

TOXICITY CHARACTERISTIC LEACHING PROCEDURE ANALYSIS OF  
DYE CONTAINING SLUDGES

by

John D. Nelson

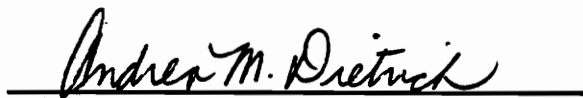
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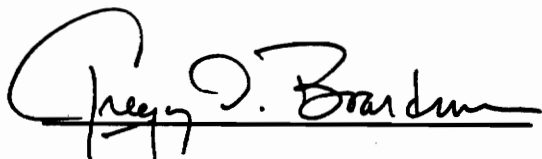
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TOXICITY CHARACTERISTIC LEACHING PROCEDURE ANALYSIS OF DYE  
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John D. Nelson

Committee Chair : Dr. Andrea M. Dietrich

Environmental Engineering

(ABSTRACT)

The ability to leach dyestuffs contained in municipal sludge using the Toxicity Characteristic Leaching Procedure (TCLP) was investigated. In addition to the dyestuffs, metals and other organic compounds which also leached were identified.

Only small amounts of color were detected in the TCLP extracts; the mean ADMI color values for undigested and aerobically digested sludges were 240 and 156 ADMI color units respectively. Concentrations of individual dyes that may have leached into the TCLP extracts were below detection limits. The reactive vinyl sulfone aniline moiety, which is released as a reduction product from the Remazol dyes used in the cellulosic textile dyeing industry, was found in the leachate from the sludge not treated by extended aerobic digestion. In the leachate from the sludge treated by extended aerobic digestion the reactive vinyl sulfone aniline reduction product was not found, suggesting that

this compound was destroyed or rendered immobile by aerobic digestion. Metals leached from the sludge in trace amounts from 0.05  $\mu\text{g/L}$  up to 1 mg/L. Several organic compounds detected in influent wastewater and in leachate from undigested sludge were not found in the leachate from digested sludge.

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## 1.0 INTRODUCTION

The use of reactive azo dyes are increasing due to the consumer demand for higher quality textile products (Zollinger, 1991). Reactive azo dyes produce bright colors on cotton textiles that are resistant to fading through wear, washing, and weathering. The very properties that make these dyes so popular among consumers are cause for concern by the textile manufacturer when disposing of the spent dyebath effluent.

Textile dyebath effluents treated by Publicly Owned Treatment Works (POTWs) are regulated by color at the end of the plant where the effluent is discharged into the receiving stream. However, the POTW sludge is not currently regulated. Since 43.5% of all POTWs, dispose of their sludge in municipal landfills, it would follow that the same percentage of POTWs treating textile effluents would dispose of their sludge in a similar manner (EPA, 1989). Land disposal of municipal sludge will soon become a matter of regulation under the proposed section 503 rules governing the standards for the disposal of sewage sludge.

Under the proposed rules, if a municipal sludge exhibits toxicity characteristics as defined by the Toxicity Characteristic Leaching Procedure (TCLP), then it will be

considered hazardous and be subject to disposal under the confines of the Resource Conservation and Recovery Act (RCRA) (EPA, 1989). Since some of the dyes used by the textile industry are metal complexed and some of the dye reduction byproducts are priority pollutants this rule could produce increased costs for the disposal of textile wastewater effluents for the dye industry.

The TCLP was developed by the U.S. EPA to evaluate the mobility of contaminants from a solid waste matrix if it were codisposed in a municipal landfill. The test simulates a landfill leachate that would be produced in a municipal landfill if the cap were to fail and allow the introduction of moisture. The procedure is regulated under the toxicity characteristic rule which was finalized after public comment in March 1990.

In this research dye containing sludges were analyzed using the Toxicity Characteristic Leaching Procedure. The objectives of this study were threefold: first, to determine if any dyestuffs in the sludges were released into the TCLP leachate; second, attempt to identify any organic compounds in the leachate; third, to determine if any metals in the sludges were released into the leachate. The sludge from

the Martinsville, Virginia POTW was analyzed in this study. A flow diagram of the plant is shown in Figure 1.

The Martinsville POTW treats on the average of 6.1 million gallons per day (MGD) of municipal and industrial sewage. Approximately 70-75% of the flow is from industrial inputs with 50% of that from three industrial textile dyeing operations in the area. The largest of the dyeing operations uses reactive azo dyes almost exclusively. The sludge from the treatment plant is digested aerobically, dewatered by a belt-filter press, and disposed in the local municipal landfill.

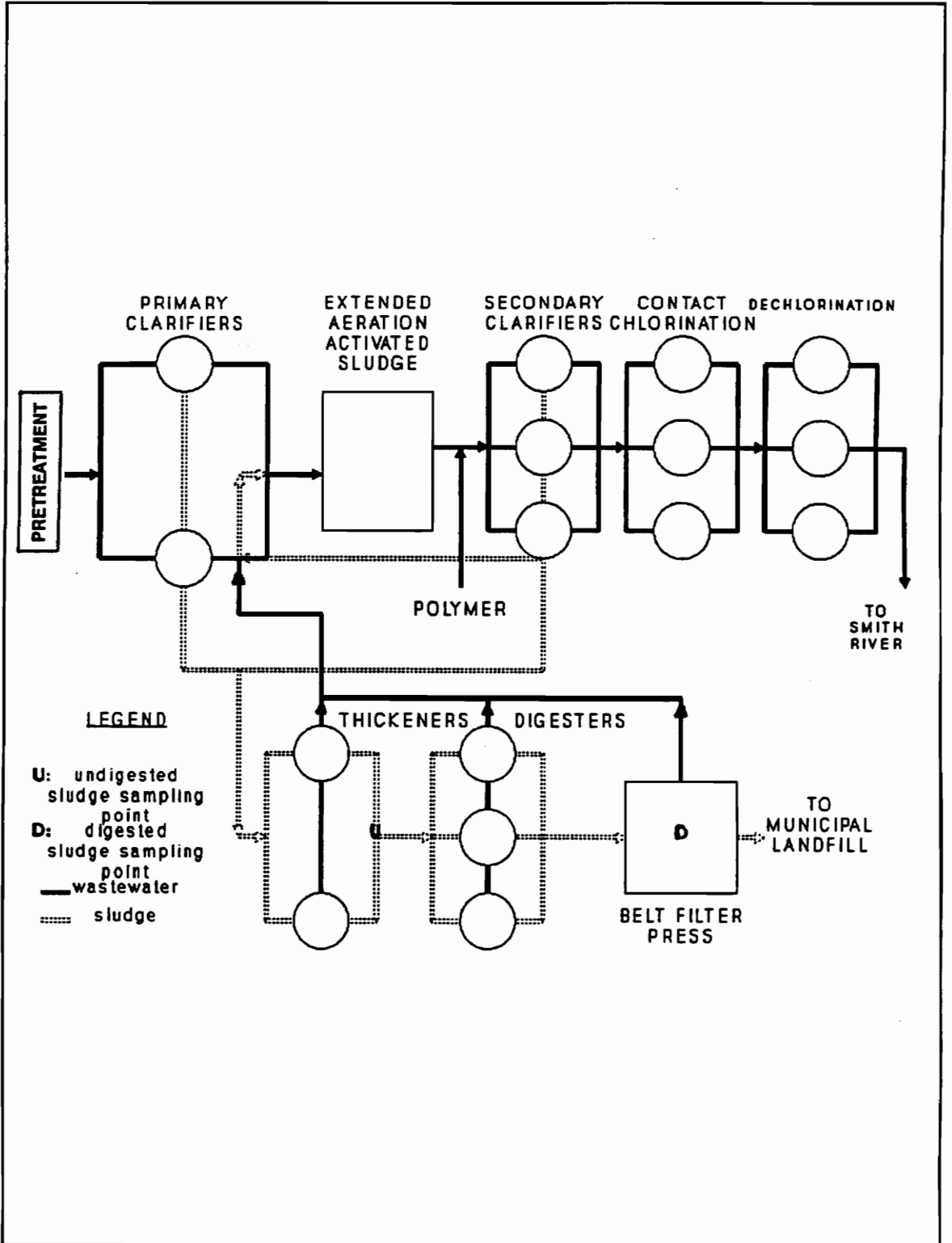


Figure 1. Martinsville, VA POTW Flow Diagram

## 2.0 LITERATURE REVIEW

### 2.1 Chemistry of Azo Dyes

Dyes in general may be classified on the basis of structure or application method. Azo dyes are a class of dyes based on the structure of the compounds containing a nitrogen double bond (Zollinger, 1991). These azo groups may link benzene rings, naphthalene rings, or various other aromatic heterocycles (Zollinger, 1991). Azo dyes are the largest structural class of dyes marketed in the world today (Zollinger, 1991). The large amount of azo dyes produced has led to increased interest in their fate and effect upon the environment.

Azo dyes are found in many of the classes based on application method. The classes that azo dyes can be found in are: acid, vat, direct, azoic, metal complex, disperse, and reactive dyes (Abraham, 1977). The two classes most important to this research are the metal complex azo dyes and the reactive azo dyes. These two classes will be discussed further. The reader is directed to references listed earlier for information on other classes of azo dyes.

### 2.1.1 Properties and Synthesis of Azo Dyes

As discussed previously, azo dyes have a nitrogen double bond linking various aromatic heterocycles. It is this azo structure,  $-N=N-$ , that acts as the chromophore in the dye molecule (Abraham, 1977). There can be more than one azo linkage in the dye molecule rendering the terms dis or tris, for two or three azo linkages (Zollinger, 1991). Normally substituent groups are attached to the aromatic or nitrogen in the dye molecule. These substituent groups could be  $-OH$ ,  $-NH_2$ , or  $-Cl$ . The location and type of substituent groups effect the various properties of the dye such as color or fastness (Zollinger, 1991).

Azo dyes are synthesized by a two step process of diazotization and then azo coupling (Zollinger, 1991). In the first step, diazotization, an aromatic or heteroaromatic primary amine is converted into the diazonium ion by the action of nitrous acid in an aqueous acid medium (Abraham, 1977). The diazonium ion produced by the first step is a relatively weak electrophile (Zollinger, 1991). The second step, azo coupling, occurs when the diazonium ion is coupled with a nucleophilic compound (Zollinger, 1991). The nucleophilic compounds are aromatics with electron donors such as  $OH$  or  $NH_2$ . There are several other methods of azo dye synthesis, however, none are industrially significant

(Zollinger, 1991).

### 2.1.2 Properties and Uses of Reactive Azo Dyes

Reactive azo dyes constitute a large portion of all reactive dyes on the market today (Zollinger, 1991). In the dyeing of cellulosic fibers the growth rate of consumption of reactive dyes is four times the rate for other cellulosic fiber dyes (Renfrew and Taylor, 1990). This makes the study of effects of reactive azo dyes in the environment all the more important.

According to Zollinger, "Reactive dyes are colored compounds which contain one or two groups capable of forming covalent bonds between a carbon or phosphorus atom of the dye ion or molecule and an oxygen, nitrogen or sulfur atom of a hydroxy, an amino or a mercapto group, respectively, of the substrate" (Zollinger, 1991). This means that a covalent bond is normally formed by four different types of reactions depending on the composition of the dye molecule. These reactions are nucleophilic substitution, nucleophilic addition, several addition and elimination steps with the nucleophilic group of fiber, and ester formation of a phosphonic acid group (Zollinger, 1991). Of the four reaction mechanisms only the first two are industrially significant in the textile industry today (Zollinger, 1991).



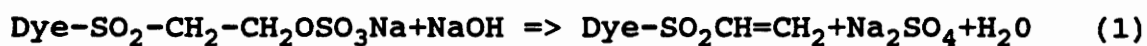
In order for the covalent bond to form between the reactive dye molecule and the fiber, the fiber must have suitable groups which can be substituted. These groups are normally -OH, -SH, and -NH<sub>2</sub> which are found primarily in cellulosic and protein fibers (Hildebrand, 1972). Once the covalent bond is formed between the dye and the fiber it is very stable. This strong bond between the fiber and the dye molecule gives reactive dyes their desirable characteristics of high wet fastness and bright saturated colors (Shore, 1986).

While there are several advantages to dyeing with reactive dyes there are also some definite disadvantages. First, the reaction of the dye with water competes with the reaction of the dye with the fiber. This is called hydrolysis. The hydrolyzed dye cannot react with the textile substrate and must be removed from the textile by washing (Zollinger, 1991). Second, the affinity of reactive dyes must be matched to the conditions of application. If affinity is too high then the uniform penetration of the fiber and washing of the hydrolyzed dye will be troublesome. If affinity is too low then a lower rate of fixation will be achieved (Zollinger, 1991). Third, the wet fastness relies on the stability of the dye-fiber bond. The bonds formed between the dye and the fiber are susceptible to an ensuing slower hydrolysis reaction under alkaline or acidic

conditions. This hydrolysis reaction will affect the fixation since the previous bonds formed can be hydrolyzed. For a high degree of fixation these competing hydrolysis reactions must be minimized (Zollinger, 1991).

### 2.1.3 Remazol Dye Characteristics and Uses

The Remazol dyes are a group of reactive dyes that have a vinyl sulfone reactive group. The dye gives a vinyl group when placed in solution with a base (Abraham, 1977):

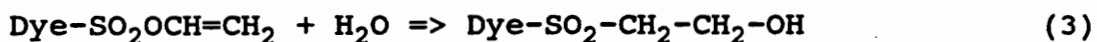


The reactive form of the dye then reacts to form the covalent bond with the cellulose through the reaction mechanism of a carbonium ion formation. This formation is assisted by the taking of an electron by the vinyl sulfone group which then reacts with the anionic center in the cellulose fiber; this reaction is a nucleophilic addition (Abraham, 1977):



The competing reaction, as mentioned previously, is hydrolysis. This reaction occurs at elevated temperature

between the hydroxide ion of water in the dye bath and the reactive group of the vinyl sulfone dye (Flege, 1970):



Under optimal conditions the degree of fixation ranges between 75 and 80% (Weber *et al.*, 1990). This means that approximately 20 to 25% of the dye reaches the dye bath effluent. A large portion of the dye will be the hydrolyzed form. A small portion however may be the reactive form of the vinyl sulfone. Vinyl sulfones, as mentioned before, are electrophilic compounds and as such may be toxic in the aqueous environment (Weber *et al.*, 1990).

#### 2.1.4 Dye Components of Navy 106

The three dye components of Navy 106 dye are reactive remazol dyes. These are; Remazol Black B, Remazol Red RB, and Remazol Golden Yellow 3RA. These dyes are also known as Color Index (C.I.) Reactive Black 5, C.I. Reactive Red 198, C.I. Reactive Orange 16.

Remazol Black B was one of the first generation of reactive dyes. It is produced by several manufacturers since its structure is no longer proprietary. The textile mill at Martinsville, VA, uses this dye more often than

other dyes (Loyd, 1992). This dye was the first commercial dye with two reactive groups. These were probably added to increase the fixation of the dye to cellulosic fibers (Zollinger, 1991). The structure of the dye is shown in Figure 2A. It contains two azo groups, a central H-acid coupling group, and two diazo groups with a vinyl sulfone reactive group attached to each.

Remazol Red RB is a proprietary dye; however, a postulated structure is depicted in Figure 2B (Reife, 1992). The proposed dye structure is monazo, has a central H-acid coupling group, one vinyl sulfone group, and one reactive triazine group. The vinyl sulfone group is attached to the diazo group.

Remazol Golden Yellow 3RA has a structure that is known. This is presented in Figure 2C (Parry, 1992). It is monazo and has an H-acid coupling group. It has one vinyl sulfone group attached to the diazo group.

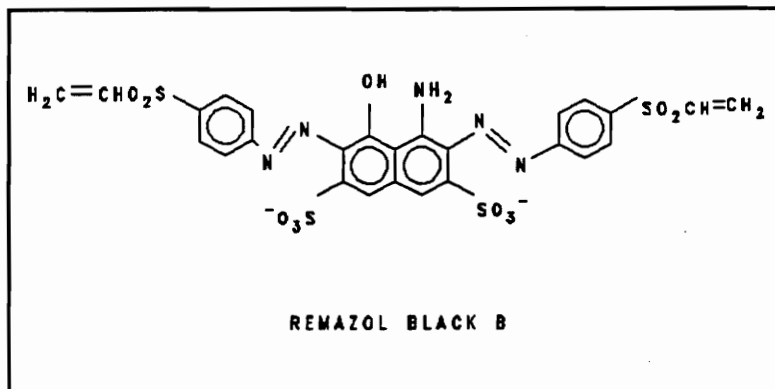


Figure 2A Remazol Black B (Vinyl Sulfone Form)

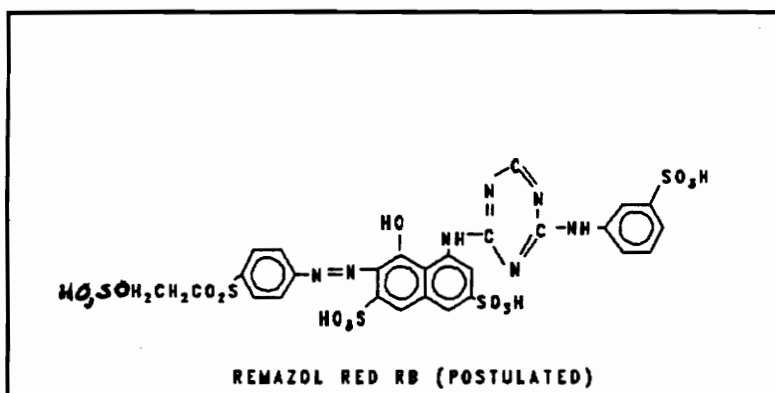


Figure 2B Remazol Red RB (Parent Acid Form)

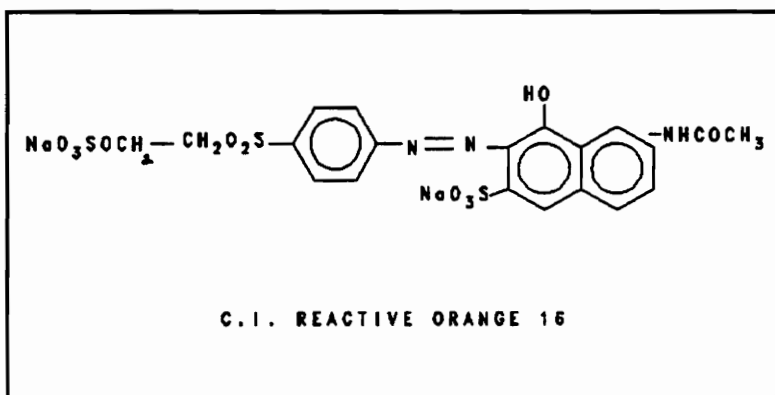


Figure 2C Remazol Golden Yellow 3RA (Parent Na Salt Form)

### 2.1.5 Characteristics of Metal Complexed Dyes

Two structural classes of metal complexed dyes are important in the cotton dyeing industry today, these are; phthalocyanine and azo complexed metal dyes. The mechanism of reaction that occurs to attach the dye molecule to the fiber is one of chelation. The metal complexed dye molecule will contain electron donors, or ligands, that will detach from the dye molecule and free bonds on the metal atom depending on the coordination number. The fiber will then attach to the complex by van der Waals forces. The van der Waals forces are directly proportional to the size of the dye molecule forming the complex. The van der Waals forces will effect the wet and light fastness (Venkataraman, 1952; Abrahart, 1977; Zollinger, 1991).

Because of their toxicity, heavy metal complexed dyes are coming under increased scrutiny (Reife, 1992). The most common complexing metals in dyes are chromium, and copper, both of which are considered priority pollutants (Wentz, 1989). However, because of the popularity of the finished textile product produced by the use of metal complexed dyes, their use will probably continue in the future.

## 2.2 Behavior of Dye Wastes in a Landfill

There is a general lack of research regarding the fate and transport of dyes contained in wastewater sludges disposed in landfills. The U.S. EPA estimates that of the approximately 15,300 publicly owned treatment works (POTWs), 43.5% dispose of their sludge in municipal landfills (EPA, 1989). Wastewater from textile dyeing operations are usually treated by biological treatment operations at a local POTW (Tincher, 1988). Therefore, a large portion of textile wastewater residual sludges will probably end up in a municipal landfill.

### 2.2.1 Municipal Landfill Characteristics

Municipal landfills are complex environments that vary based on site geology, hydrogeology, municipal wastestream characteristics, and site climatic conditions to just name a few variables. As a result, it is hard to draw conclusions about how a particular waste will behave in a landfill (Rathje, 1991).

In general, the components of a modern municipal landfill are: a natural soil foundation to support the weight of the landfill; one or two synthetic liners to contain leachate; a leachate collection system to remove

leachate from inside the landfill; two layers of compacted clay to serve as an additional liner system; the solid waste, formed into cells by covering with compacted soil to reduce leachate production from infiltration; once the landfill is closed, a final cap of compacted clay and topsoil to reduce the amount of leachate due to infiltration (Pfeffer, 1992).

Under optimal conditions and assuming no failures in the components of the landfill, all leachate produced would be captured by the leachate collection system. If a failure in the cap or in the liner system were to occur the leachate could migrate through the vadose zone and affect groundwater aquifers. This forms the basis of the mismanagement scenario that the U.S. EPA has used to base its new toxicity characteristic rule (EPA, 1990).

The composition of the leachate will affect the leaching of organic compounds and that of heavy metals. One of the more important parameters that will affect the leaching potential of a waste is the pH of the leachate. Gardner and Conrad evaluated three New York City landfills and found the leachate pH range to be 3.7 to 8.5 (Gardner and Conrad, 1986). This roughly corresponds to the pH range found in the Fresh Kills New York Landfill which was 5.8 to 8.1 (Suflita et al., 1992).

The Fresh Kills Landfill was the subject of an



extensive multidisciplinary study of the characteristics of a landfill. While it is hard to draw conclusions about all landfills based on the study of one landfill, as mentioned previously, the results found depict the complex nature of a landfill environment. The study of the Fresh Kills Landfill evaluated samples of solid waste from 14 different locations within the landfill. The results of the solid waste evaluation revealed that moisture was an important factor in the amount of anaerobic degradation that occurred in the landfill. The higher the moisture content in an area, the more biodegradation of the solid waste that had taken place (Suflita et al., 1992).

