979).

Tortura, Gerald J., Funke, Berdell R., and Case, Christine L., Microbiology: An Introduction 2nd Ed., The Benjamin/Cummings Publishing Company, Inc., Menlo Park, CA, pp. 200-203 (1986).

Verschueren, Karel, Handbook of Environmental Data on Organic Chemicals, 2nd edition. Van Nostrand Reinhold Company, New York, N.Y. (1983).

Zar, Jerrold H., Biostatistical Analysis. Prentice-Hall International, Inc., London, England (1974).

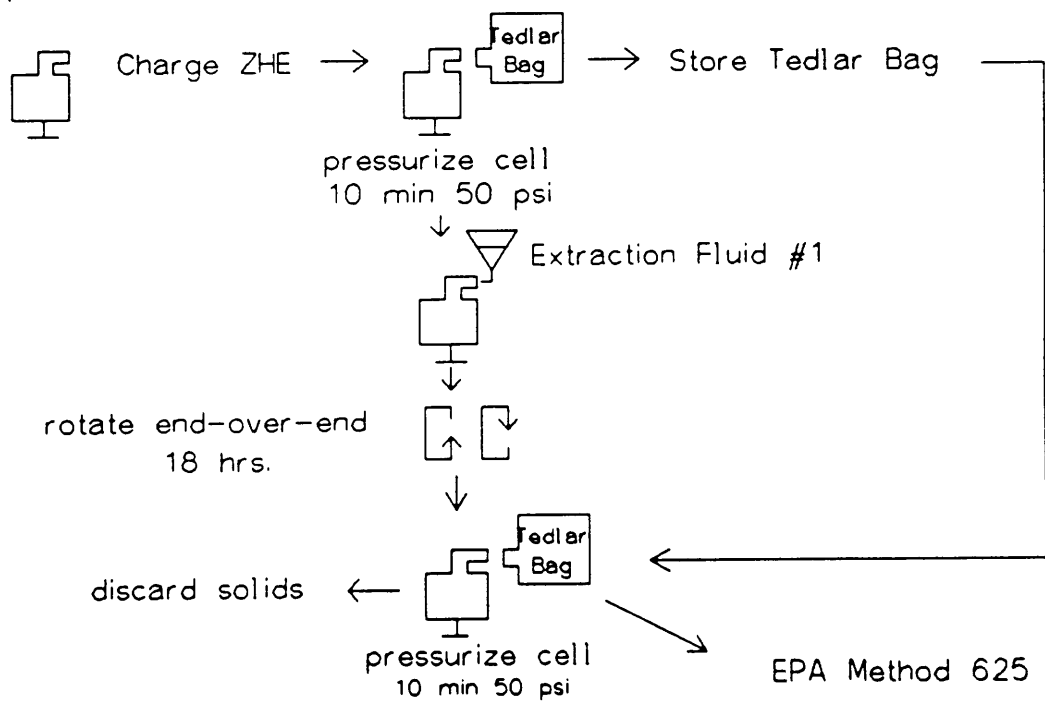


APPENDIX A

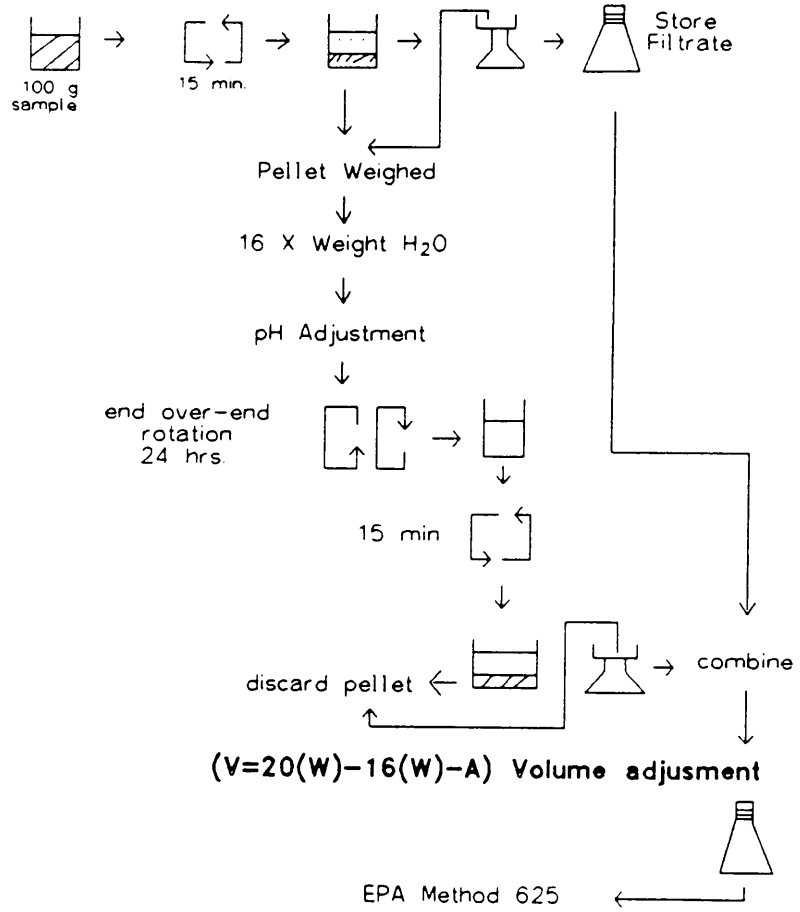
Schematic:  
TCLP  
EP  
EPA Method 625

## TCLP PROCEDURE

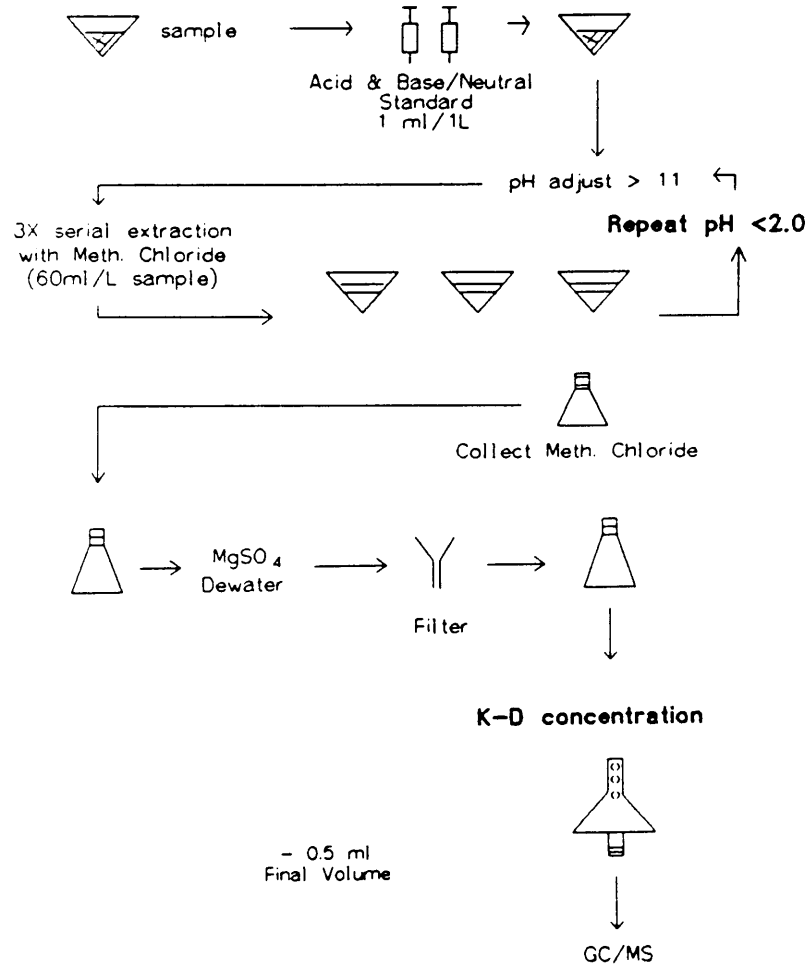
- preliminary solid determination



## EP TOXICITY TEST

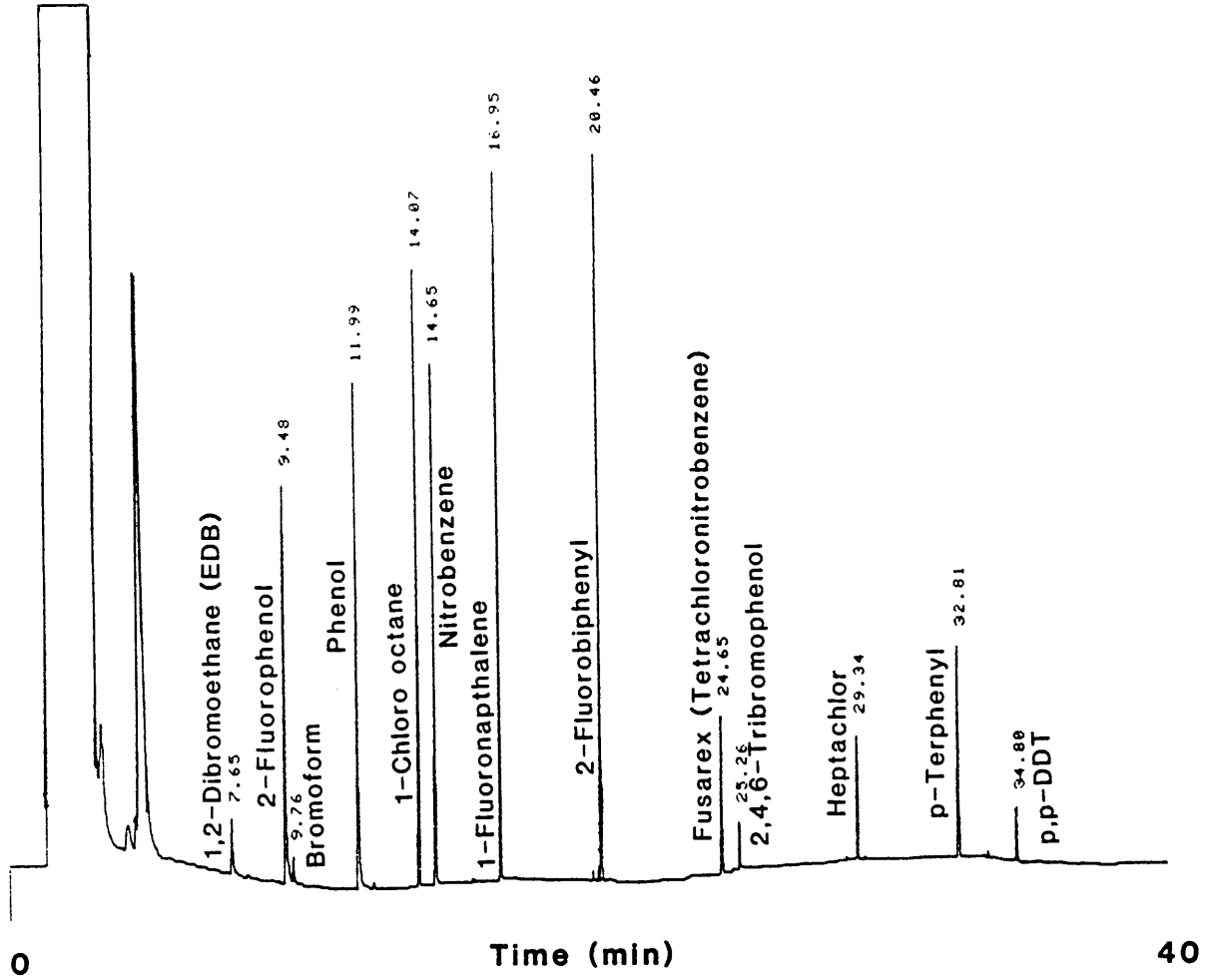


## EPA Method 625 Liquid\Liquid Extraction

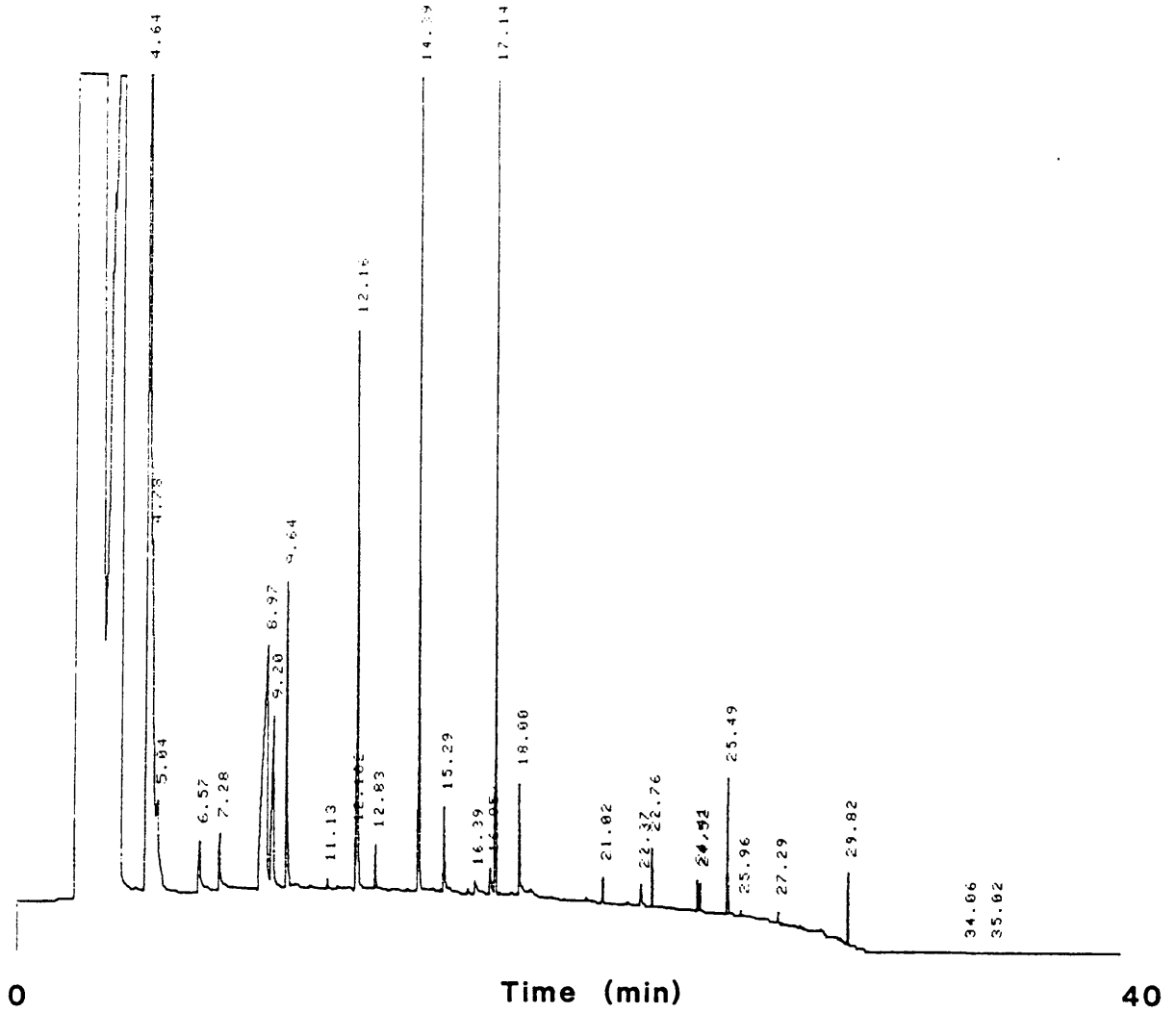


