

61749

ATTACHMENT O  
PART 2 OF 2

PCB BIOTRANSFORMATION IN  
AQUATIC SEDIMENTS:  
NEW BEDFORD HARBOR AND  
OTHER SITES



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APPENDIX I

TASK 11

PCB BACKGROUND INFORMATION  
RELEVANT TO THE NEW BEDFORD HARBOR PROJECT

(Y & A Project NMF-3003/Balsam Project 6002)

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DRAFT

## PREFACE

During the preparation of the interim and final reports for various tasks of this project, it became apparent that a basic understanding of fundamental PCB background information was necessary to assure the consistent interpretation of data evaluations. This document has been prepared to help accomplish that goal.

Additionally, much of the information in this document relates in one way or another to several of the various tasks assigned to Yoakum & Associates, Inc. (YAI). By providing this document for use as a background reference, the presentation of redundant information can be eliminated in individual reports.

Much of the information presented is available in the published literature; the basic references used during the preparation of this document are listed in the reference section. However, the source of a number of the chromatograms used to demonstrate pertinent pattern alterations will not be identified because of proprietary constraints relating to unpublished data. Permission has been obtained by YAI for the use of these chromatograms for illustrative purposes.

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## TERMS

"Additive Effect": To heighten or increase the intensity of a peak in a chromatogram (enhancement).

Aerobe: A microorganism that live only in air or free oxygen.

Aerobic microbial (bio)degradation: The reduction of a chemical component from a higher to a lower type by the action of aerobic microbes.

Anaerobe: A microorganism that flourishes without free air.

Anaerobic microbial (bio)degradation: The reduction of a chemical component from a higher to a lower type by the action of anaerobic microbes.

Anaerobic biotransformations: Changes brought about as the result of the action of anaerobic bacteria.

Anaerobic dechlorination: A specific PCB microbial degradation process whereby chlorine is selectively removed from a congener as the result of anaerobic microbial actions.

Aroclor: Trade name (Monsanto) for a series of commercial PCB and polychlorinated terphenyl mixtures marketed in the United States.

Aroclor degradation: A reductive modification with respect to the proportions of the individual PCB congeners present in the specific Aroclor.

Aroclor transformation: Any change (either reduction or enhancement) in the unique characteristic of the composition of a specific Aroclor.

Chromatogram: A tracing of the detector output from a chromatograph which consists of a series of peaks with time.

Chromatographic pattern alteration: Any change or modification which occurs in the chromatogram produced by a known reference material (e.g., a specific Aroclor).

Congener: One of the 209 PCBs or other group of compounds, not necessarily the same homolog.

Degrade: To reduce from a higher to a lower type.

Enhance: To heighten or increase in intensity.

## TERMS

Environmental aging (weathering): The process whereby the Aroclor(s) present in an environmental sample undergoes modification with respect to the proportions of individual PCB congeners present as the result of partial vaporization, adsorption onto surfaces, and/or extraction into water. True molecular solution in water is shown (on chromatograms) as the non-selective loss of the more volatile and more water-soluble congeners from the Aroclors in the sediments.

"High-end drop-off": The pattern alteration observed when higher chlorinated PCB congeners (usually penta- and hexa-) undergo anaerobic dechlorination.

High resolution gas-liquid chromatography: Gas chromatography with a capillary column.

Homolog: One of the 10 degrees of chlorination of PCBs ( $C_{12}H_nCl$  through  $C_{12}Cl_{10}$ ) or other group of compounds varying by systematic addition of a substituent.

Isomer: Any PCB or other compound which has the same molecular formula, different positional substitutions. 2,2'-Dichlorobiphenyl and 2,3-dichlorobiphenyl are isomeric; 4-chlorobiphenyl and 2,3,4-trichlorobiphenyl are not.

"Low-end drop-off": The pattern alteration observed when lower chlorinated PCB congeners are removed from samples by weathering.

Pattern alterations: Changes in a characteristic chromatographic pattern. The effect of the changes will be reflected by peak enhancements, reductions, or both. (See chromatographic pattern alterations.)

Polychlorinated biphenyl (PCB): One of 209 individual compounds having the molecular formula  $C_{12}H_nCl_{10-n}$ , where  $n = 0-9$ . This definition includes monochlorobiphenyls, but not biphenyl.

PCB degradation: A conversion whereby a PCB congener of a higher chlorine content is reduced (converted) to one of a lower chlorine content.

PCB "enrichment": A term used to describe compositional distribution differences between vapor phase and solid or liquid phase Aroclors. The vapor phase is enriched with lower chlorinated congeners relative to a specific Aroclor standard.

PCB transformation: Any change whereby a PCB congener is converted into another compound.

## TERMS

Qualitative: Having to do with establishing the presence of identity of a compound.

Quantitative: Having to do with measuring the amount or concentration of a compound in a sample.

Retention time: Time between injection and detection of a compound on a chromatographic system under specified conditions, expressed in seconds or minutes.

Transformation: Any change which gives a different appearance.

Weathering: A process which gives a compositional change in an Aroclor residue (see environmental aging).



## ABBREVIATIONS

p,p'DDE	1,1--Dichloro-2,2-bis (p-chlorophenyl) ethylene
p,p'DDT	1,1,1-Trichloro-2,2-bis (p-chlorophenyl) ethane
DDTR	A combination including DDT, DDD, and DDE
EC	Electron capture (detector)
EPA	(U.S.) Environmental Protection Agency
GC	Gas-liquid chromatography (column type unspecified)
GC/EC	Gas chromatography/electron capture
GC/MS	Gas-liquid chromatography/mass spectrometry (ionization mode unspecified)
HCB	Hexachlorobenzene
HRGC	High resolution gas-liquid chromatography
NBH	New Bedford Harbor
PCB	Polychlorinated biphenyl
RIC	Reconstructed ion chromatogram (in GC/MS)
RT	Retention time

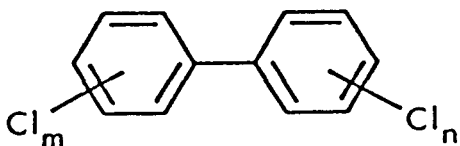
## BACKGROUND INFORMATION RELEVANT TO THE NEW BEDFORD HARBOR PROJECT

### 1.0 INTRODUCTION

The purpose of this document is to provide a brief overview of relevant polychlorinated biphenyl (PCB) properties and other pertinent facts. The treatment of these subjects is not intended to be comprehensive but rather to present sufficient background information to give the reader a better understanding of the topics which have been and/or will be covered in reports prepared in support of the New Bedford Harbor Project (YAI Project NMF-3003).

### 2.0 WHAT ARE PCBs?

The polychlorinated biphenyls (PCBs) are a class of chlorinated, aromatic compounds with biphenyl as the basic structural unit. Chlorination of the group can produce 209 discrete PCBs, called congeners, in which one to ten chlorine atoms are attached to a biphenyl unit.



$$m + n = 1 \text{ to } 10$$

The term "PCB" is a commonly used abbreviation which can refer to the entire class or any subset of one or more compounds. The entire class of 209 PCBs forms a set of "congeners." When PCBs are subdivided by degree of chlorination, the term "homolog" is used; e.g., the trichlorobiphenyl homolog. PCBs of a given homolog with different chlorine substitution positions are called "isomers." For example, there are twenty-four trichlorobiphenyl isomers. The composition of chlorinated biphenyls by homolog is found in Table 1.

Table 1. Composition of PCBs by Homolog

<u>Chlorine Substitution Level (Homolog)</u>	<u>Number of Possible Isomers</u>
Mono-	3
Di-	12
Tri-	24
Tetra-	42
Penta-	46
Hexa-	42
Hepta-	24
Octa-	12
Nona-	3
Deca-	<u>1</u>
Total:	209

The nomenclature for the biphenyl ring system involves the numbering system shown in Figure 1, where one ring system is assigned unprimed numbers and the other primed numbers. An example of the structure and nomenclature for an arbitrarily chosen pentachlorobiphenyl is illustrated in Figure 2.

Another important PCB nomenclature system pertains to the chlorine substitution position on one ring relative to the other ring. These positions are designated as ortho-, meta-, and para- and are abbreviated as o-, m-, and p-, respectively. The locations of these substitutional positions on the biphenyl ring system are shown in Figure 3.

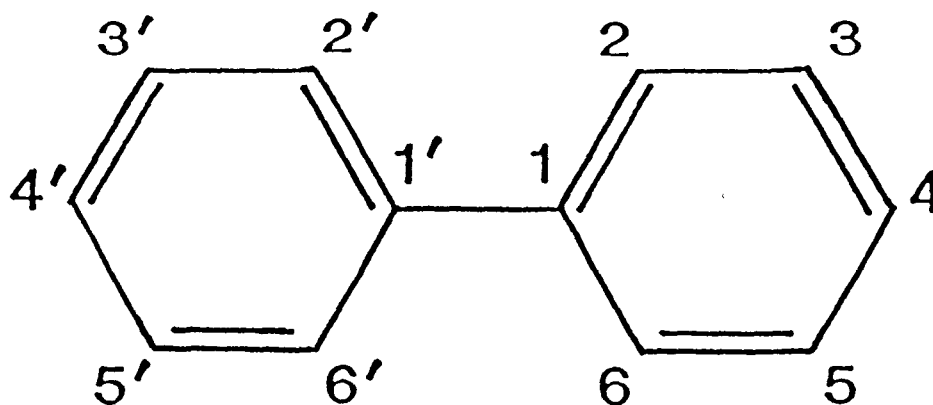


Figure 1. Numbering in the Biphenyl Ring System

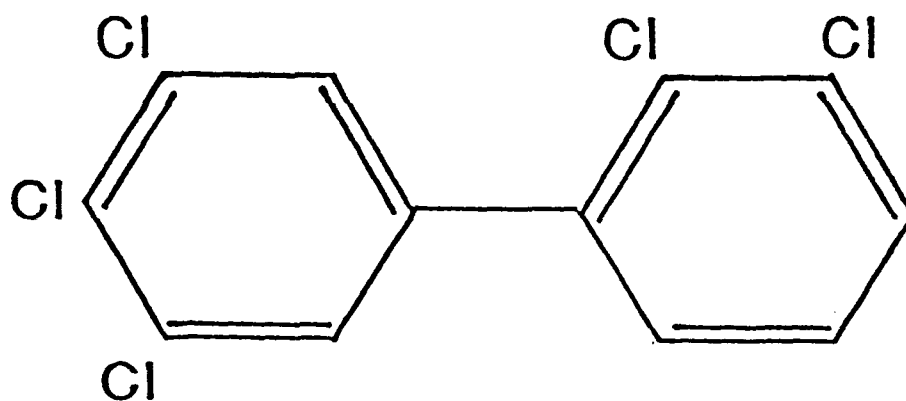


FIGURE 2. Structure of 2,3,3',4',5'-pentachlorobiphenyl

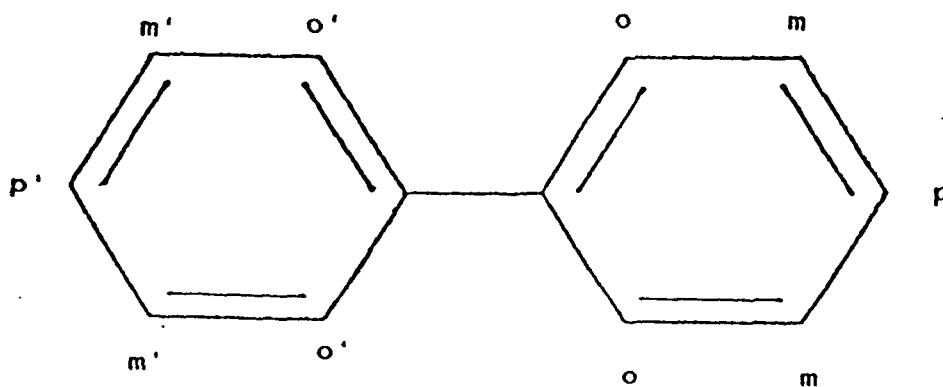


Figure 3. Substitution Positions on the Biphenyl Ring System

### 3.0 WHAT ARE AROCLORS?

Commercial production of PCBs began in 1929. They were synthesized by chlorination of biphenyl with chlorine gas in the presence of a catalyst, such as iron filings or iron chloride. The chlorination process produced complex mixtures of chlorobiphenyls which were influenced by the ratio of chlorine to biphenyl. Since the chlorination of biphenyl was carried out to a fixed weight gain, an invariance of original composition resulted for the various PCB products produced. The major world producer was the Monsanto Corporation, which manufactured PCBs from 1929 to 1977. Monsanto PCB products were marketed under the trade name Aroclor<sup>®</sup>. The most common Aroclor preparations included 1242, 1248, 1254, and 1260, with Aroclor 1242 being the most popular blend. The first two digits, 12, define the molecular structure of the Aroclor preparation and represent the number of carbon atoms in the biphenyl group (see Figure 1). The last two digits are an approximate percent by weight chlorine content in the PCB preparation (see Table 2).

Table 2. Chlorine Content of Aroclor Preparations\*

Aroclor	Approx. Cl (Weight %)	Avg. Number Cl/Molecule	Avg. Molecular Weight (g/mole)
1221	20.5-21.5	1.15	201
1232	31.5-32.5	2.04	232
1242	42	3.10	267
1248	48	3.90	300
1254	54	4.96	327
1260	60	6.30	375
1262	61.5-62.5	6.80	389
1268	68	8.70	453

\*Manufacturer's specifications

In 1971, Monsanto introduced a new PCB product, Aroclor 1016, for use as a replacement for Aroclor 1242. Aroclor 1016 was not named according to the established protocol. This new PCB product contained approximately

41% chlorine by weight, but the penta-, hexa-, and heptachlorobiphenyl content had been significantly reduced from those found in Aroclor 1242. The approximate compositions of Aroclors by homologs are presented in Table 3.

Table 3. Average Molecular Composition  
(wt.% ) of Some Aroclors

Homolog (Chlorines)	Aroclor						
	1221	1232 <sup>a</sup>	1016	1242	1248	1254	1260
0 (Biphenyl)	10						
1	50	26	2	1			
2	35	29	19	13	1		
3	4	24	57	45	22	1	
4	1	15	22	31	49	15	
5				10	27	53	12
6					2	26	42
7						4	38
8							7
9							1

<sup>a</sup>Five percent unidentified (Biphenyl?).

#### 4.0 PCBs IN THE ENVIRONMENT

PCBs found global applications because of their physical stability, chemical inertness and excellent dielectric properties. The stability of these compounds, which made them most desirable for industrial use, is also responsible for their environmental occurrence. PCBs may be considered ubiquitous pollutants. Once in the environment, PCBs accumulate in the biomass because of their lipid solubility and resistance to degradation.

In living matter, PCBs accumulate in tissues and organs of high lipid content. The accumulation appears to be higher in the case of penta- and more highly chlorinated biphenyls. Tetra- and less chlorinated biphenyls are more

readily metabolized. Metabolic rates are both isomer- and homolog-dependent. In general, the higher the homolog, the slower the metabolism.

Other properties of PCBs which are important in controlling their transport and distribution in the environment are solubility, vaporization and sorption. Solubility of PCBs in water is low and generally decreases with increasing chlorine content. Aqueous solubilities for selected Aroclors are given in Table 4.

Table 4. Solubility of Several Aroclors

<u>Aroclor</u>	<u>Solubility (ppb)</u>
1221	3,500
1232	1,450
1016	332
1242	288
1248	54
1254	42
1260	2.7

Source: Chou and Griffin (1986)

Vaporization of PCBs is extremely dependent on vapor pressures, which are directly related to the number and position of chlorine atoms on the biphenyl structure. Generally, the fewer chlorine molecules associated with the biphenyl structure, the lower its molecular weight and boiling point, and the higher its vapor pressure. PCBs, as a class of compounds, have very low vapor pressures. Vaporization rates for six common Aroclors are found in Table 5.

Table 5. Vaporization Rates of Six Aroclors Measured at 100°C

Aroclor (12.28 cm <sup>2</sup> surface)	Vaporization Rate (g/cm <sup>2</sup> /hr)
1221	0.00174
1232	0.000874
1242	0.000338
1248	0.000152
1254	0.000053
1260	0.000009

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Source: Shawhney (1986)

For a given Aroclor, the PCB congeners with the fewest chlorine atoms per molecule will be enriched in the vapor phase relative to the original Aroclor source. In environmental samples where PCBs are sorbed on soil or sediment surfaces, the rate of vaporization is greatly reduced and depends upon the sorption surface.

The transport and fate of PCBs in aquatic systems and their partitioning in different compartments of the environment depend to a large degree on sorption reaction. Generally, sorption increases with increase in chlorine content of the chlorobiphenyl, and with surface area and organic carbon content of the sorbent.

## 5.0 PCB ANALYSIS OF NEW BEDFORD HARBOR SAMPLES

Chemical analysis in support of the New Bedford Harbor (NBH) project has been performed, almost exclusively, by packed column gas chromatography using the electron capture (GC/EC) detector. Recent special studies have used capillary columns to improve separation of PCB congeners. A third approach,



used for the analysis of water samples, has been gas chromatography/mass spectrometry (GC/MS) for the determination of "isomer groups" (homologs) in the samples.