#### 2.2.1 Evaluation of Dyeing Waste Behavior in Landfills

Tincher (1988) studied the fate of dyes that entered the landfill from sludge residuals generated by the biological treatment of textile waste waters. The experiment consisted of a simulated landfill facility constructed of clay pipe 12 feet long and two and one half feet in diameter. The column was filled with gravel and sand at the bottom. This layer was topped by a 2 foot layer of clay to simulate the landfill liner. The sludge was placed on top of this layer in two foot lifts and covered with six inches of clay to simulate the formation of

landfill cells. These landfill cells were followed by a two foot cover of topsoil to simulate the landfill cap (Tincher, 1988).

The sludge placed in the columns came from three wastewater treatment plants that treated greater than 75% textile wastewater in their influents. A control column consisting of sludge from a wastewater plant that treated domestic waste only was also established. The four columns were subjected to simulated rainfall infiltration through the controlled application of 120 gallons of distilled water per year. The columns were operated for a three year period and retained sludge, column effluent, and column interiors were evaluated for dyes and possible degradation products. The landfill contents and effluent were monitored for 24 dyes. These dyes included acid, direct, disperse and reactive types (Tincher, 1988).

The samples were concentrated by evaporating one liter of liquid and dissolving the residue in 10 ml of methanol for acid, direct, and reactive dyes, and 10 ml of benzene for the disperse dyes. The 100-fold concentrated samples were then analyzed using High Performance Liquid Chromatography. No dyes or dye degradation products were found in the samples at greater than the detection limits. The conclusion of the study was that the dyes were strongly sorbed by the wastewater sludge (Tincher, 1988).

Ganesh (1992) studied the fate of azo dyes in sludges. In this work, aerobic and anaerobic digestion batch tests were conducted using Reactive Black 5 in non-textile municipal sludge, Navy 106 dye in non-textile municipal sludge, and Navy 106 in a sludge from a POTW treating predominantly (approximately 75%) textile wastewater. In each batch test a control reactor was operated with two experimental reactors at different American Dye Manufacturers Index (ADMI) color values. No dye was added to the control reactor (Ganesh, 1992).

The sludges from the various batch reactor tests were subjected to EPA Method 1311, also known as the Toxicity Characteristic Leaching Procedure (TCLP). This test will be described later in more detail. The basic concept of the TCLP is to simulate the ability of a waste to leach into groundwater from a municipal landfill if a failure of the cap and liner were to occur (EPA, 1990). The procedure consists of rotation of the waste and a dilute acetic acid extraction fluid for 18 hours in a glass jar. The extract is filtered and analyzed for various parameters. Ganesh analyzed for the ADMI color value of the extract. The conclusion of the work was that little or no dye leached into the TCLP extract based on the low measured ADMI values (Ganesh, 1992).

### 2.3 History and Regulatory Basis of the Toxicity Characteristic Leaching Procedure (TCLP)

The Toxicity Characteristic Leaching Procedure was developed by the U.S. EPA as a second generation leaching test to be used in determining if groundwater contamination would result from improper waste management (EPA, 1986). The first generation test was the Extraction Procedure Toxicity test (EP). This test was promulgated by EPA in response to the mandate given by Congress in the Resource Conservation Recovery Act of 1976 to identify wastes which pose hazards to human health and environment if improperly managed (EPA, 1986).

The EP test had some shortcomings in the test method which reduced the reproducibility and increased the cost of the test (EPA, 1986). Congress recognized these shortcomings and in the Hazardous and Solid Waste Amendments of 1984 directed the EPA to develop a second generation test that more accurately predicts leaching potential (EPA, 1986). The EPA started development of the TCLP as early as 1981 when it entered into an interagency agreement with U.S. Department of Energy's Oak Ridge National Laboratory (ORNL) (Kimmell, 1987).

### 2.3.1 Development of the TCLP Test Protocol

Oak Ridge National Laboratory split the TCLP development program into three phases. The intent of the TCLP development program was to develop a test method using the model and assumptions on which the EP test was based. The objectives of the program were: to model the mobility of organic constituents from a waste; that the test be inexpensive to conduct; that the test produce an extraction fluid that could be subject to biological toxicity testing; that it could also be used to model the mobility of inorganic constituents from the waste (Kimmell and Friedman, 1986).

Phase I involved the operation of four field lysimeters filled with domestic and commercial waste to generate municipal waste leachate. This leachate was pumped into columns containing four types of industrial wastes which were: 1) heavy ends and column bottoms from the production of trichloroethylene and perchloroethylene; 2) paint production sludge; 3) a mixture of petroleum refining incinerator ash and American Petroleum Institute (API) separator sludge; and 4) an electroplating wastewater treatment sludge. The columns were constructed of borosilicate glass and contained the wastes sandwiched between 5 and 7 cm of sand to prevent entrainment of waste

by the leachate and to evenly distribute the leachate across the waste. The leachate from each column was sampled twice a week during the first thirty days of leaching and once a week until the end of the experiment. After 79 days of operation the samples were analyzed for concentrations of the target compounds (Francis et al., 1986).

Oak Ridge National Laboratories also ran various laboratory leaching procedures at the same time the lysimeter/column experiments were in progress. The same four industrial wastes were subjected to four different types of laboratory extractions with four different types of extraction media. The four extraction media were: 0.1 M sodium acetate pH 5 buffer, carbon dioxide-saturated deionized distilled water, deionized distilled water, and actual municipal waste leachate. The four laboratory extractions were conducted at four extractant to waste ratios of 2.5, 5, 10, and 20 to 1. The results of these lab extractions or leaching procedures were compared to the target concentrations obtained by the field lysimeters. The two tests that best replicated the field lysimeter concentrations for target compounds were selected for further evaluation in phase two of the study (Kimmell and Friedman, 1986).

Phase two of the program was designed to evaluate and verify the results of phase one. In phase two of the study,

seven industrial wastes were subjected to the lysimeter/column leaching tests at a 20:1 liquid to solid ratio. These seven wastes were then subjected to the two laboratory leaching procedures that were selected in phase one, which were the sodium acetate buffer and the carbon dioxide saturated water. In addition, the seven wastes were also subjected to the EP test. The laboratory tests were once again compared to the concentrations of target compounds established from the lysimeter/column leaching tests of the seven industrial wastes. The test matching the target concentrations the best, as well as meeting the project's objectives the best, was chosen as the draft TCLP. Concluding phase two was the distribution of the draft TCLP for public comment to industry, academia, environmental groups, and others with interest in the test. (EPA, 1986).

The draft TCLP that was chosen from the work in phase two of the evaluation is very similar to the final TCLP. The procedure employs a batch extraction. The solid waste is combined with a sodium acetate pH 5 buffer or a dilute acetic acid, depending on the characteristics of the waste in a 20 to one extraction fluid to waste ratio. The mixture is rotated in an end over end rotary apparatus for 18 hours at 30 rpm. The mixture of waste and extraction fluid is filtered after rotation through a 0.6 to 0.7  $\mu\text{m}$  glass fiber filter to separate the solid phase from the liquid phase.

The liquid phase of the extract is then evaluated for organic compounds and inorganic constituents. A device called the Zero Head Extractor (ZHE) is used for the evaluation of volatile organic compounds.

Phase three of the program consisted of the evaluation of the draft TCLP, which is similar to the final TCLP, for ruggedness and precision. The evaluation of precision consisted of two laboratories each extracting replicate samples of two wastes. The two wastes were: 1) an API separator sludge with electroplating waste containing non volatile organic and inorganics, and 2) an ammonia still lime sludge containing various polycyclic aromatic hydrocarbons and various inorganic compounds. Both wastes were spiked with various volatile organic compounds (EPA, 1986).

The results of the precision evaluation revealed that there was no statistical difference at a 95% confidence interval between laboratories for the non volatile analytes and metals. The variability between samples was found to increase with decreasing concentration of non-volatile organic compounds. Variability between samples analyzed for metals was found to be affected by the pH of the leaching fluid. The results of the precision evaluation for volatile compounds were inconclusive (Blackburn et al., 1987)

A ruggedness evaluation was conducted during phase



three. The objective of that evaluation was to determine the sensitivity of the test to departures from the procedures of the test under routine lab conditions. The ruggedness was performed by one laboratory using different aliquots of the same waste used to evaluate precision. Various parameters were varied during the evaluation, including: liquid/solid ratio, extraction time, extraction fluid acidity, extractor vessels, and filters (EPA, 1986).

The results of the evaluation demonstrated that the TCLP for analysis of semi-volatile organics was rugged. The parameters chosen did not affect the analysis of semi-volatile organics with a few exceptions. The metals on the other hand could be affected by two parameters. Acidity of the extraction fluid affected the amount of metals that leached. Bottle type also affected the extraction of metals. Borosilicate glass provided better ruggedness compared to flint glass (ERCO, 1986).

### 2.3.2 Regulatory Implementation of the TCLP

The TCLP was promulgated in a final rule published in the March 29, 1990 Federal Register. The TCLP is used to analyze for 39 regulated chemicals listed in Table 1. As of today, all small and large quantity hazardous waste generators are subject to the provisions of the Toxicity

Table 1  
TCLP Regulated Compounds

COMPOUND	REGULATORY LEVEL (mg/L)
Arsenic	5.0
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresol	200.0
m-Cresol	200.0
p-Cresol	200.0
Cresol	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13
Endrin	0.02
Heptachlor (and its hydroxide)	0.008

Source: *Federal Register*, March 29, 1990

Table 1, (Continued)  
TCLP Regulated Compounds

COMPOUND	REGULATORY LEVEL (mg/L)
Hexachlorobenzene	0.13
Hexachloro-1,3-butadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl chloride	0.2

Source: *Federal Register*, March 29, 1990

Characteristics rule, which is the governing regulation of the TCLP (EPA, 1990). Sludge from POTWs are not included in the Toxicity Characteristics rule, however, in the proposed sludge disposal rules set forth in 40 CFR Parts 257 and 503 the EPA has decided that all POTWs must use the TCLP to determine if their sludge is hazardous. If the sludge has been determined to be hazardous based on TCLP, then it will be regulated under the Resource Conservation and Recovery Act (EPA, 1989).

#### 2.4 The Use of the TCLP in Evaluating Various Wastes for Metals

Since the implementation of the TCLP there has been an increase in the literature concerning the performance of the test for extracting metals. Although pH seems to effect the variability of the test, other parameters such as particle size, agitation time, and the nature of the waste could also effect the variability of the test.

In one study done by researchers at the U.S. Army Engineer Waterways Experimentation Station, two types of heavy metal containing wastes were subjected to the TCLP. The study compared the TCLP to the EP test. The results showed that the TCLP using extraction fluid 1 (dilute acetic

acid buffered with sodium hydroxide) was generally more aggressive toward metals than the EP test (Bricka et al., 1992).

The effect of particle size was not considered as a parameter in the ruggedness test conducted for EPA. Prange and Garvey (1990) evaluated the effect of particle size on an arsenic waste and a cadmium waste each stabilized with portland cement. Five different particle sizes were evaluated ranging from 0.5 to 9.5 mm. The results demonstrated a significant difference in the leaching of the two metals depending on particle size. A larger amount of metals leached from the two wastes if the particle size was larger. The range of particle sizes tested were those allowed by the TCLP protocol. Thus to reduce experimental variability it is important to maintain uniform particle size (Prange and Garvey, 1990).

A study was done with two industrial sludges to evaluate the effects of pH variations and agitation time. One sludge was from a chemical processing plant, the other sludge was from the wastewater treatment facility of an electronic microchip manufacturing plant. The results of this investigation showed that pH is the most critical factor with regard to the leaching of metals from a waste. Although the results were inconclusive regarding agitation time, the researchers observed that in general, the longer

the extraction time the greater the amount of metals that leached (Basu et al., 1990).

Chromium leaching ability of 82 samples from the leather industry was examined using the TCLP and compared to the EP test. The samples ranged from wet and dry leather shavings and dust to the sludge from precipitating tannery effluent streams. The samples were measured for moisture, total chromium content, and leaching ability using the TCLP and the EP test. The TCLP leaching levels were generally higher than the EP test leaching levels. The evaluation also found that for acidic wastes (pH<5) the TCLP was more aggressive than the EP test. Wastes with lower moisture content tended to leach less chromium (Menden and Rutland, 1988).

## 2.5 The Use of the TCLP in Evaluating Wastes for Organic Compounds

In comparison to the amount of literature in the area of metals analysis using the TCLP there is a relative lack of literature involving the analysis of organic compounds. The discussion of organic compounds will be limited to semi-volatile organic compounds. This may be due to the difficult nature of analysis of organic compounds. In general the TCLP has been shown to provide similar results

when compared to the EP test; however, it may be sensitive to the same changes in parameters as for metal components.

The TCLP demonstrated high variability for the recovery of six sludge surrogate compounds added to samples taken from three POTWs. The standards added were bromoform, 1-chlorooctane, DDT, ethylene dibromide, fusarex, and heptachlor. The recoveries of the surrogates were generally low and ranged between 0 and 30 percent. There was no difference in the recoveries of the semi-volatile compounds between the TCLP and EP test. The researchers hypothesized that the type of sludge matrix was critical in the recovery of various compounds (Alderman, 1989; Chesnutt, 1989; Dietrich et al., 1992).

Five commercial Treatment, Storage and Disposal Facilities (TSDFs) residuals were examined using the TCLP. The wastes treated varied greatly and included electroplating waste, fly ash, and incineration waste. The results showed no difference between the EP test and the TCLP for semi-volatile organics although the TCLP was shown to be more aggressive in some instances (Shively and Crawford, 1989).

A statistical analysis was conducted using the data generated for the EPA multi-laboratory collaborative study in phase three of the TCLP protocol development program. This was compared to the results obtained from a single

laboratory precision evaluation. The results for the analysis of the semi-volatile organic compounds demonstrated excellent precision with 90 percent of the results exhibiting a relative standard deviation of less than 25 percent. The single laboratory study found that better precision was obtained when using the more acidic extraction fluid 2. They also found that the high acetate content did not present problems with the analytical procedures used to detect semi-volatiles (Newcomer et al., 1990).

The TCLP was studied as a tool to predict the effectiveness to remediate a superfund site using five different treatment technologies. The ten organic compounds evaluated were: acetone, chlorobenzene, 1,2-dichloroethane, ethylbenzene, styrene, tetrachloroethylene, xylene, anthracene, bis(2-ethylhexyl)phthalate, and pentachlorophenol. The results showed that on average, the TCLP extract contained about 8% of the maximum available semi-volatile contaminants for leaching. The results also demonstrated that for organic compounds the higher the boiling point the lower the ability of the compound to leach into the extract (Thurnau and Esposito, 1989).

## 2.6 Regulations Governing POTW Effluents

The Martinsville POTW as well as all POTWs in the



United States are regulated under the provisions of the Clean Water Act. The U.S. EPA and the States implement this act through the National Pollution Discharge Elimination System (NPDES). This program, which is regulated by the Commonwealth of Virginia in the case of the Martinsville POTW, establishes maximum levels for contaminants that may be discharged into a receiving body of water from a POTW. The contaminants regulated by the program include: ADMI color values, heavy metal concentrations, Biochemical Oxygen Demand (BOD), suspended solids concentrations, Chemical Oxygen Demand (COD), and other parameters (Metcalf & Eddy, 1991).

## 2.7 Summary and Justification

The behavior of wastewater sludges containing dyestuffs disposed in a landfill environment have been studied in column studies and using the TCLP. However, none of these studies have combined the use of the TCLP and the analysis of the leachate for individual contaminants. The TCLP is the current mandated test procedure to evaluate the behavior of a solid waste when codisposed in a municipal landfill. The procedure has been demonstrated to be relatively effective in determining the leaching ability of individual contaminants. Since a large portion of textile dyeing

effluents are treated by municipal treatment plants, the problem of disposing residuals will become a major issue when the Sewage Sludge Disposal Rules become final. The TCLP will be the procedure that those municipalities will depend on to monitor the quality of their sludge before final disposal in a landfill.

### 3. METHODS AND MATERIALS

In this chapter, details will be given of the experimental design, sampling methods, and analytical procedures used to evaluate the fate of dye-containing sludges using the Toxicity Characteristic Leaching Procedure (TCLP).

#### 3.1 Experimental Design

Sludge from the Martinsville, Virginia Publicly Owned Treatment Works (POTW) was evaluated using the TCLP. The Martinsville POTW was selected because 70-75% of the influent treated by the plant is from industrial inputs with 50% of that consisting of waste dye baths from textile dyeing companies. The wastewater treated by the POTW is settled first in a primary settling tank. The supernatant is sent to an activated sludge treatment process, while waste sludge from both the 10 settling tanks and activated sludge is gravity thickened to an average of 3 percent solids. Figure 1 depicted the treatment scheme of the Martinsville POTW. The thickened sludge undergoes extended aerobic digestion for 28-31 days, after which the digested sludge is dewatered in a belt filter press to about 19

percent dry solids. The dewatered sludge is disposed of in a municipal landfill.

To evaluate the potential effects of disposing the sludge in a municipal landfill, the Martinsville POTW sludge was assessed using the TCLP. As discussed previously in the literature review, the TCLP was developed to evaluate hazardous wastes codisposed with municipal wastes. Sludges from POTWs are not regulated under the Toxicity Characteristic Rule, however the TCLP can be used to evaluate the fate of the waste in a municipal landfill.

Sludge from the gravity thickener, before digestion in an extended aeration process, was collected and analyzed (see site "U" in Figure 1). Aerobically digested and dewatered sludge from the belt filter press was collected and analyzed (see site "D" in Figure 1). A comparison was made to determine the effects of digestion on the components contained in the sludge matrix.

### 3.2 Sample collection and preparation

Undigested sludge from the gravity thickener was collected on three sampling dates; July 30, August 28, and September 15, 1992. Each time the sludge was collected in a five gallon carboy directly from the underflow drain of the thickener into the carboy. The sludge was stored in a

refrigerator at 4°C prior to sample preparation. Sludge samples were dewatered in the laboratory to an average solids concentration of 11% in an International Equipment CS centrifuge (Needham Heights, MA). This dewatered, undigested sludge was stored in an amber glass bottle at 4°C prior to analysis.

Samples of the dewatered, digested sludge were collected April 2, May 12, and June 4, 1992. Amber glass bottles were used to collect samples from the belt filter press after dewatering, these sludge samples averaged 19% solids. Sample was placed directly into the bottle from the belt filter press. Samples awaiting analysis were stored in a refrigerator at 4°C.

### 3.3 Reagents and Equipment

Reagents used in the experiments described were of the highest quality obtainable. Methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) was Optima brand from Fisher Scientific (Pittsburgh, PA). Trace metal grade acetic and nitric acids, sulfuric acid, hydrogen peroxide (30%), sodium hydroxide, sodium thiosulfate (anhydrous), ferrous sulfate, boiling chips, and filter papers were from Fisher Scientific (Pittsburgh, PA). TCLP glass fiber 0.7 $\mu$  filters and Metrical 0.45 $\mu$  membrane filters were from Gelman Sciences (Ann Arbor, MI). All reagent

dilutions were made with water purified using the Millipore Super-Q purification system, Millipore Corporation (Medford, MA.).

Internal and surrogate recovery standards were obtained from Chem Service (West Chester, PA) and diluted with methylene chloride. All pH measurements were made using a Fisher brand pH meter (Fisher Scientific).

The apparatus for the TCLP consisted of the DC-20 end over end rotator and RA-119 2L plastic coated borosilicate glass bottles. All TCLP equipment was purchased from Analytical Testing and Consulting Services, Inc. (Warrington, PA.). The pressure filtration was done using the C-102 Zero Head Extractor also from Analytical Testing and Consulting Services Inc.

#### 3.4 General Laboratory Procedures

To minimize contamination, all glassware was meticulously cleaned with soap and water and rinsed three times with distilled water and three times with Milli-Q water. All glassware and plastic bottles used for metals analyses were immersed in a 10% nitric acid and distilled water bath for at least 24 hours, and rinsed with Milli-Q water. All glassware were allowed to dry in a drying oven at 120°C, then covered with aluminum foil (for organics

analysis) or paraffin wrap (for metals analysis) to eliminate the possibility of contamination from airborne particulates.

All jar and vial caps were teflon lined. Teflon tape was used on all glassware connections to prevent contamination and to eliminate the possibility of sample loss. To ensure that the precautions taken to avoid lab contamination were successful, replicate blanks were analyzed for each experimental procedure. If any gross contamination was present the experiment would be repeated.

### 3.5 EPA Method 1310, Toxicity Characteristic Leaching Procedure (TCLP)

The TCLP method can be used to evaluate the leaching ability of volatile and semi-volatile organic compounds in addition to inorganic compounds contained in a solid waste (EPA, 1990). Since large molecular weight dyes and dye by-products of water soluble reactive dyes were the focus of this research, volatile compounds were not analyzed. Thus, the discussion of the TCLP method will focus on the procedures required for the analysis of semi-volatile organic compounds and inorganic constituents in the Martinsville sludge samples. The TCLP method used in this research will be summarized in this section; a more detailed

description of the TCLP method is contained in *Federal Register* Volume 55, Number 126, pages 26986-26998, June 29, 1990.

### 3.5.1 Apparatus and Materials

1. Agitation Apparatus: Analytical Testing and Consulting Services, Inc., DC-20, eight place, multi-purpose compact rotary apparatus. This allows the rotation of a sample end over end at  $30 \pm 2$  rpm.
2. Extraction Vessel: Analytical Testing and Consulting Services, Inc., RA-119, 2.4L, Borosilicate Glass Safety Coated, TCLP extraction bottle.
3. Filtration: Pressure filtration at 50 psi in an Analytical Testing and Consulting Services, Inc., Model C-102 Mechanical Zero Headspace Extractor (ZHE). Pressure was applied manually using a torque wrench for a ten minute period. The sample was filtered through a Gelman Sciences 0.6-0.8  $\mu\text{m}$  borosilicate glass fiber filter.
4. Extraction fluids:



Fluid #1: 22.8 mL glacial acetic acid (trace metal grade) was added to 500 mL of Milli-Q water and 257.2 mL of 1.0N sodium hydroxide. The mixture was diluted to a final volume of 4 liters with a pH of  $4.93 \pm 0.05$ .

Fluid #2: 22.8 mL glacial acetic acid (trace metal grade) was added to 500 mL of Milli-Q water, and then diluted to a final volume of 4 liters, with a pH of  $2.88 \pm 0.05$ .