APPENDIX B  
Fishersville Chromatograms

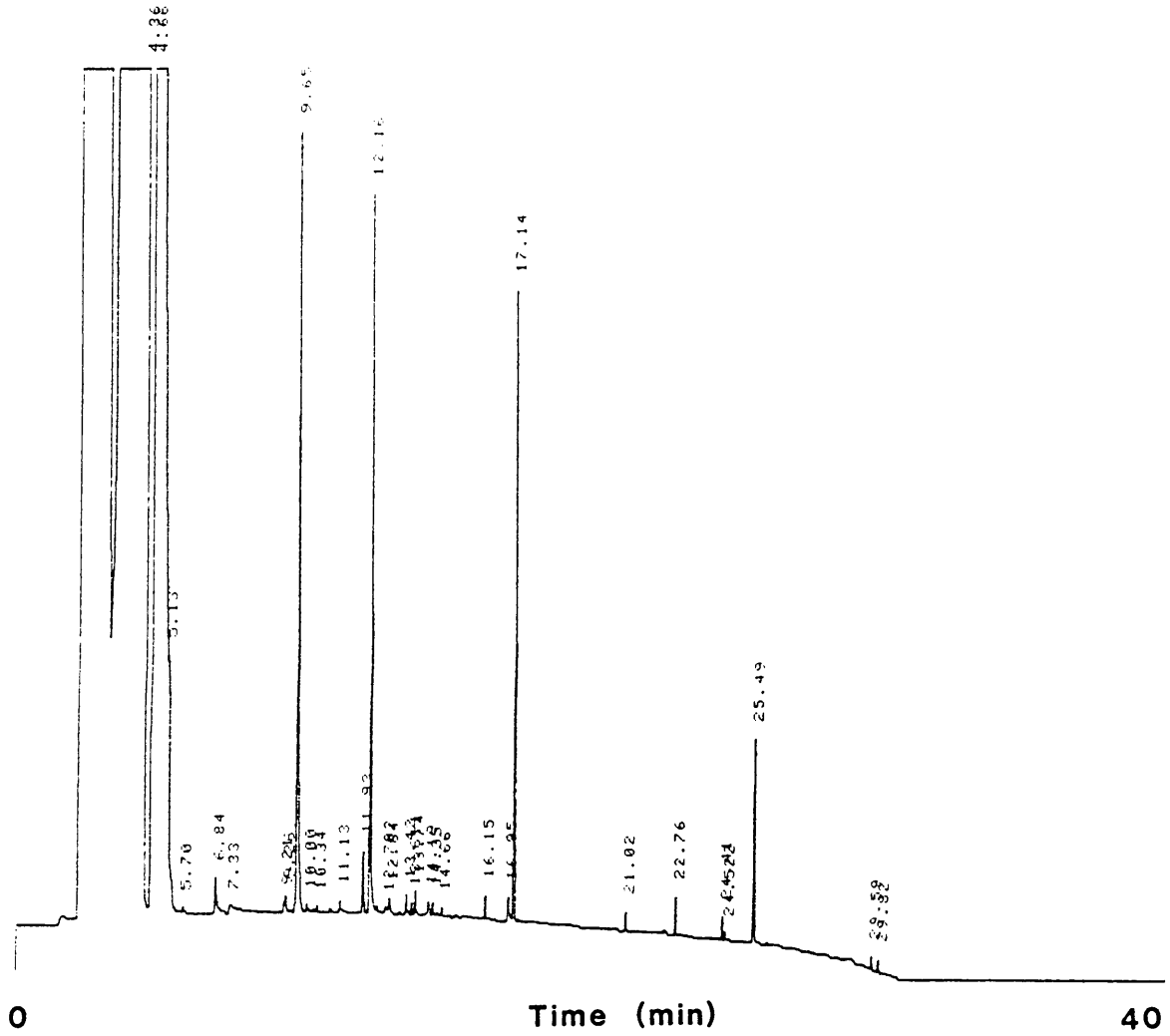
## Internal Standard



TCLP: Fishersville Acid

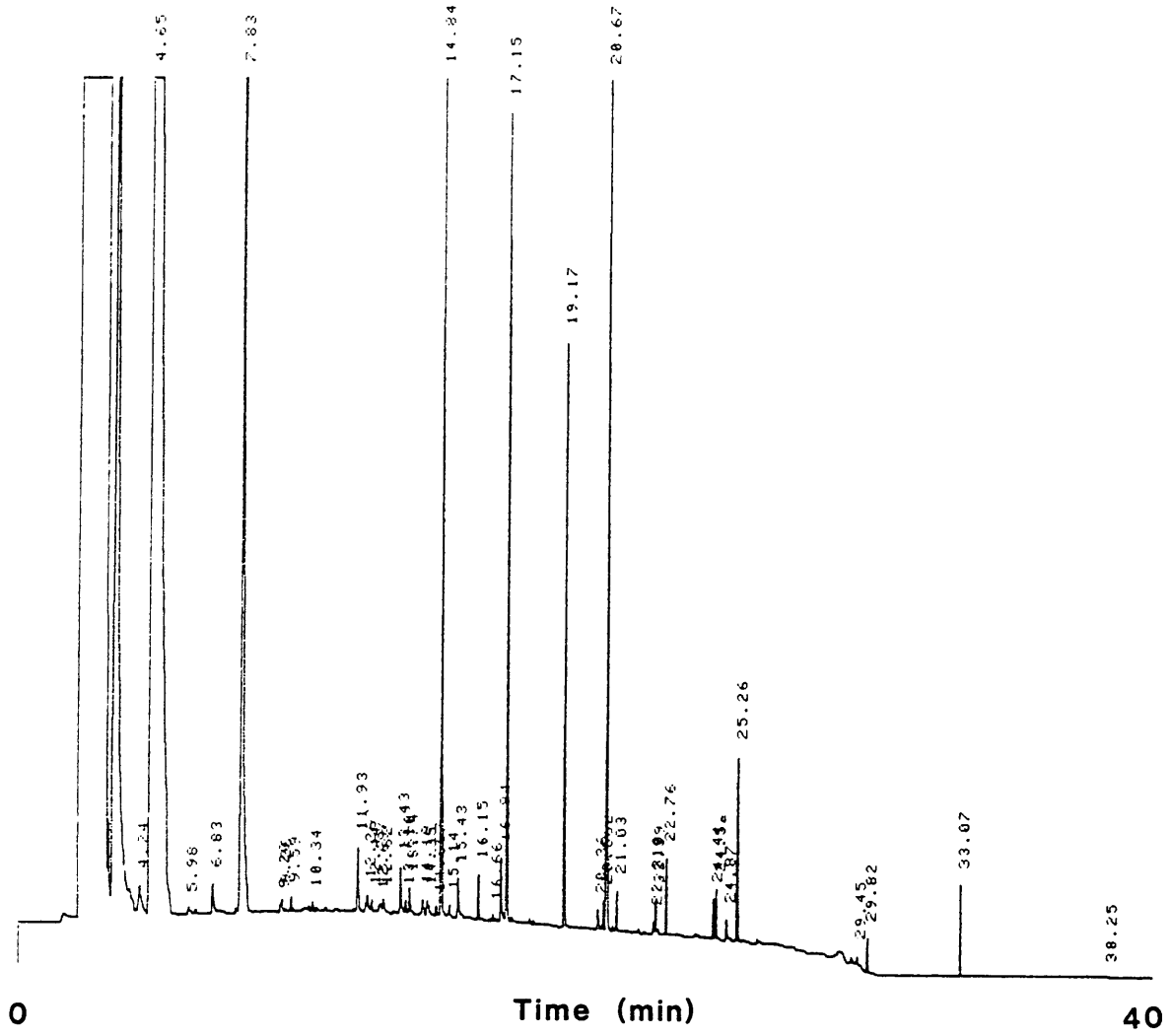


TCLP: Fishersville Acid Blank

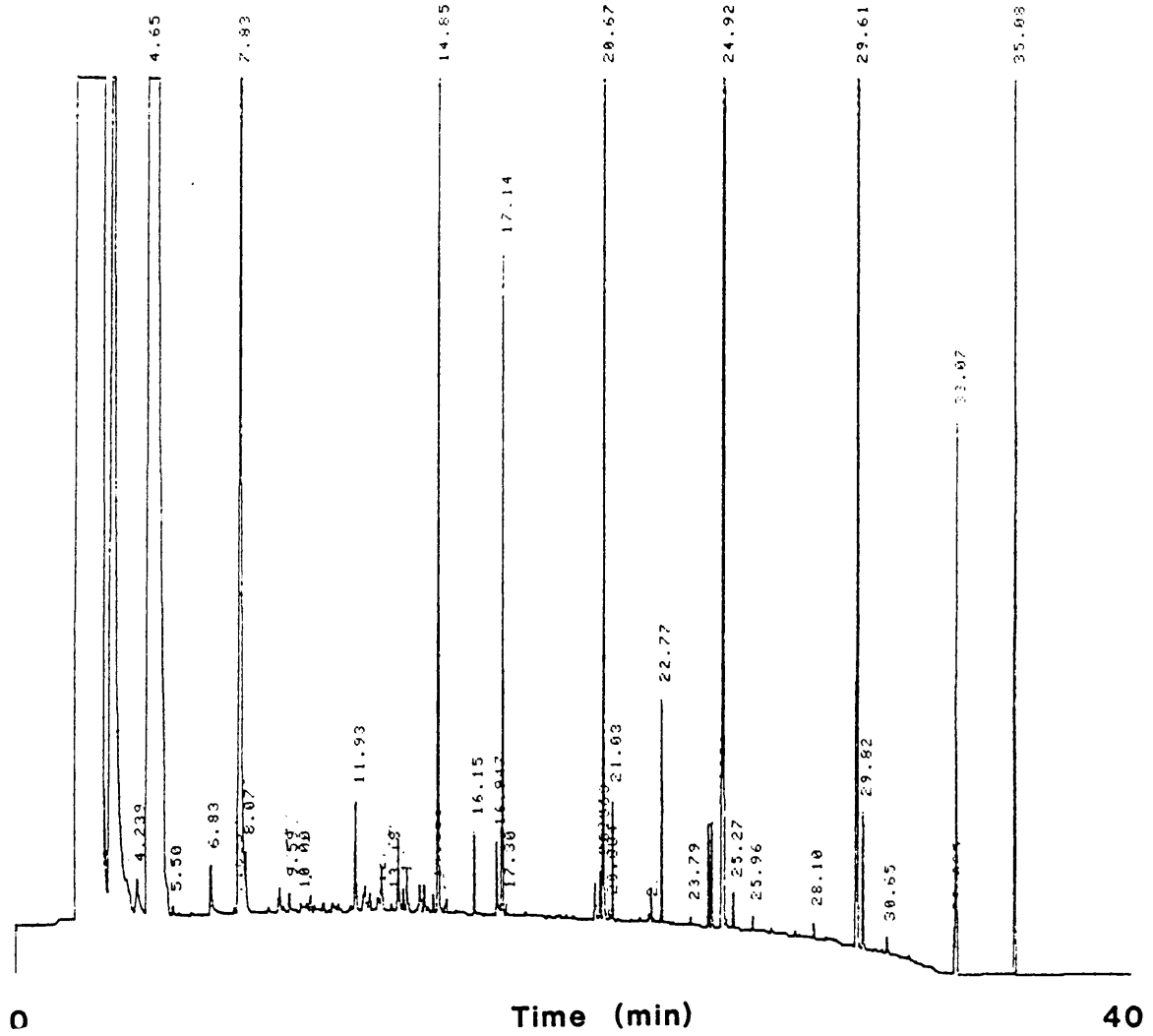




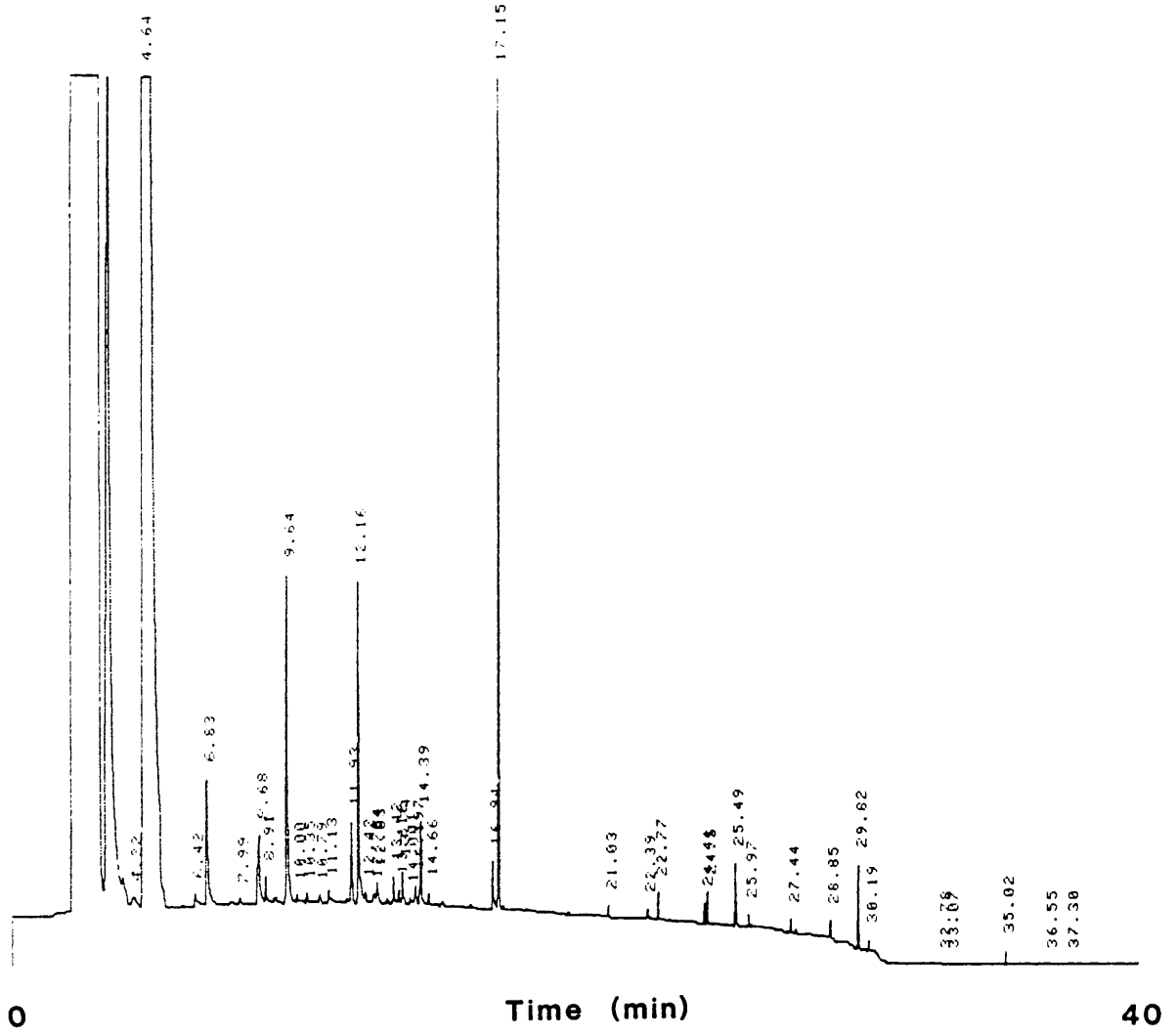
TCLP: Fishersville Base/Neutral



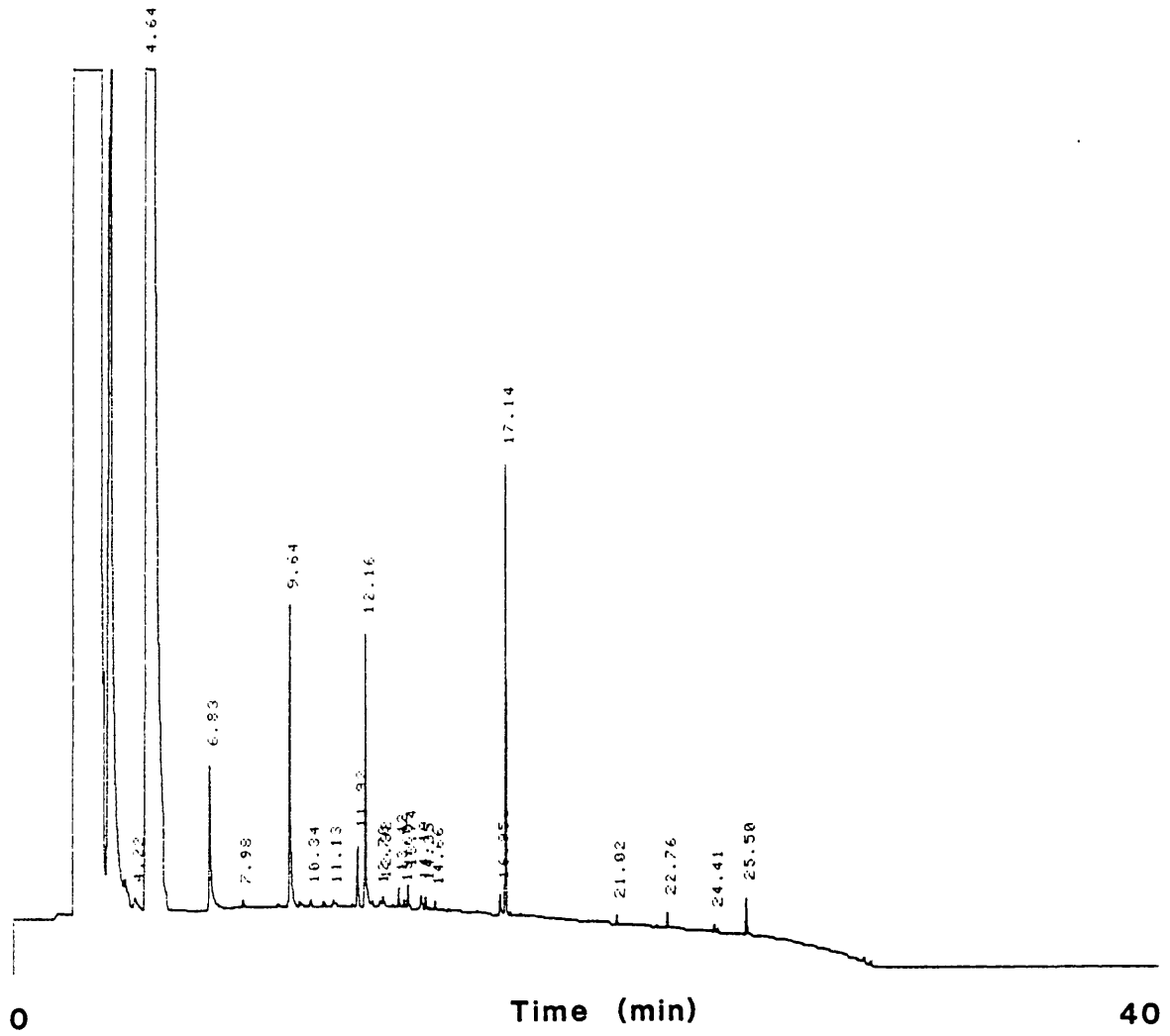
## TCLP: Fishersville Base/Neutral Blank