Clearly, no one technique is the best for all analyses and selection of the analysis mode to be used depends on the project needs. For an analysis where "total PCB" is the desired output, packed column GC/EC has been by far the most popular and useful analytical procedure for over 20 years. However, if congener-specific analysis is required, as is the case for the PCB degradation study, capillary column GC/EC is the technique of choice. Even with the superior separation afforded by capillary columns, the problem of co-elution of PCB congeners is not completely solved. Further identity confirmation may require the use of a definitive technique such as GC/MS.

#### 5.1 Analysis of PCBs by Packed Column GC/EC

Since the vast majority of the New Bedford Harbor samples have been analyzed by packed column GC/EC, this section will discuss the procedure and cover the difficulties most frequently associated with the determination of PCBs in environmental samples using this technique.

##### 5.1.1 Principles of the Technique

The function of the gas chromatograph (GC) is to separate complex mixtures and detect the individual components. The separation is accomplished by the column and the components are detected by the detector. The detection output consists of a series of peaks observed over time (a chromatogram). The separated peaks exit ("elute") from the GC column and are detected at different times. Measurement of the time required to elute through a given column yields a retention time (RT) which is reproducible for a given compound. GC analyses use elevated temperature so compound volatility affects the retention time. PCBs generally elute in order of chlorination: monochlorobiphenyls first, decachlorobiphenyl last; but there is considerable overlap in the middle homologs. The intensity of the peaks is generally proportional to the amount of the compound present.

#### 5.1.1.1 Separation of PCBs

The quality of the chromatography provided by a packed column is adequate for low resolution separation of the various Aroclors into discrete "fingerprints" for identification and/or quantitation.

#### 5.1.1.2 Detection of PCBs

The analysis of PCBs generally requires both selectivity and sensitivity of the GC detector. Even after cleanup, PCBs are usually a minor component of environmental and biological samples. They are frequently mixed with other halocarbons (e.g., DDE), hydrocarbons (especially oils) and lipids. Therefore, the detector must selectively detect PCBs in the presence of other compounds present at orders of magnitude higher concentration. In addition, the levels of PCBs typically observed in environmental and biological samples are in the parts per million and parts per billion concentration range.

Because of its extreme sensitivity and selectivity toward chlorine containing compounds, the electron capture detector (ECD) is the most common detector used for GC analysis of PCBs. The primary advantage of the EC detector is its ability to essentially ignore the vast majority of other sample components present in the sample extract. Although the EC detector is considered a selective detector, it does detect many non-PCB compounds (including halogenated organics, phthalate esters, polynuclear aromatics, and other compounds) which may be differentiated from PCBs only on the basis of retention time. The pattern alterations caused by these interferences will be covered in Section 6.0.

The main disadvantage of the EC detector is the disproportionality in response to different PCB congeners. Detector response is highly dependent on the degree and location of chlorination and can vary as much as two to four orders of magnitude between mono- and polychlorinated species. The EC response to 1 ng of five selected dichlorobiphenyls injected on the same GC column is illustrated in Figure 4. Dependent on the relative location of the two chlorine atoms on the biphenyl nucleus, a wide range of detector responses was obtained demonstrating the marked differences which exist within the same molecular weight group.

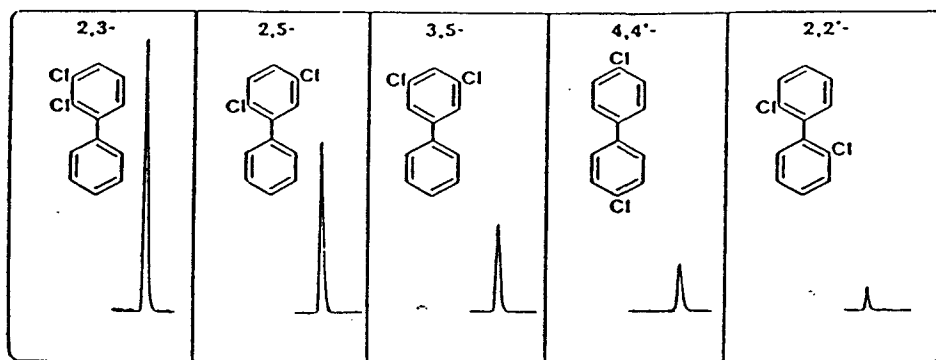


Figure 4. EC Responses for 1ng Injected On-column of Selected PCBs

Source: Cairns, et al. (1986)

The EC detector also shows increased sensitivity to the total number of chlorines in the PCB. The difference in response among homologs increases significantly from the mono- to trichlorobiphenyls. However, response factors for tetra- through heptachlorobiphenyls usually differ by no more than a factor of two.

#### 5.1.2 Major Problems Relating to PCB Determinations

Since Aroclors are complex mixtures of PCBs, they give a large number of peaks when analyzed by GC/EC. The complications induced by analyzing mixtures of PCBs rather than any single specific isomer are a serious impediment to both the identification and quantitation of the PCB residues present in environmental samples. As a consequence, PCB analysis is something of an art and considerable expertise is required of the analyst if reliable data are to be produced.

##### 5.1.2.1 Identification of Aroclors in Environmental Samples

Although the chromatographic patterns produced by the different Aroclors are distinctive, the most serious problem in identifying PCB residues is the inability to correlate the results with a known reference standard. The chromatograms obtained from samples containing PCBs frequently do not match the Aroclor standards. Many times, as is the case for the New Bedford Harbor samples, the PCB residues are a composite of two or more Aroclors. In addition,

some change in the composition of a commercial Aroclor may have occurred during use. On discharge to the environment, the Aroclors, whether used or not, can undergo further modification in respect to the proportions of individual PCB congeners present. Each congener will behave in different ways. The lower molecular weight compounds evaporate more rapidly, are more soluble in water and also react and degrade more readily. Even among the more highly chlorinated compounds, individual congeners do not behave and react uniformly. Samples which have undergone changes of this type are referred to as "weathered." As a consequence of these changes, the analysis of PCBs by packed column GC/EC becomes more difficult because of pattern alterations. Indiscriminate comparison of a weathered sample chromatogram with that of a standard Aroclor frequently provides results which can only be regarded as a compromise as to the identity of the Aroclor(s) present. In many situations it may be both inaccurate and misleading.

#### 5.1.2.2 Quantitation of Aroclors in Environmental Samples

As is the case in Aroclor identification, the selection of the appropriate standard(s) for the quantitation of PCBs in environmental samples is critical to the reliability of the data generated. Quantitation can be attempted only after the Aroclor(s) has been identified, although the required level of confidence in the identification can vary widely. When quantitation of PCBs in weathered samples is required, the accuracy of the data generated is directly related to the ability of the analyst to interpret PCB elution profiles correctly. The majority of PCBs found in environmental samples only resemble certain Aroclors in chromatographic pattern but do not match them exactly. Because of the disproportionality of the EC detector response (Section 5.1.1.2), the choice of a suitable reference standard can significantly affect the final analytical result.

Having made the necessary judgmental decision as to the most suitable standard to use, quantitation is accomplished by comparison of chromatographic profiles. The comparison can be carried out in a number of ways, including the use of total peak area, the area of one or more peaks, or the peak height of one or more peaks.

Since quantitation is usually the most labor-intensive step in the analysis of PCBs, the most widely used approaches to quantitation in recent years have involved the electronic integration of peaks in the chromatogram. However, the simplest automated integration routine sums the area of all peaks within a given retention time window. The total area is then compared to the corresponding area for an Aroclor standard and the concentration reported. Using this procedure, it is common practice to allow the major peaks of the sample chromatogram to be "off-scale." When this occurs, it is impossible to ascertain the true pattern of the sample and pattern alterations are unnoticed and ignored. When non-PCB peaks are present in the samples, a high bias occurs in the data.

A peak-by-peak comparison approach to quantitation rather than an integration window approach usually provides considerable improvement in the reliability of results generated by GC/EC. This approach was originally suggested by Webb and McCall (1973) and it is the quantitation method of choice for patterns not representing a single Aroclor.

Comparison of a chromatogram of a weathered sample with that of a standard Aroclor can only provide a crude assessment of the total quantity of PCBs present. In particular, it is important to note that quantitation in terms of a particular Aroclor should not imply that contamination by that Aroclor has necessarily occurred. The reporting of NBH PCB data as Aroclor 1248 appears to be a case in point as discussed in more detail in Section 6.1.

## 5.2 Analysis of PCBs by Capillary Column GC/EC

In recent years capillary columns have been developed for use in gas chromatography. Since the separation of individual PCB congeners is much more effective with these columns than with packed columns, the technique is called high resolution gas chromatography (HRGC). When the technique is properly used, substantially more resolution and information is provided by a capillary column chromatogram than a packed column chromatogram. An example of the packed column and capillary column chromatogram of a NBH sample is illustrated in Figure 5.

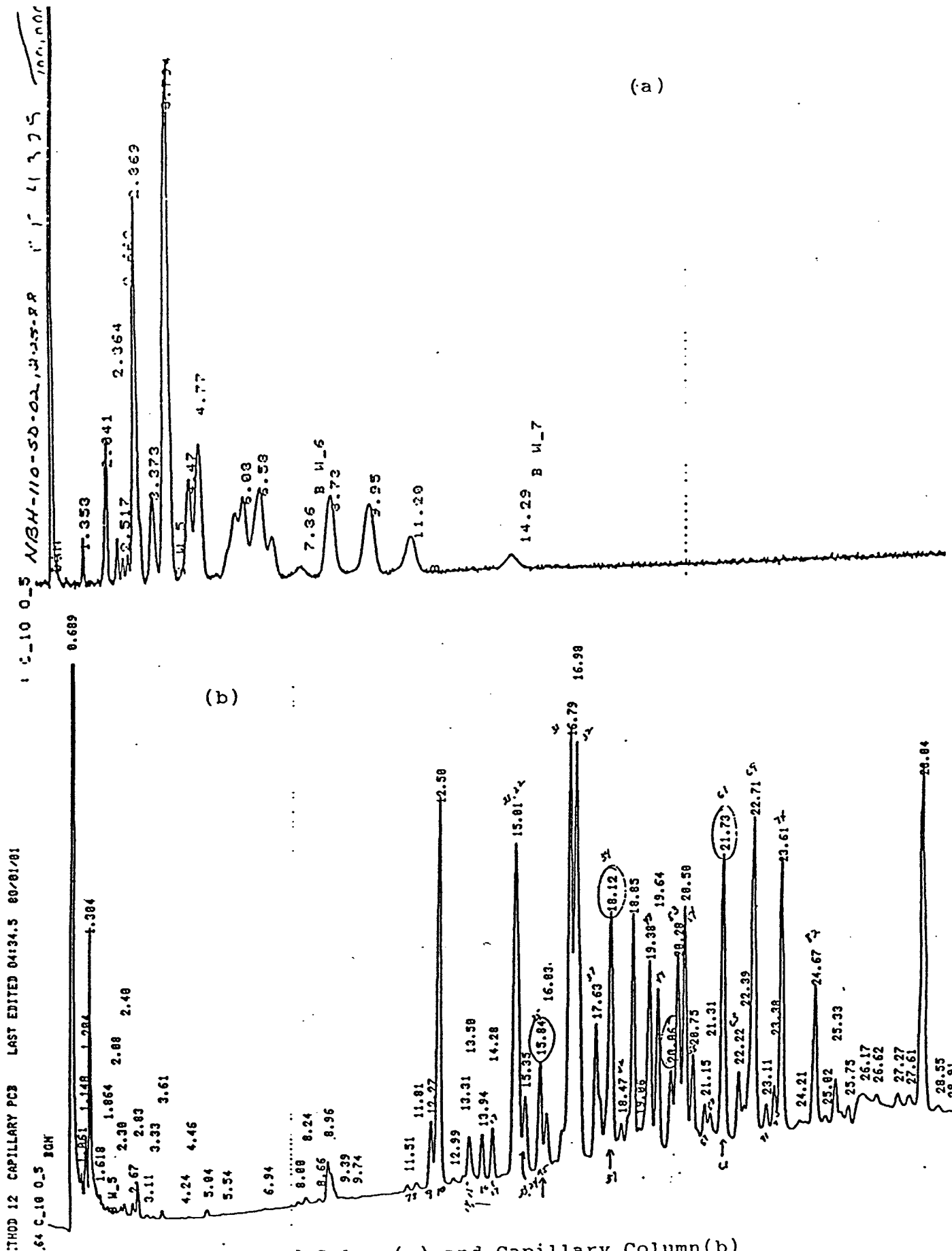


Figure 5. Packed Column(a) and Capillary Column(b) Chromatograms for NBH-110-02

Generally speaking, any PCB analysis which can be done by packed column GC may also be done by HRGC. The HRGC provides better resolution, and thus better qualitative reliability. Packed column GC yields a simpler chromatogram and is generally considered easier to use and more cost-effective. Pattern alterations are frequently more easily observed in the packed column chromatograms.

A special research project to determine the extent of anaerobic degradation of PCBs in NBH sediment samples is on-going. Since the study required individual PCB congener identification, capillary column GC/EC was required. Although the separation of the individual PCB congeners was substantially improved over the packed column chromatogram, co-elution of some isomers was apparent and confirmation of congener identity will require the use of GC/MS.

### 5.3 Analysis of PCBs by Gas Chromatography/Mass Spectrometry (GC/MS)

Electron impact mass spectrometry ranks second only to electron capture in popularity as a GC detector for PCBs. Mass spectrometry is particularly well suited to the detection of PCBs because of their intense molecular ion and the characteristic chlorine cluster. When operating in the full spectrum mode, sensitivity is considerably less than that of the EC detector.

Because of severe alterations of Aroclor patterns in water samples, a GC/MS procedure has been developed which determines the PCB content of samples by "isomer group" (homolog) levels. Representative congeners from each homolog group are utilized as single standards to quantitate all isomers in a given homolog. Battelle used this approach (EPA Method 680) for the analysis of the NBH filtrate samples.

## 6.0 ALTERATIONS IN THE GC/EC PATTERNS OF AROCLORS

The most serious problem encountered in the identification and subsequent quantitation of PCB residues in environmental samples is alterations of the characteristic GC/EC Aroclor patterns. Traditionally, GC/EC data have

been evaluated by visual pattern recognition. Increasingly, formal computerized pattern recognition routines are used to compare the PCB composition of samples.

The major causes of pattern alterations observed in NBH project samples are

- o the presence of two or more Aroclors in the same sample,
- o environmental aging or "weathering,"
- o metabolism in biological samples,
- o the presence of EC sensitive, non-PCB compounds in certain samples, and
- o degradation of Aroclors in sediment samples.

A brief discussion of these alterations and representative chromatograms illustrating the altered patterns are included in this section.

#### 6.1 Aroclor Mixtures in the Same Sample

When two or more Aroclors are mixed together, the alteration to the GC pattern is an additive or enhancement effect on peaks. This phenomenon is illustrated in Figure 6. Chromatogram (a) is an injection of 0.6 ng Aroclor 1248. Chromatogram (c) is 0.9 ng Aroclor 1254. The middle chromatogram (b) results from an injection containing a mixture of 0.6 ng Aroclor 1248 plus 0.9 ng Aroclor 1254.

To the casual observer, the middle chromatogram (b) in Figure 6 bears a striking resemblance to a number of NBH degraded sediment chromatograms. This similarity led to the erroneous reporting of the presence of Aroclor 1248 in numerous NBH sediment samples.

When Aroclor 1248 is reported to be present in a sample, but cannot be implicated as a significant PCB contamination source, chromatographic pattern alterations due to PCB transformation in other Aroclors are usually indicated. This is especially true when Aroclor 1016/1242 and Aroclor 1254 are present as mixtures in sediment samples (as is the case for upper Acushnet Estuary samples). Three sediment samples from New Bedford Harbor (one inner harbor



[illegible]

0.9 ng Aroclor 1254

Chromatogram showing 21 peaks labeled 1 through 21. The x-axis is labeled 'min' and the y-axis is labeled 'A.U.'.

Peak Number	Retention Time (min)
1	1.3
2	1.6
3	2.32
4	2.94
5	3.10
6	3.32
7	3.53
8	3.70
9	3.91
10	4.12
11	4.33
12	4.54
13	4.75
14	4.96
15	5.17
16	5.38
17	5.59
18	5.80
19	6.01
20	6.22
21	6.43

Hand-drawn NMR spectrum of 1,4-dichlorobenzene. The x-axis is labeled "PPM" and ranges from 0 to 10. The spectrum shows four distinct signals: a doublet at approximately 7.2 ppm, a doublet at approximately 7.6 ppm, a singlet at approximately 4.3 ppm, and a singlet at approximately 3.7 ppm. The signals are labeled with their chemical shifts: 7.20, 7.16, 7.01, 7.23, 7.12, 7.14, 7.13, 4.2, 4.20, 3.68, 3.59, and 3.37.