### 3.5.2 TCLP Preliminary Evaluation of Waste Sample

A 100 gm aliquot of sludge was pressure filtered through a preweighed 0.6-0.8  $\mu$  borosilicate glass fiber filter inserted in a ZHE device. Pressure was applied at 10 psi increments every two minutes up to 50 psi total manual pressure applied. Any extruded liquid phase was collected in a preweighed container. The percent solids as defined by the procedure were calculated as follows:

$$\text{Percent TCLP solids} = \frac{\text{weight of aliquot} - \text{weight of liquid phase}}{\text{weight of aliquot}} \times 100$$

The type of extraction fluid to use was determined by combining a 5.0 gm sample of sludge with 96.5 mL of Milli-Q water in a 500 mL beaker. The pH was measured after this

mixture was stirred vigorously for 5 minutes using a magnetic stirrer. If the sample pH was less than 5, extraction fluid #1 was chosen. If the sample pH was greater than 5, then 3.5 mL of 1N Hydrochloric acid was added to the mixture. The mixture was then heated to 50°C for 10 minutes. After cooling to room temperature the pH of the mixture was measured again. If the sample had a pH less than 5, extraction fluid #1 was chosen. If the sample mixture had a pH greater than 5, extraction fluid #2 was chosen.

### 3.5.3 TCLP Procedure

Three 100 gram samples of waste were placed in three TCLP extraction bottles. The extraction fluid, determined in the preliminary evaluation of the waste sample, was added according to the following:

$$\text{Weight of extraction fluid} = \frac{20 \times \% \text{TCLP solids} \times \text{weight of waste}}{100}$$

A fourth blank TCLP extraction bottle was filled with extraction fluid only. The TCLP extraction bottles were sealed with teflon tape and covered with teflon lined caps. The bottles were then placed in the agitation apparatus and rotated for 18±2 hours.

After agitation the mixture in the TCLP extraction bottles was separated into its component liquid and solid phases by filtering through a 0.6-0.8  $\mu$  borosilicate glass fiber filter. The solid phase was discarded and the liquid phase extract was separated into aliquots for various organic and inorganic analyses. A one liter aliquot of each sample was placed in an amber glass jar and stored at 4°C prior to analysis using EPA Method 625. A 250 ml aliquot of each sample was acidified with nitric acid to pH less than 2 and stored at 4°C for analysis for metals. The remainder of the liquid phase of the extract from each sample was set aside and stored in acid washed plastic containers for additional analyses.

### 3.6 EPA Method 625 Liquid-Liquid Extraction Procedure

EPA Method 625 was designed to evaluate water and wastewater samples for semi-volatile organic compounds. The procedure involves a serial liquid-liquid extraction of non-polar and semi-polar compounds into methylene chloride from an aqueous sample. After extraction, the sample is concentrated using a Kuderna-Danish concentrator (EPA, 1984) (EPA, 1986).

By adjusting the pH, sample is extracted into two fractions, the base/neutral fraction and the acid fraction.

At pH greater than 11 most base compounds are unionized and will separate with the neutral compounds into the methylene chloride. At pH less than 2 the acid compounds will be in their unionized form and will be extracted into the methylene chloride.

### 3.6.1 Liquid-Liquid Extraction Procedure

Before extraction began three base/neutral extraction standards and three acid extraction standards were added to each one liter aliquot of TCLP sample. The three base/neutral standards, 2-fluorobiphenyl,  $d_5$ -nitrobenzene, and p-terphenyl- $d_{14}$  were added to a final concentration of 10  $\mu\text{g/L}$ . The three acid standards, 2-fluorophenol,  $d_6$ -phenol, and 2-4-6-tribromophenol were added to a final concentration of 20  $\mu\text{g/L}$ .

The sample with the added standards was poured into a 2 L separatory funnel. A Pasteur pipette was used to add 10N sodium hydroxide to raise the pH above 11. Sixty milliliters of methylene chloride was added to the sample bottle and shaken for thirty seconds, removing any remaining organic compounds from the bottle. This was added to the separatory funnel. The sample and methylene chloride in the separatory funnel were shaken for two minutes, then the phases were allowed to separate for ten minutes. After ten

minutes, the methylene chloride phase was collected in a 250 mL erlenmeyer flask and labeled as the base/neutral fraction. The extraction procedure was performed three times for each one liter TCLP sample at pH above 11.

The pH of the TCLP sample was then reduced below 2 using 1:1 sulfuric acid and reagent water. The sample was extracted three times with methylene chloride, as before with the base/neutral fraction. The methylene chloride phase was collected in a separate erlenmeyer flask and labeled as the acid fraction.

### 3.6.2 Kuderna-Danish Concentration

Prior to concentration in a Kuderna-Danish concentrator each fraction of the sample was "dried" with anhydrous sodium sulfate to remove any water that may be retained in the methylene chloride. The sample was poured through the anhydrous sodium sulfate and then filtered through a Whatman #1 filter. The filter and the erlenmeyer flask were rinsed with a several milliliters of methylene chloride to provide complete removal of any remaining sample.

A Kuderna-Danish concentrator was assembled for each fraction separated. The concentrator consisted of a 10 mL collection flask attached to a 500 mL evaporating flask, which in turn was attached to a three ball Snyder column.

The concentrator was partially immersed in a 1000 mL beaker of water at 60-65°C. A few boiling chips were added to the sample in the concentrator to avoid "bumping".

Each fraction was concentrated down to about 1 mL of methylene chloride. The concentrator was rinsed with about a milliliter of methylene chloride from a pasteur pipette and collected into a sample vial. Each fraction was concentrated further to exactly 1 mL using nitrogen gas bubbled into the sample. Methylene chloride extracts were stored in 10 mL sample vials at 4°C prior to GC/MS analysis.

### 3.7 EPA Method 3050 Acid Digestion of Sludge

Each sample of sludge collected after the first two sampling periods was subjected to an acid digestion to compare total metals contained in the sludge matrix versus the metals that were leached into the TCLP fluid. In Method 3050 a one gram wet weight sample of sludge was digested with nitric acid and hydrogen peroxide (EPA, 1986).

The sludge sample was added to a 250 mL erlenmeyer flask with ten mL of 1:1 nitric acid to reagent water. The slurry was mixed thoroughly, covered with a watchglass, and heated to 95°C for 15 minutes. The mixture was allowed to cool to room temperature, 5 mL of concentrated nitric acid were added, then the covered flask was heated for 30

minutes. This last step was repeated once again to allow for complete oxidation. A ribbed watchglass was placed on the erlenmeyer flask and the solution was evaporated to 5 mL.

After the solution was allowed to cool, 2 mL of reagent water and 3 mL of 30% hydrogen peroxide were added. The solution was heated to start the peroxide reaction. As the effervescence from the peroxide reaction subsided the ribbed watchglass was replaced and the solution was evaporated to 5 mL. After the solution was cooled, the mixture was diluted to 100 mL. The dilute digestate was filtered through a Whatman No. 41 filter. The sample was prepared for metal analysis by flame or graphite furnace atomic absorption spectrophotometer.

### 3.8 Analysis of Extracts by Capillary Gas Chromatography and Mass Spectrometry

After extraction of the TCLP samples the base/neutral and acid fractions were analyzed using Gas Chromatography/Mass Spectrometry (GC/MS). A Hewlett-Packard (Avondale, PA) 5980 Series II gas chromatograph interfaced with a Hewlett-Packard 5970B Mass Selective Detector controlled by a Hewlett-Packard 9000 data system. The mass spectra collected during the analysis were analyzed using the Wiley

Library of mass spectra using a Probability Based Matching Program contained in the HP 9000 data system. The program matches the mass spectra with those contained in the computer database and reports the probability of match.

1. Chromatographic Conditions

Column: J&W Scientific 30 Meter DB-5, 1  $\mu\text{m}$  film

Sample Volume: 2  $\mu\text{L}$

Injector: 250°C; Splitless injection purge on after  
3 minutes

Temperature Program: 40°C for four minutes, ramp 8°C  
per minute, 260°C for 17  
minutes, Total run time 48.5  
minutes.

2. Electron Impact Conditions

Ionizing Electron Energy: 70 eV

Accelerating Voltage: 4kV

Mass Range: 45-425 amu

Source Temperature: 200°C

Source Pressure:  $4 \times 10^{-5}$  torr

Scan Rate: 0.9 scans/sec

3.9 Analysis of Extracts by High Performance Liquid  
Chromatography

The TCLP sample base/neutral and acid extracts of TCLP



fluid were analyzed using High Performance Liquid Chromatography (HPLC). A Hewlett-Packard HP1090 Liquid Chromatograph equipped with a Diode Array Detector was used to detect dye compounds that are not readily volatilized and thus cannot be analyzed using GC/MS. The Diode Array Detector can simultaneously detect wavelengths in both the ultraviolet and visible ranges of the electromagnetic spectrum. Data reduction and manipulation were performed on an Hewlett-Packard 9000 Chemstation data system. A program to evaluate azo dyes using reverse phase liquid chromatography was used and is described in the following section (Bell et al., 1992).

1. Chromatographic Conditions:

Column: Octadecylsilyl, C<sub>18</sub>

Mobile Phase: methanol 25 mMol acetate buffer; 20/80 for one minute, 100/0 for 14 minutes, 20/80 for six minutes.

Flow Rate: 1.0 mL per minute

Injection Volume: 15  $\mu$ L

Detection: Spectrum range from 200 nm to 600 nm at a sampling interval of 640 scan/ms

Program Time: 21 minutes

### 3.10 Analysis of TCLP Extracts Using Flame and Graphite Furnace Atomic Absorption Spectrophotometry

The TCLP extracts were analyzed for inorganic metals using Flame and Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS). Two inorganic elements, copper and iron, were analyzed by Flame Atomic Absorption Spectrophotometry. Mercury was analyzed using Cold Vapor Atomic Absorption Spectrophotometry. The remaining metals were analyzed by GFAAS since those were present in trace amounts or required specialized atomic absorption conditions that could not be performed in the flame AAS.

A Perkin-Elmer (Norwalk, CT) model 703 Flame Atomic Absorption Spectrophotometer was used to analyze for copper and iron. Wavelength and slit settings were adjusted according to the Perkin-Elmer manual for each element. The wavelength and slit settings for copper were 324.8 nm and 0.7 nm respectively. The wavelength and slit settings for iron were 248.3 nm and 0.2 nm. Two prepared sets of standards and each sample were analyzed by aspirating directly into the flame and the absorbance measured. Absorbance data were converted to concentration by the instrument.

Mercury was analyzed by the Cold Vapor Atomic Absorption Spectrometric Method, as described in section

3112 B. of *Standard Methods* (1989), by Don Marickovich, PhD Student in the Environmental Engineering and Environmental Sciences Division at Virginia Polytechnic Institute and State University. The reported detection limit was 0.2  $\mu\text{g/L}$ .

All other metals were analyzed by Marilyn Grender, Analytical Chemist in the Environmental Engineering and Environmental Sciences Division, using a Perkin-Elmer 5100 Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS) with Zeeman Background Correction. A listing of the GFAAS conditions are listed in Table 2. Matrix modifiers are added to the sample to eliminate any matrix effects when analyzing for some metals in the GFAAS; these matrix modifiers are also specified in Table 2.

Table 2  
GFAAS Operating Conditions

METAL	WAVE-LENGTH (nm)	SLIT (nm)	SITE*	PYROLYSIS TEMP (°C)	ATOMIZATION TEMP (°C)	MATRIX MODIFIER
Ag	328.1	0.7	P	1000	1800	0.015 mg Pd & 0.01 mg Mg(NO <sub>3</sub> ) <sub>2</sub>
Al	309.3	0.7	P	1600	2500	0.05 mg Mg(NO <sub>3</sub> ) <sub>2</sub>
As	193.7	0.7	P	1300	2400	0.015 mg Pd & 0.01 mg Mg(NO <sub>3</sub> ) <sub>2</sub>
Ba	553.6	0.4	W	1200	2550	none
Cd	228.8	0.7	P	900	1600	0.2 mg (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> & 0.01 mg Mg(NO <sub>3</sub> ) <sub>2</sub>
Cr	357.9	0.7	P	1650	2600	0.05 mg Mg(NO <sub>3</sub> ) <sub>2</sub>
Pb	283.3	0.7	P	850	1800	0.2 mg (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> & 0.01 mg Mg(NO <sub>3</sub> ) <sub>2</sub>
Se	196.0	2.0	P	600/1100	2100	0.015 mg Pd & 0.01 mg Mg(NO <sub>3</sub> ) <sub>2</sub>

\*P=Platform, W=Wall

### 3.11 American Dye Manufacturers Institute (ADMI) Color Value

The color of the TCLP extracts was evaluated using the ADMI color value method as described in section 2120 E. (Proposed) of *Standard Methods for the Examination of Water and Wastewater* (1989). In this procedure each sample pH was adjusted to 7.6 and filtered through a Gelman Sciences Metrical 0.45  $\mu\text{m}$  filter. The percent transmittances at 438, 540, and 590 nm were measured using a Bausch & Lomb Spectronic 20 spectrophotometer. A standard of 500 ADMI color value was read for quality control. The color value was calculated using the tristimulus, Munsell, and intermediate values. A sample calculation of the ADMI value is included in Appendix C., and a more detailed explanation of the procedure for calculating those values is described in *Standard Methods* (1989).

### 3.12 Analysis of Sludge from Fenton's Reagent Oxidation

An abbreviated TCLP analysis was made of sludge produced from a Fenton's reagent oxidation of Nylon Black BW dyebath, a chromium complexed azo dye. Fenton's reagent is

a mixture of ferrous sulfate and hydrogen peroxide. The ferrous sulfate was added to the pH 3.0, 60°C dyebath and allowed to mix for a few minutes. Hydrogen peroxide was then added sequentially in a 10 to 1 weight ratio with the ferrous sulfate. This yielded 4750 ppm of 30% hydrogen peroxide and 475 ppm ferrous per 200 ml sample of dyebath. The solutions were stirred by a magnetic stirrer for 30 minutes at which time no visible change was observed. The solids produced in the reaction were allowed to settle.

The solution containing the solids and the liquid sample was centrifuged at 2000 rpm for one hour. The supernatant was decanted and the solids were weighed and combined in an erlenmeyer flask with TCLP extraction fluid number one, in a 1 to 20 weight ratio. The entire mixture was placed in a shaker table and agitated for 18 hours. After that time the solution was filtered through a 0.6 to 0.8  $\mu\text{m}$  borosilicate glass fiber filter. The abbreviated TCLP extracts, the supernatants from the centrifuge, and samples of the dyebath were analyzed for chromium in the Flame AAS with nitrous oxide and acetylene as the flame gasses. The wavelength and slit settings were 357.9 nm and 0.7 mm respectively.

### 3.13 Statistical Methods

A "nested" Analysis of Variance (ANOVA) was performed to establish the difference between the undigested and digested samples. Since the sampling periods were different in each type of sample, the variable, sampling period, was represented as "TIME" and was nested under the variable, type of sludge, represented as "PROCESS". The "nested" ANOVA was performed on each metal analyzed and the ADMI color values measured. The ANOVA was made at a 95% confidence level ( $\alpha=0.05$ ). The p-values obtained by the analysis for each treatment were considered significant if less than 0.05. The "nested" ANOVA was run on SYSTAT/SYGRAPH (SYSTAT INC., Evanston, IL) a statistical program that can be used on an IBM compatible Personal Computer (PC).

A paired t-test on SYSTAT was used to evaluate the variance of metal concentrations between the acid digested sludge samples and the TCLP extracts of those same sludge samples. The t-test was also evaluated at a 95% confidence interval, so the p-values obtained were considered significant if less than 0.05.

#### 4.0 RESULTS AND DISCUSSION

Results and discussion of the TCLP analysis of the dye containing sludges are presented in this section. Each sludge; undigested Martinsville POTW sludge, digested Martinsville POTW sludge, and the Fenton Reagent sludge of Black BW wastewater; will be discussed according to the analytical methodology conducted (e.g. ADMI, GC/MS, HPLC, AAS). Since the Fenton's reagent sludge was only analyzed for chromium the results of that experiment will be discussed in the section on metals analysis. The undigested and digested sludges were not paired according to sampling date, that is to say that, each sludge sample was collected independently on a separate date. The digested sludge samples were collected and analyzed before the undigested sludge samples.

As discussed in the previous section on methods and materials the following analyses were performed to determine the respective characteristics of the TCLP extracts:

- ADMI Color of TCLP Extract
  - Spectrophotometry
- Organics present in TCLP Extract



Extracted by EPA Method 625 (Base/Neutral and Acid extractable fractions)

-GC/MS for Semi-volatiles

-HPLC for dyes

- Metals present in TCLP Extract

- Flame AA for Cu, Fe

- Graphite Furnace AA for As, Al, Ba, Cd, Cr, Pb, Se, Ag

- Cold Vapor AA for Hg

- Metals present in sludges

- Flame AA for Cu, Cr, Fe, Al

- Graphite Furnace AA for As, Ba, Cd, Pb, Se, Ag

In this section samples of digested dewatered sludge collected on April 2, May 12, and June 4, 1992 are referred to as Samples A, B, and C respectively. Samples of undigested sludge collected on July 30, August 28, and September 15, 1992 are referred to as samples D, E, and F respectively.

#### 4.1 Color Analysis of TCLP Samples

Color of the TCLP extracts were analyzed using the American Dye Manufacturers Institute method. The color hue of the extracts were also visually assessed.

The results of the ADMI method are listed in Table 3. A nested analysis of variance, similar to that used to analyze the metals concentration, was used to analyze the color values measured for the digested and undigested sludge TCLP extracts. The p-values of the nested ANOVA are reported in Table 4. The computer output of the ANOVA is listed in Appendix D.

In general the color of the digested extracts was less than the color of the undigested extracts. The variation may be due to type of sludge or to the sampling period based on the results of the nested ANOVA. The amount of variation due to the type of sludge according to the F-ratio is higher than that of the variation due to sampling period. This suggests that the type of sludge may have more of an effect on measured color.

The initial color of the dewatered digested sludge was a dark purple. This color was the same color as the activated sludge and the color of the influent to the primary clarifier. The color of the sludge collected from the thickener initially was the same purple color, however the color shifted to a sea green during transport from the POTW to the laboratory, a two hour trip. In one instance the sludge collected from the thickener was the same sea green color as the sludge was collected from the underflow drain.

Table 3  
ADMI Color Values of TCLP Samples

SAMPLE <sup>a</sup>	ADMI VALUE (COLOR UNITS)	MEAN $\pm$ SD (COLOR UNITS)	OVERALL MEAN $\pm$ SD (COLOR UNITS)
<b>DIGESTED SLUDGE</b>			
A1	116	83 $\pm$ 24	156 $\pm$ 56
A2	59		
A3	74		
B1	184	201 $\pm$ 18	
B2	226		
B3	192		
C1	205	186 $\pm$ 15	
C2	184		
C3	168		
<b>UNDIGESTED SLUDGE</b>			
D1	244	251 $\pm$ 7	240 $\pm$ 33
D2	261		
D3	249		
E1	228	264 $\pm$ 31	
E2	304		
E3	260		
F1	223	204 $\pm$ 13	
F2	196		
F3	194		

a Triplicate samples from each sampling date were analyzed, thus samples A1, A2, A3 represent triplicate TCLP extracts of sludge obtained on April 2, 1992

Table 4  
ANOVA Results: ADMI Color Value, Color Units

p-VALUE, PROCESS <sup>a</sup>	p-VALUE, TIME(PROCESS) <sup>b</sup>
<0.001	<0.001

a PROCESS=DIGESTED OR UNDIGESTED

b TIME(PROCESS)=SAMPLING PERIOD within PROCESS

If  $p < 0.05$  then treatment is statistically different

The color of both digested and undigested TCLP extracts after filtering was a slight yellow green. Since there were aromatic amines present in both the undigested and digested TCLP extracts, the yellow hue may originate from those. In comparing the ADMI values with those found by Ganesh (1992), a close relationship can be found. Color values in similar TCLP extracts of other aerobically digested sludge ranged from 33 to 200 ADMI color units (Ganesh, 1992). The color of the undigested sludge extracts were higher. The degradation products detected in the TCLP extracts of the undigested sludge probably contributed to the color, thus increasing the color value. In addition, by visual observation the color was a darker shade of green in the undigested TCLP extracts. The green hue may be from the presence of the degradation products in the extracts. Since the extracts from both the undigested sludge and digested sludge were of a light color, very few, if any, dyes were present. This supports what was found using the HPLC. There is no ADMI standard regulated by the U.S. EPA in the TCLP method, however, there is an ADMI standard for effluent from the Martinsville POTW of 200 ADMI color units.

#### 4.2 Detected Trace Organic Compounds by GC/MS

Trace organic compounds detected by GC/MS in the TCLP extracts are listed in Table 5. The table shows compounds that were detected in both the undigested and digested sludge from the Martinsville, VA, POTW. The table shows that under each column for digested and undigested sludge the results were based on triplicate TCLP analyses of three different sludge samples.

Compounds were identified using a probability based matching library included in the GC/MS data system. All compounds listed as identified were considered a confident identification (probability greater than 70%) based on the library. Compounds that were considered poor matches (probability less than 70%) were excluded from the list. Any compounds that were found to be in the blank TCLP extract were not reported since those compounds were probably contaminants from the reagents, glassware, or plasticware that may have contacted the samples or extracts. Quality Control/Quality Assurance data regarding the analysis of semi-volatiles are reported in Appendix A. Representative mass spectra of reported compounds are included in Appendix B.