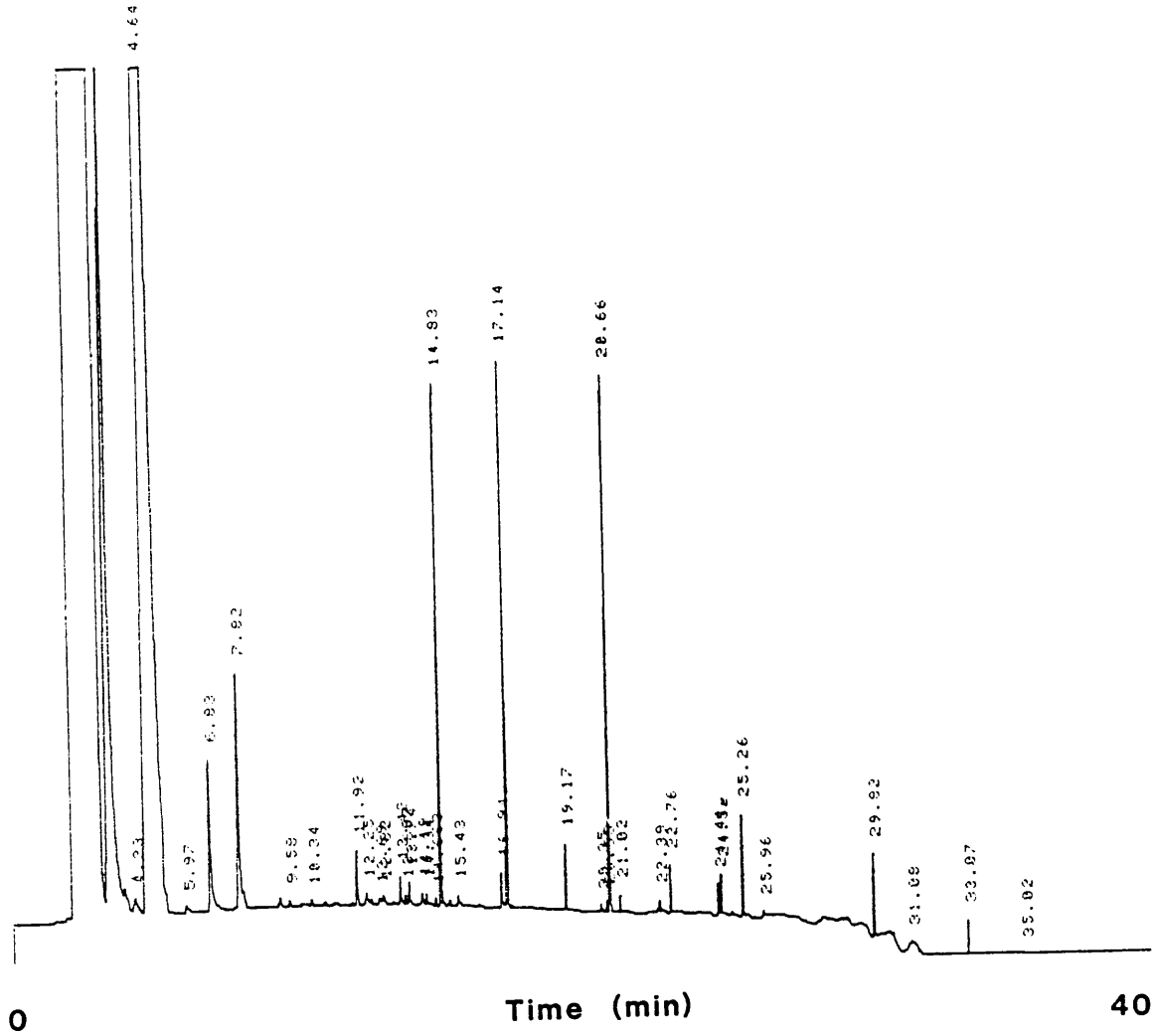
EP: Fishersville Acid

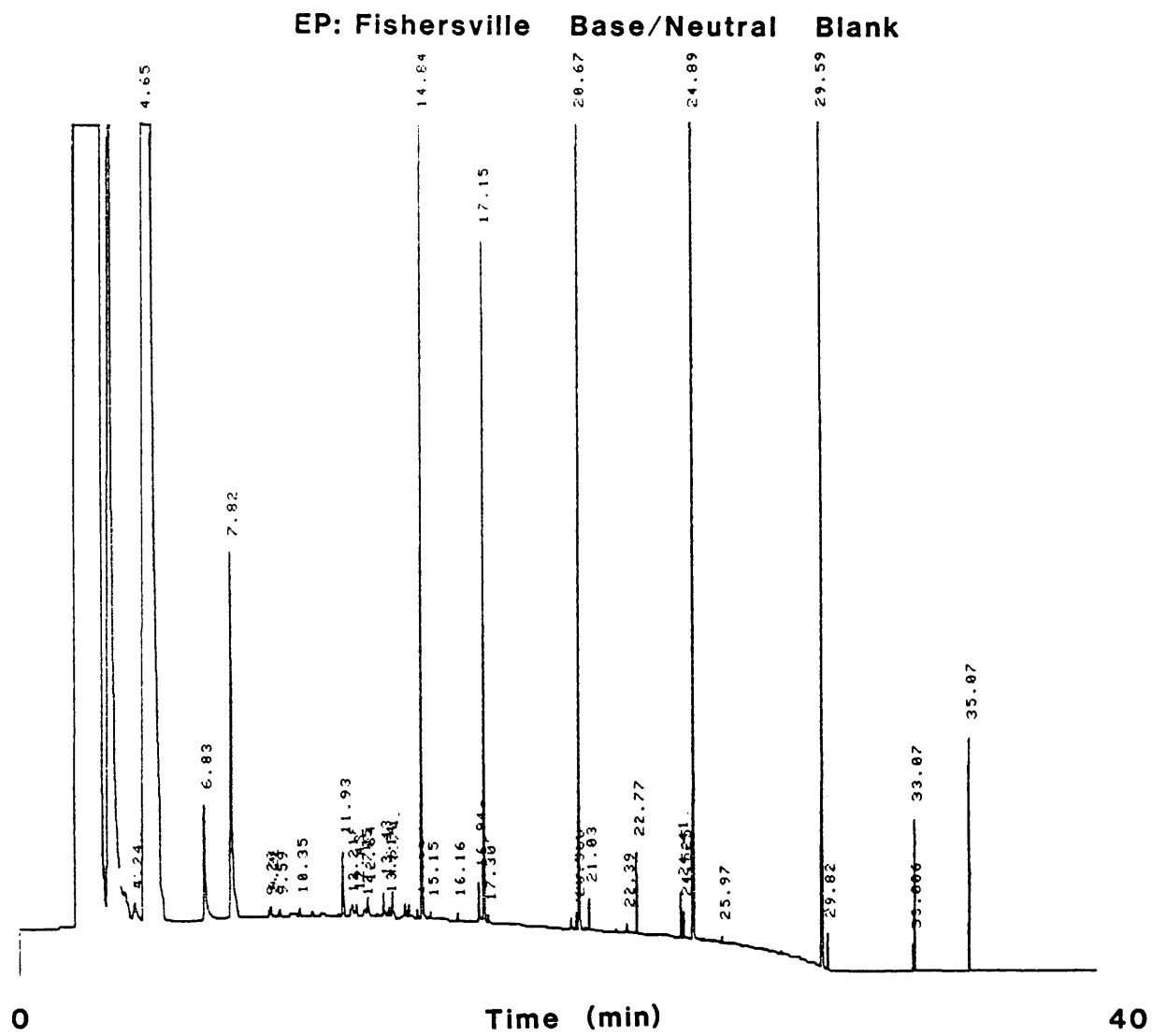


## EP: Fishersville Acid Blank



EP: Fishersville Base/Neutral





## APPENDIX C

### Spectra:

#### Detected Trace Organic Compounds

Dichlorodimethoxybenzene  
Dimethylpentanol  
Tetramethylbutylphenol  
4-Methylphenol