Figure 6. Illustration of Pattern Enhancement that occurs when Aroclors are mixed.

and two outer harbor) were analyzed for PCBs in a collaborative study sponsored by EPA (Alford-Stevens, 1985). Six laboratories analyzed the samples using packed column GC/EC, and four used capillary column GC/MS. All 10 laboratories identified the Aroclors present in the samples as mixtures of either 1016 and/or 1242 and 1254. It is significant that the presence of Aroclor 1248 in the samples was not reported by any of the participants, all of whom were considered by EPA to be experts in the field of PCB analysis. For this reason, it appears that a number of the laboratories involved in the NBH project lacked the expertise to make Aroclor identifications which are fully reliable.

Strikingly different patterns can result just from varying the ratio of Aroclors in the mixture. This is illustrated in Figure 7 where the (a) chromatogram results from an Aroclor 1242/Aroclor 1254 mixture ratio of 1.78 and the (b) chromatogram results from an Aroclor 1242/Aroclor 1254 mixture ratio of 0.35. The comparison of the patterns for the Aroclor 1242/Aroclor 1254 mixture ratio 1.78 standard and New Bedford Harbor sediment sample NBS-112-02 in Figure 8 illustrates a near perfect pattern match. No apparent degradation is evident in this sample.

Because of the compositional similarities between Aroclor 1242 and Aroclor 1016, it is difficult, if not impossible, to distinguish between Aroclor 1016 and/or Aroclor 1242 in an environmental sample if Aroclor 1254 is also present in that sample. The packed column GC/EC chromatograms of Aroclor 1016, Aroclor 1242, and Aroclor 1254 are shown in Figure 9. The differences in the chromatograms of Aroclor 1016 and Aroclor 1242 all occur beyond peak retention time 4.82 minutes. Since peak overlap from Aroclor 1254 begins to occur at retention time 3.76 minutes, the pattern difference between Aroclor 1016 and Aroclor 1242 is obscured by the additive effect of the peaks from Aroclor 1254 when it is present in a sample which also contains Aroclor 1016 and/or Aroclor 1242. A comparison of the chromatograms in Figure 10 clearly shows that even without the complication of environmental aging, it is impossible to distinguish between the Aroclor 1242/Aroclor 1254 mixture (a) and the Aroclor 1016/Aroclor 1254 mixture (b) based on packed column GC/EC patterns.

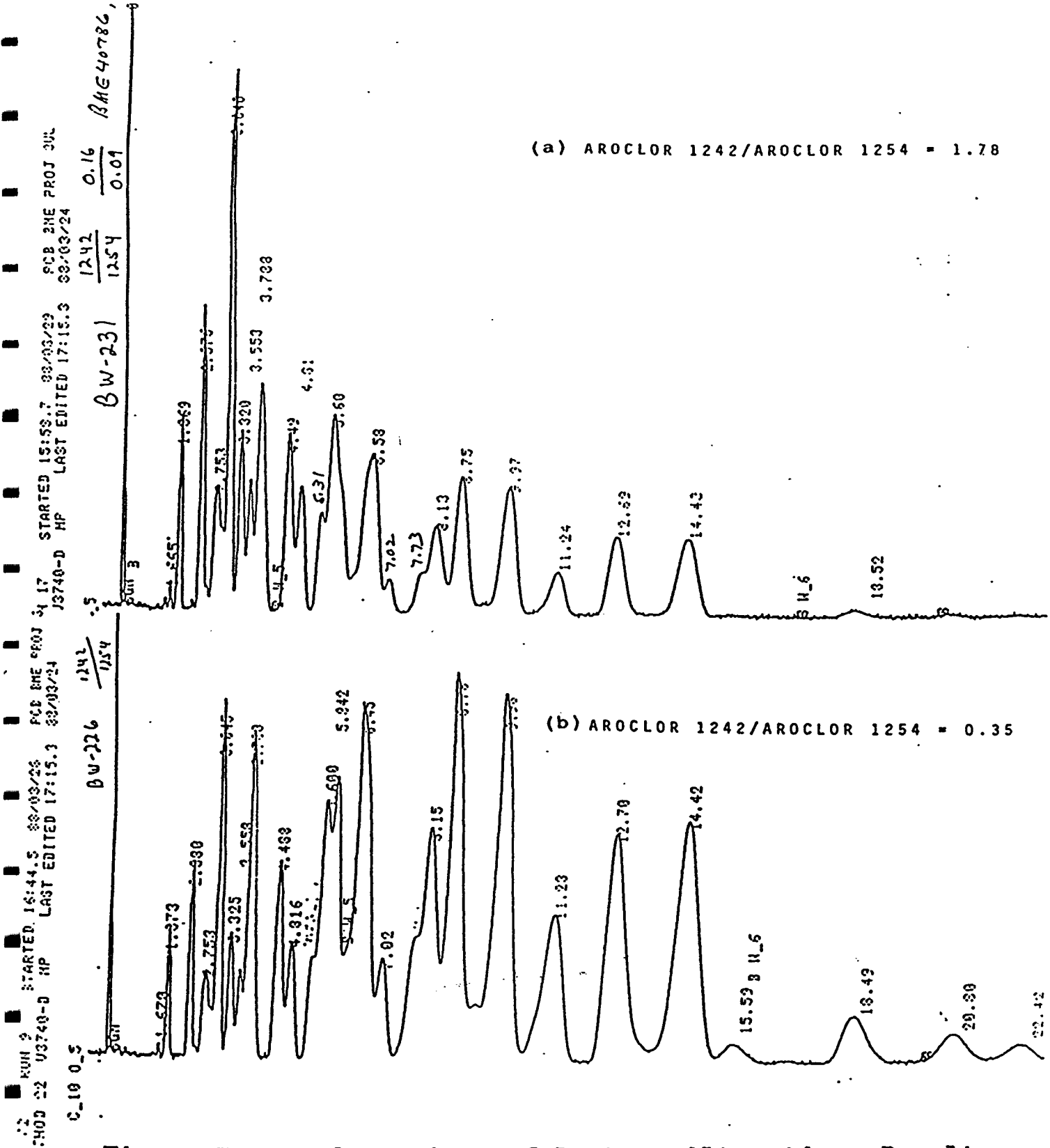
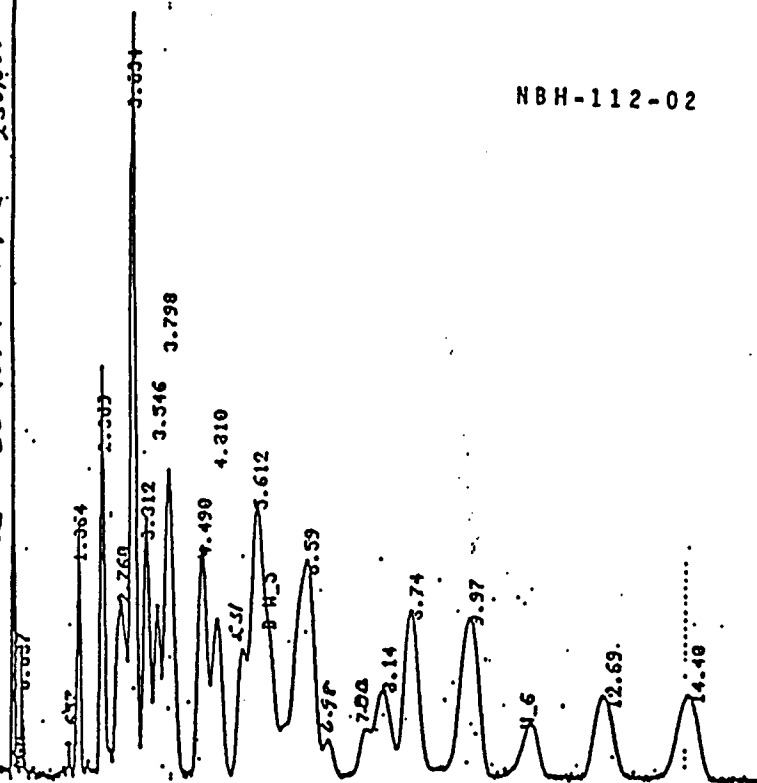


Figure 7.

Comparison of Pattern Alterations Resulting from Two Different Aroclor 1242/1254 Mixtures

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 400 22 U3740-D HP LAST EDITED 17:15.3 83/03/24

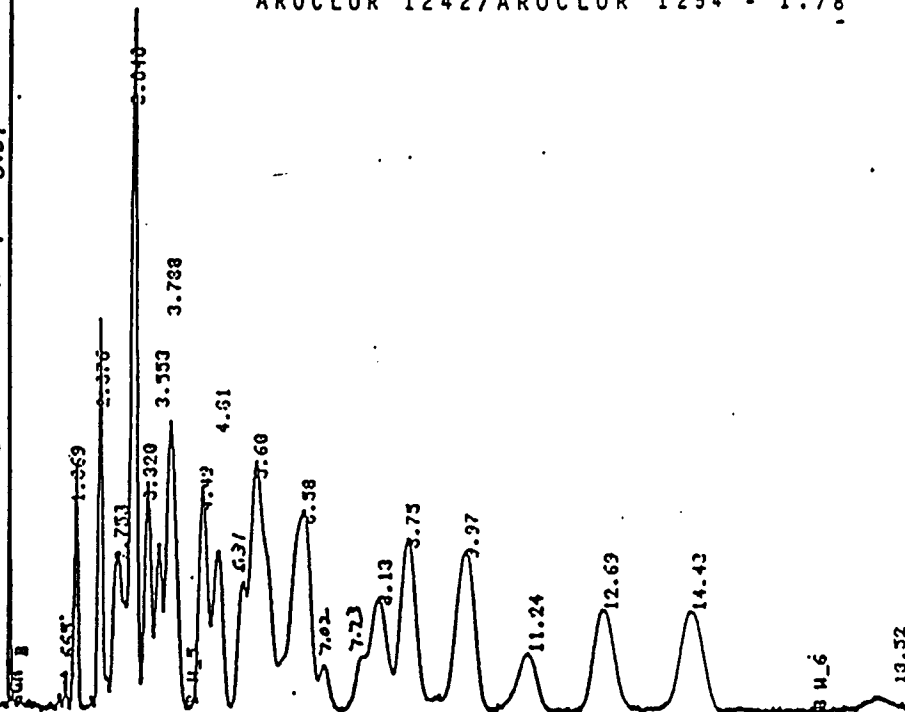
1 C-10 0.5 NBH-112-50-02 EE 4329 Hy (P) 250,000 BME H0005 0.45



NBH-112-02

10 RUN 17 STARTED 13:53.7 83/03/29 PCB BNE PROJ 3UL  
 400 22 U3740-D HP LAST EDITED 17:15.3 83/03/24

1 C-10 0.5 BW-231 1242 1254 0.16 0.09 BME 40782, BM E4020 0.160



AROCLOR 1242/AROCLOR 1254 - 1.78

Figure 8. Comparison of Patterns for Sample NBH-112-02 and 1.78 Ratio Aroclor 1242/1254 Standard

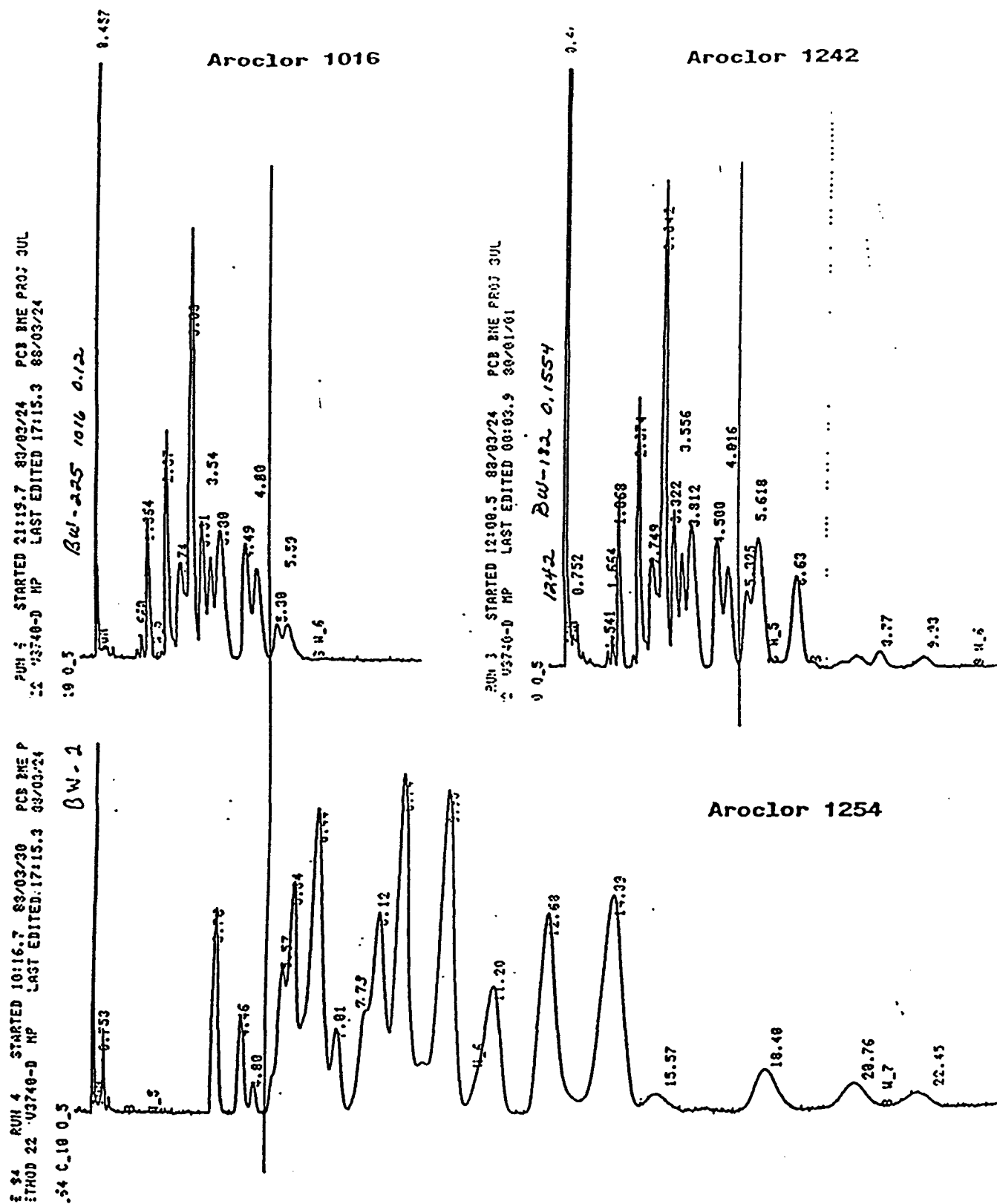


Figure 9. Standard Chromatograms - Aroclor 1016, Aroclor 1242, and Aroclor 1254

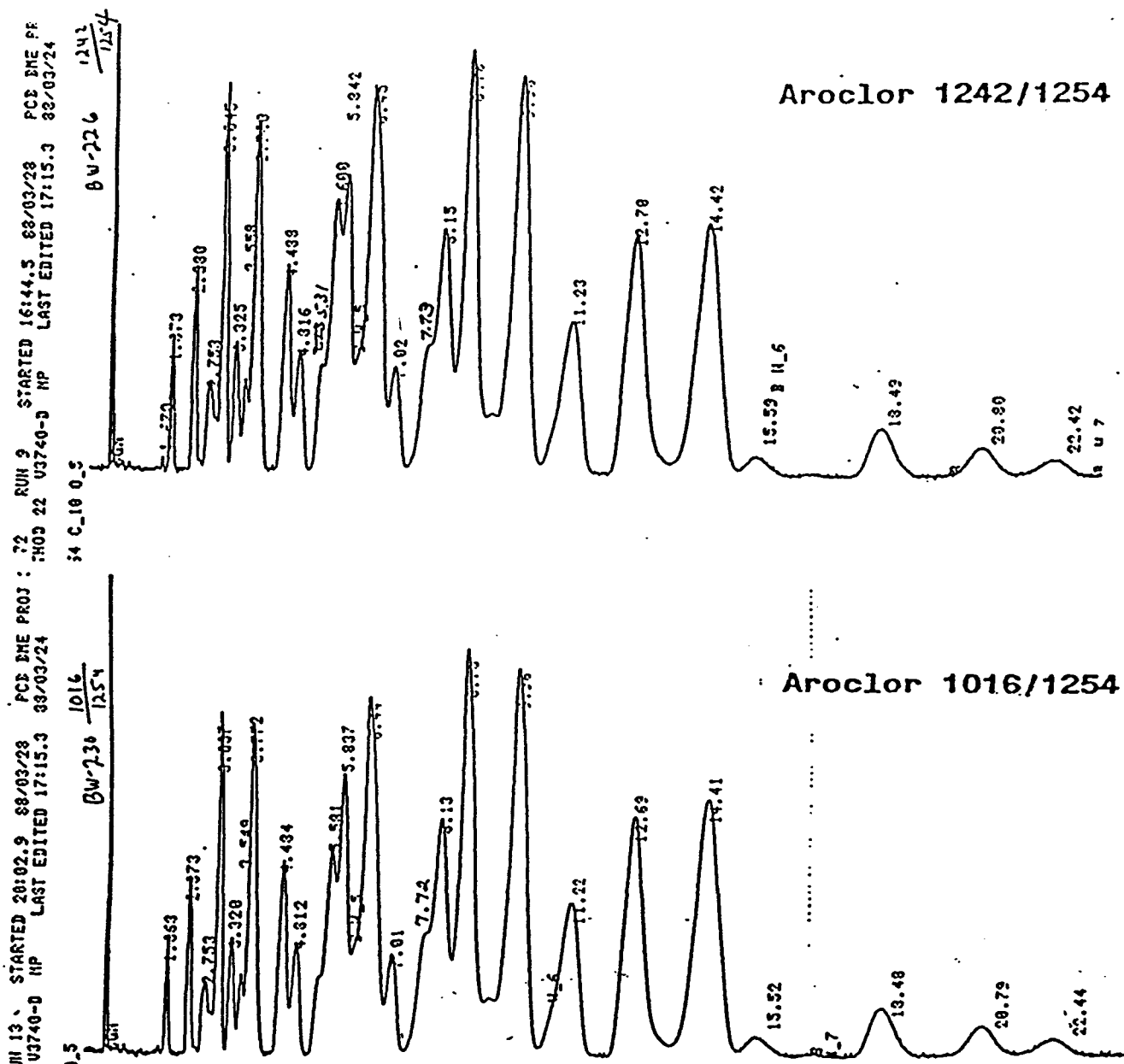


Figure 10.