Table 5  
Compounds Identified in Undigested and Digested Sludges

COMPOUND <sup>a</sup>	Number of Undigested Samples in which Compound Detected (n=9)	Number of Digested Samples in which Compound Detected (n=9)
p-(2-Hydroxyethylsulfone)-Aniline, [2-(HES)aniline](B)	8	0
p-(2-ethylenesulfone)-Aniline(B) [Loss of water from 2-(HES)aniline]	9	0
Benzaldehyde(N)	0	6
Benzeneacetic Acid(A)	9	7
4-Methoxybenzeamine(B)	3	1
4-Methoxy-N-Methyl-Benzeamine(B)	9	8
Benzoic Acid(A)	7	3
Butanoic Acid(A)	7	0
2-Methylbutanoic Acid(A)	6	0
Camphor(N)	8	0
Decanoic Acid(A)	4	0
Dodecanoic Acid(A)	3	0
Hexanoic Acid(A)	2	2
2-Ethylhexanoic Acid(A)	9	4
1H-Indole(B)	9	0
3-Methyl-1H-Indole(B)	5	0
3-Methoxy-4,7-Dimethyl-1H-Isoindole(B)	9	7
1,2,3-Trimethyl-1H-Indole(B)	1	1
1,3,3-Trimethyloxindole(B)	1	4
p-Menth-3-en-1-ol(N)	3	0
[4-(Dimethylamino)phenyl]-Phenyl-Methanone(B)	9	0
Pentanoic Acid(A)	7	0
4-Methylphenol (p-cresol)(A)	8	0
Tri-Butyl Ester of Phosphoric Acid(N)	9	6
alpha-Pinene(N)	3	0
8-Ethylquinoline(B)	6	0
1-alpha-Terpineol(N)	9	0
Dimethyl Trisulfide(N)	2	0

<sup>a</sup> B=base, N=neutral, A=acid as determined by EPA method 625 and chemical structure

According to EPA Method 625, the detection limits for semi-volatile compounds contained in a wastewater matrix can range from 10  $\mu\text{g/L}$  to 50  $\mu\text{g/L}$ . Compounds in the TCLP extract probably will not be detected in concentrations below that range.

In general, there were more detected trace organic compounds in the undigested sludge compared to the digested sludge. Twenty seven different organic compounds were detected in undigested sludge. Only eleven organic compounds were detected in digested sludge; ten of these were also present in the TCLP extract of the undigested sludge. This suggests that extended aerobic digestion was able to destroy several compounds to concentrations below detection limits. Extended aerobic digestion also did not form significant new organic compounds.

No known dyes were detected by the GC/MS. This was to be expected since the dye molecules are large and are not easily placed into a gaseous state to be detected by GC analysis. The extracts were a slight green color as noted in the previous section. This color could not be directly attributed to any dyes that may have leached into the sludge. Some of the color may have been caused by the aromatic amines that were in the extract or by the reduction



product, p-(2-hydroxyethylsulfone)-aniline that was detected.

Even though samples of undigested and digested sludge were not coordinated to represent paired samples, the character of the wastewater inputs to the Martinsville POTW is such that one would expect the wastewater composition to be relatively similar during normal operations. In addition, a great deal of equalization takes place throughout the process so that by the time sludge is collected for thickening its composition is relatively homogenous. Pad dyeing of cotton fabrics with Remazol dyes requires the addition of pine oil, fabric sizing agents, tributyl phosphate, and surfactants. In addition, the presence of the vinyl sulfone reactive group, regardless of the dye color and the actual molecular structure of the dye, is expected in wastewater from dyeing with Remazol dyes. Since the textile industrial inputs to the POTW constantly use Remazol dyes in both pad dyeing and jet dyeing operations, then there would be a similar source of textile wastewater to the POTW throughout the year. Thus, a qualitative comparison between the undigested and digested sludges would be a valid comparison.

Even though the dyes could not be detected by GC/MS, the reduction product of all Remazol dyes, p-(2-hydroxyethylsulfone)-aniline (MW 201) was detected in the

TCLP extract of the undigested sludge in eight of the nine total samples. Remazol dyes contain a reactive vinyl sulfone aniline moiety. Since a large portion of the industrial input to the Martinsville POTW is dye washwater from reactive dyeing of cotton fiber textiles, these reduction products would be expected. The reduction product with a loss of water, p-(2-ethylenesulfone)-aniline (MW 183) was detected in all nine TCLP extracts of the undigested sludge. The loss of water could have been caused by the injection of the sample into the injection port of the GC/MS. The further evidence of heat as the cause of water loss is that only the p-(2-hydroxyethylsulfone)-aniline was detected by HPLC (see section 4.3).

These aniline-based reduction products were not detected in the TCLP extracts of the digested sludge. This may mean that the reduction products were destroyed by the digester or were rendered immobile, so that the products would not leach into the TCLP extraction fluid.

Several aromatic amines, such as 4-methoxybenzenamine and 4-methoxy-n-methyl-benzenamine, were detected in both the undigested and digested sludge TCLP extracts. The percent reduction of the 4-methoxy-N-methyl-benzenamine in the digestion process was calculated to be 72%. These aromatic amines may be dye degradation products from the reduction of azo bonds. According to Zollinger (1991),

indoles are also possible degradation products of azo dyes undergoing reduction (Zollinger, 1991). Indoles were detected in both the undigested and digested samples, although more indole based compounds were detected in the undigested sludge. The percent reduction of 3-methoxy-4,7-dimethyl-1H-isoindole in the digestion process was calculated to be 66%. This suggests that extended aerobic digestion destroys some of the indole compounds, particularly the simple, low molecular weight indole compounds.

Previous work by Bell (1992) in the analysis of Navy 106 wastewater showed that both the p-(2-hydroxyethylsulfone)-aniline and the p-(2-ethylenesulfone)-aniline were present in Navy 106 wastewater as detected by GC/MS (Bell *et al.*, 1992). In addition, these two compounds were detected in bench scale anaerobically treated Navy 106 washwater (Bell *et al.*, 1992). Since Navy 106 is a large portion of the industrial effluent treated by the Martinsville POTW these two reduction compounds would be expected to remain in the sludge matrix.

In addition to the reduction products, two other compounds found in Navy 106 washwater were found in the sludge (Bell *et al.*, 1992). Tri-butyl ester of phosphoric acid was found in both the undigested and digested sludge. Tri-butyl ester of phosphoric acid is a common cellulose

plasticizer (Merck, 1983). Since the compound was identified in both sludge types, the compound is probably resistant to extended aerobic digestion. Further evidence of this is the percent reduction computed between the undigested and digested samples was only 6%. This compound was also found in river water which received textile effluents (Dietrich *et al.*, 1988), further suggesting that this compound is not readily biodegradable. Another compound found in Navy 106 washwater was 1-alpha-terpineol; this compound was only detected in the undigested sludge. 1-Alpha-terpineol is the major ingredient in pine oil which is added to the dye bath to clean the hydrolyzed dyes off of the cellulose textile after dyeing (Zollinger, 1991). The 1-alpha-terpineol was probably destroyed by extended aerobic digestion, since it was not found in the digested sludge.

The only regulated TCLP pollutant that was detected in the sludge from the Martinsville POTW sludge was 4-methylphenol (p-cresol). This compound was only found in the undigested sludge, suggesting that it is degraded by extended aerobic digestion. The compound 4-methylphenol, was previously identified in TCLP extracts of municipal, non-industrial sludges (Dietrich *et al.*, 1993).

Many of the remaining compounds identified were organic acids; pentanoic acid, benzoic acid, butanoic acid, decanoic acid, among others. These are commonly found in municipal

sewage as microbial biodegradation products (Grant and Long, 1981).

#### 4.3 Detected Trace Organic Compounds by High Performance Liquid Chromatography (HPLC)

The acid fraction and base/neutral fractions of the TCLP extracts were analyzed by HPLC for any dyes that may be in the matrix. In all samples analyzed there were no known dyes present at detectable concentrations. The detection limits for Remazol Black B and Remazol Red RB was determined by Bell (1992) to be 4.9 mg/L at 525 nm and 2.6 mg/L at 590 nm respectively. In the extracts from the undigested sludge the only detectable compound by HPLC was the p-(2-hydroxyethylsulfone)-aniline. A typical liquid chromatogram and the resulting ultraviolet-visible spectrum of a sample containing p-(2-hydroxyethylsulfone)-aniline are shown in Figures 3a and 3b. The p-(2-hydroxyethylsulfone)-aniline was found in both the acid fraction and the base/neutral fraction. This may be due to some bleedover from the base/neutral liquid-liquid extraction.

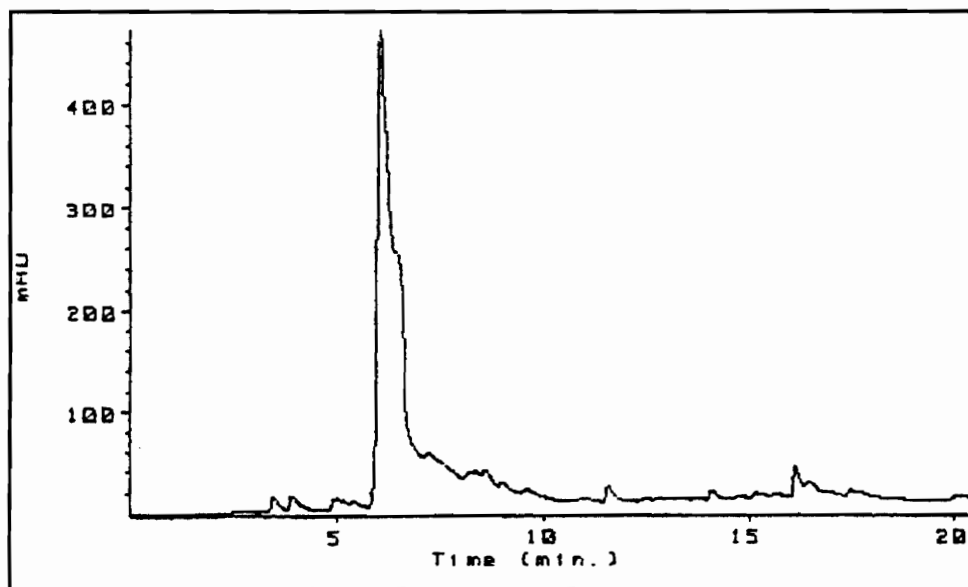


Figure 3a. Sample HPLC Chromatogram of p-(2-Hydroxyethylsulfone)-Aniline

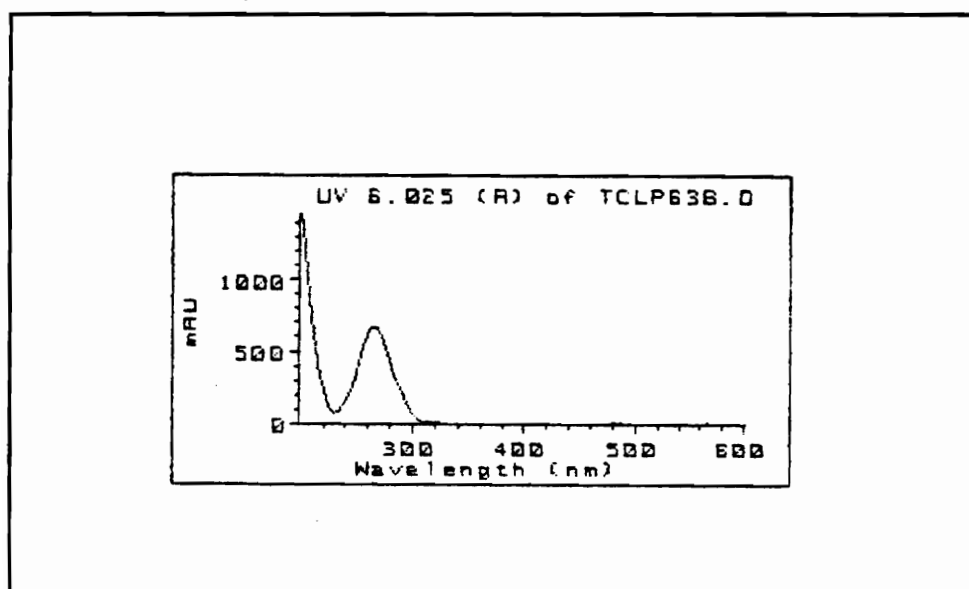


Figure 3b. Sample UV-Vis Spectrum of p-(2-Hydroxyethylsulfone)-Aniline

The UV-Vis spectrum and retention time of the p-(2-hydroxyethylsulfone)-aniline is similar to both the spectrum detected in the Navy 106 washwater and that of a purified dye compound obtained from reducing remazol dyes (Bell et al., 1992). Since no dyes were present in either the undigested sludge or the digested sludge extracts, the dyes probably adhered to the sludge matrix or were rendered resistant to leaching into the TCLP extract.

The known aniline-based dye reduction products were not detected in the digested sludge TCLP extracts. Since the reduction products were not detected in the digested sludge, the digester probably further degraded the aromatic amines.

#### 4.4 Detected Metals in TCLP Samples

The eight regulated TCLP metals; arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver; were detected at trace levels in both the undigested and digested samples. The three other metals analyzed, aluminum, copper, and iron, were detected as well. The results of the metals analysis of TCLP samples are reported in Tables 6 to 16. Analysis of variance of each metal is reported in Table 17. A nested ANOVA was used to evaluate the data. A nested ANOVA is a multivariable factorial analysis of variance with

Table 6  
Arsenic Concentrations<sup>a</sup> in TCLP Samples

SAMPLE <sup>b</sup>	CONCENTRATION ( $\mu\text{g/L}$ )	MEAN $\pm$ SD ( $\mu\text{g/L}$ )	OVERALL MEAN $\pm$ SD ( $\mu\text{g/L}$ )
<b>DIGESTED SLUDGE</b>			
A1	3.8	3.53 $\pm$ 0.309	2.62 $\pm$ 0.73
A2	3.1		
A3	3.7		
B1	2.8	2.37 $\pm$ 0.419	
B2	2.5		
B3	1.8		
C1	2	1.97 $\pm$ 0.125	
C2	2.1		
C3	1.8		
<b>UNDIGESTED SLUDGE</b>			
D1	1.7	1.63 $\pm$ 0.047	1.83 $\pm$ 0.43
D2	1.6		
D3	1.6		
E1	1.3	1.57 $\pm$ 0.205	
E2	1.6		
E3	1.8		
F1	2.9	2.30 $\pm$ 0.432	
F2	2.1		
F3	1.9		

a ESTIMATED DETECTION LIMIT: 1  $\mu\text{g/L}$ ; TCLP Regulatory LIMIT=5.0 mg/L

b Triplicate samples from each sampling date were analyzed, thus, samples A1, A2, A3 represent triplicate TCLP extracts of sludge obtained on April 2, 1992



Table 7  
Aluminum Concentrations<sup>a</sup> in TCLP Samples

SAMPLE <sup>b</sup>	CONCENTRATION ( $\mu\text{g/L}$ )	MEAN $\pm$ SD ( $\mu\text{g/L}$ )	OVERALL MEAN $\pm$ SD ( $\mu\text{g/L}$ )
<b>DIGESTED SLUDGE</b>			
A1	458	519 $\pm$ 65.7	385 $\pm$ 103
A2	488		
A3	610		
B1	312	311 $\pm$ 14.7	
B2	292		
B3	328		
C1	322	326 $\pm$ 10.5	
C2	340		
C3	315		
<b>UNDIGESTED SLUDGE</b>			
D1	532	521 $\pm$ 8.99	775 $\pm$ 223
D2	522		
D3	510		
E1	782	780 $\pm$ 40.00	
E2	828		
E3	730		
F1	965	1023 $\pm$ 147	
F2	1225		
F3	880		

a ESTIMATED DETECTION LIMIT:1  $\mu\text{g/L}$

b Triplicate samples from each sampling date were analyzed, thus, samples A1, A2, A3 represent triplicate TCLP extracts of sludge obtained on April 2, 1992

Table 8  
Barium Concentrations<sup>a</sup> in TCLP Samples

SAMPLE <sup>b</sup>	CONCENTRATION ( $\mu\text{g/L}$ )	MEAN $\pm$ SD ( $\mu\text{g/L}$ )	OVERALL MEAN $\pm$ SD ( $\mu\text{g/L}$ )
<b>DIGESTED SLUDGE</b>			
A1	556	590 $\pm$ 154	669 $\pm$ 108
A2	420		
A3	793		
B1	738	728 $\pm$ 6.94	
B2	725		
B3	722		
C1	652	688 $\pm$ 33.1	
C2	732		
C3	680		
<b>UNDIGESTED SLUDGE</b>			
D1	1300	1237 $\pm$ 66.4	1596 $\pm$ 322
D2	1265		
D3	1145		
E1	1924	1901 $\pm$ 23.8	
E2	1868		
E3	1910		
F1	1994	1649 $\pm$ 285	
F2	1296		
F3	1658		

a ESTIMATED DETECTION LIMIT:5  $\mu\text{g/L}$ ; TCLP Regulatory Limit=100 mg/L

b Triplicate samples from each sampling date were analyzed, thus, samples A1, A2, A3 represent triplicate TCLP extracts of sludge obtained on April 2, 1992

Table 9  
Cadmium Concentrations<sup>a</sup> in TCLP Samples

SAMPLE <sup>b</sup>	CONCENTRATION ( $\mu\text{g/L}$ )	MEAN $\pm$ SD ( $\mu\text{g/L}$ )	OVERALL MEAN $\pm$ SD ( $\mu\text{g/L}$ )
<b>DIGESTED SLUDGE</b>			
A1	2.3	1.55 $\pm$ 0.543	2.53 $\pm$ 1.78
A2	1.04		
A3	1.3		
B1	7.04	4.21 $\pm$ 2.21	
B2	1.64		
B3	3.96		
C1	1.76	1.83 $\pm$ 0.124	
C2	2		
C3	1.72		
<b>UNDIGESTED SLUDGE</b>			
D1	0.96	0.937 $\pm$ 0.056	0.93 $\pm$ 0.50
D2	0.99		
D3	0.86		
E1	0.64	1.19 $\pm$ 0.771	
E2	0.65		
E3	2.28		
F1	0.72	0.667 $\pm$ 0.062	
F2	0.7		
F3	0.58		

a ESTIMATED DETECTION LIMIT:0.05  $\mu\text{g/L}$ ; TCLP Regulatory Limit=1.0 mg/L

b Triplicate samples from each sampling date were analyzed, thus, samples A1, A2, A3 represent triplicate TCLP extracts of sludge obtained on April 2, 1992

Table 10  
Chromium Concentrations<sup>a</sup> in TCLP Samples

SAMPLE <sup>b</sup>	CONCENTRATION ( $\mu\text{g/L}$ )	MEAN $\pm$ SD ( $\mu\text{g/L}$ )	OVERALL MEAN $\pm$ SD ( $\mu\text{g/L}$ )
<b>DIGESTED SLUDGE</b>			
A1	4.3	6.1 $\pm$ 2.34	4.3 $\pm$ 2.0
A2	9.4		
A3	4.6		
B1	5.1	4.12 $\pm$ 0.66	
B2	3.7		
B3	3.7		
C1	2.4	2.5 $\pm$ 0.37	
C2	2.1		
C3	3.0		
<b>UNDIGESTED SLUDGE</b>			
D1	2.5	2.33 $\pm$ 0.24	2.5 $\pm$ 0.2
D2	2.5		
D3	2.0		
E1	3.0	2.67 $\pm$ 0.24	
E2	2.6		
E3	2.4		
F1	2.6	2.5 $\pm$ 0.082	
F2	2.4		
F3	2.5		

a ESTIMATED DETECTION LIMIT:0.5  $\mu\text{g/L}$ ; TCLP Regulatory Limit=5.0 mg/L

b Triplicate samples from each sampling date were analyzed, thus, samples A1, A2, A3 represent triplicate TCLP extracts of sludge obtained on April 2, 1992

Table 11  
Copper Concentrations<sup>a</sup> in TCLP Samples

SAMPLE <sup>b</sup>	CONCENTRATION (mg/L)	MEAN $\pm$ SD (mg/L)	OVERALL MEAN $\pm$ SD (mg/L)
<b>DIGESTED SLUDGE</b>			
A1	1.03	1.02 $\pm$ 0.074	0.78 $\pm$ 0.19
A2	0.92		
A3	1.1		
B1	0.78	0.75 $\pm$ 0.022	
B2	0.73		
B3	0.74		
C1	0.61	0.58 $\pm$ 0.040	
C2	0.6		
C3	0.52		
<b>UNDIGESTED SLUDGE</b>			
D1	0.05	0.04 $\pm$ 0.008	0.04 $\pm$ 0.01
D2	0.04		
D3	0.03		
E1	0.04	0.04 $\pm$ 0.000	
E2	0.04		
E3	0.04		
F1	0.05	0.05 $\pm$ 0.005	
F2	0.06		
F3	0.05		

a ESTIMATED DETECTION LIMIT:0.02 mg/L

b Triplicate samples from each sampling date were analyzed, thus, samples A1, A2, A3 represent triplicate TCLP extracts of sludge obtained on April 2, 1992

Table 12  
Iron Concentrations<sup>a</sup> in TCLP Samples

SAMPLE <sup>b</sup>	CONCENTRATION (mg/L)	MEAN $\pm$ SD (mg/L)	OVERALL MEAN $\pm$ SD (mg/L)
<b>DIGESTED SLUDGE</b>			
A1	0.13	0.15 $\pm$ 0.012	0.13 $\pm$ 0.01
A2	0.16		
A3	0.15		
B1	0.14	0.13 $\pm$ 0.008	
B2	0.12		
B3	0.13		
C1	0.12	0.12 $\pm$ 0.008	
C2	0.13		
C3	0.11		
<b>UNDIGESTED SLUDGE</b>			
D1	2.4	2.73 $\pm$ 0.403	3.60 $\pm$ 0.75
D2	2.5		
D3	3.3		
E1	4.1	3.90 $\pm$ 0.216	
E2	4.0		
E3	3.6		
F1	4.3	4.17 $\pm$ 0.579	
F2	4.8		
F3	3.4		

a ESTIMATED DETECTION LIMIT:0.03 mg/L

b Triplicate samples from each sampling date were analyzed, thus, samples A1, A2, A3 represent triplicate TCLP extracts of sludge obtained on April 2, 1992

Table 13  
Lead Concentrations<sup>a</sup> in TCLP Samples

SAMPLE <sup>b</sup>	CONCENTRATION ( $\mu\text{g/L}$ )	MEAN $\pm$ SD ( $\mu\text{g/L}$ )	OVERALL MEAN $\pm$ SD ( $\mu\text{g/L}$ )	
<b>DIGESTED SLUDGE</b>				
A1	2.1	2.57 $\pm$ 0.34	2.27 $\pm$ 0.70	
A2	2.7			
A3	2.9			
B1	1.4	1.4 $\pm$ 3.8E-10		
B2	1.4			
B3	1.4			
C1	3.4	2.83 $\pm$ 0.42		
C2	2.4			
C3	2.7			
<b>UNDIGESTED SLUDGE</b>				
D1	7.2	6.97 $\pm$ 0.17		
D2	6.9			
D3	6.8			
E1	6	5.73 $\pm$ 0.21		
E2	5.7			
E3	5.5			
F1	5.2	5 $\pm$ 0.51		
F2	5.5			
F3	4.3			

a ESTIMATED DETECTION LIMIT:1  $\mu\text{g/L}$ ; TCLP Regulatory Limit=5.0 mg/L

b Triplicate samples from each sampling date were analyzed, thus, samples A1, A2, A3 represent triplicate TCLP extracts of sludge obtained on April 2, 1992