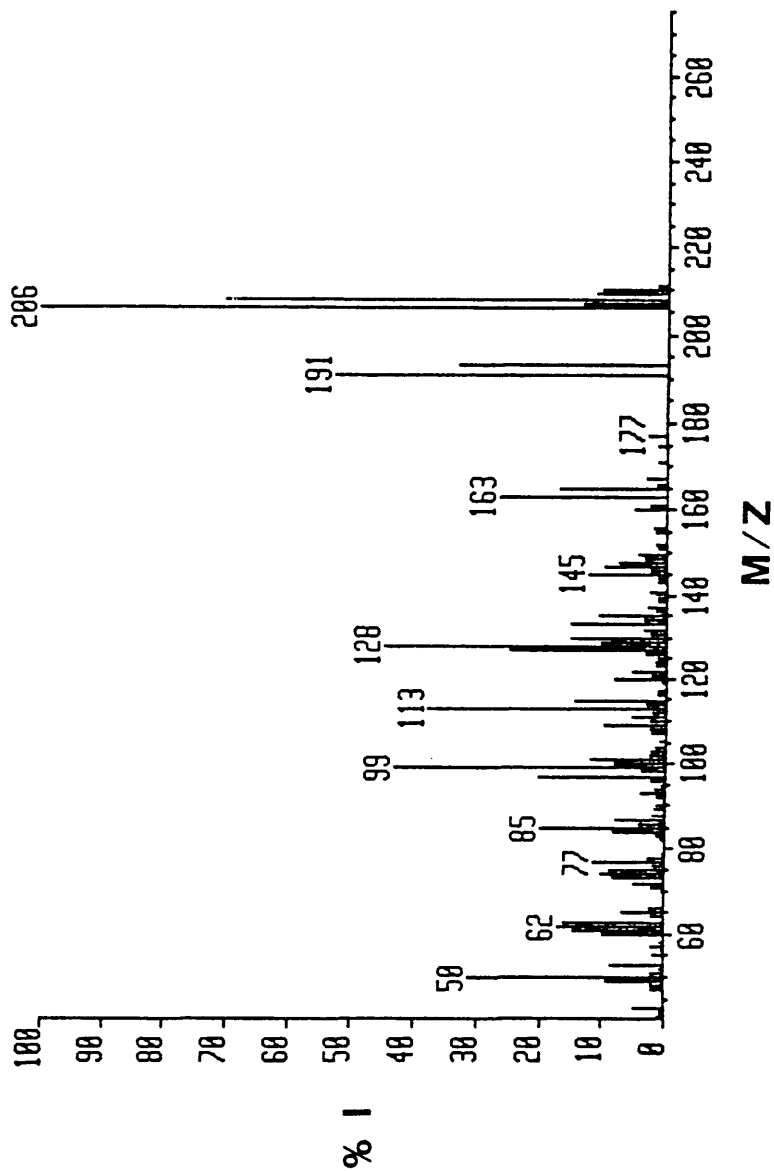
#### Contaminants

Benzaldehyde  
Benzonitrile  
Dibutylphthalate

#### Artifacts

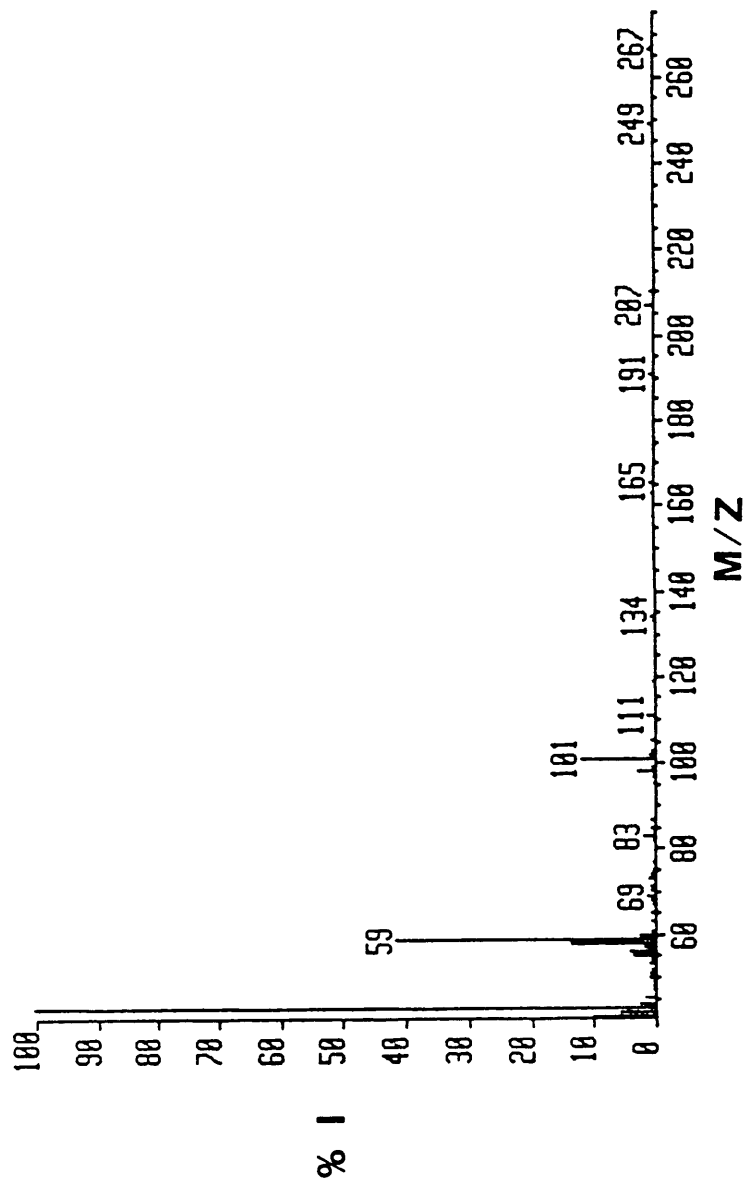
Cyclohexene  
Cyclohexenone  
Chlorocyclohexenol