Comparison of Chromatograms for  
 Aroclor 1242/1254 and Aroclor 1016/1254  
 Mixtures

It has been suggested that through the use of the higher resolution afforded by capillary column GC/EC, it is possible to ascertain the difference between a mixture of Aroclor 1016 and Aroclor 1254 and a mixture of Aroclor 1242 and Aroclor 1254 in environmentally aged samples. However, an attempt to verify this suggestion has been unsuccessful.

## 6.2 Environmental Aging or "Weathering"

Environmental aging or "weathering" of Aroclors in environmental samples is demonstrated by alterations in the standard Aroclor patterns. When alterations do occur, they are due to the fact that Aroclors do not behave as a homogeneous substance. Differences in volatility and water solubility of the individual PCBs tend to fractionate the residue. A weathered sample has undergone modification with respect to the proportions of individual PCB congeners present.

Loss of more volatile or soluble congeners yields a residue which demonstrates low-end drop-off and, usually, a high-end enhancement of peaks. An environmentally aged sediment sample containing Aroclor 1016 is illustrated in Figure 11. This pattern shows both significant low-end drop-off and high-end enhancement of peaks. An example of an Aroclor 1260 residue which has undergone losses of its more volatile congeners is shown in Figure 12. It is by no means implied, however, that all environmental samples which contain Aroclors will demonstrate aging or weathering. The pattern of the sample shown in Figure 13 demonstrates a perfect match with the Aroclor 1260 standard.

A phenomenon termed "enrichment" is typically observed in air samples, where the earlier eluting peaks are enhanced due to vaporization as shown in Figures 14-17. In addition to the enrichment of the earlier eluting peaks, these chromatograms also show high end "drop-off" alterations.

Water samples which have been in contact with PCB contamination in sediments will frequently show this same enrichment of the earlier eluting peaks due to the preferential solubility of the lower chlorinated PCB congeners of the Aroclor. A preferential adsorption of higher chlorinated PCBs onto the surfaces

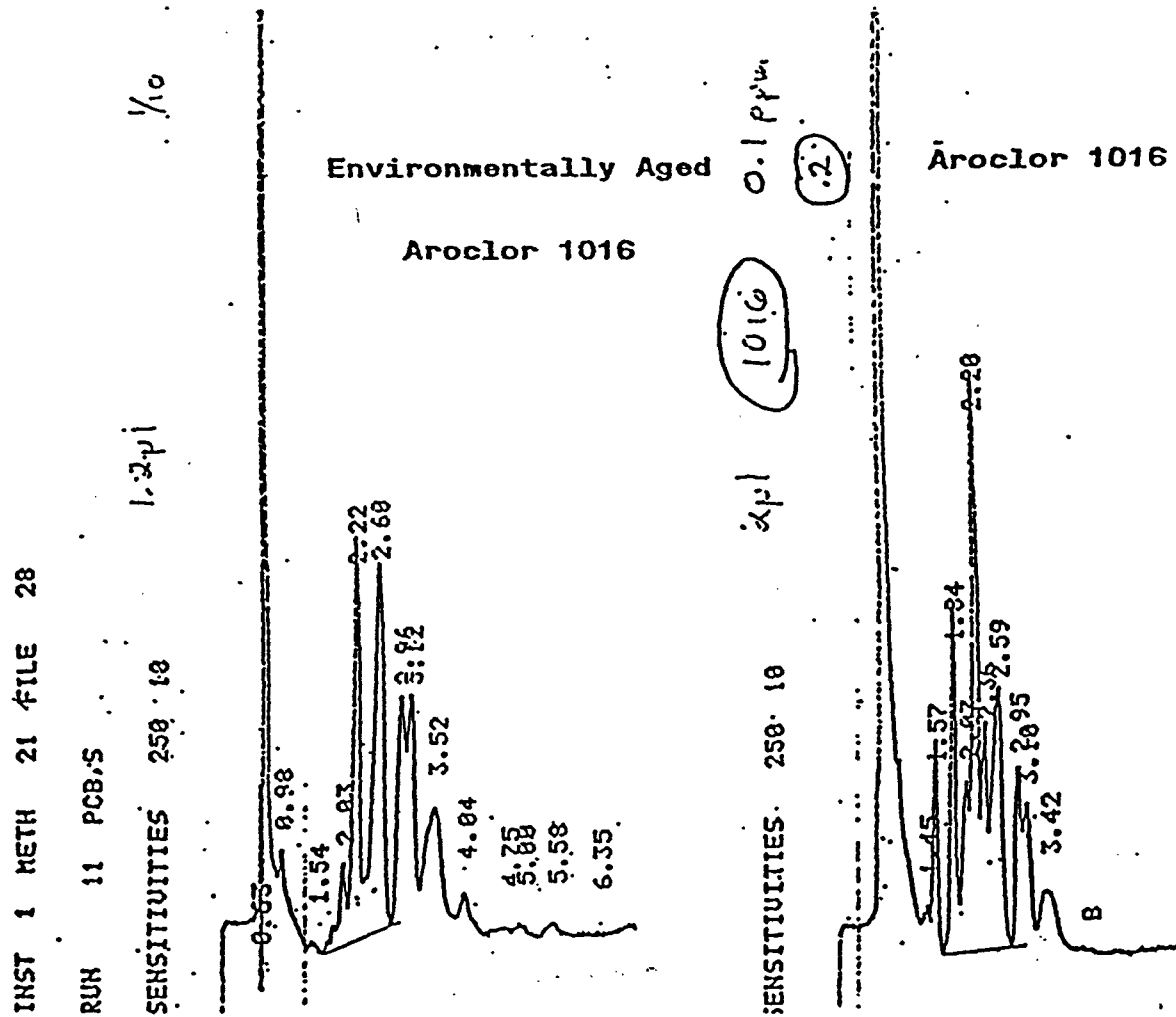


Figure 11. Environmentally Aged Aroclor 1016



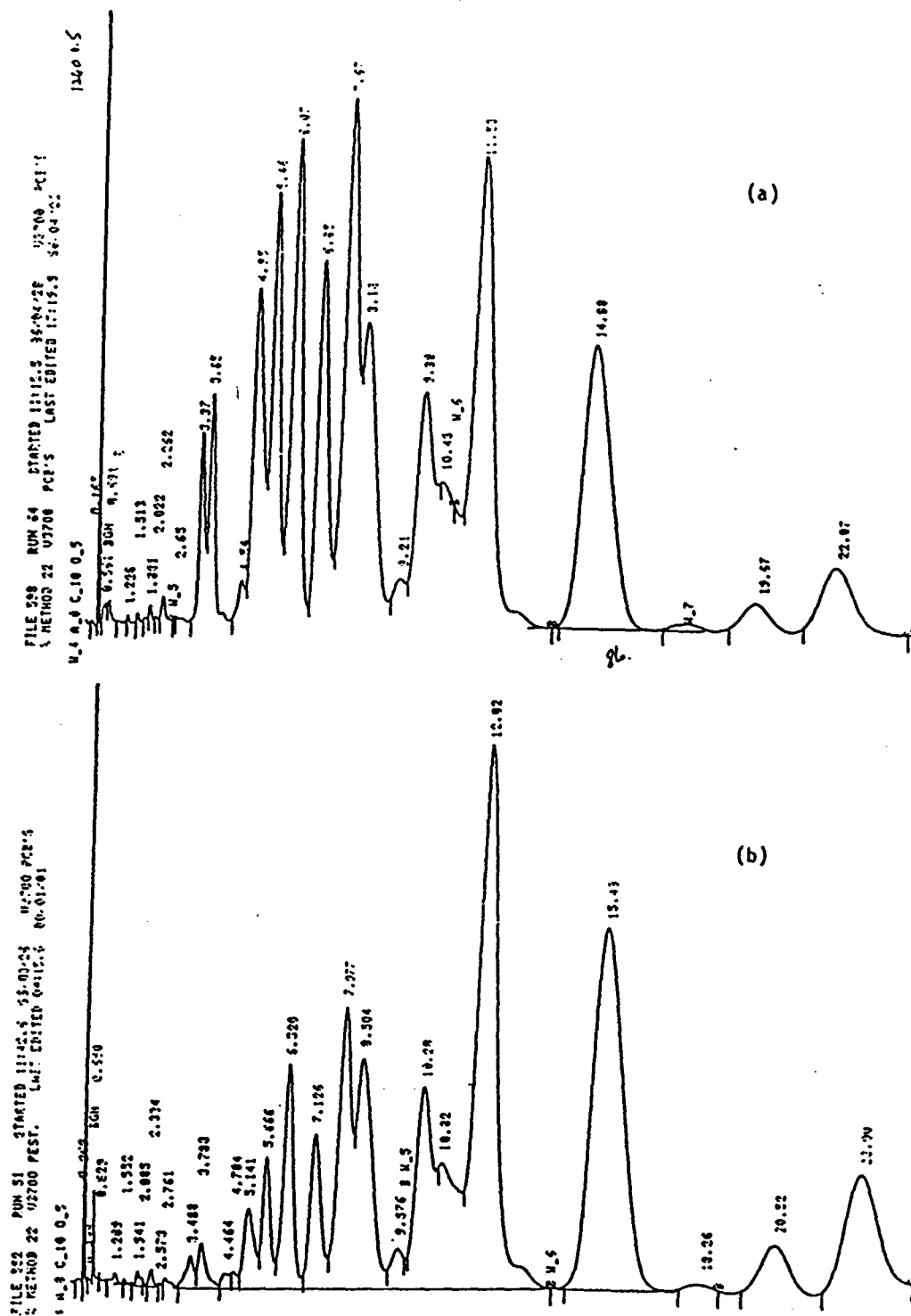


Figure 12. Aroclor 1260 Standard(a) and Heat Altered Aroclor 1260 Residue(b)

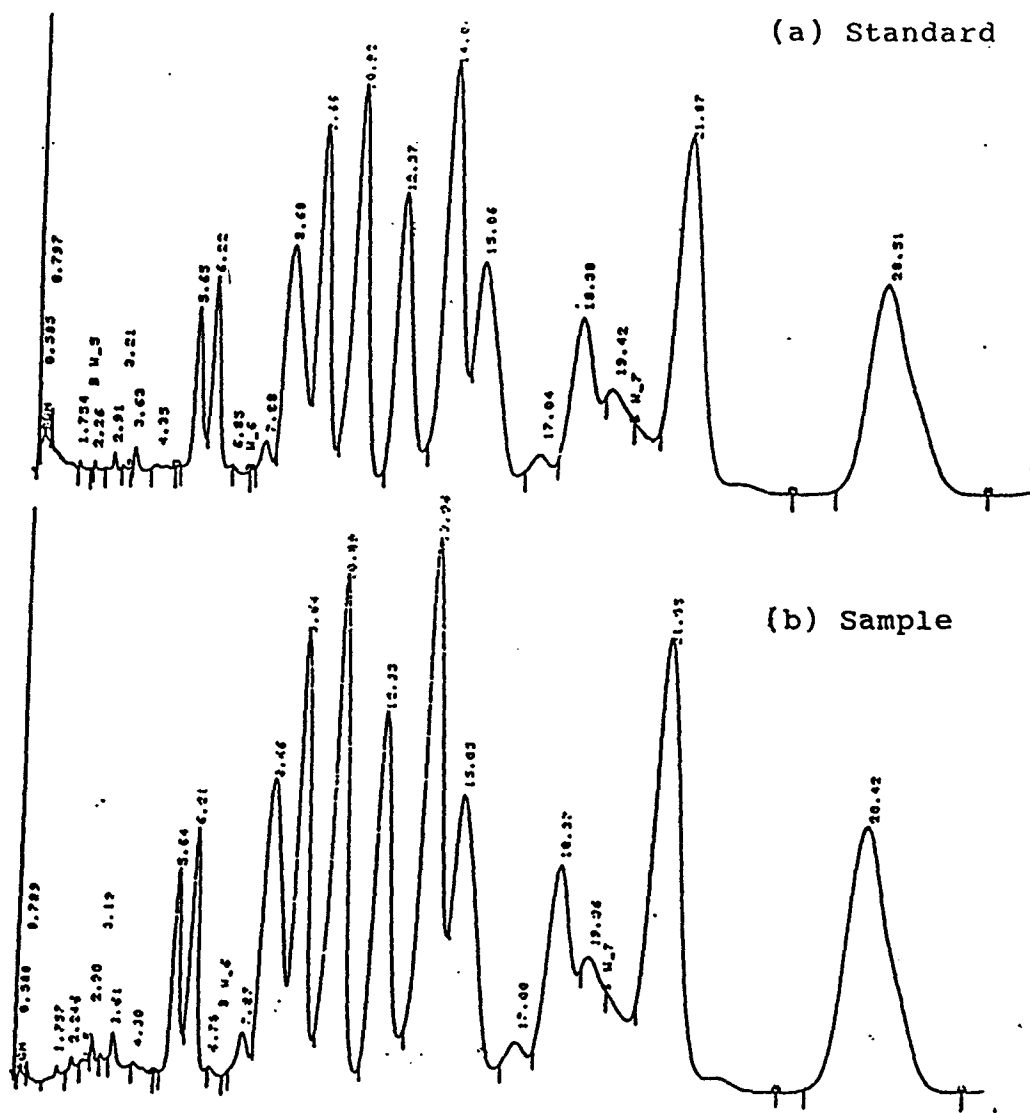


Figure 13. Comparison of Chromatograms of Aroclor 1260 Standard(a) and Environmental Sample(b)