Table 14  
Mercury Concentrations<sup>a</sup> in TCLP Samples

SAMPLE <sup>b</sup>	CONCENTRATION ( $\mu\text{g/L}$ )	MEAN $\pm$ SD ( $\mu\text{g/L}$ )	OVERALL MEAN $\pm$ SD ( $\mu\text{g/L}$ )
<b>DIGESTED SLUDGE</b>			
A1	0.05 <sup>c</sup>	0.15 $\pm$ 0.146 <sup>c</sup>	0.07 $\pm$ 0.10 <sup>c</sup>
A2	0.05 <sup>c</sup>		
A3	0.36 <sup>c</sup>		
B1	0.05 <sup>c</sup>	0.017 $\pm$ 0.024 <sup>c</sup>	
B2	ND <sup>d</sup>		
B3	ND <sup>d</sup>		
C1	0.04 <sup>c</sup>	0.04 $\pm$ 0.00 <sup>c</sup>	
C2	0.04 <sup>c</sup>		
C3	0.04 <sup>c</sup>		
<b>UNDIGESTED SLUDGE</b>			
D1	0.04 <sup>c</sup>	0.087 $\pm$ 0.034 <sup>c</sup>	0.07 $\pm$ 0.04 <sup>c</sup>
D2	0.11 <sup>c</sup>		
D3	0.11 <sup>c</sup>		
E1	0.05 <sup>c</sup>	0.083 $\pm$ 0.034 <sup>c</sup>	
E2	0.07 <sup>c</sup>		
E3	0.13 <sup>c</sup>		
F1	0.04 <sup>c</sup>	0.043 $\pm$ 0.020 <sup>c</sup>	
F2	0.02 <sup>c</sup>		
F3	0.07 <sup>c</sup>		

a ESTIMATED DETECTION LIMIT:0.2  $\mu\text{g/L}$ ; TCLP Regulatory Limit=0.2 mg/L

b Triplicate samples from each sampling date were analyzed, thus, samples A1, A2, A3 represent triplicate TCLP extracts of sludge obtained on April 2, 1992

c These values are below the detection limit of 0.2 mg/L and thus represent an estimate of the actual Hg concentration in the TCLP extract

d ND= not detected



Table 15  
Selenium Concentrations<sup>a</sup> in TCLP Samples

SAMPLE <sup>b</sup>	CONCENTRATION ( $\mu\text{g/L}$ )	MEAN $\pm$ SD ( $\mu\text{g/L}$ )	OVERALL MEAN $\pm$ SD ( $\mu\text{g/L}$ )
<b>DIGESTED SLUDGE</b>			
A1	2.9	1.63 $\pm$ 1.02 <sup>c</sup>	1.22 $\pm$ 0.71 <sup>c</sup>
A2	1.6 <sup>c</sup>		
A3	0.4 <sup>c</sup>		
B1	0.8 <sup>c</sup>	0.83 $\pm$ 0.047 <sup>c</sup>	
B2	0.8 <sup>c</sup>		
B3	0.9 <sup>c</sup>		
C1	0.7 <sup>c</sup>	1.2 $\pm$ 0.37 <sup>c</sup>	
C2	1.3 <sup>c</sup>		
C3	1.6 <sup>c</sup>		
<b>UNDIGESTED SLUDGE</b>			
D1	0.6 <sup>c</sup>	1.07 $\pm$ 0.37 <sup>c</sup>	0.58 $\pm$ 0.42 <sup>c</sup>
D2	0.3 <sup>c</sup>		
D3	0.3 <sup>c</sup>		
E1	0.6 <sup>c</sup>	0.4 $\pm$ 0.14 <sup>c</sup>	
E2	0.3 <sup>c</sup>		
E3	0.3 <sup>c</sup>		
F1	0.3 <sup>c</sup>	0.27 $\pm$ 0.05 <sup>c</sup>	
F2	0.3 <sup>c</sup>		
F3	0.3 <sup>c</sup>		

a ESTIMATED DETECTION LIMIT:2  $\mu\text{g/L}$ ; TCLP Regulatory Limit=1.0 mg/L

b Triplicate samples from each sampling date were analyzed, thus, samples A1, A2, A3 represent triplicate TCLP extracts of sludge obtained on April 2, 1992

c These values are below the detection limit of 2  $\mu\text{g/L}$  and thus represent an estimate of the actual Se concentration in the TCLP extract

Table 16  
Silver Concentrations<sup>a</sup> in TCLP Samples

SAMPLE <sup>b</sup>	CONCENTRATION ( $\mu\text{g/L}$ )	MEAN $\pm$ SD ( $\mu\text{g/L}$ )	OVERALL MEAN $\pm$ SD ( $\mu\text{g/L}$ )
<b>DIGESTED SLUDGE</b>			
A1	ND <sup>d</sup>	0.03 $\pm$ 0.05 <sup>c</sup>	0.1 $\pm$ 0.0 <sup>c</sup>
A2	ND <sup>d</sup>		
A3	0.1 <sup>c</sup>		
B1	ND <sup>d</sup>	0.07 $\pm$ 0.05 <sup>c</sup>	
B2	0.1 <sup>c</sup>		
B3	0.1 <sup>c</sup>		
C1	0.1 <sup>c</sup>	0.10 $\pm$ 2.4E-11 <sup>c</sup>	
C2	0.1 <sup>c</sup>		
C3	0.1 <sup>c</sup>		
<b>UNDIGESTED SLUDGE</b>			
D1	ND <sup>d</sup>	ND <sup>d</sup>	ND <sup>d</sup>
D2	ND <sup>d</sup>		
D3	ND <sup>d</sup>		
E1	ND <sup>d</sup>	ND <sup>d</sup>	
E2	ND <sup>d</sup>		
E3	ND <sup>d</sup>		
F1	ND <sup>d</sup>	ND <sup>d</sup>	
F2	ND <sup>d</sup>		
F3	ND <sup>d</sup>		

a ESTIMATED DETECTION LIMIT:0.2  $\mu\text{g/L}$ ; TCLP Regulatory Limit=5.0 mg/L

b Triplicate samples from each sampling date were analyzed, thus, samples A1, A2, A3 represent triplicate TCLP extracts of sludge obtained on April 2, 1992

c These values are below the detection limit of 0.2  $\mu\text{g/L}$  and thus represent an estimate of the actual Ag concentration in the TCLP extract.

d ND= not detected

Table 17  
ANOVA Results: Metal Concentrations

METAL	p-VALUE (PROCESS) <sup>a</sup>	p-VALUE (TIME(PROCESS)) <sup>b</sup>
As	0.001*	0.001*
Al	<0.001*	<0.001*
Ba	<0.001*	0.005*
Cd	0.016*	0.120
Cr	0.011*	0.053
Cu	<0.001*	<0.001*
Fe	<0.001*	0.005*
Pb	<0.001*	<0.001*

a PROCESS=DIGESTED OR UNDIGESTED

b TIME(PROCESS)=SAMPLING PERIODS within PROCESS

\* Statistically significant at  $\alpha=0.05$

Note: Results of the metals analyses for Mercury (Table 14), Selenium (Table 15), and Silver (Table 16) were not statistically compared as all the individual concentrations for the TCLP extracts were below the detection limits.

incomplete factorials. One factor is "nested" under another so that not all combinations of the two factors are observed. The categorical variables included whether the sludge sample was undigested or digested (variable name=PROCESS), and the sampling period was "nested" in the digested or undigested variable (variable name=TIME(PROCESS)). A complete listing of ANOVA results is presented in Appendix D.

Three metals were detected below estimated detection limits, as shown in the previous tables. These were, mercury, selenium, and silver. Because those metals were detected below detection limits it is hard to draw any conclusions about the significance of that data; however, the data are presented for the benefit of the reader. All the regulated TCLP metals, arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver, were below regulatory limits.

Since the sampling times were different for each type of sludge the nested ANOVA was used to evaluate for variance. The analysis of variance was inconclusive however, since there was statistically significant variance for both sampling period and type of sludge. While no conclusions can be drawn from this analysis, a few observations may be made. In the case of several metals;

barium, cadmium, chromium, iron, selenium, and silver; the variance of the sampling period was smaller than the variance of the type of sludge. In the case of copper, chromium, cadmium, and arsenic, the digested sludge TCLP extract had a higher concentration of those metals than the undigested TCLP extract. In the case of lead, iron, barium, and aluminum the opposite effect was observed. This may be due to variations in influent from industrial sources. The metal contents in the wastewater influents to the POTW is very sporadic, for instance the textile inputs sometimes use copper complexed dyes if an order for a certain fabric color is made. In addition to the metal inputs from the use of metal complexed dyes by the textile dyeing industries, a metal plating facility inputs to the POTW that is primarily a copper effluent, this may cause some variability. It may also be due to matrix effects of the sludge on the mobility of the type of metal.

#### 4.5 Metals Analysis of Acid Digested Sludges

The two sludges evaluated from the Martinsville, VA, POTW were evaluated for total metal content by EPA Method 3050 using a nitric acid/hydrogen peroxide digestion (EPA, 1986). The sludges from the last four sampling periods were evaluated. As a result one set of digested sludge and three

sets of undigested sludge were evaluated by the method. The mean results are shown in Table 18. These results were compared to the metals concentrations for the same sludge samples to evaluate the leaching ability of the TCLP. Since the two sets of data only differed by type of treatment, a paired t-test was used to evaluate the variance of the two procedures. The p-values obtained are also reported in Table 18. The computer output from the paired t-test analysis is included in Appendix D. Mercury was not evaluated since it was below detection limits in the TCLP extracts. All TCLP extract concentrations were converted to mass of contaminant per mass of sludge analyzed for purposes of comparison.

The results of the comparison of the TCLP to Method 3050 showed that, the acid digestion method was the more aggressive test with respect to determination of metals content. For all but one element, barium, the results were statistically significant. These results were expected, since the TCLP is used to test mobility of the compound in a landfill.

Table 18  
 Paired t-Test: Metals Concentration  
 TCLP Extract of Sludge to Acid Digestion of Sludge (n=12)

METAL	TCLP MEAN±SD	ACID DIGESTED MEAN±SD	% RECOVERED BY TCLP [TCLP] x(100%) [Acid digest]	p-VALUE
As	0.037±0.008 (µg/g)	0.228±0.049 (µg/g)	16.2%	<0.001*
Al	13.25±5.48 (µg/g)	1850±256 (µg/g)	0.72%	<0.001*
Ba	27.37±9.64 (µg/g)	38.4±12.2 (µg/g)	71%	0.110
Cd	0.023±0.011 (µg/g)	0.094±0.037 (µg/g)	24.4%	<0.001*
Cr	0.05±0.006 (µg/g)	2.37±0.589 (µg/g)	2.1%	<0.001*
Cu	0.004±0.005 (mg/g)	0.292±0.079 (mg/g)	1.4%	<0.001*
Fe	0.055±0.033 (mg/g)	1.21±0.254 (mg/g)	4.5%	<0.001*
Pb	0.103±0.031 (µg/g)	5.51±1.84 (µg/g)	18.7%	<0.001*
Se	0.015±0.010 (µg/g)	0.138±0.071 (µg/g)	10.9%	<0.001*
Ag	0.0005±0.0009 (µg/g)	3.15±1.25 (µg/g)	0.016%	<0.001*

\* Statistically significant at  $\alpha=0.05$

Since one set of sludge from the digester was examined, any observations to be made concerning total metals in the undigested sample versus the digested sample could not be justified.

#### 4.6 Chromium Analysis of Fenton's Reagent with Nylon Black BW Wastewater Sludge

An abbreviated TCLP analysis of a sludge formed with a Fenton's Reagent reaction of Nylon Black BW, a chromium complexed azo dye. As mentioned previously in the methods and materials section, a Fenton's reaction was performed with 1:10 ferrous to hydrogen peroxide and 200 milliliters of Black BW dye wastewater. The resulting solution was centrifuged at 2000 rpm, the supernatant was decanted, and evaluated for chromium content. The solids were removed and placed with a 20:1 ratio of TCLP extraction fluid #1 to solids. The combined mixture was shaken on a shaker table for 18 hours, filtered through a 0.6 to 0.8  $\mu\text{m}$  borosilicate glass fiber filter and also evaluated for chromium content. All samples were analyzed for chromium content in the Flame AAS with nitrous oxide and acetylene as the flame gasses with a detection limit of 0.05 mg/l.



The oxidation with the Fenton's reagent caused the Black BW dyebath to reduce color (by visual observation only). The resulting solution after 30 minutes had a dark brown color, as compared to the dark black color of the Black BW dyebath. The solids produced in the reaction were suspended in solution and were a fine flocculent. After centrifugation the solids all collected at the bottom of the centrifuge bottle and were a dark black in color.

A mass balance was made using the results from four samples of Black BW wastewater analyzed. The initial four samples of 200 mL of Black BW washwater had a mean chromium content of 3.44 mg  $\pm$ 0.043 mg. The four samples of supernatant had a mean chromium content of 3.28 mg  $\pm$ 0.94 mg. The TCLP extracts had a mean chromium content of 0.055 mg  $\pm$ 0.05 mg.

Assuming that mass was conserved, 95% of the chromium stayed in the supernatant of the samples, 2% of the chromium leached into the TCLP fluid and 3% either stayed in the sludge matrix or was lost in handling. The results suggest that chromium complexed dyes treated with Fenton's reagent release the chromium into solution, ultimately ending up in the supernatants of the dewatering process. Very little chromium is found in the sludge matrix.

## 5.0 CONCLUSIONS

An analysis was made on the leaching potential of dye-containing sludges. In this analysis, sludge from gravity thickeners and dewatered sludge from the aerobic digesters of a POTW treating textile wastewater were evaluated by the EPA's Toxicity Characteristic Leaching Procedure (TCLP). In addition, sludge from a Fenton's reaction with metal dye containing washwater was analyzed using an abbreviated TCLP.

The following conclusions may be made from the results of this study:

1. The ADMI color values of the TCLP extracts from both digested and undigested sludges were less than 300 ADMI units, suggesting that dyes were not leached. Further evidence of this is that known dyes were not found by HPLC at detectable levels in either sludge type.

2. A vinyl sulfone degradation product (e.g., p-(2-hydroxyethylsulfone)-aniline) of Remazol dyes was detected in the TCLP extract of the sludge prior to aerobic digestion, but was not released into the TCLP leachate at detectable levels after aerobic digestion. This may be due to sorption by the biomass or due to the degradation of the product by extended aerobic digestion.

3. In the TCLP extract of undigested sludges, 27 organic

chemicals were detected; 10 of these same organic chemicals were also detected in the digested sludges, plus one additional chemical. Thus, digestion by extended aeration appeared to degrade many, but not all organic compounds, without producing new TCLP-extractable organic chemicals.

4. 4-Methylphenol was the only TCLP regulated organic chemical found in the TCLP extract of undigested sludges; no regulated organic chemicals were leached from the digested sludges.

5. None of the TCLP regulated metals (As, Ba, Cd, Cr, Pb, Hg, Se, Ag) were detected in either sludge type above the regulatory limit.

6. For As, Al, Cd, Cr, Cu, Fe, Pb, Se, and Ag, comparison of the concentrations of metals in the TCLP extracts to the total metals determined by acid digestion indicated that <1 % to about 25 % of the metal content of the sludge could be extracted by TCLP. Barium was an exception as 71 % of this metal was extracted from the sludge by TCLP.

7. Chromium contained in Nylon Black BW washwater remained in solution after treatment using a Fenton's reagent oxidation. A subsequent TCLP analysis of the solids produced by the reaction, and a mass balance of the entire process, showed that 95 % of the chromium stayed in solution, 2 % was leached into the TCLP extract, and 3 % remained in the sludge matrix or was lost.

## 6.0 RECOMMENDATIONS

Several issues were raised in the course of this work that would provide opportunities for further research and are summarized here:

1. The role of varying inputs to the Martinsville POTW restricted the ability to draw specific conclusions regarding the differences in the leaching characteristics of undigested and digested sludge. A pilot scale treatment plant using controlled dye wastewater inputs could provide sludges of uniform composition. The sludges produced would provide a better comparison of the behavior of undigested and digested sludges in a TCLP analysis.

2. The amount of copper that could be extracted from digested sludge was much higher when compared to the amount that leached from the undigested sludge. This suggests that if the copper is held in complexed dyes it would remain in the sludge matrix, unless the copper containing dyes were degraded by extended aerobic digestion. After extended aeration, the copper would be more readily extracted by the TCLP test. Although this is a reasonable hypothesis, the experimental design used in this research precluded testing this hypothesis

since the undigested and digested sludge samples were not obtained in a paired experimental design. A coordinated evaluation of the behavior of metalized dyes in sludges could provide answers to this question.

3. The color of the undigested sludge would shift from dark purple to a sea green, indicating a change in the chemistry of the sludge. This may be due to effects caused by anaerobic conditions in the sludge matrix. The effects of anaerobic and aerobic conditions on sludges should be investigated.

4. With the protocol worked out for conducting the TCLP test, these procedures should be used for testing the effectiveness of any in-process treatment of segregated dye wastes.

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**APPENDIX A.**  
**QUALITY CONTROL/QUALITY ASSURANCE**

Mean percent recoveries and the standard deviations for Acid and Base/Neutral surrogate standards used in EPA Method 8270 are reported in Table A-1. In addition to the percent recoveries measured, the range of acceptance for water and wastewater for the EPA method quality control criteria are reported for each surrogate. The surrogates were added only to sixteen of the eighteen samples analyzed. Since the organic compounds detected in the sample extracts were not being quantified this should not affect the outcome of the detected compound results.

The only compound that was within tolerance for EPA recovery limits was the 2,4,6-tribromophenol. The remainder of the compounds were below percent recovery limits. Since the TCLP extract is a very difficult matrix to analyze the results are not surprising. Some possible explanations of the lower percent recoveries could be sludge particles, that were suspended in the TCLP extract after filtering, entraining the surrogates. There were surfactants in the TCLP extracts, mainly hexanoic acid, that caused a certain amount of emulsion during the liquid-liquid separation. The emulsion formed may have trapped some of the surrogates, thus reducing the amount of compound recovered.

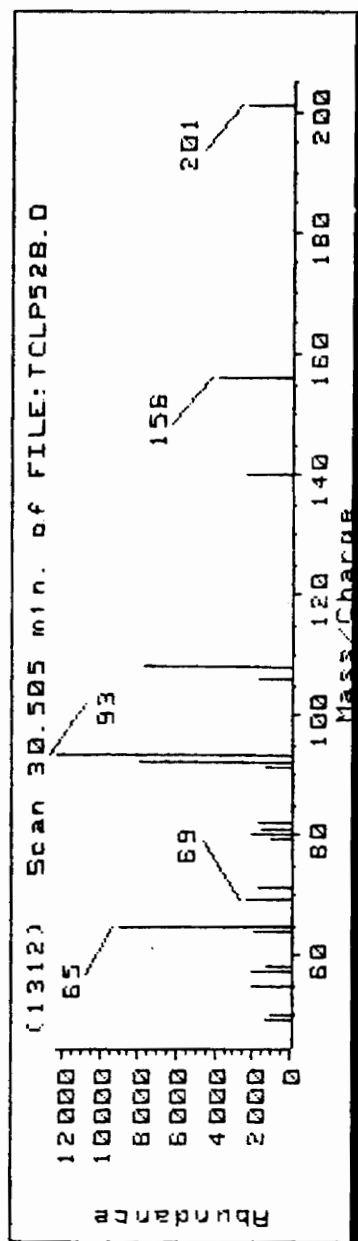
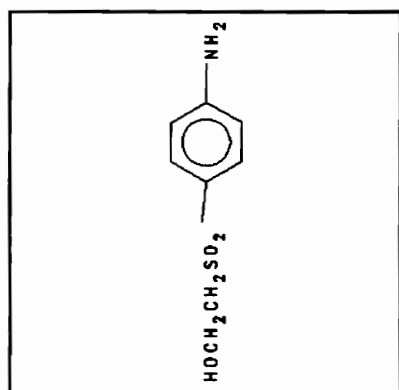
TABLE A-1  
PERCENT RECOVERIES OF SURROGATE STANDARDS

COMPOUND	MEAN %RECOVERY	EPA RECOVERY LIMITS*
BASE/NEUTRAL EXTRACTABLE COMPOUNDS		
Nitrobenzene-d <sub>5</sub>	15.37 ±7.81 (n=16)	35-114
2-Fluorobiphenyl	10.18 ±4.61 (n=16)	43-116
p-Terphenyl-d <sub>14</sub>	14.42 ±7.62 (n=16)	33-141
ACID EXTRACTABLE COMPOUNDS		
Phenol-d <sub>5</sub>	5.40 ±1.96 (n=16)	10-94
2-Fluorophenol	10.90 ±4.32 (n=16)	21-100
2-4-6-Tribromopenol	25.36 ±17.08 (n=16)	10-123

\* Based on method 8270 in EPA Manual SW846 Test methods for Evaluating Solid Waste-Physical/Chemical Methods

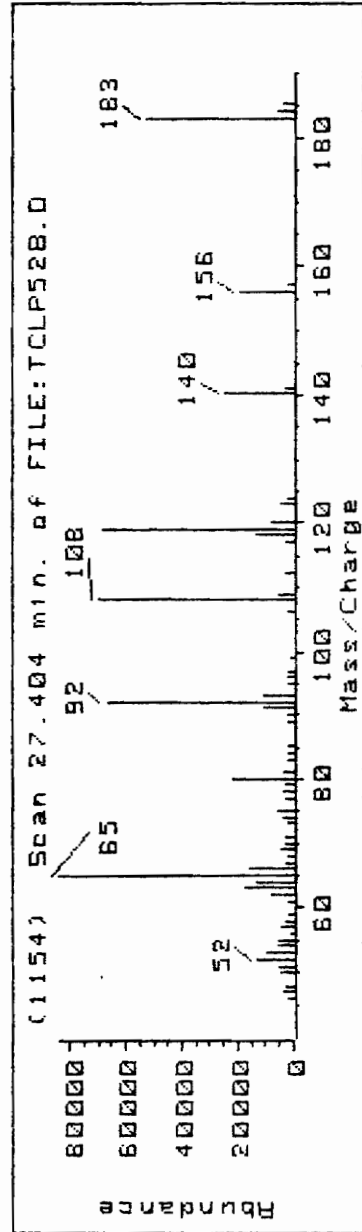
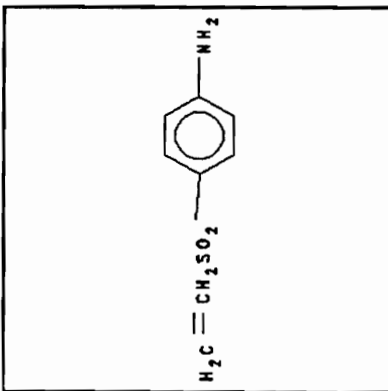
**APPENDIX B**