## DICHLORODIMETHOXYBENZENE

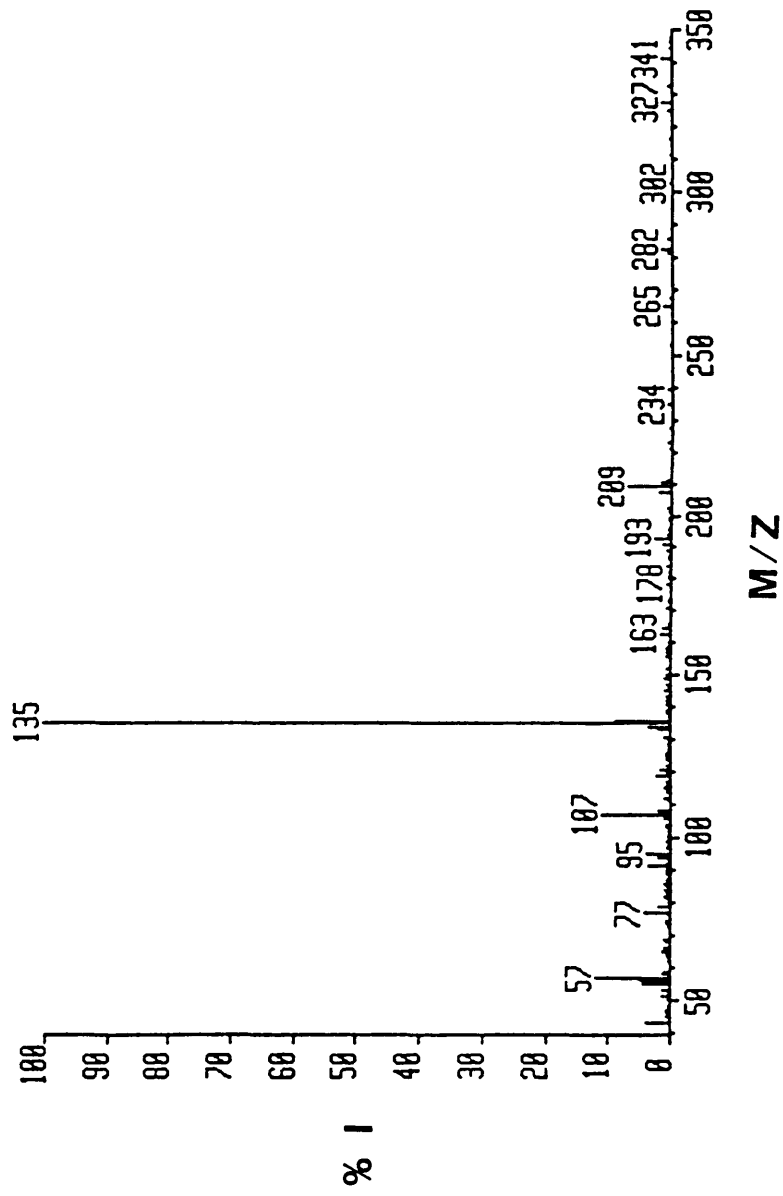




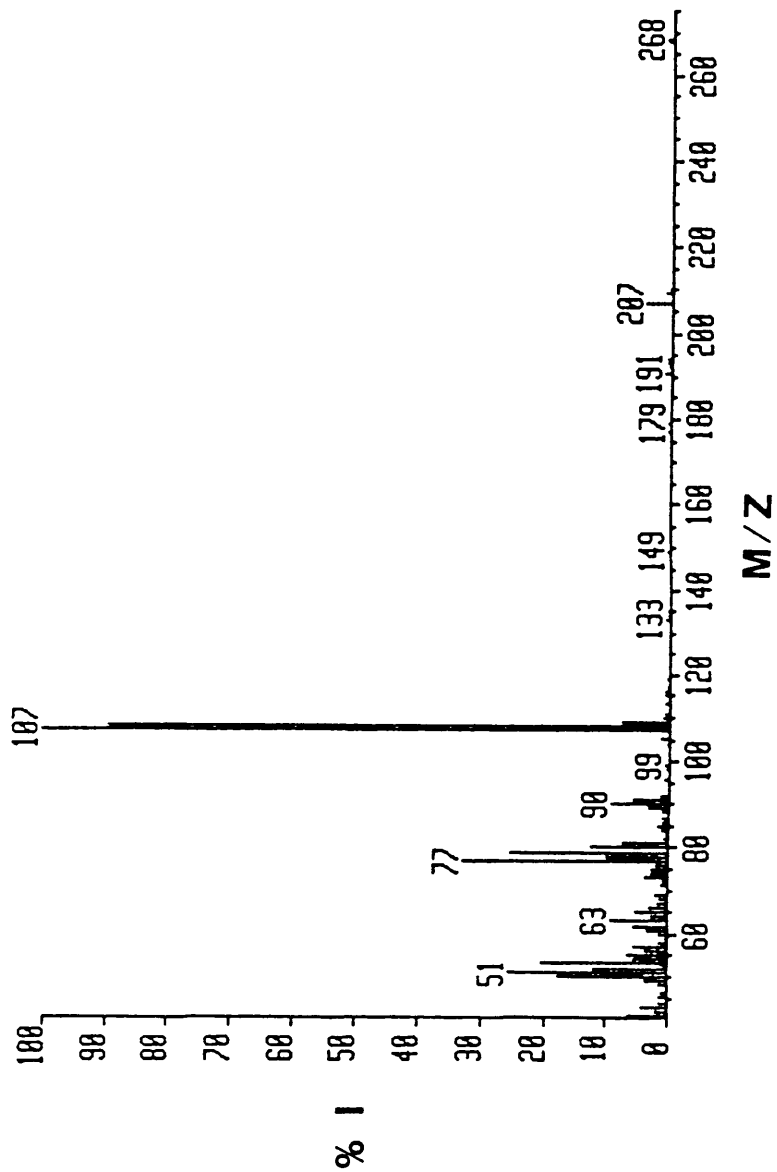
## 2,4-DIMETHYL-2-PENTANOL



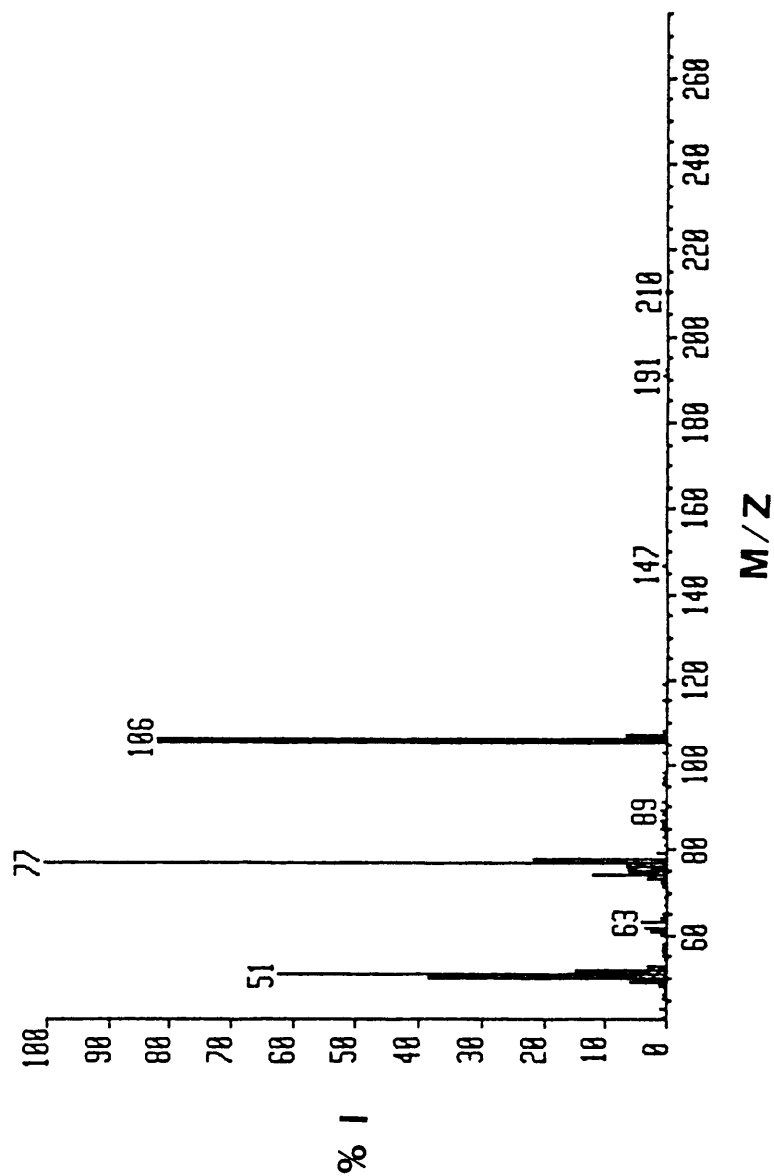
## 4-(2,2,3,3-TETRAMETHYLBUTYL)-PHENOL



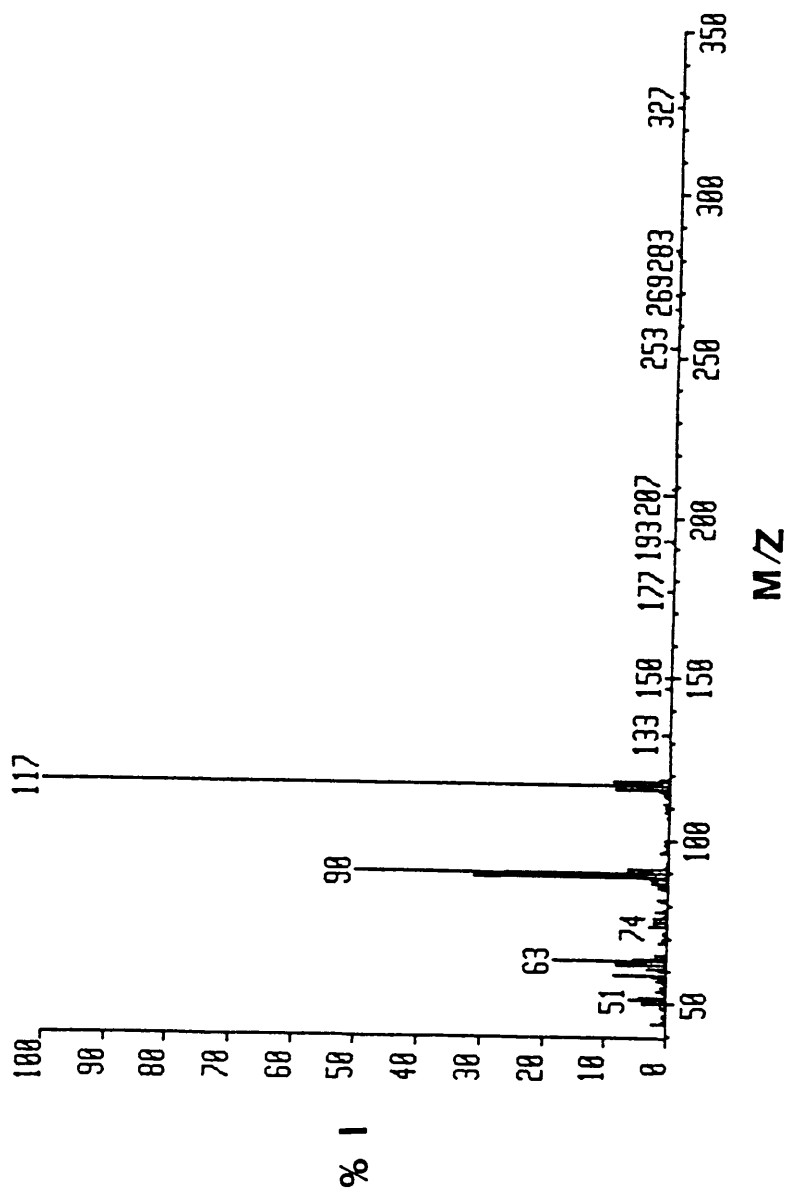
## 4-METHYL PHENOL



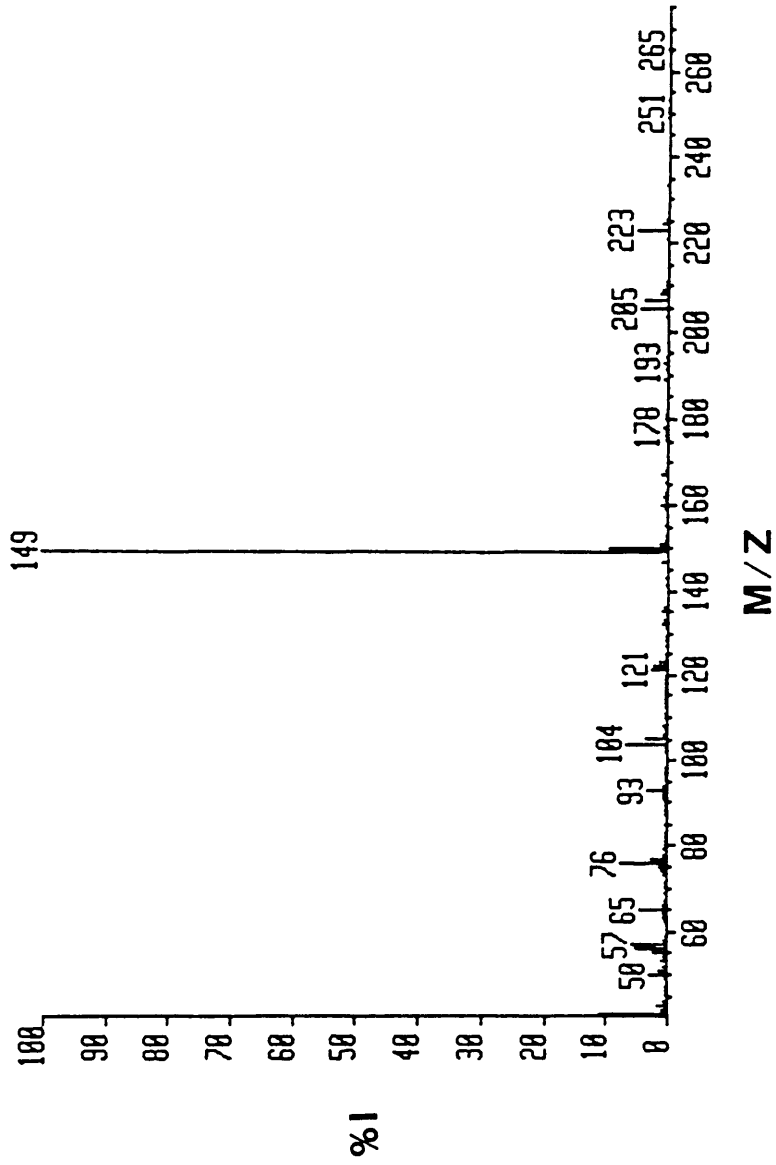
## BENZALDEHYDE



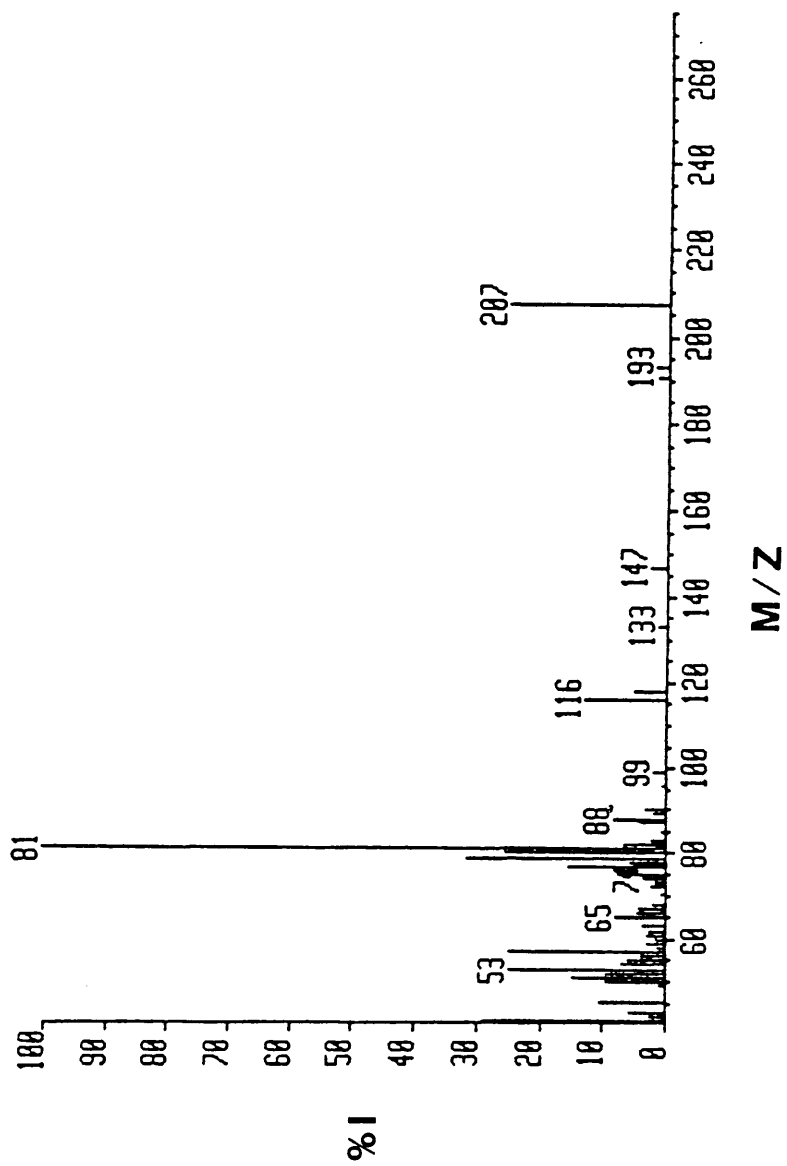
## 2-METHYL BENZONITRILE



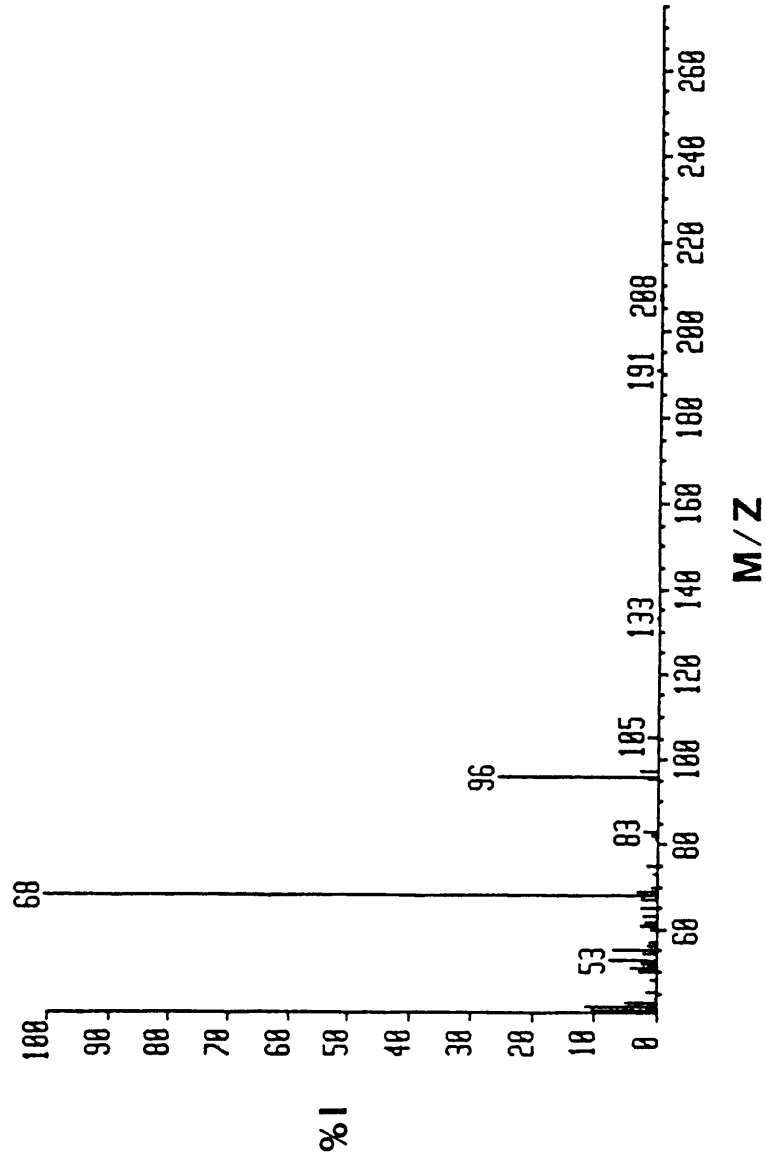
## DIBUTYL PHTHALATE ESTER



## CYCLOHEXENE

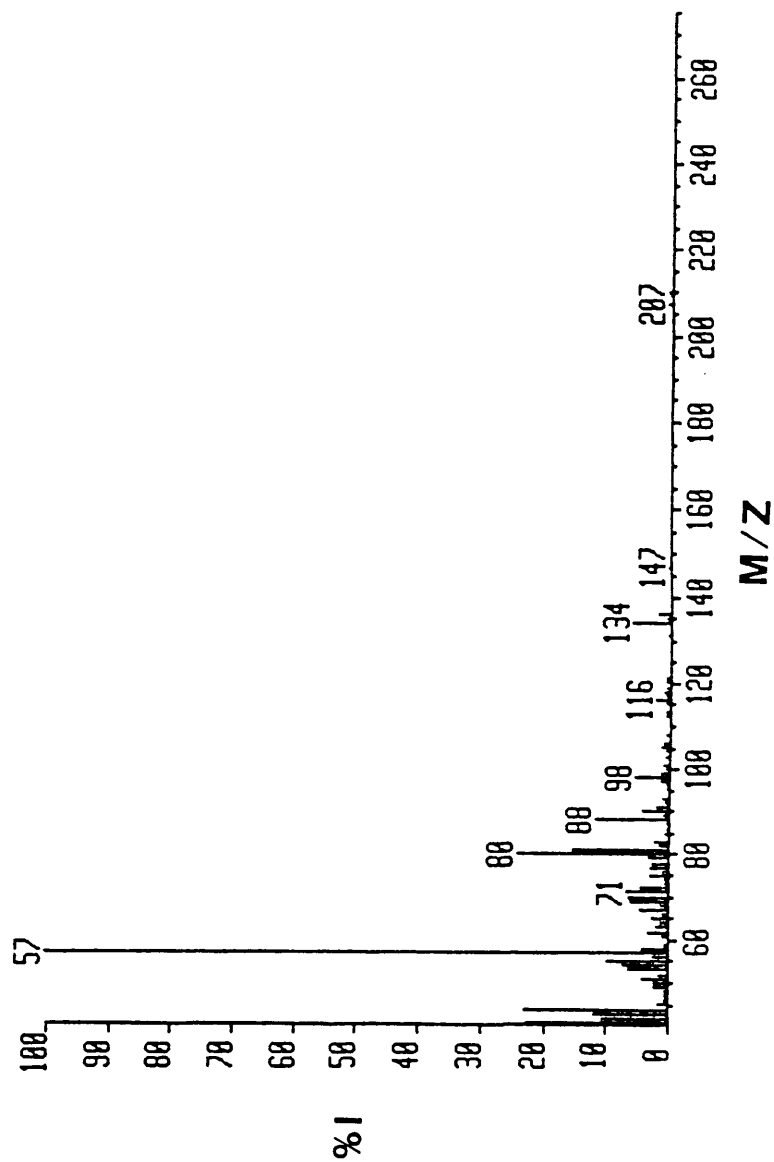


## CYCLOHEXENONE





## CHLOROCYCLOHEXANOL



**APPENDIX D**

**Statistics:  
ANOVA Results  
t-Test Analysis  
Linear Regression**

## ANOVA Results

## SYSTAT PROGRAMMING VARIABLES:

FINREC = Final Percent Recovery

TESTNO = Systat command to delineate a sample from a particular test:  
TCLP and EP triplicate sludge samples.

SITENO and SITEN2 = Systat commands to sort surrogate recovery from the  
four sites. Each site was assigned a number because the program  
needed consecutive ranking numbers

TESTNO\*SITENO and TEST\*SITEN2 = Interaction of test and site on recovery  
of the various sludge surrogates.

## ANOVA RESULTS

## EDB

DEP VAR: FINREC N: 18 MULTIPLE R: .909 SQUARED MULTIPLE R: .827

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
TESTNO	321.359	1	321.359	4.164	0.064
SITEN2	3778.519	2	1889.259	24.479	0.000
TESTNO*					
SITEN2	330.749	2	165.375	2.143	0.160
ERROR	926.137	12	77.178		