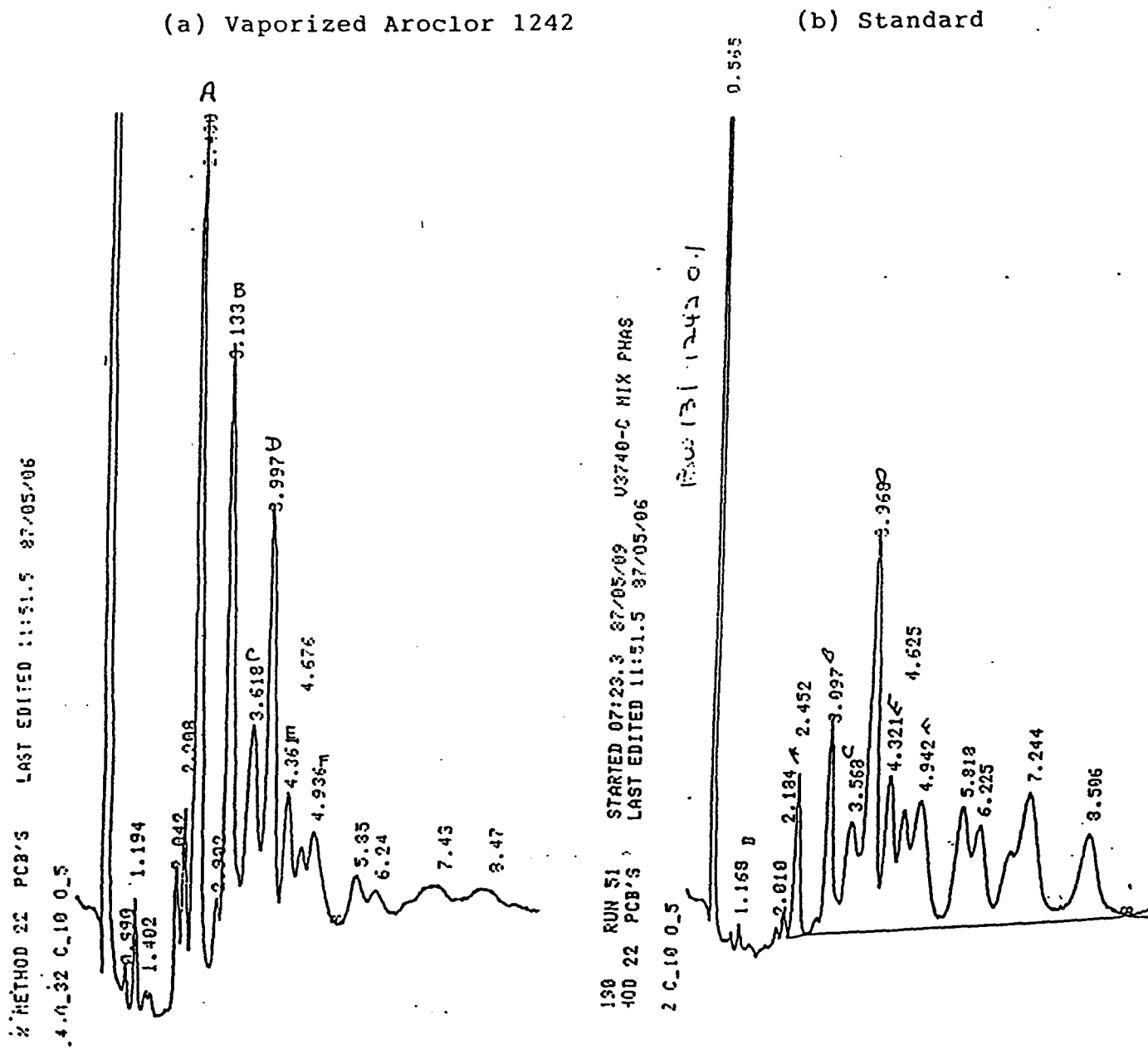


Figure 14. Example of "Enrichment" of Earlier Eluting Peaks in Chromatogram of Vaporized Aroclor 1242 in Air(a) vs. Aroclor 1242 Liquid Phase Standard

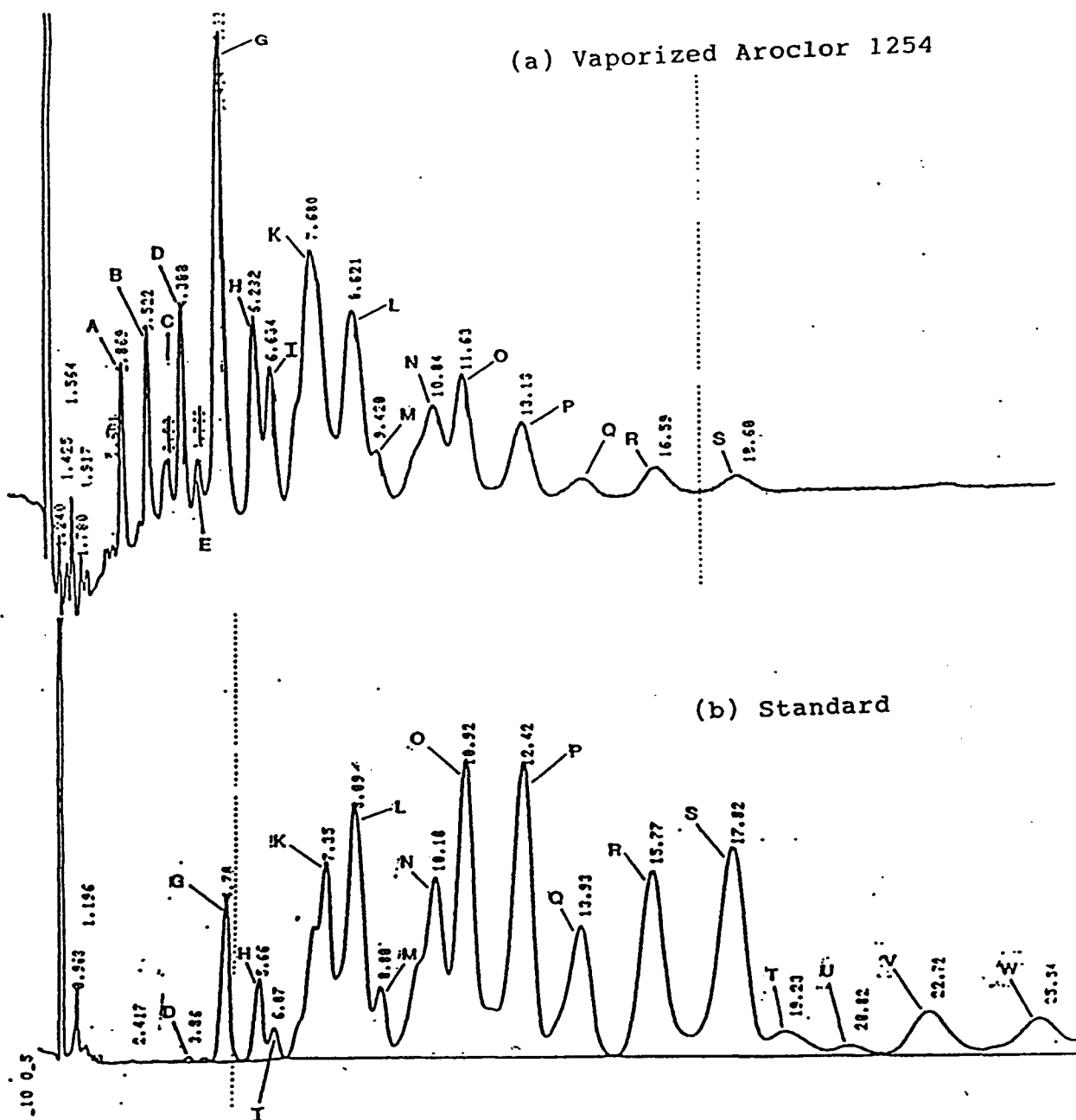
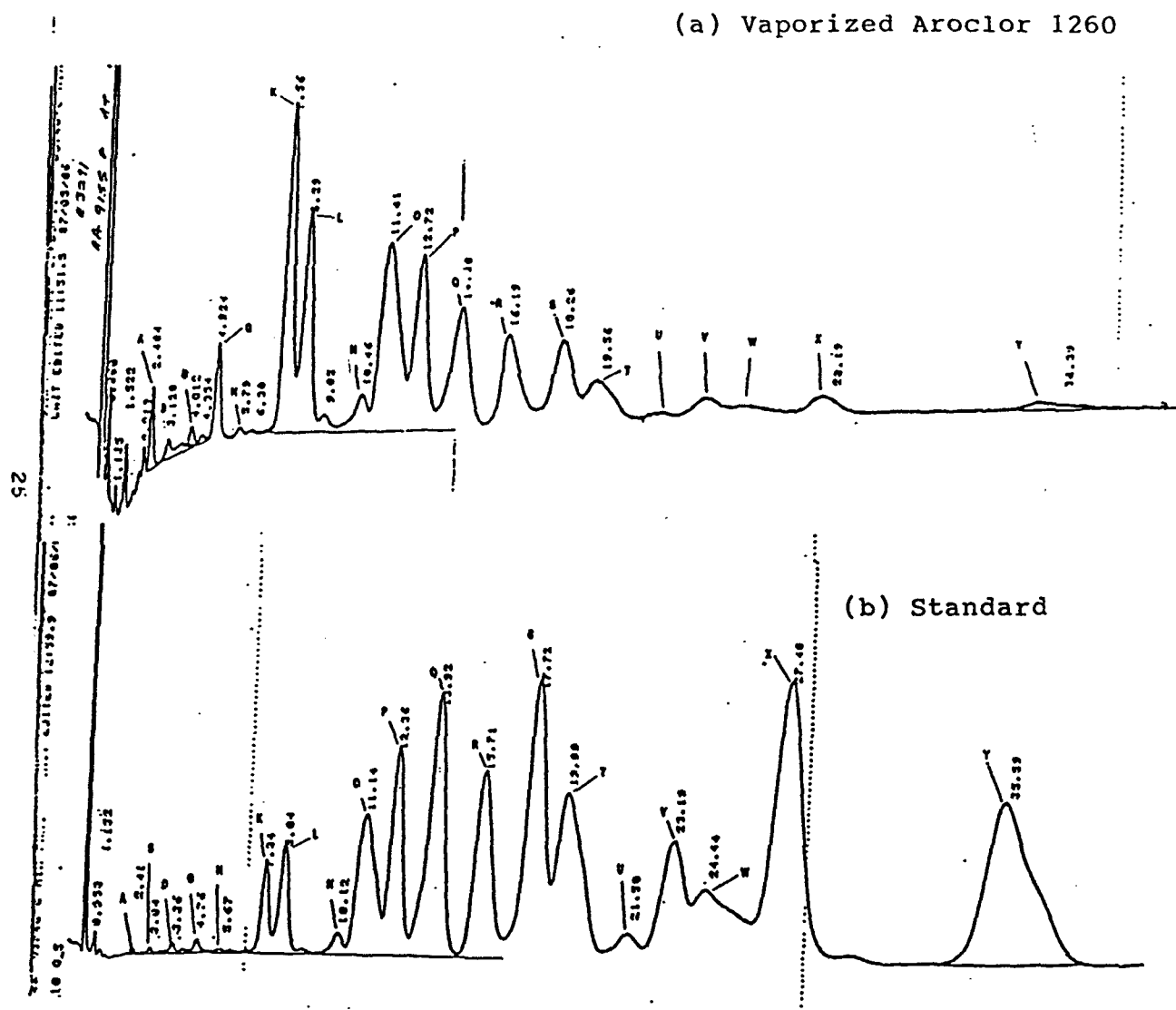


Figure 15. Illustration of "Enhancement" of Earlier Eluting Peaks in Chromatogram of Vaporized Aroclor 1254 in Air(a) vs. Aroclor 1254 Liquid Phase Standard(b)



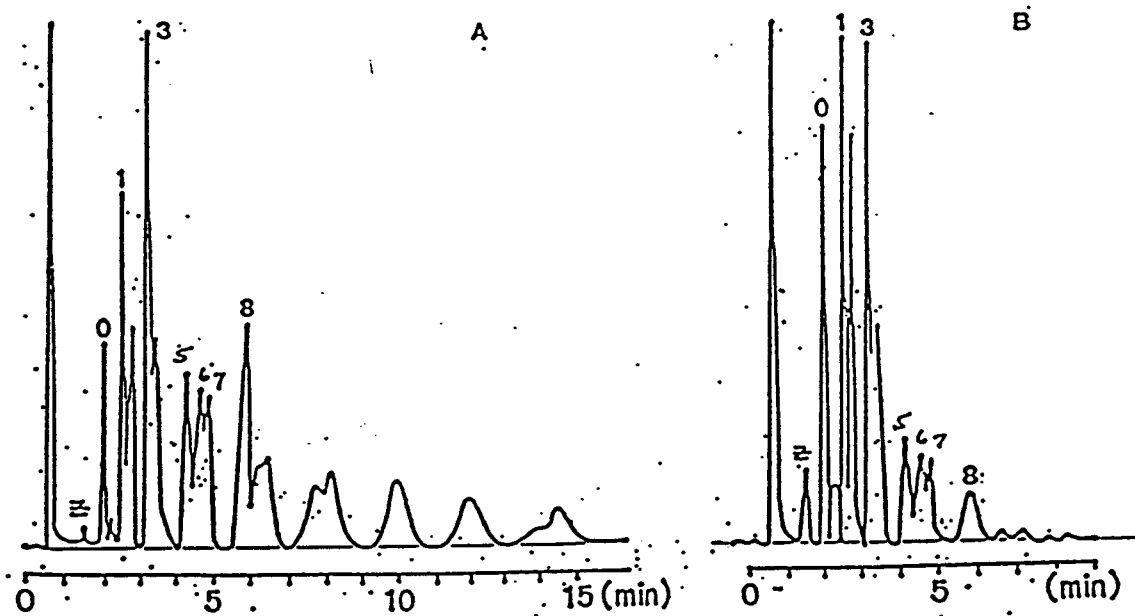


Figure 17. Gas Chromatograms of Sewage Bottom Mud (A) and of Air above the Sewage (B) (Toyonaka City, Osaka; June, 1972)

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Source: Tatsukawa (1976)

of sediment and soils can also occur which contributes to pattern alterations of weathered samples.

### 6.3 Metabolism in Biological Samples

PCBs have accumulated in living matter because of their lipid solubility. This accumulation appears to be higher in the case of penta- and more highly chlorinated biphenyls. Aroclor pattern alterations occur in biological samples because the metabolic rates for PCBs are both isomer- and homolog-dependent. The higher the homolog, the slower the metabolism. A typical chromatogram for a blood serum sample from the Greater New Bedford Public Health Effects Study (GNBPHEs) (Figure 18) demonstrates that tetra- and less chlorinated biphenyls are more readily metabolized.

### 6.4 Non-PCB Compound Interference

As discussed in Section 5.1.1.2, while the electron capture detector is a chlorine sensitive detector, it can respond to certain non-PCB compounds. Consequently, non-PCB interferences, when present above detectable levels, can cause pattern alterations.

#### 6.4.1 Non-PCB Interferences in Biological Samples

Frequently, non-PCB interferences are found in biological samples and are due to the presence of chlorinated pesticides and/or their metabolites. This problem occurred in the analysis of samples from the GNBPHEs and is illustrated in Figure 19. Two compounds, hexachlorobenzene (HCB) and p,p'DDE, were consistently found in the samples. In addition, p,p'DDT (peak 174) was detected on occasion.

The additive or "enhancement" effect which results when DDT and its metabolites [chromatogram (a)] are added to an Aroclor 1260 standard [chromatogram (b)] is shown in Figure 20. Chromatogram (c) is the altered pattern which occurs. The close similarity between chromatogram (c) from Figure 20 and an actual fish sample is shown in Figure 21. The fish sample contains Aroclor 1260, a small amount of Aroclor 1254, o,p'DDE, p,p'DDE, o,p'DDT, and p,p'DDT. Quantitation of this sample by electronic integration of

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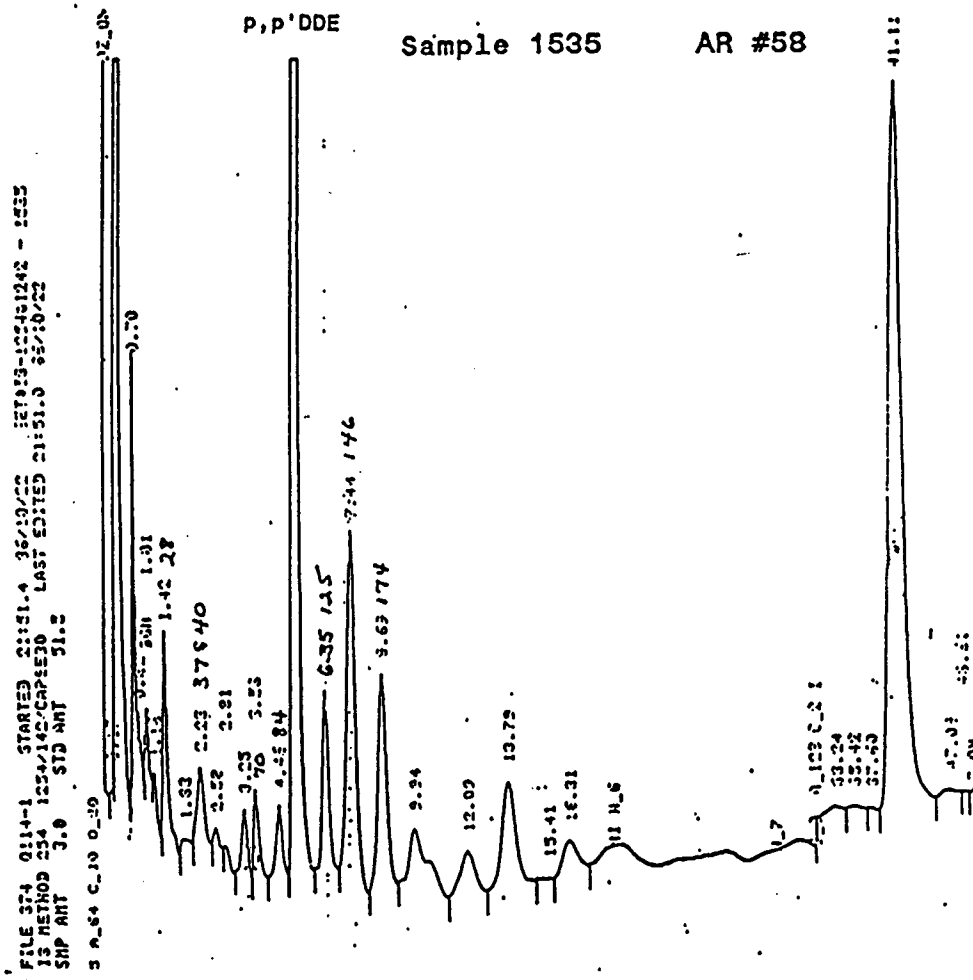