**MASS SPECTRA**  
**AND**  
**CHROMATOGRAMS**

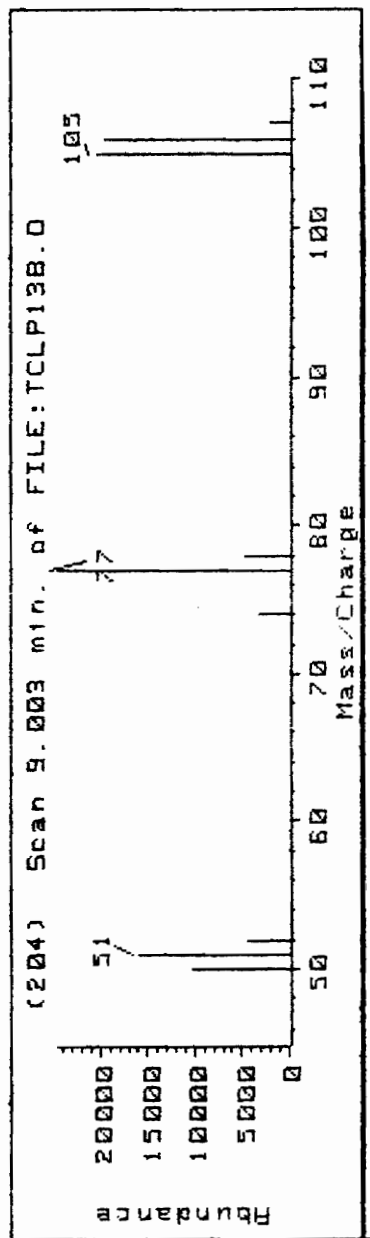
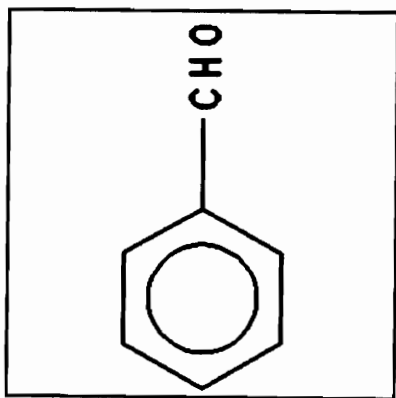


p-2 (Hydroxyethylsulfone)-aniline (MW201)

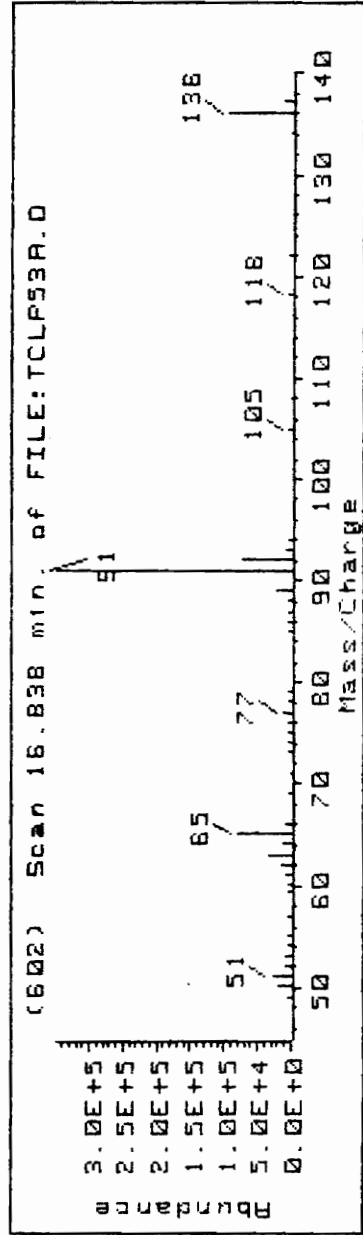
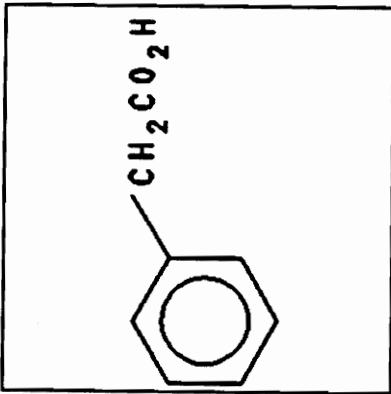




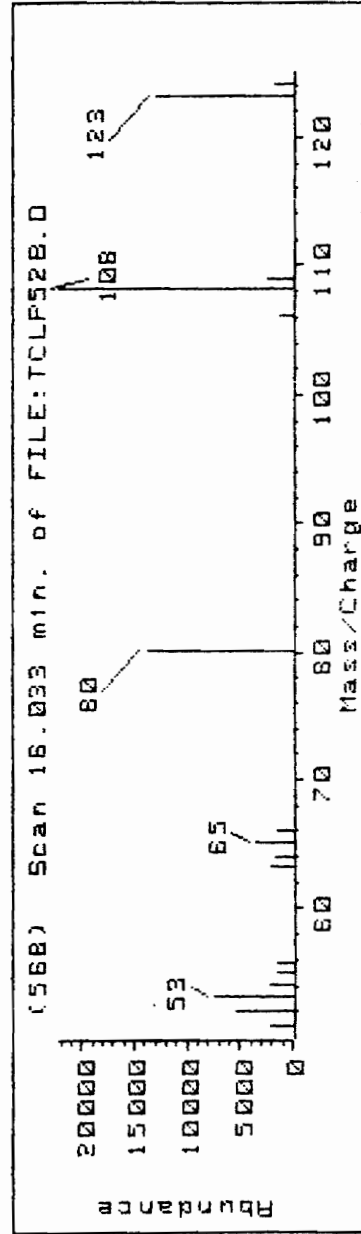
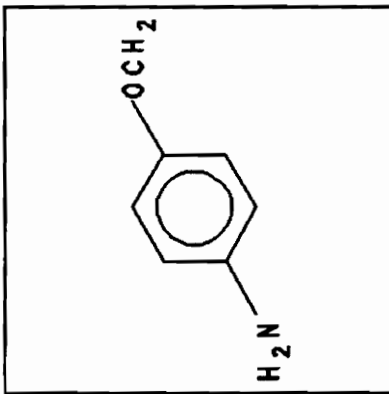
p-(2-ethylenesulfone)-aniline (MW183)



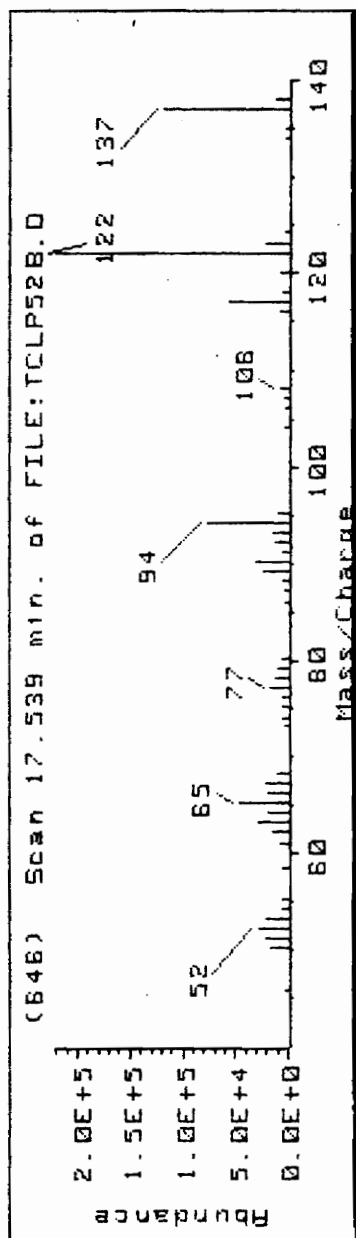
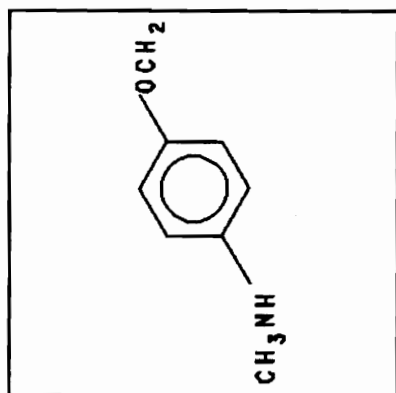
Benzaldehyde



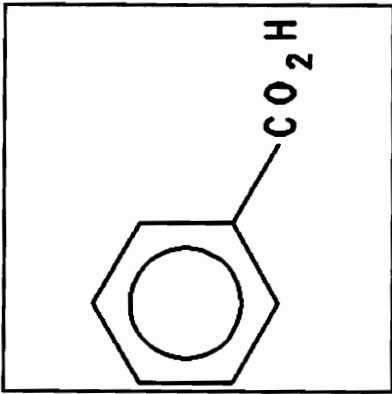
Benzeneacetic Acid



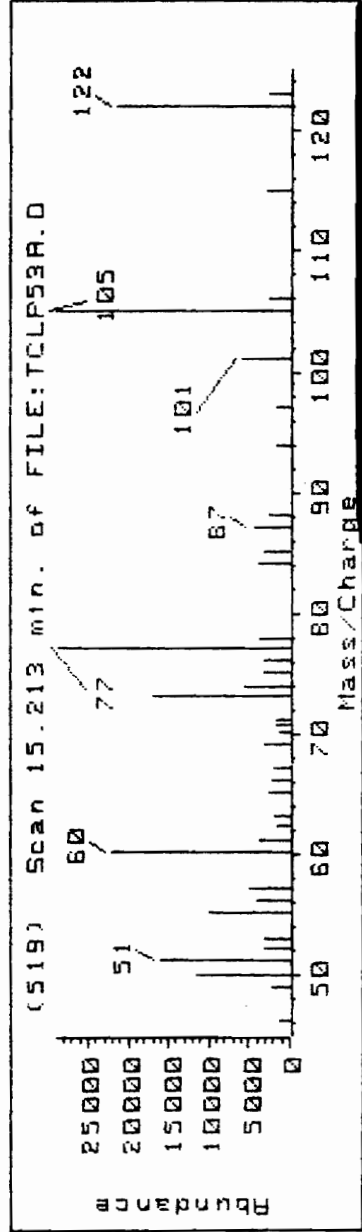
4-Methoxybenzenamine



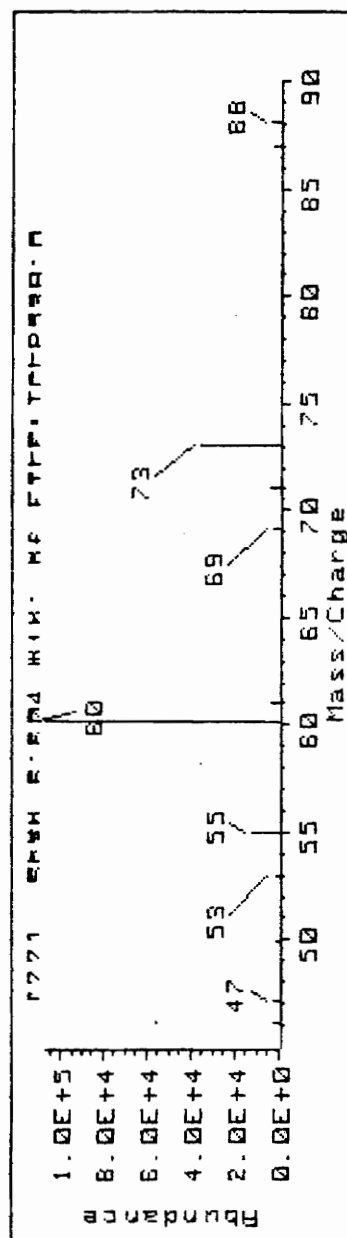
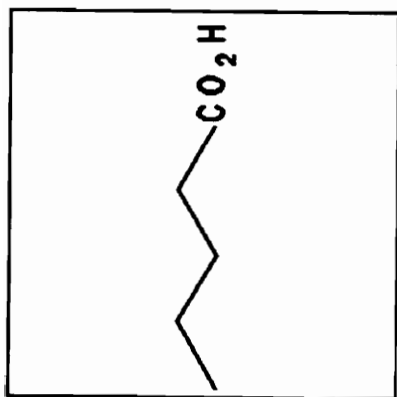
4-Methoxy-N-methyl-benzenamine



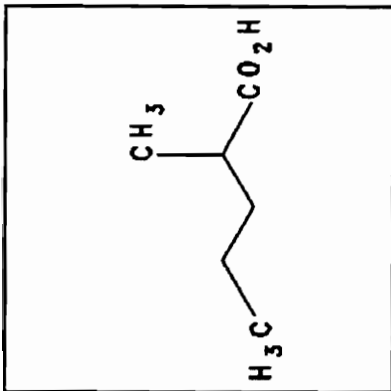
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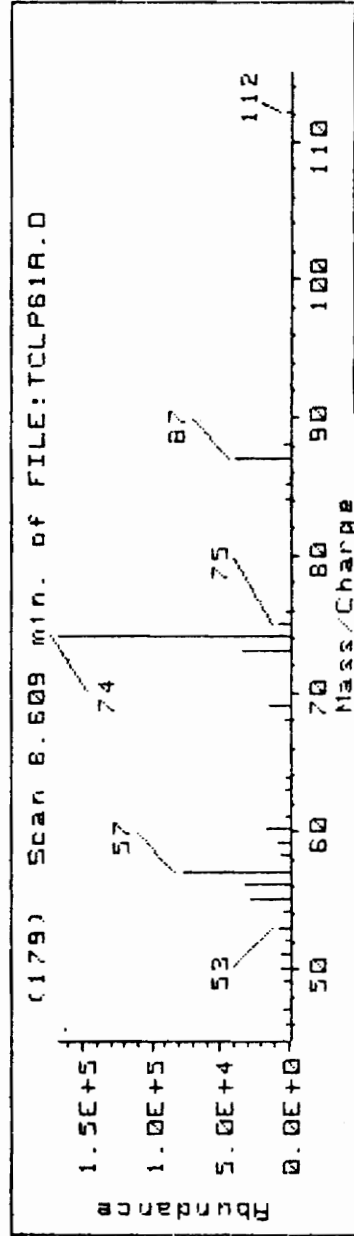
Benzoic Acid



Butanoic Acid

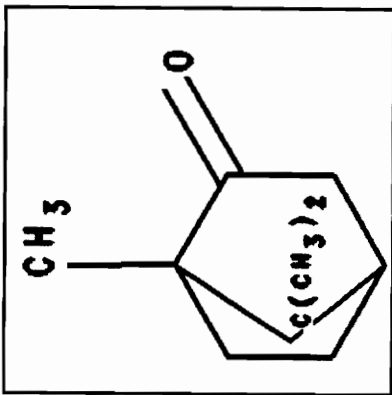


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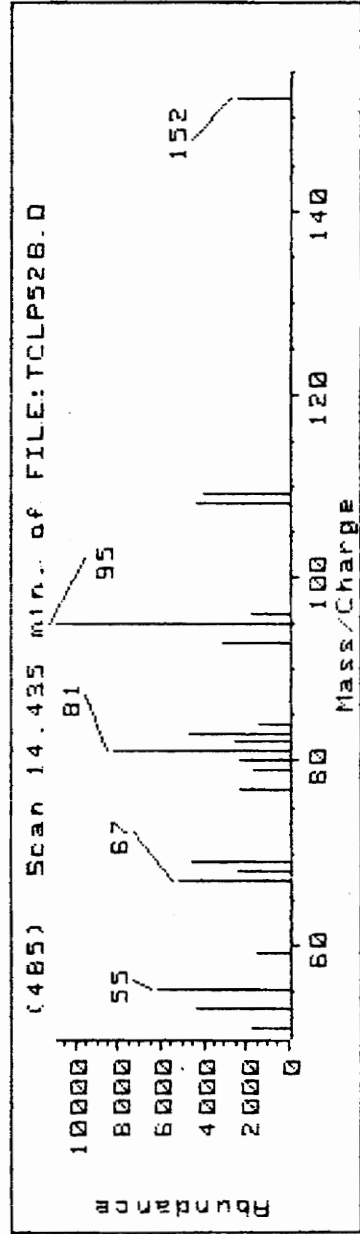


2-Methylbutanoic Acid

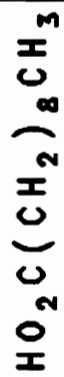




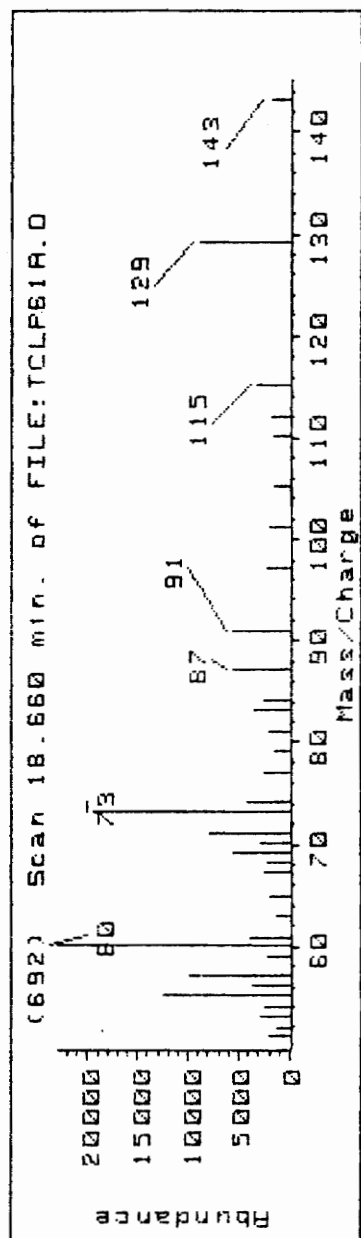
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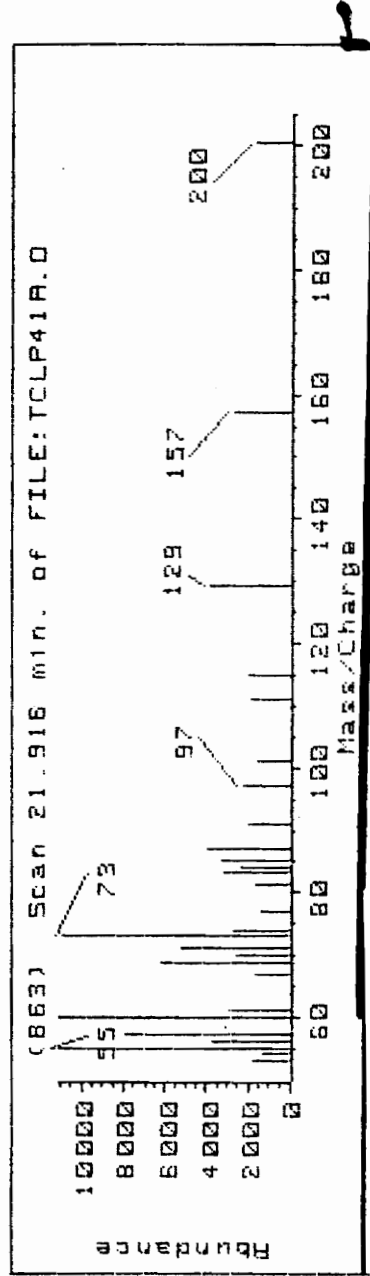
Camphor



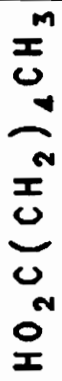
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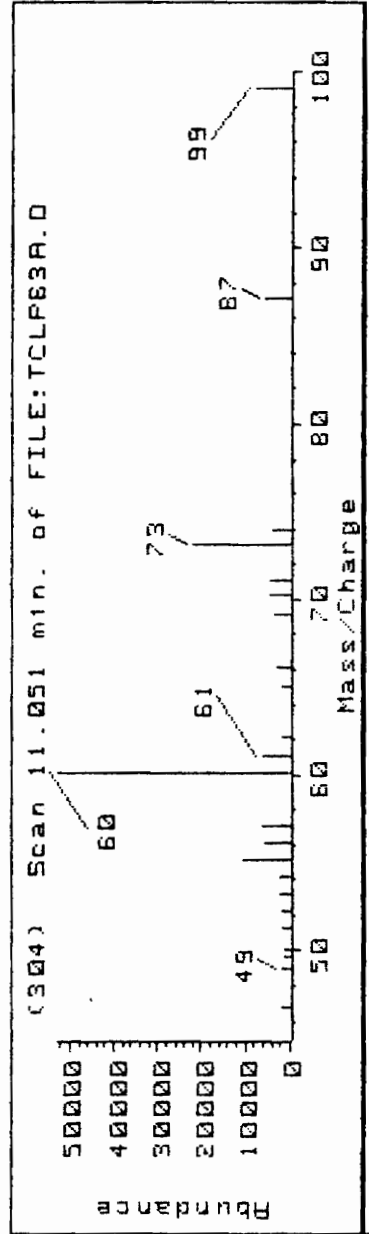
Decanoic Acid