## Bromoform

DEP VAR: FINREC N: 12 MULTIPLE R: .638 SQUARED MULTIPLE R: .407

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
TESTNO	399.000	1	399.000	1.133	0.318
SITENO	1499.293	1	1499.293	4.256	0.073
TESTNO*					
SITENO	32.956	1	32.956	0.094	0.768
ERROR	2817.899	8	352.237		

## 1-Chlorooctane

DEP VAR: FINREC N: 12 MULTIPLE R: .504 SQUARED MULTIPLE R: .254

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
TESTNO	0.985	1	0.985	0.139	0.719
SITENO	13.640	1	13.640	1.922	0.203
TESTNO*					
SITENO	4.663	1	4.663	0.657	0.441
ERROR	56.768	8	7.096		

## ANOVA RESULTS

## Fusarex

DEP VAR: FINREC N: 24 MULTIPLE R: .808 SQUARED MULTIPLE R: .652

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
TESTNO	2.941	1	2.941	2.550	0.130
SITENO	13.038	3	4.346	3.768	0.032
TESTNO* SITENO	18.629	3	6.210	5.383	0.009
ERROR	18.456	16	1.154		

---

## Heptachlor

DEP VAR: FINREC N: 18 MULTIPLE R: .698 SQUARED MULTIPLE R: .487

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
TESTNO	0.013	1	0.013	0.357	0.561
SITEN2	0.319	2	0.159	4.524	0.034
TESTNO* SITEN2	0.070	2	0.035	0.996	0.398
ERROR	0.423	12	0.035		

---

## DDT

DEP VAR: FINREC N: 18 MULTIPLE R: .512 SQUARED MULTIPLE R: .262

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
TESTNO	2.700	1	2.700	0.718	0.413
SITEN2	4.177	2	2.088	0.555	0.588
TESTNO* SITEN2	9.136	2	4.568	1.215	0.331
ERROR	45.133	12	3.761		

---

**t-Test Analysis****POOLED t-TEST RESULTS**

Percent Recovery in the blank reagent water to that in the triplicate sludge samples listed by sludge surrogate.