Figure 18. Predominant GNBPHES Sample  
(Pattern A)



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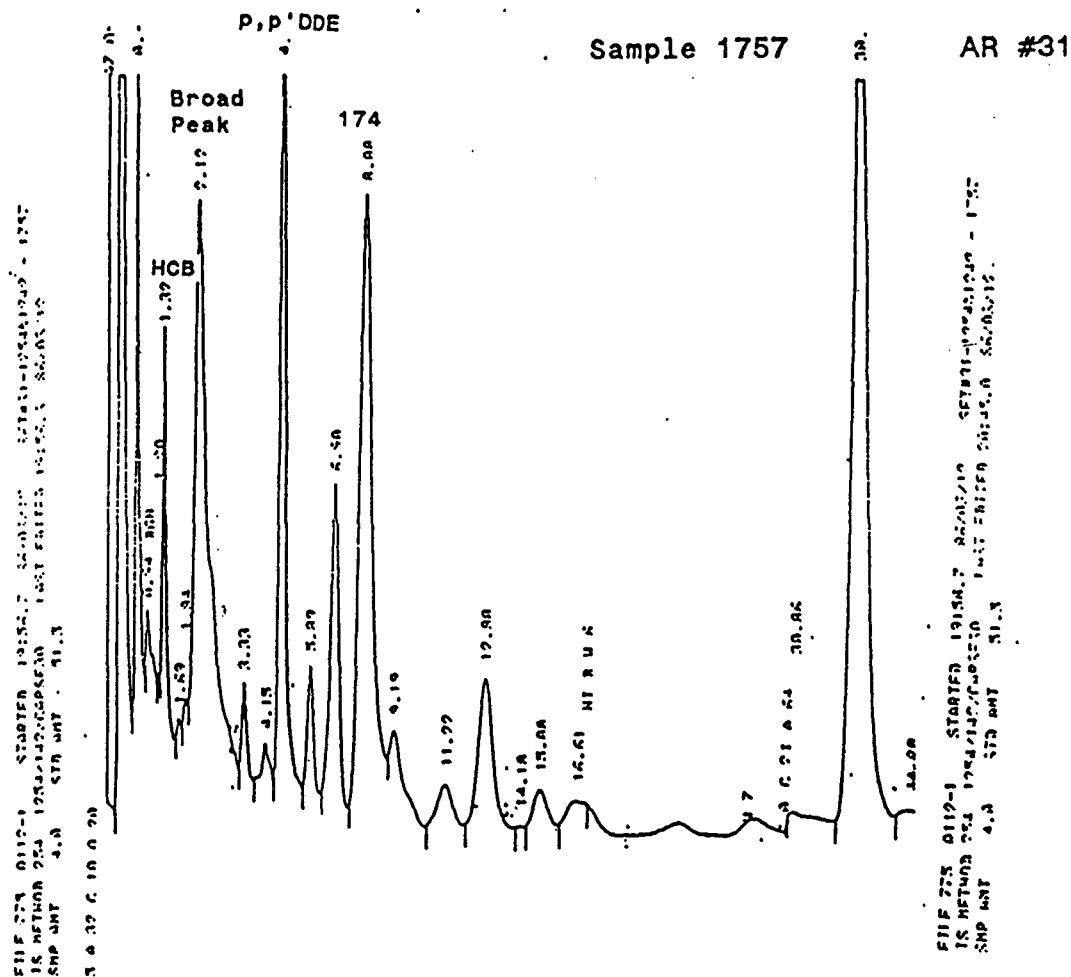
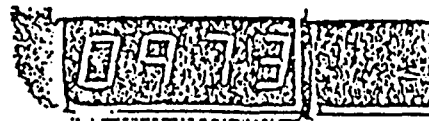


Figure 19. Sample Containing Significant Interferences

RETENTION TIMES 250 10 1.775  $\mu$ i DDTR 0.1  $\mu$ g

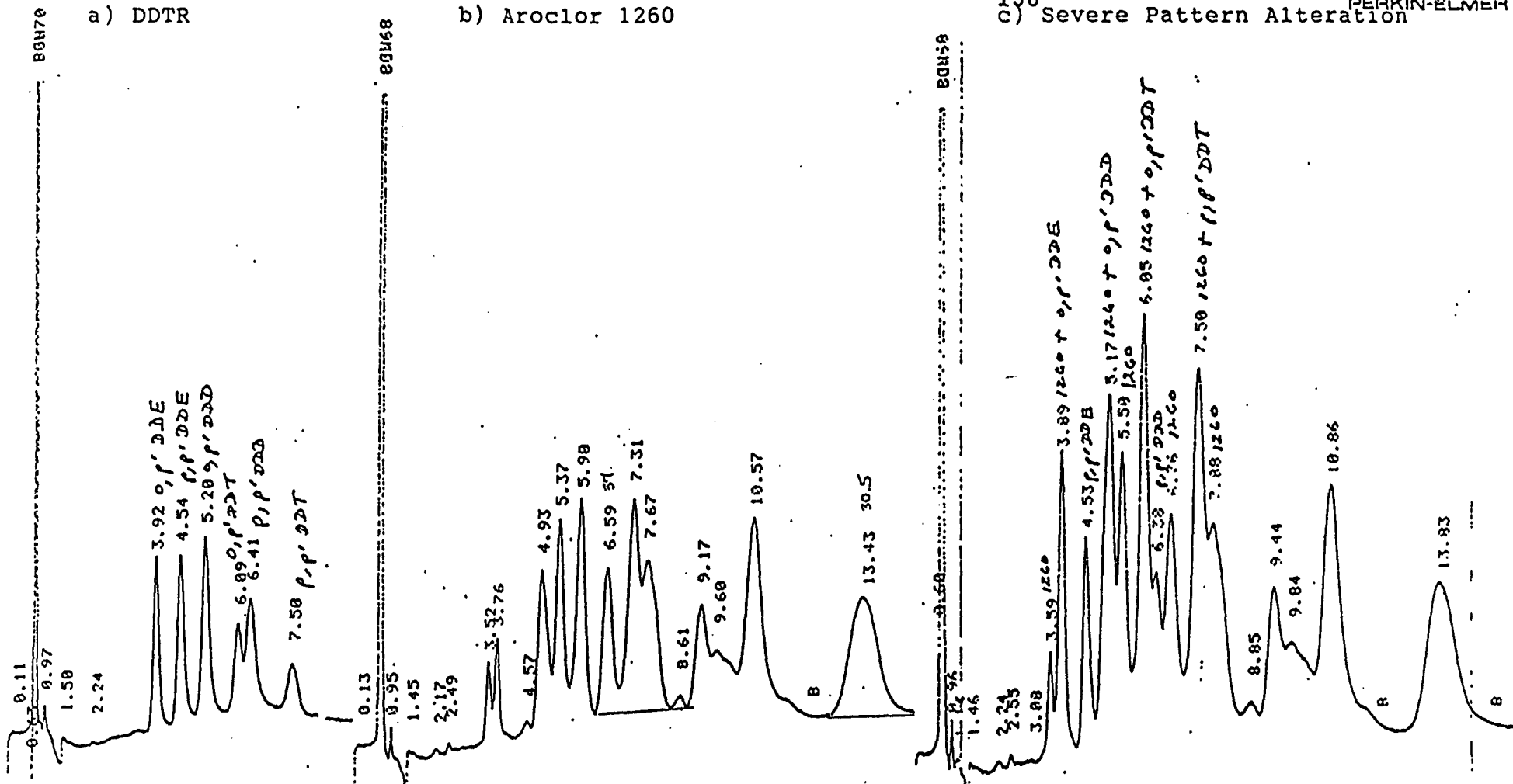
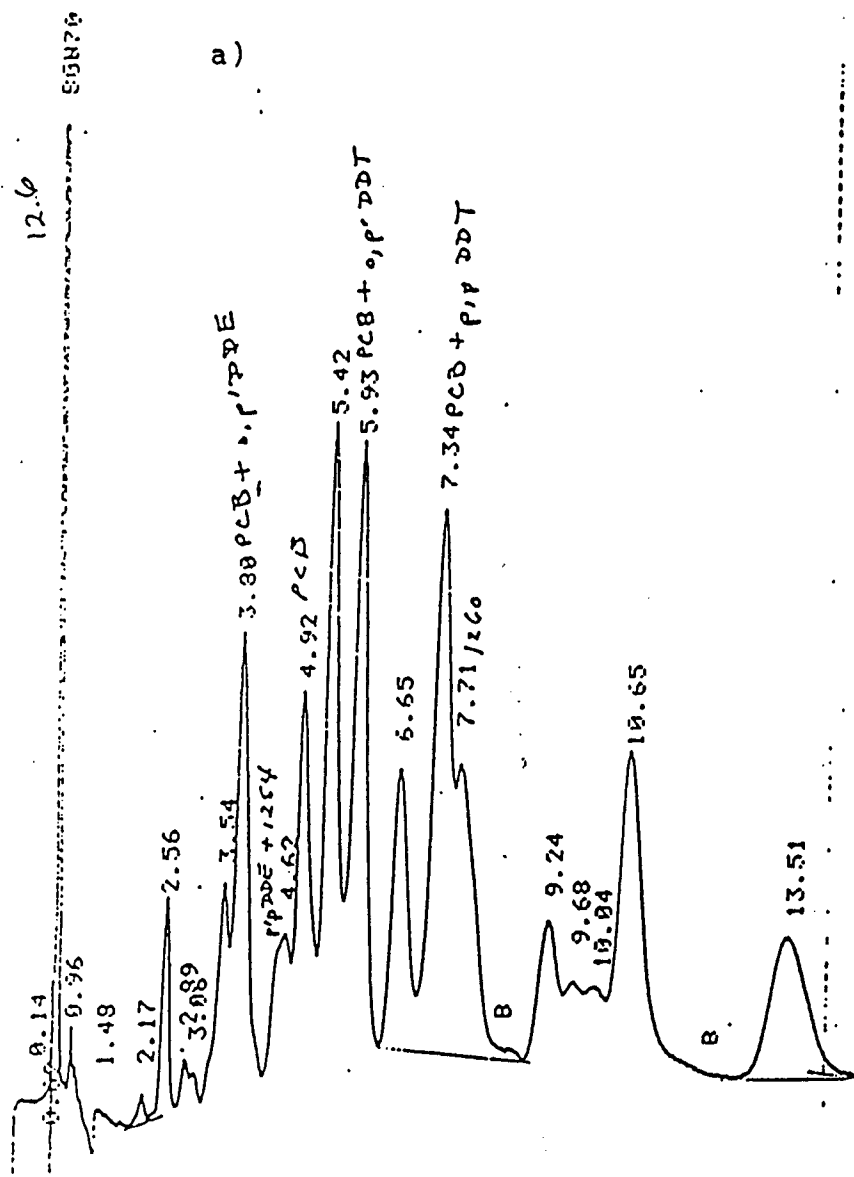
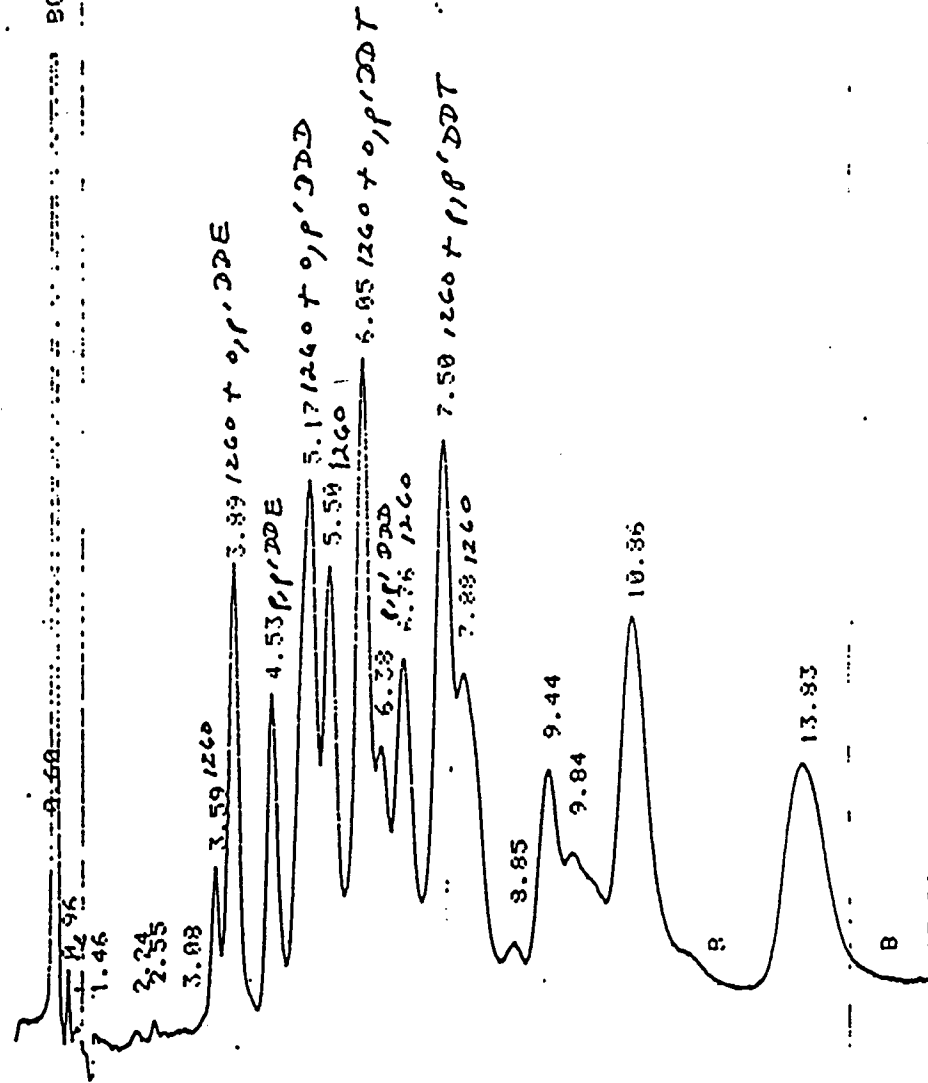


Figure 20. Illustration of Non-PCB Compound Interference: a) DDTR plus b) Aroclor 1260 equals c) Severe Alteration of Aroclor 1260 Pattern

130 PERKIN-ELMER  
c) Severe Pattern Alteration

SENSITIVITIES 250 10

2.05  $\mu$ l SL 6607A  $\frac{1}{5}$ SENSITIVITIES 250 10 2.2  $\mu$ l 1260 0.26 ppm + 2  $\mu$ l DDT 0.15  $\mu$ l

PERKIN-ELMER

Figure 21. Comparison of a) Fish Sample and b) Aroclor 1260 Standard containing DDT

the total area of the Aroclor 1260 window resulted in a significantly high data bias because the DDTR contribution was ignored.

#### 6.4.2 Non-PCB Interferences in Sediment Samples

Pattern alterations due to the presence of non-halogen containing compound interferences are routinely observed in sediment chromatograms. Phthalate esters and polynuclear aromatic compounds including anthracene, fluoranthene, and pyrene have been identified in Aroclor-contaminated samples.

Sulfur is a common contaminant in sediment samples. Its presence, however, is easily recognized at high concentrations because of its uniquely characteristic chromatographic pattern. Figure 22 illustrates sulfur interference patterns observed in the NBH sediment samples. The sulfur concentration in the samples decreases progressively from chromatograms (a) through (e). The problem is easily recognized in chromatograms (a) and (b). As the sulfur concentration decreases and the PCB concentration increases, it is much more difficult to recognize the sulfur interference. Chromatograms of the three samples shown in Figure 23 all have sulfur interference (color-coded green). These samples were collected in the upper estuary of the Acushnet River.

Sulfur interference was observed in the chromatograms of samples taken from other regions of the harbor. The chromatogram in Figure 24, for Sample AF214 from a sampling site in the outer harbor area (Buzzard's Bay), illustrates both sulfur interference and Aroclor 1254 transformations. The Aroclor 1254 pattern alterations (color-coded blue) can be seen by comparing the sample chromatogram (b) to the Aroclor 1254 standard (c). Interference peaks in the sample due to sulfur interference are color-coded green, and are comparable to the similarly highlighted peaks in the demonstrated chromatogram (a).