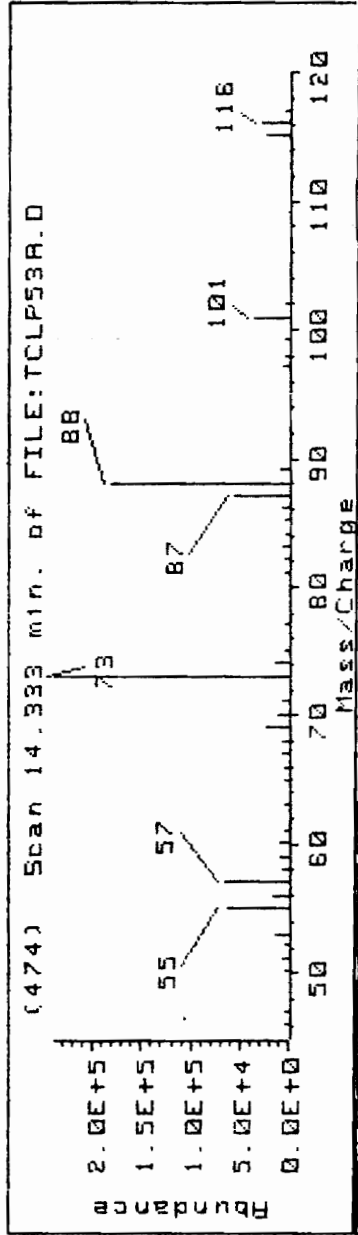
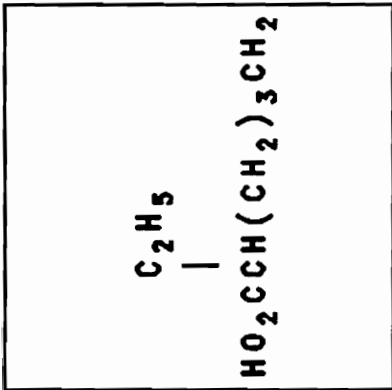
Dodecanoic Acid



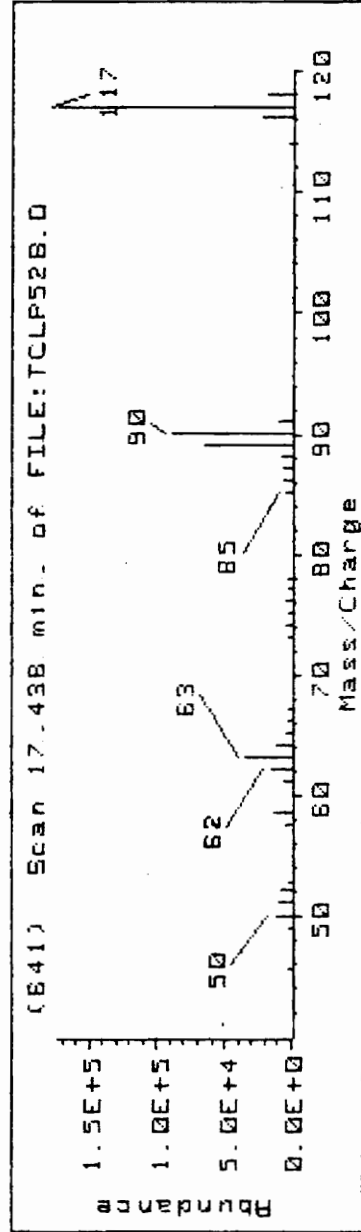
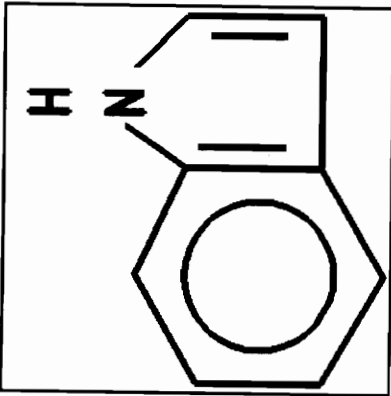
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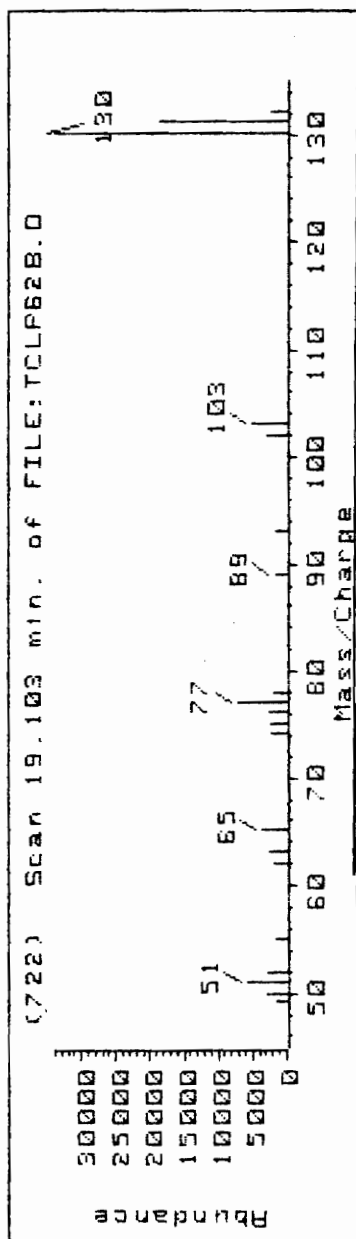
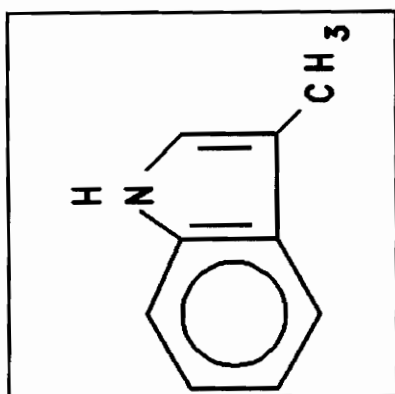
Hexanoic Acid



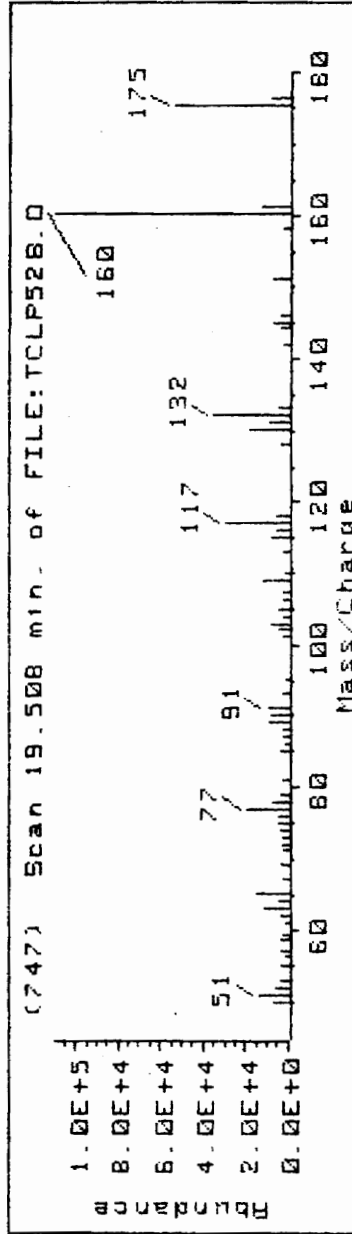
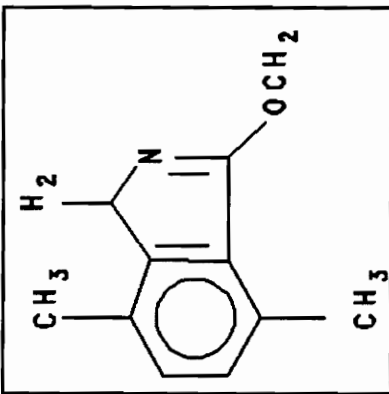
2-Ethylhexanoic Acid



1H-Indole

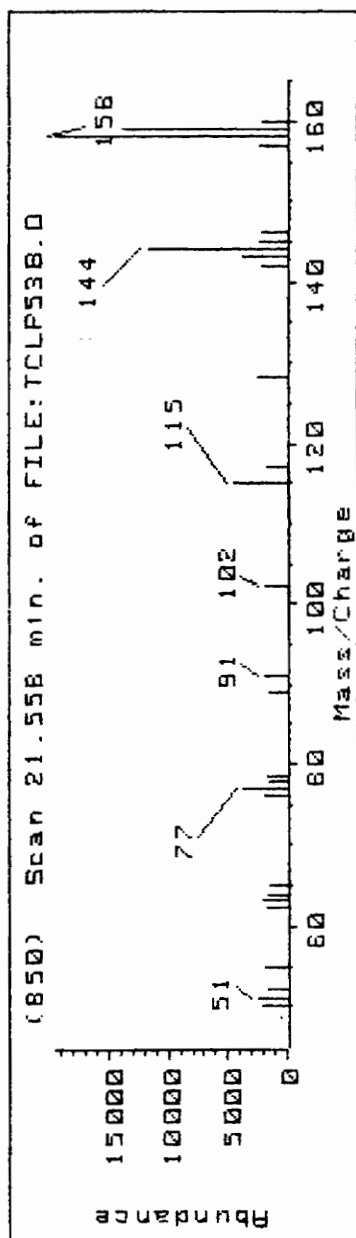
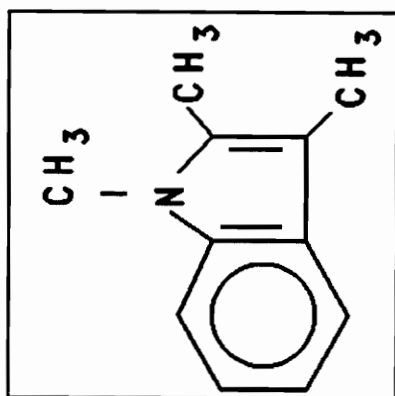


3-Methyl-1H-Indole

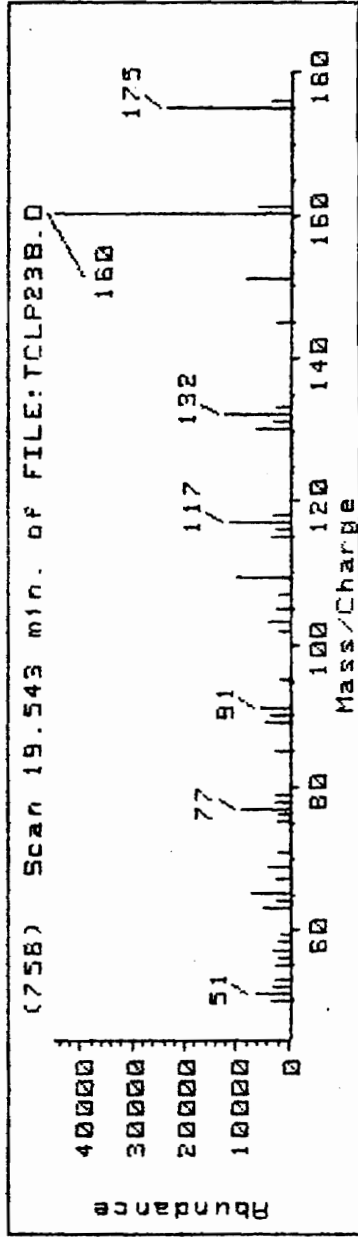
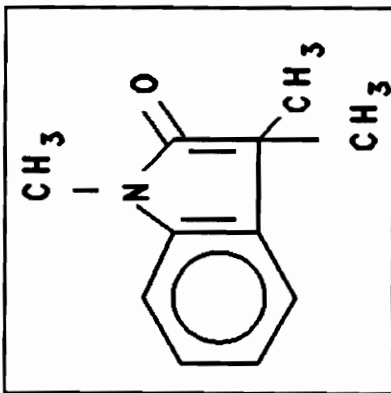


3-Methoxy-4,7-Dimethyl-1H-Indole

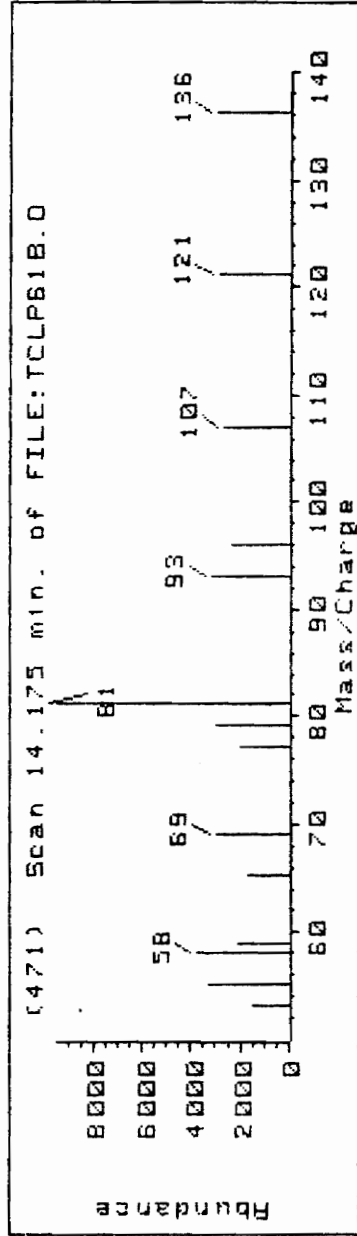
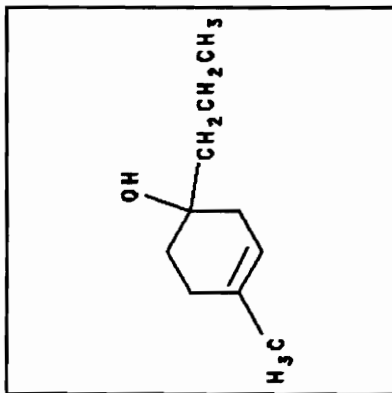




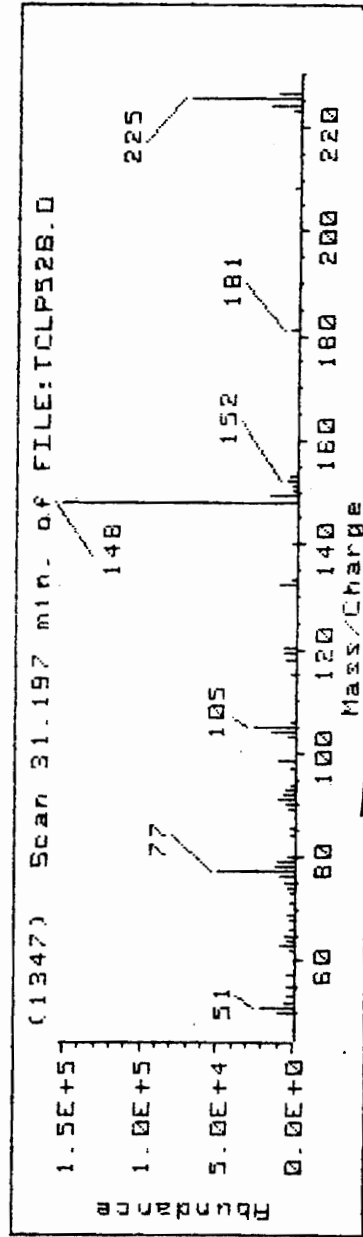
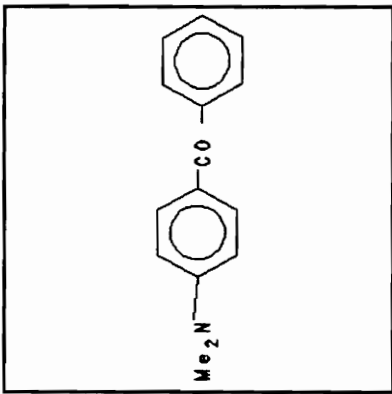
1,2,3-Trimethyl-1H-Indole



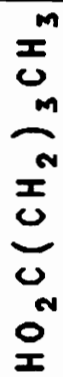
1,3,3-Trimethylindole



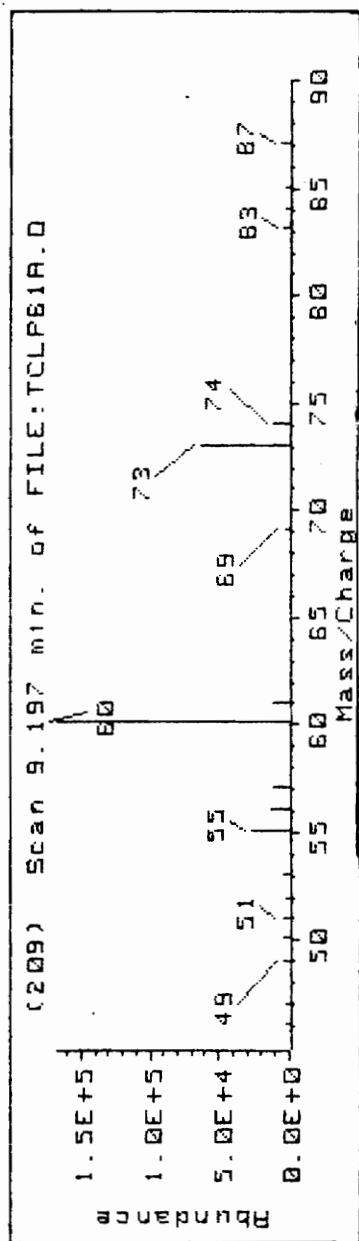
p-Menth-3-en-1-ol



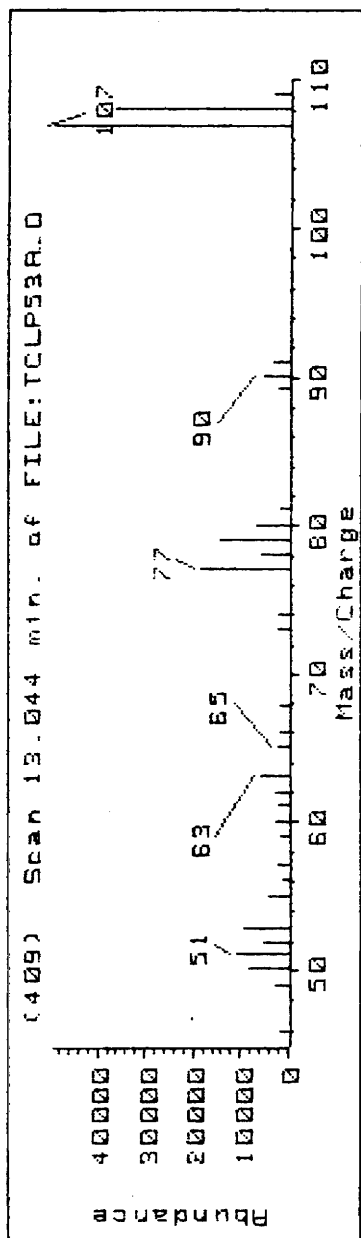
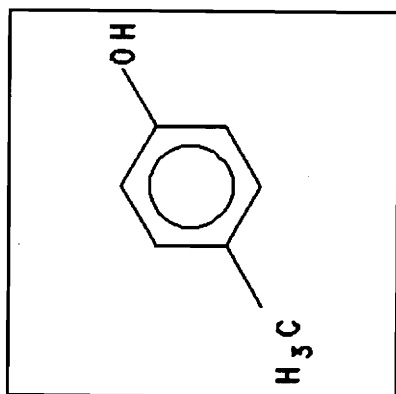
[4-(Dimethylamino)phenyl]-Phenyl-Methanone



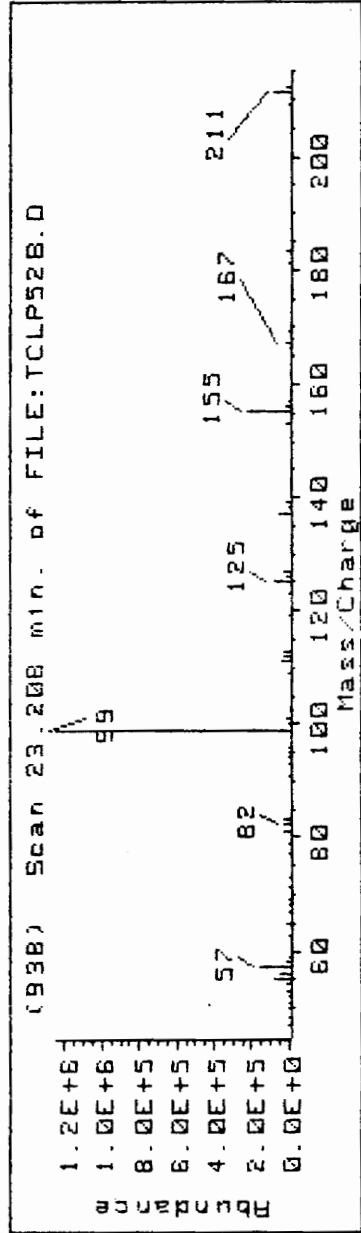
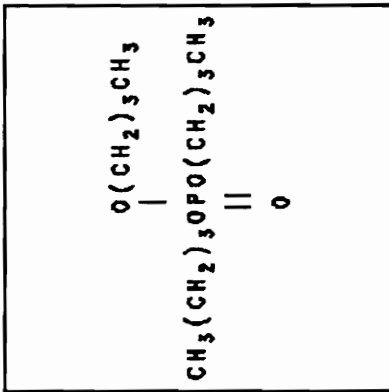
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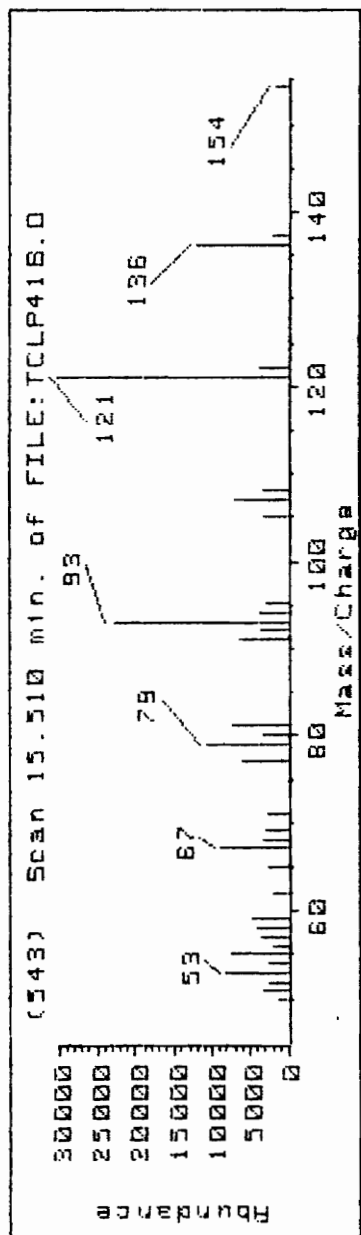
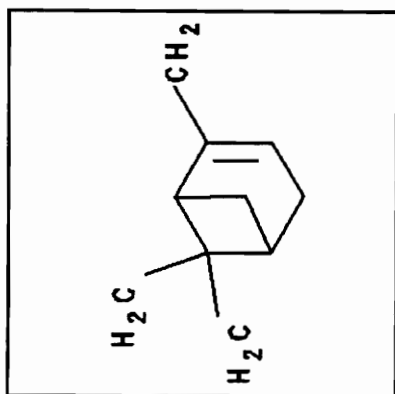
Pentanoic Acid