**SYSTAT PROGRAMMING VARIABLE:**

FINREC = Final Percent Recovery

**t-Test Sludge Surrogates TCLP**  
**% Recovery (Blank vs. Sludge Sample)**

THE FOLLOWING RESULTS ARE FOR:  
 COMPOUND\$ = 1-CHLOROOCCTA

INDEPENDENT SAMPLES T-TEST ON FINREC GROUPED BY BLANK

GROUP	N	MEAN	SD
2.000	6	1.117	0.691
1.000	2	1.815	2.155

SEPARATE VARIANCES T = -0.451 DF = 1.1 PROB = .727  
 POOLED VARIANCES T = -0.790 DF = 6 PROB = .459

THE FOLLOWING RESULTS ARE FOR:  
 COMPOUND\$ = BROMOFORM

INDEPENDENT SAMPLES T-TEST ON FINREC GROUPED BY BLANK

GROUP	N	MEAN	SD
2.000	6	33.391	16.087
1.000	2	22.048	10.650

SEPARATE VARIANCES T = 1.135 DF = 2.8 PROB = .345  
 POOLED VARIANCES T = 0.907 DF = 6 PROB = .399

THE FOLLOWING RESULTS ARE FOR:  
 COMPOUND\$ = DDT

INDEPENDENT SAMPLES T-TEST ON FINREC GROUPED BY BLANK

GROUP	N	MEAN	SD
2.000	9	1.049	2.624
1.000	3	5.157	4.276

SEPARATE VARIANCES T = -1.569 DF = 2.5 PROB = .231  
 POOLED VARIANCES T = -2.036 DF = 10 PROB = .069

THE FOLLOWING RESULTS ARE FOR:  
 COMPOUND\$ = EDB

INDEPENDENT SAMPLES T-TEST ON FINREC GROUPED BY BLANK

GROUP	N	MEAN	SD
2.000	9	18.741	21.453
1.000	3	26.323	22.468

SEPARATE VARIANCES T = -0.512 DF = 3.3 PROB = .641  
 POOLED VARIANCES T = -0.525 DF = 10 PROB = .611

**TCLP:**

THE FOLLOWING RESULTS ARE FOR:  
 COMPOUNDS = FUSAREX

INDEPENDENT SAMPLES T-TEST ON FINREC GROUPED BY BLANK

GROUP	N	MEAN	SD
2.000	12	1.979	1.874
1.000	4	17.635	10.662

SEPARATE VARIANCES T = -2.922 DF = 3.1 PROB = .060  
 POOLED VARIANCES T = -5.207 DF = 14 PROB = .000

THE FOLLOWING RESULTS ARE FOR:  
 COMPOUNDS = HEPTACHLOR

INDEPENDENT SAMPLES T-TEST ON FINREC GROUPED BY BLANK

GROUP	N	MEAN	SD
2.000	9	0.084	0.121
1.000	3	7.833	8.979

SEPARATE VARIANCES T = -1.495 DF = 2.0 PROB = .274  
 POOLED VARIANCES T = -2.894 DF = 10 PROB = .016



**t-Test Sludge Surrogates EP**  
**% Recovery (Blank vs. Sludge Sample)**

THE FOLLOWING RESULTS ARE FOR:  
 COMPOUND\$ = DDT

INDEPENDENT SAMPLES T-TEST ON FINREC GROUPED BY BLANK

GROUP	N	MEAN	SD
2.000	9	0.274	0.649
1.000	3	19.577	27.757

SEPARATE VARIANCES T = -1.204 DF = 2.0 PROB = .352  
 POOLED VARIANCES T = -2.330 DF = 10 PROB = .042

THE FOLLOWING RESULTS ARE FOR:  
 COMPOUND\$ = EDB

INDEPENDENT SAMPLES T-TEST ON FINREC GROUPED BY BLANK

GROUP	N	MEAN	SD
2.000	9	10.290	13.007
1.000	3	21.007	13.233

SEPARATE VARIANCES T = -1.220 DF = 3.4 PROB = .300  
 POOLED VARIANCES T = -1.232 DF = 10 PROB = .246

THE FOLLOWING RESULTS ARE FOR:  
 COMPOUND\$ = FUSAREX

INDEPENDENT SAMPLES T-TEST ON FINREC GROUPED BY BLANK

GROUP	N	MEAN	SD
2.000	12	1.279	1.023
1.000	4	27.387	20.025

SEPARATE VARIANCES T = -2.606 DF = 3.0 PROB = .080  
 POOLED VARIANCES T = -4.855 DF = 14 PROB = .000

THE FOLLOWING RESULTS ARE FOR:  
 COMPOUND\$ = HEPTACHLOR

INDEPENDENT SAMPLES T-TEST ON FINREC GROUPED BY BLANK

GROUP	N	MEAN	SD
2.000	9	0.137	0.295
1.000	3	22.592	23.910

SEPARATE VARIANCES T = -1.627 DF = 2.0 PROB = .245  
 POOLED VARIANCES T = -3.149 DF = 10 PROB = .010

EP:

THE FOLLOWING RESULTS ARE FOR:  
 COMPOUNDS = 1-CHLOROCTA

INDEPENDENT SAMPLES T-TEST ON FINREC GROUPED BY BLANK

GROUP	N	MEAN	SD
2.000	6	1.689	3.813
1.000	2	13.482	19.067

SEPARATE VARIANCES T = -0.869 DF = 1.0 PROB = .542  
 POOLED VARIANCES T = -1.694 DF = 6 PROB = .141

THE FOLLOWING RESULTS ARE FOR:  
 COMPOUNDS = BROMOFORM

INDEPENDENT SAMPLES T-TEST ON FINREC GROUPED BY BLANK

GROUP	N	MEAN	SD
2.000	6	21.858	24.723
1.000	2	10.902	4.635

SEPARATE VARIANCES T = 1.032 DF = 5.8 PROB = .343  
 POOLED VARIANCES T = 0.592 DF = 6 PROB = .575

## Linear Regression

### $r^2$ VALUES

Proportion of the variability explained by certain physical/chemical parameters listed by test, EP or TCLP.

### SYSTAT PROGRAMMING VARIABLES:

FINREC = Final Percent Recovery

SQUARED MULTIPLE R =  $r^2$  values

N = number of observations

CONSTANT = the y-axis intercept ,B, in the straight line equation

$$Y = MX + B$$

LOGVP = log Vapor Pressure

LOGSOLU = log Solubility

LOGHENRY = log Henry's Law Constant

LOGKOW = log  $K_{ow}$

LOGKOC = log  $K_{oc}$

BP = Boiling Point, nine cases missing because boiling point data for heptachlor was not available

## log Vapor Pressure

THE FOLLOWING RESULTS ARE FOR:  
TEST\$ = EP

DEP VAR: FINREC N: 51 MULTIPLE R: .434 SQUARED MULTIPLE R: .189  
ADJUSTED SQUARED MULTIPLE R: .172 STANDARD ERROR OF ESTIMATE: 10.843

VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	9.252	1.980	0.000		4.672	0.000
LOGVP	1.904	0.564	0.434	.100E+01	3.376	0.001

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	1340.017	1	1340.017	11.398	0.001
RESIDUAL	5760.648	49	117.564		

THE FOLLOWING RESULTS ARE FOR:  
TEST\$ = TCLP

DEP VAR: FINREC N: 51 MULTIPLE R: .537 SQUARED MULTIPLE R: .289  
ADJUSTED SQUARED MULTIPLE R: .274 STANDARD ERROR OF ESTIMATE: 13.038

VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	14.764	2.372	0.000		6.225	0.000
LOGVP	3.015	0.676	0.537	.100E+01	4.462	0.000

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	3384.101	1	3384.101	19.908	0.000
RESIDUAL	8329.530	49	169.990		

## log Solubility

THE FOLLOWING RESULTS ARE FOR:  
TESTS = EP

DEP VAR: FINREC N: 51 MULTIPLE R: .438 SQUARED MULTIPLE R: .192  
ADJUSTED SQUARED MULTIPLE R: .175 STANDARD ERROR OF ESTIMATE: 10.822

VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	4.014	1.541	0.000	.	2.606	0.012
LOGSOLU	2.984	0.875	0.438	.100E+01	3.410	0.001

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	1362.069	1	1362.069	11.630	0.001
RESIDUAL	5738.597	49	117.114		

THE FOLLOWING RESULTS ARE FOR:  
TESTS = TCLP

DEP VAR: FINREC N: 51 MULTIPLE R: .518 SQUARED MULTIPLE R: .268  
ADJUSTED SQUARED MULTIPLE R: .253 STANDARD ERROR OF ESTIMATE: 13.225

VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	6.635	1.880	0.000	.	3.529	0.001
LOGSOLU	4.534	1.069	0.518	.100E+01	4.239	0.000

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	3143.303	1	3143.303	17.972	0.000
RESIDUAL	8570.329	49	174.905		

## log Henry's Law Constant

THE FOLLOWING RESULTS ARE FOR:  
TEST\$ = EP

DEP VAR: FINREC N: 51 MULTIPLE R: .243 SQUARED MULTIPLE R: .059  
ADJUSTED SQUARED MULTIPLE R: .040 STANDARD ERROR OF ESTIMATE: 11.677

VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	10.470	3.542	0.000	.	2.956	0.005
LOGHENRY	1.810	1.032	0.243	.100E+01	1.754	0.086

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	419.361	1	419.361	3.076	0.086
RESIDUAL	6681.305	49	136.353		

THE FOLLOWING RESULTS ARE FOR:  
TEST\$ = TCLP

DEP VAR: FINREC N: 51 MULTIPLE R: .316 SQUARED MULTIPLE R: .100  
ADJUSTED SQUARED MULTIPLE R: .081 STANDARD ERROR OF ESTIMATE: 14.671

VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	16.796	4.296	0.000	.	3.910	0.000
LOGHENRY	2.926	1.257	0.316	.100E+01	2.329	0.024

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	1167.180	1	1167.180	5.423	0.024
RESIDUAL	10546.451	49	215.234		

## log Kow

THE FOLLOWING RESULTS ARE FOR:  
TESTS - EP

DEP VAR: FINREC N: 51 MULTIPLE R: .359 SQUARED MULTIPLE R: .129  
ADJUSTED SQUARED MULTIPLE R: .111 STANDARD ERROR OF ESTIMATE: 11.235

VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	19.596	5.658	0.000	.	3.464	0.001
LOGKOW	-3.633	1.349	-0.359	.100E+01	-2.693	0.010

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	915.540	1	915.540	7.253	0.010
RESIDUAL	6185.125	49	126.227		

THE FOLLOWING RESULTS ARE FOR:  
TESTS - TCLP

DEP VAR: FINREC N: 51 MULTIPLE R: .346 SQUARED MULTIPLE R: .120  
ADJUSTED SQUARED MULTIPLE R: .102 STANDARD ERROR OF ESTIMATE: 14.508

VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	24.036	6.537	0.000	.	3.677	0.001
LOGKOW	-4.052	1.571	-0.346	.100E+01	-2.579	0.013

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	1400.281	1	1400.281	6.653	0.013
RESIDUAL	10313.351	49	210.477		

## log Koc

THE FOLLOWING RESULTS ARE FOR:  
TEST\$ = EP

DEP VAR: FINREC N: 51 MULTIPLE R: .438 SQUARED MULTIPLE R: .192  
ADJUSTED SQUARED MULTIPLE R: .175 STANDARD ERROR OF ESTIMATE: 10.821

VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	23.763	5.717	0.000	.	4.157	0.000
LOGKOC	-5.426	1.591	-0.438	.100E+01	-3.411	0.001

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	1362.566	1	1362.566	11.636	0.001
RESIDUAL	5738.100	49	117.104		

THE FOLLOWING RESULTS ARE FOR:  
TEST\$ = TCLP

DEP VAR: FINREC N: 51 MULTIPLE R: .427 SQUARED MULTIPLE R: .183  
ADJUSTED SQUARED MULTIPLE R: .166 STANDARD ERROR OF ESTIMATE: 13.979

VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	28.657	6.541	0.000	.	4.381	0.000
LOGKOC	-6.070	1.835	-0.427	.100E+01	-3.308	0.002

## ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	2138.255	1	2138.255	10.942	0.002
RESIDUAL	9575.377	49	195.416		



## Boiling Point

THE FOLLOWING RESULTS ARE FOR:  
 TESTS = EP  
 9 CASES DELETED DUE TO MISSING DATA.

DEP VAR: FINREC N: 42 MULTIPLE R: .336 SQUARED MULTIPLE R: .113  
 ADJUSTED SQUARED MULTIPLE R: .090 STANDARD ERROR OF ESTIMATE: 12.323

VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	18.818	6.000	0.000	.	3.136	0.003
BP	-0.063	0.028	-0.336	.100E+01	-2.253	0.030

### ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	771.187	1	771.187	5.078	0.030
RESIDUAL	6074.569	40	151.864		

THE FOLLOWING RESULTS ARE FOR:  
 TESTS = TCLP  
 9 CASES DELETED DUE TO MISSING DATA.

DEP VAR: FINREC N: 42 MULTIPLE R: .368 SQUARED MULTIPLE R: .135  
 ADJUSTED SQUARED MULTIPLE R: .114 STANDARD ERROR OF ESTIMATE: 15.438

VARIABLE	COEFFICIENT	STD ERROR	STD COEF	TOLERANCE	T	P(2 TAIL)
CONSTANT	25.603	6.782	0.000	.	3.775	0.001
BP	-0.080	0.032	-0.368	.100E+01	-2.503	0.017

### ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
REGRESSION	1493.184	1	1493.184	6.265	0.017
RESIDUAL	9533.718	40	238.343		

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the scanned document**