The observance of sulfur interference in the chromatograms of NBH sediment samples was surprising since sulfur can be completely removed, or at least significantly reduced, when the appropriate clean-up procedures are employed. All EPA approved analytical methodology for the determination of





### a) Sulfur Interference

b) Sample AF 214

c) Aroclor 1254

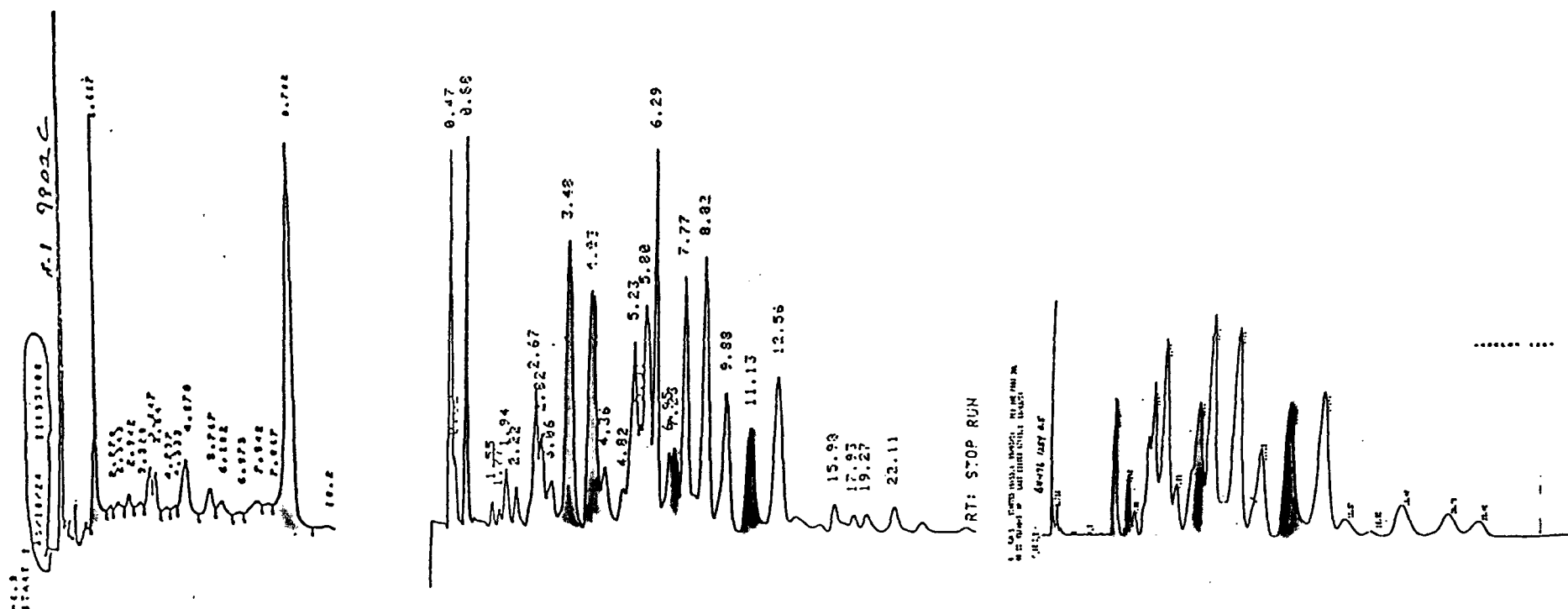


Figure 24. Illustration of Aroclor 1254 Alterations and Sulfur Interference in Sample AF214 from Buzzards Bay

PCB by GC/EC requires that clean-up procedures be used for the removal of sulfur prior to the analysis of the sample extracts.

#### 6.5 Microbial Degradation in Sediment Samples

Aroclor pattern alterations in sediment samples can occur as the result of both aerobic and anaerobic microbiological action. The most significant alteration which has occurred in NBH sediment samples is that due to anaerobic dechlorination. The chromatograms of samples undergoing anaerobic biotransformations frequently demonstrate the presence of new peaks in the pattern as well as "high-end" drop-off due to the degradation of higher chlorinated PCBs. Peak enhancements, reductions, and even disappearances also occur. Anaerobic alteration patterns in sediment samples are distinctively different from those found in "weathered" soil samples (volatilization and adsorption alterations) and river and groundwater samples (solubility, volatility, and aerobic microbial degradation alterations).

Pattern alterations resulting from anaerobic degradation can be observed in packed column GC/EC chromatograms. The chromatogram for sample NBH-111-02 (Figure 25) illustrates moderate transformation of both Aroclor 1242 and Aroclor 1254. A comparison of an Aroclor 1254 standard and sample NBH-106 is shown in Figure 26. Significant transformation of Aroclor 1254 has occurred in sample NBH-106.

The phenomenon of anaerobic transformation of Aroclors in sediments appears to be widespread, but its occurrence is not widely reported in the literature. Anaerobic transformation of Aroclors in the sediments of Silver Lake in Pittsfield, Massachusetts was observed in 1980 by Yoakum (1982). Further study by Brown (1987) and co-workers subsequently confirmed the occurrence of anaerobic dechlorination in these sediments. Both aerobic and anaerobic PCB transformations in sediments from the upper Hudson River (between Ft. Edwards and Troy, NY) have been reported (Brown, 1984). In addition to Silver Lake and the Hudson River, Brown (1987) has reported the observance of chromatographic pattern alterations indicative of anaerobic dechlorination of PCB residues in aquatic sediments from four other PCB spill sites: Waukegan Harbor (Waukegan, IL), Hoosic River (North Adams, MA), Sheboygan River



RUN 35 STARTED 22:17.1 83/03/25 PCB BHE PROJ 3UL  
:2 U3740-D MP LAST EDITED 17:15.3 83/03/24

0 0.5 NBH-111-SD-02, 2-25-88 EE4327 50,000 H<sub>2</sub>(F)

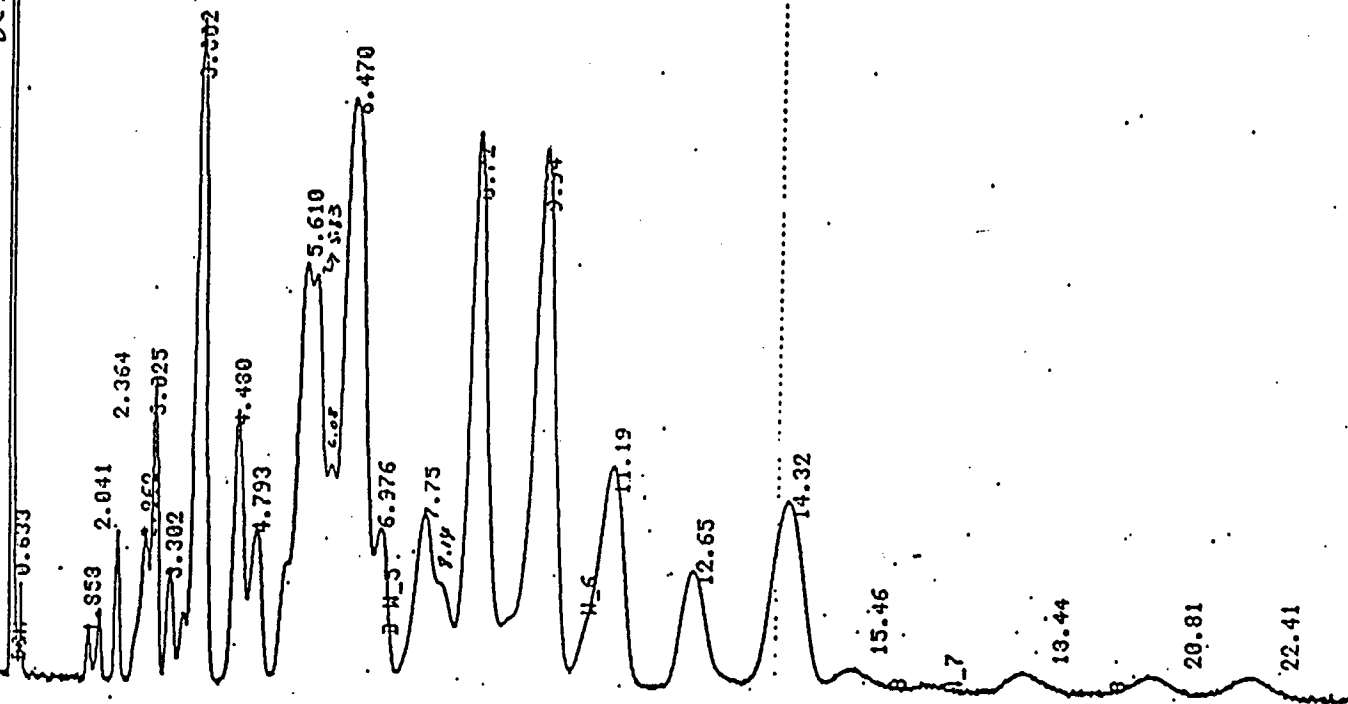


Figure 25. Packed Column GC/EC Chromatogram of NBH-111-02

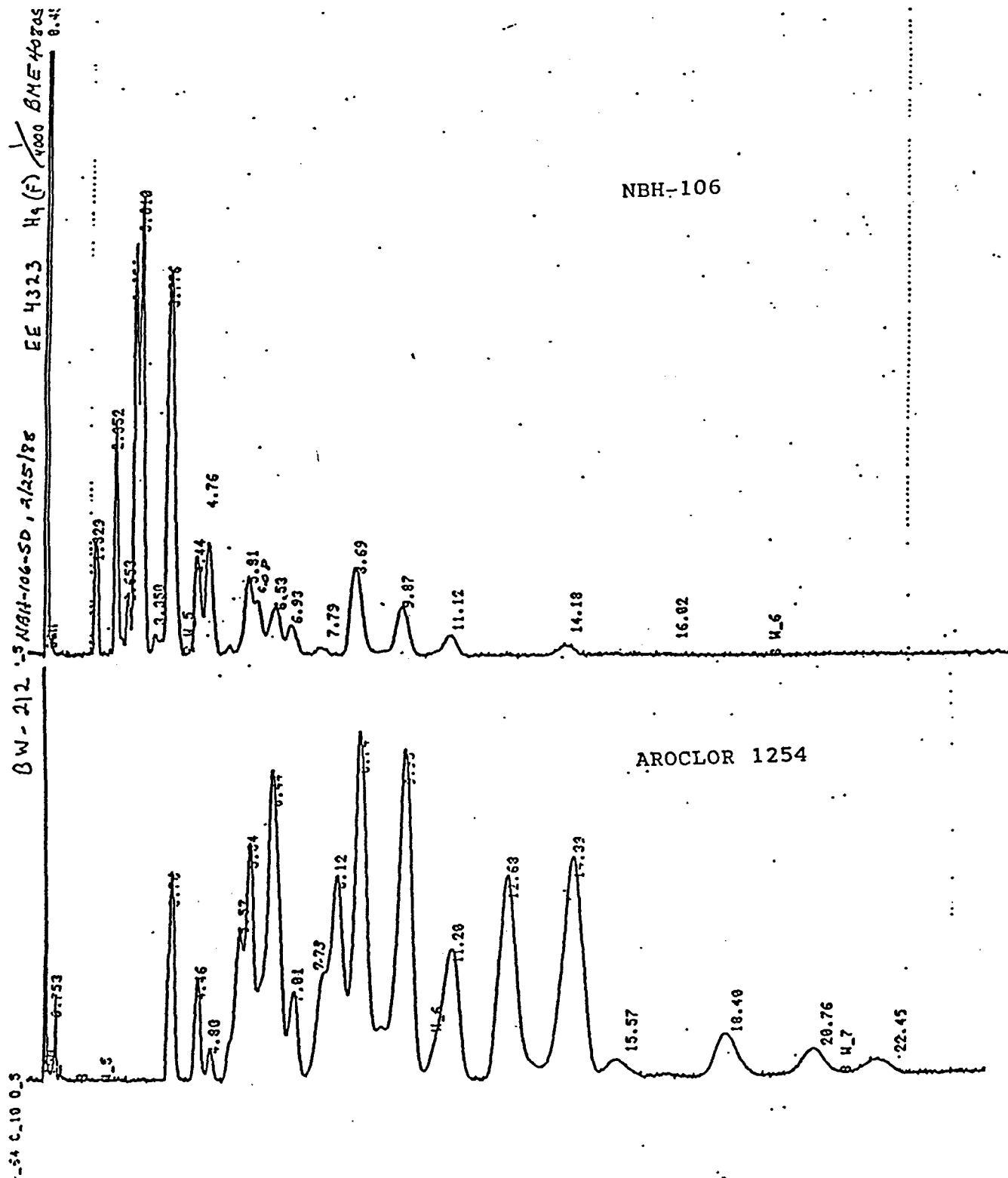


Figure 26. Comparison of Sample NBH-106 and Aroclor 1254 Standard

(Sheboygan, WI), and the Acushnet Estuary (New Bedford, MA). The failure to identify and report the pattern alterations associated with anaerobic degradation in sediments is undoubtedly due, at least in part, to the data reduction techniques currently employed by most laboratories. Pattern alterations cannot be observed when the major component peaks of the chromatograms are allowed to produce "off-scale" responses. This is common practice when Aroclor quantitations are performed by total area integrations of retention time windows.

In addition to the observation of anaerobic dechlorination of Aroclors in Silver Lake sediments, the same phenomenon was confirmed at two other sites by Yoakum for Aroclor 1260 in 1980 and for Aroclor 1242 and/or Aroclor 1016 in 1981. Reconstructed ion chromatograms (RICs) from the GC/MS confirmation of the anaerobic degradation of Aroclor 1242 and/or Aroclor 1016 are shown in Figure 27. The top RIC is from the Aroclor 1016 standard and the sediment sample is the bottom RIC. The sample contained increased amounts of mono- and dichlorobiphenyls, concentration alterations of the trichlorobiphenyls, significantly reduced tetrachlorobiphenyls and no detectable pentachlorobiphenyls.

Confirmation of anaerobic degradation of Aroclor 1254 and Aroclor 1260 in sediments by GC/MS is presented in Figures 28 and 29. Two levels of biotransformation of Aroclor 1254 (plus a lesser amount of Aroclor 1260) are shown in Figure 28 [RIC (a) & (c)]. Although both samples are from the same site, pattern (c) exhibits more degradation than does pattern (a). The anaerobic transformation of Aroclor 1260 was confirmed by RIC (a) in Figure 29. An Aroclor 1242 standard was included in both Figures 28 and 29 for comparison purposes.

The sources of the sediments used for the GC/MS confirmation studies were a settling pond (Figure 27), a discharge lake (Figure 28), and a wastewater discharge lagoon (Figure 29). The Aroclor discharges came from manufacturing facilities for electrical capacitors and transformers and a military installation.

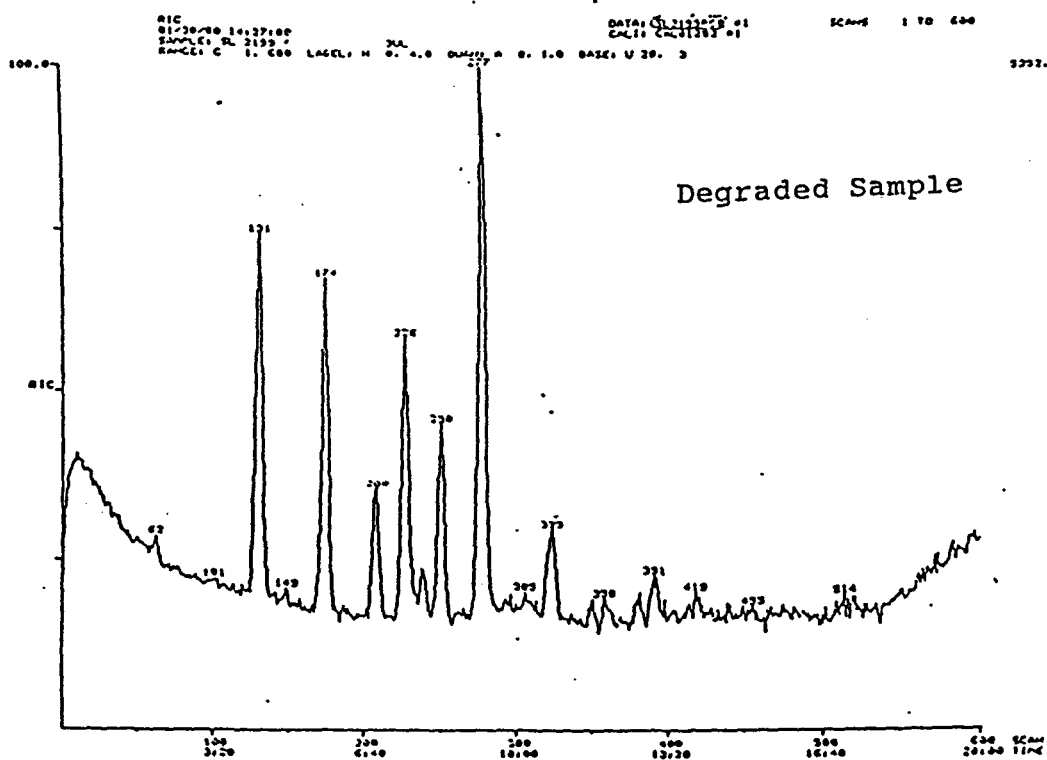
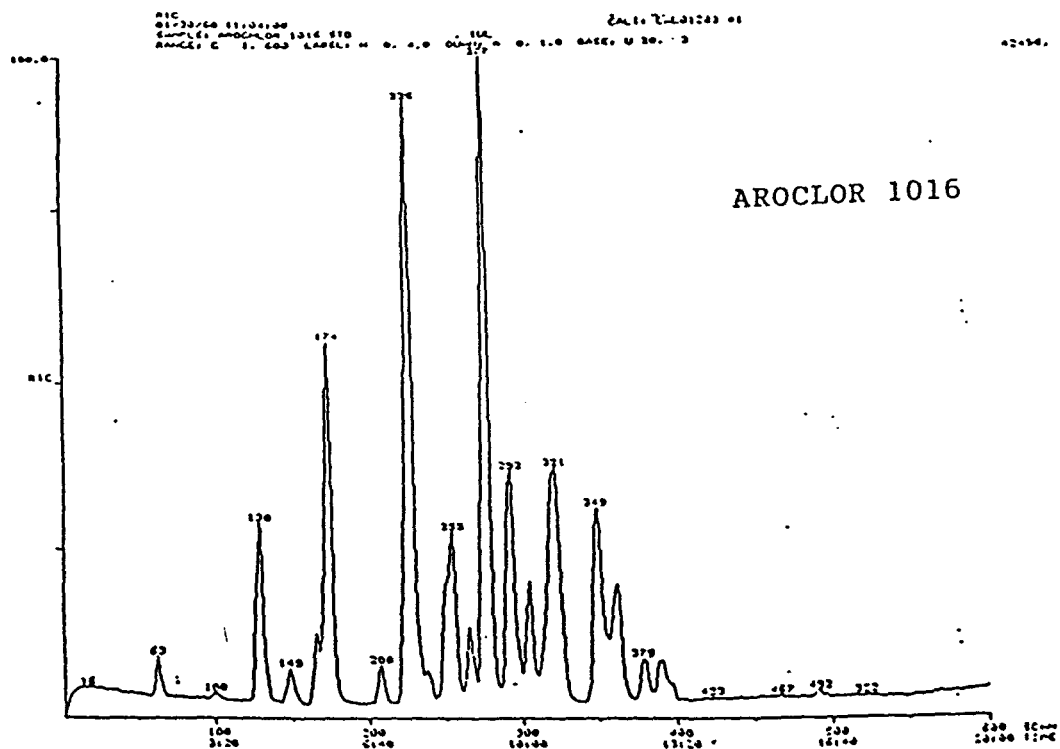