4-Methylphenol (p-Cresol)

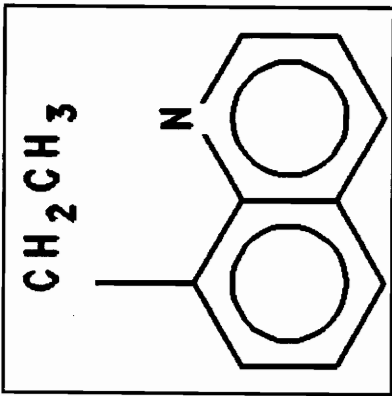


Tri-Butyl Ester of Phosphoric Acid

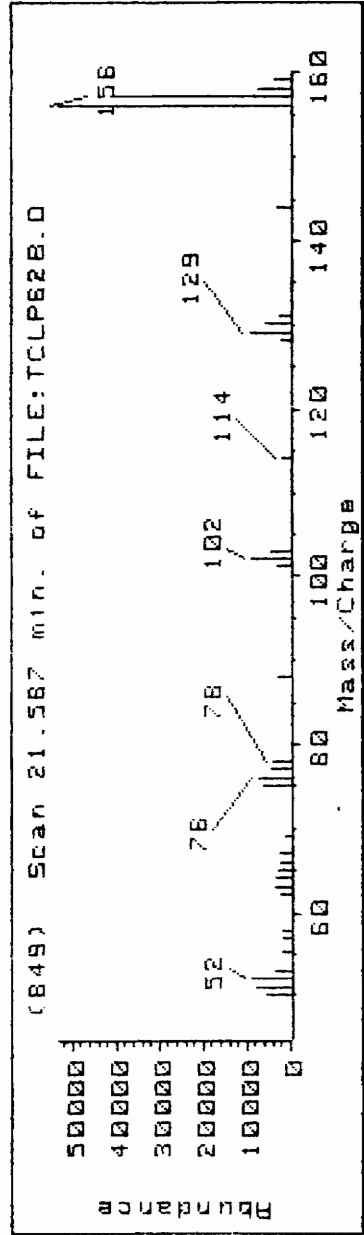


alpha-Pinene

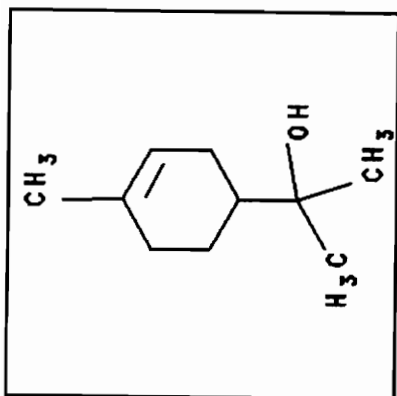




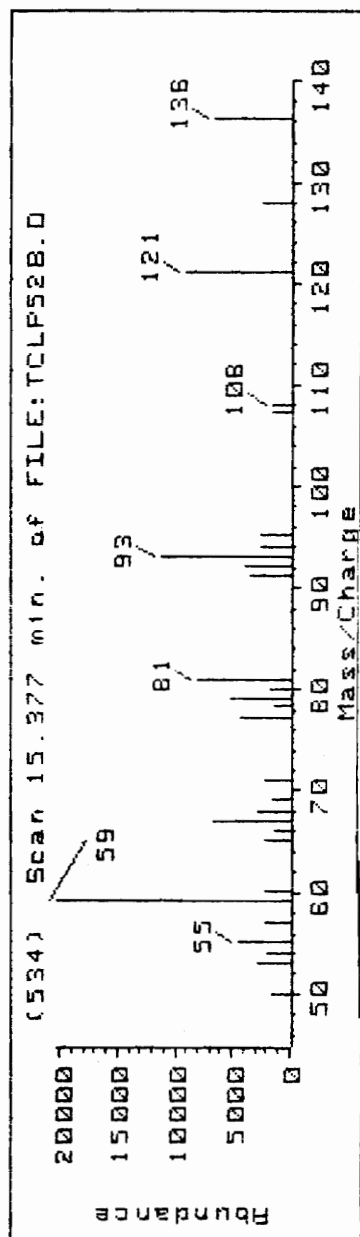
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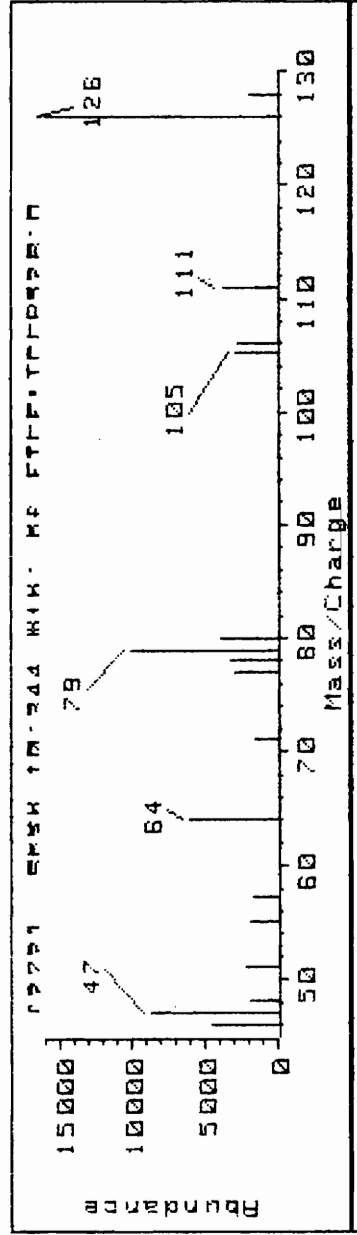
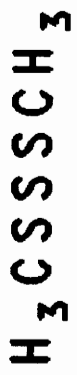
8-Ethylquinoline



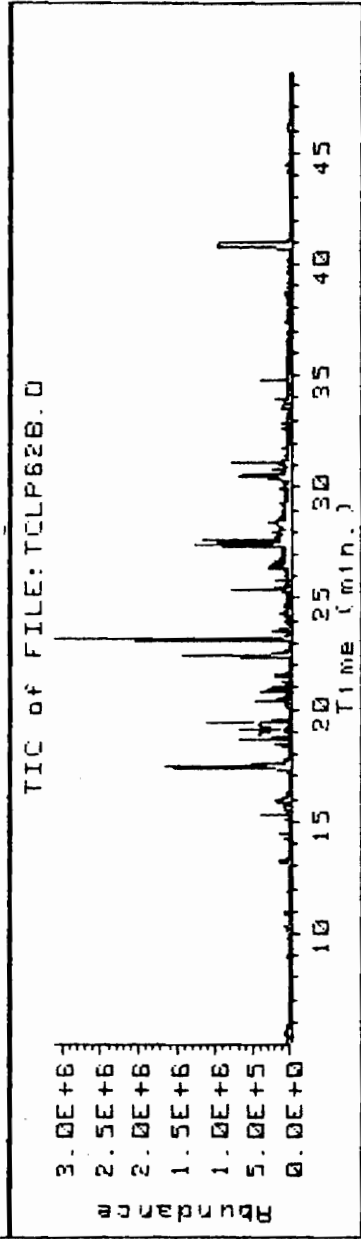
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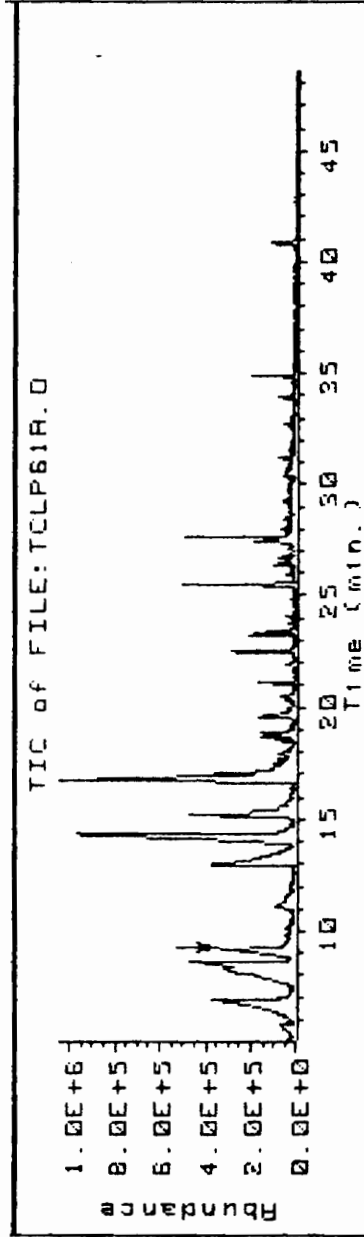
1- $\alpha$ -terpineol



Dimethyl Trisulfide



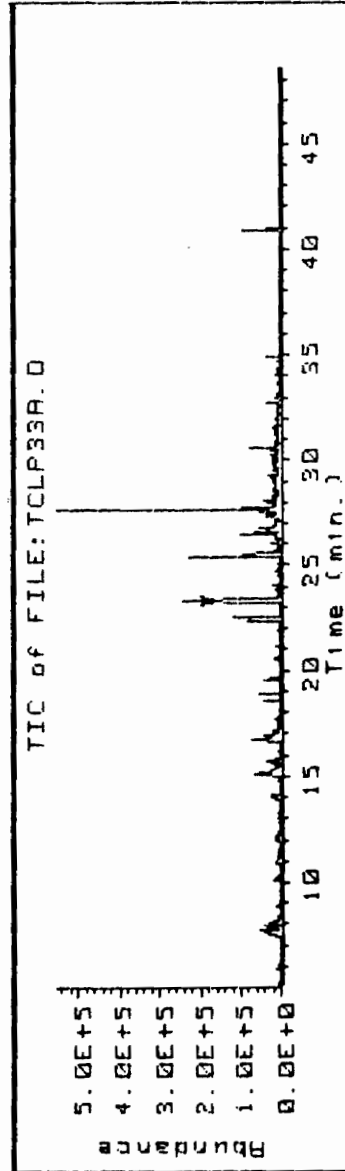
Typical Base/Neutral Fraction Chromatogram (Undigested Sludge)



Typical Acid Fraction Chromatogram (Undigested Sludge)



Typical Base/Neutral Fraction Chromatogram (Digested Sludge)



Typical Acid Fraction Chromatogram (Digested Sludge)

APPENDIX C  
ADMI COLOR CALCULATION



Color Values were analyzed using the American Dye Manufacturers Institute (ADMI) method. In this method three different wavelengths are measured, 590 nm, 540 nm, and 438 nm. Tristimulus values are determined based on the transmittance at each of these wavelengths. These tristimulus values relate the measured color to a position in color-space. Color-space is a term to describe shades in the textile industry. Color-space is defined to be a 3 dimensional matrix in which the axes are labeled L, A, and B. The L-axis measures the contrast of the shade. The A-axis measures the red-green position. The B-axis measures the yellow-blue position.

Distilled water is used as a pure solvent reference point (0,0,0). The color value is calculated to be the distance from that reference point in color-space. Munsell values based on the tristimulus value is calculated using a curve-fit equation. A Quattro-Pro (Borland International, Inc., Scotts Valley, CA.) spreadsheet was used to make the color calculations. The transmittance values and dilution ratios were entered into the spreadsheet. The cell formulae are as follows:

A1: '590 %T

B1: '540 %T

```

C1: '438 %T
D1: +C1*0.1899 + A1*0.791
E1: @SQRT(D1/98.06)
F1: @ABS((30.646*E1) + (-97.172*E1^2) + (292.949*E1^3)+
(-608.85*E1^4) + (870.83*E1^5) + (-840.79*E1^6) +
(521.73*E1^7) + (-187.64*E1^8) + (29.73*E1^9) - 1.5324)
G1: +B1
H1: @SQRT(G1/100)
I1: @ABS((30.646*H1) + (-97.172*H1^2) + (292.949*H1^3)+
(-608.85*H1^4) + (870.83*H1^5) + (-840.79*H1^6) +
(521.73*H1^7) + (-187.64*H1^8) + (29.73*H1^9) - 1.5324)
J1: +C1*1.835
K1: @SQRT(J1/118.11)
L1: @ABS((30.646*K1) + (-97.172*K1^2) + (292.949*K1^3)+
(-608.85*K1^4) + (870.83*K1^5) + (-840.79*K1^6) +
(521.73*K1^7) + (-187.64*K1^8) + (29.73*K1^9) - 1.5324)
M1: @SQRT((0.23*(9.902-I1))^2 + ((9.904-9.902) - (F1-I1))^2
+(0.4*((9.902-9.91)-(I1-L1)))^2)
N1: 1272 (Fave)
O1: 5 (DILUTION RATIO)
P1: +M1*N1*O1

```

The cells F1, I1, and L1 compute the Muncell values based on ninth order equations. The cell N1 is a factor which depends on the spectrophotometer in use. The cell P1 is the resulting ADMI color value.

**APPENDIX D**

**STATISTICS:**

**ANOVA Results**

**t-Test Results**

LEVELS ENCOUNTERED DURING PROCESSING ARE:

PROCESS

1.000 2.000

TIME

1.000 2.000 3.000 4.000 5.000 6.000

#####

DEP VAR: ADMI N: 18 MULTIPLE R: 0.948 SQUARED MULTIPLE R: 0.898

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
PROCESS	31333.389	1	31333.389	53.572	0.000
TIME (PROCESS)	30540.444	4	7635.111	13.054	0.000
ERROR	7018.667	12	584.889		

#####

LEVELS ENCOUNTERED DURING PROCESSING ARE:

PROCESS

1.000 2.000

TIME

1.000 2.000 3.000 4.000 5.000 6.000

#####

DEP VAR: ARSENIC N: 18 MULTIPLE R: 0.913 SQUARED MULTIPLE R: 0.833

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
PROCESS	2.801	1	2.801	21.635	0.001
TIME (PROCESS)	4.962	4	1.241	9.584	0.001
ERROR	1.553	12	0.129		

#####

LEVELS ENCOUNTERED DURING PROCESSING ARE:

PROCESS

1.000 2.000

TIME

1.000 2.000 3.000 4.000 5.000 6.000

#####

DEP VAR:ALUMINUM N: 18 MULTIPLE R: 0.965 SQUARED MULTIPLE R: 0.932

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
PROCESS	684060.056	1	684060.056	98.175	0.000
TIME (PROCESS)	458861.556	4	114715.389	16.464	0.000
ERROR	83613.333	12	6967.778		

#####

LEVELS ENCOUNTERED DURING PROCESSING ARE:

PROCESS

1.000 2.000

TIME

1.000 2.000 3.000 4.000 5.000 6.000

#####

DEP VAR: BARIUM N: 18 MULTIPLE R: 0.966 SQUARED MULTIPLE R: 0.932

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
PROCESS	3912536.889	1	3912536.889	139.180	0.000
TIME (PROCESS)	735949.556	4	183987.389	6.545	0.005
ERROR	337335.333	12	28111.278		

#####

LEVELS ENCOUNTERED DURING PROCESSING ARE:  
PROCESS

	1.000	2.000				
TIME	1.000	2.000	3.000	4.000	5.000	6.000

DEP VAR: CADMIUM N: 18 MULTIPLE R: 0.766 SQUARED MULTIPLE R: 0.587

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
PROCESS	11.488	1	11.488	7.918	0.016
TIME {PROCESS}	13.297	4	3.324	2.291	0.120
ERROR	17.410	12	1.451		

LEVELS ENCOUNTERED DURING PROCESSING ARE:  
PROCESS

	1.000	2.000				
TIME	1.000	2.000	3.000	4.000	5.000	6.000

DEP VAR: CHROMIUM N: 18 MULTIPLE R: 0.803 SQUARED MULTIPLE R: 0.645

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
PROCESS	13.869	1	13.869	9.006	0.011
TIME {PROCESS}	19.642	4	4.911	3.189	0.053
ERROR	18.480	12	1.540		

LEVELS ENCOUNTERED DURING PROCESSING ARE:  
PROCESS

	1.000	2.000				
TIME						
	1.000	2.000	3.000	4.000	5.000	6.000

DEP VAR: COPPER N: 18 MULTIPLE R: 0.996 SQUARED MULTIPLE R: 0.992

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
PROCESS	2.442	1	2.442	1274.113	0.000
TIME {PROCESS}	0.295	4	0.074	38.493	0.000
ERROR	0.023	12	0.002		

LEVELS ENCOUNTERED DURING PROCESSING ARE:  
PROCESS

	1.000	2.000				
TIME						
	1.000	2.000	3.000	4.000	5.000	6.000

DEP VAR: IRON N: 18 MULTIPLE R: 0.986 SQUARED MULTIPLE R: 0.972

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
PROCESS	54.115	1	54.115	397.366	0.000
TIME {PROCESS}	3.488	4	0.872	6.403	0.005
ERROR	1.634	12	0.136		

LEVELS ENCOUNTERED DURING PROCESSING ARE:

PROCESS

1.000 2.000

TIME

1.000 2.000 3.000 4.000 5.000 6.000

#####

DEP VAR: LEAD N: 18 MULTIPLE R: 0.987 SQUARED MULTIPLE R: 0.974

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
PROCESS	59.405	1	59.405	381.889	0.000
TIME (PROCESS)	9.413	4	2.353	15.129	0.000
ERROR	1.867	12	0.156		

#####

LEVELS ENCOUNTERED DURING PROCESSING ARE:

PROCESS

1.000 2.000

TIME

1.000 2.000 3.000 4.000 5.000 6.000

#####

DEP VAR: MERCURY N: 18 MULTIPLE R: 0.570 SQUARED MULTIPLE R: 0.325

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
PROCESS	0.000	1	0.000	0.001	0.977
TIME (PROCESS)	0.036	4	0.009	1.447	0.278
ERROR	0.074	12	0.006		

#####



LEVELS ENCOUNTERED DURING PROCESSING ARE:  
PROCESS

	1.000	2.000				
TIME						
	1.000	2.000	3.000	4.000	5.000	6.000

DEP VAR:SELENIUM N: 18 MULTIPLE R: 0.703 SQUARED MULTIPLE R: 0.494

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
PROCESS	1.869	1	1.869	5.570	0.036
TIME (PROCESS)	2.064	4	0.516	1.538	0.253
ERROR	4.027	12	0.336		

LEVELS ENCOUNTERED DURING PROCESSING ARE:  
PROCESS

	1.000	2.000				
TIME						
	1.000	2.000	3.000	4.000	5.000	6.000

DEP VAR: SILVER N: 18 MULTIPLE R: 0.816 SQUARED MULTIPLE R: 0.667

ANALYSIS OF VARIANCE

SOURCE	SUM-OF-SQUARES	DF	MEAN-SQUARE	F-RATIO	P
PROCESS	0.020	1	0.020	18.000	0.001
TIME (PROCESS)	0.007	4	0.002	1.500	0.263
ERROR	0.013	12	0.001		

**ARSENIC:**

PAIRED SAMPLES T-TEST ON DIGESTED VS TCLP WITH 12 CASES

MEAN DIFFERENCE = 0.191  
SD DIFFERENCE = 0.048  
T = 13.646 DF = 11 PROB = 0.000

**BARIUM:**

PAIRED SAMPLES T-TEST ON DIGESTED VS TCLP WITH 12 CASES

MEAN DIFFERENCE = 11.035  
SD DIFFERENCE = 21.978  
T = 1.739 DF = 11 PROB = 0.110

**ALUMINUM:**

PAIRED SAMPLES T-TEST ON DIGESTED VS TCLP WITH 12 CASES

MEAN DIFFERENCE = 1836.748  
SD DIFFERENCE = 271.212  
T = 23.460 DF = 11 PROB = 0.000

**CADMIUM:**

PAIRED SAMPLES T-TEST ON DIGESTED VS TCLP WITH 12 CASES

MEAN DIFFERENCE = 0.071  
SD DIFFERENCE = 0.032  
T = 7.630 DF = 11 PROB = 0.000

**CHROMIUM:****PAIRED SAMPLES T-TEST ON DIGESTED VS TCLP WITH 12 CASES****MEAN DIFFERENCE = 2.322****SD DIFFERENCE = 0.615****T = 13.068 DF = 11 PROB = 0.000****COPPER:****PAIRED SAMPLES T-TEST ON DIGESTED VS TCLP WITH 12 CASES****MEAN DIFFERENCE = 0.288****SD DIFFERENCE = 0.078****T = 12.834 DF = 11 PROB = 0.000****LEAD:****PAIRED SAMPLES T-TEST ON DIGESTED VS TCLP WITH 12 CASES****MEAN DIFFERENCE = 5.406****SD DIFFERENCE = 1.926****T = 9.720 DF = 11 PROB = 0.000**

**SELENIUM:****PAIRED SAMPLES T-TEST ON DIGESTED VS TCLP WITH 12 CASES**

MEAN DIFFERENCE = 0.123  
SD DIFFERENCE = 0.068  
T = 6.246 DF = 11 PROB = 0.000

**SILVER:****PAIRED SAMPLES T-TEST ON DIGESTED VS TCLP WITH 12 CASES**

MEAN DIFFERENCE = 3.150  
SD DIFFERENCE = 1.310  
T = 8.331 DF = 11 PROB = 0.000

**IRON:****PAIRED SAMPLES T-TEST ON DIGESTED VS TCLP WITH 12 CASES**

MEAN DIFFERENCE = 1.158  
SD DIFFERENCE = 0.297  
T = 13.493 DF = 11 PROB = 0.000

## VITA

John D. Nelson was born September 15, 1961, in Natick Massachusetts. He attended Clarkson University in Potsdam, NY earning a Bachelor of Science in Civil and Environmental Engineering in 1983. He was commissioned an officer in the U.S. Army Corps of Engineers in 1983 serving in various command and staff positions in Germany, The Republic of Korea, and the United States. His last position before attending VPI & SU was with the Army Materiel Command Inspector General Office and The Department of Defense Inspector General Office where he served as an environmental engineer evaluating environmental issues affecting the DOD industrial community. He is currently a Captain and will be assigned to the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland, as an environmental engineer. John is a member of the American Chemical Society and the Society of American Military Engineers. He is a registered Intern Engineer in the State of New York.