Figure 27. RICs from GC/MS Confirmation of Anaerobic Degradation of Aroclor 1016 and/or Aroclor 1242

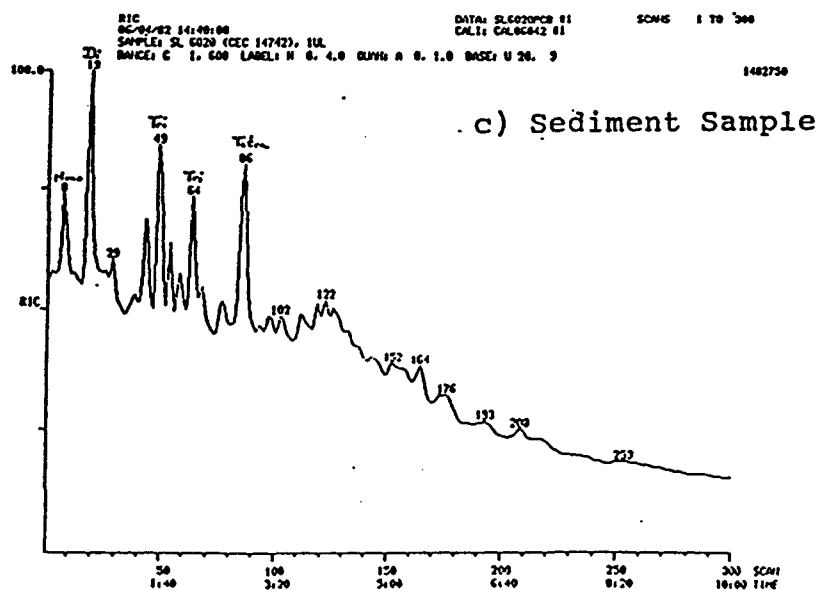
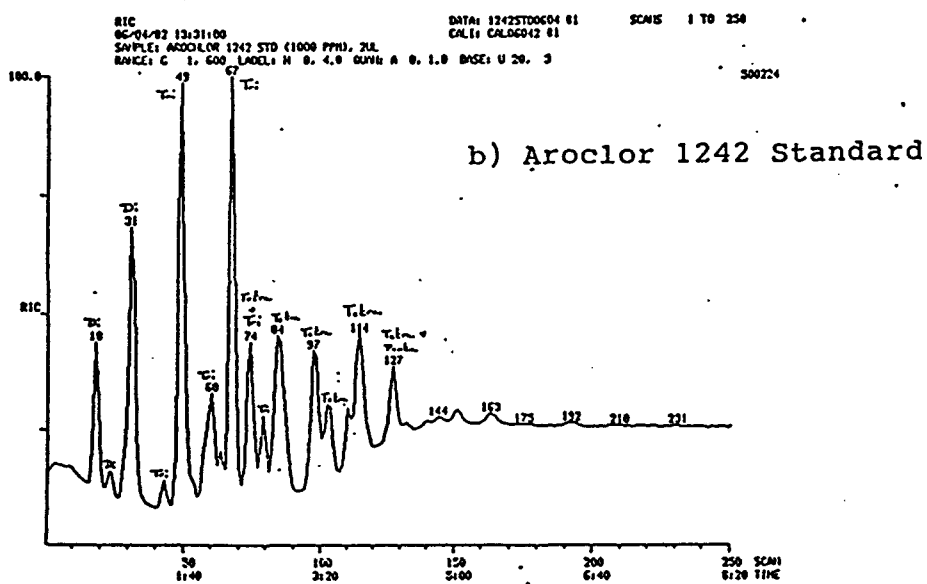
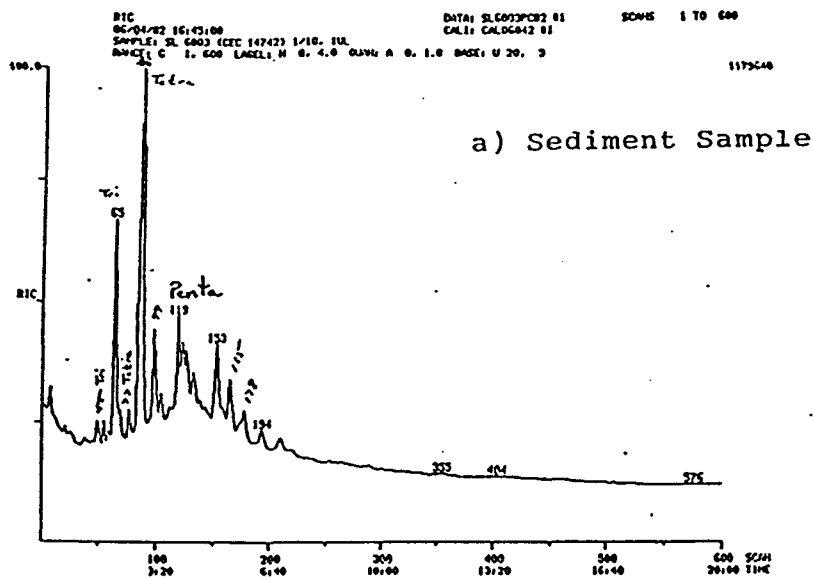


Figure 28. GC/MS Confirmation of Anaerobic Degradation

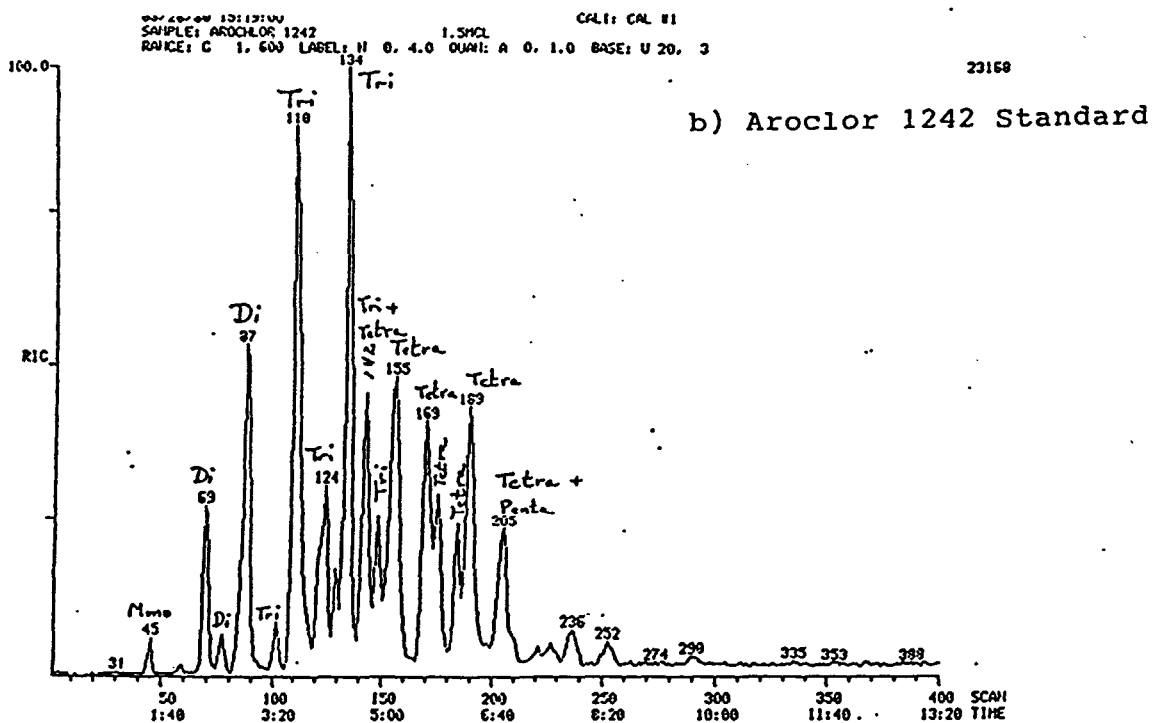
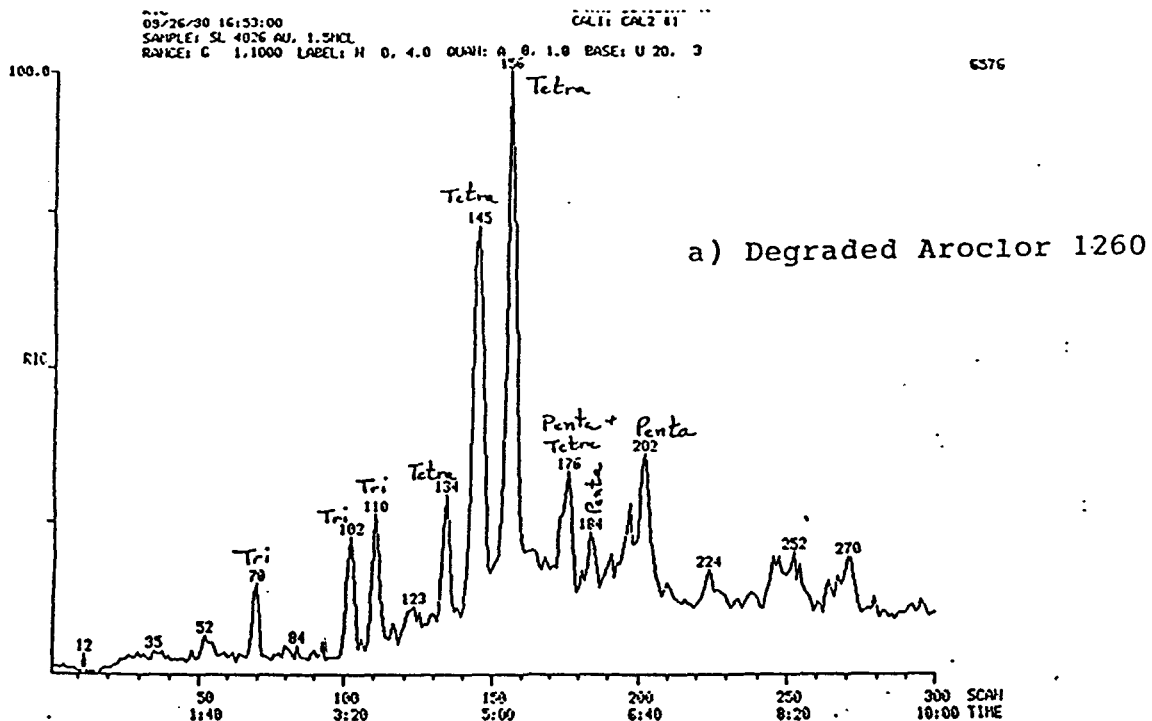


Figure 29. RIC showing Anaerobic Degradation of Aroclor 1260

#### 6.6 Analytical Ramifications of Pattern Alterations

The most serious impediment to the correct interpretation of Aroclor pattern alterations is the fact that, on numerous occasions, two or more alteration processes are operating at the same time. If these alterations are not recognized and properly taken into account, both the Aroclor identification and the PCB quantitation are subject to considerable error. In the case of the packed column chromatograms for NBH sediment samples, this appears to have occurred. The partial loss of lower chlorinated congeners (especially di- and certain trichlorobiphenyls) from Aroclor 1016/1242 due to weathering coupled with the biotransformation of the Aroclors present in the samples have produced pattern alterations resulting in chromatograms where the reported Aroclor identifications are definitely suspect.

Accurate quantitation of PCBs depends on selecting the proper standard and excluding any interferences which may be present. The reliability of the quantitation suffers when interferences are not recognized and the Aroclor(s) present are misidentified.

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14. Ibid., (1981).
15. Yoakum, A. M., Housatonic River Study - Final Report, Stewart Laboratories, Inc., Knoxville, TN (1982).



APPENDIX II

TASK 2

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EVALUATION OF PCB ANALYTICAL DATA  
FOR SAMPLES ANALYZED BY  
U. S. ARMY CORPS OF ENGINEERS  
WATER QUALITY LABORATORY  
NEW ENGLAND DIVISION

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September 6, 1989

Y & A Project NMF-3003 Task 2

**DRAFT**

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## Y & A Project NMF-3003 Task 2

### EVALUATION OF PCB ANALYTICAL DATA FOR SAMPLES ANALYZED BY U. S. ARMY CORPS OF ENGINEERS WATER QUALITY LABORATORY, NEW ENGLAND DIVISION

#### 1.0 TASK 2 BACKGROUND

The original data transmitted from Balsam Environmental Consultants, Inc. (Balsam) included the following:

- o the U. S. Army Corps of Engineers (USACE) sampling grid map,
- o a general summary of USACE analytical methods,
- o summary sheets of USACE analytical results including Quality Assurance/Quality Control (QA/QC) samples, and
- o raw analytical data consisting of integrator output and chromatograms.

A later transmittal included the complete USACE report, New Bedford Harbor Superfund Site Acushnet River Estuary Study (Condike, 1986), and related appendices (C-F).

A preliminary Yoakum & Associates, Inc. (YAI) review of the USACE chromatograms was completed in August, 1987. On 9/2/87, a request was made to Balsam that Aroclor standard chromatograms (which were missing from the data) and analytical results expressed as individual Aroclors be provided. Subsequent efforts by Balsam to secure the requested additional information were unsuccessful. As a consequence, an alternative approach to the evaluation of the chromatograms was investigated by YAI in January, 1988.

This alternative approach (described in Section 3.0) proved successful, and the USACE analytical data were evaluated in terms of the following:

1. Which Aroclors are present in the samples;
2. Are chromatographic pattern alterations observed; and
3. Is there evidence of anaerobic PCB degradation?

In addition, the raw analytical data were evaluated as to their overall quality, completeness, and reliability.

## 2.0 INITIAL DATA REVIEW

The raw data package consisted of integrator output and chromatograms for 85 samples and 16 re-runs. Raw data were also included for 21 QA/QC samples (10 spikes and 11 replicates). The data received for evaluation had the following deficiencies and/or problems:

1. The chromatograms and integrator outputs for the Aroclor standards used for the PCB determinations were missing from the data package.
2. Resolution of the chromatograms was poor. This was due in part to excessive recorder speed. However, the peak retention times indicate that the chromatographic oven temperature probably was below that required for optimum peak resolution. As a consequence of these two factors, the peaks were spread out in the horizontal direction. However, even though the peak resolution was poor, the actual peak separation afforded by the chromatographic column was good.

Without the benefit of chromatograms of the Aroclor standards used for these particular analyses, evaluation of pattern alterations in the "as received" chromatograms could not readily be performed. When it became apparent that copies of the Aroclor standards would not be made available, an alternative approach was investigated in an effort to compare the USACE chromatograms to the standards used for other New Bedford Harbor (NBH) studies.

## 3.0 ALTERNATE APPROACH TO USACE CHROMATOGRAM EVALUATION

As stated in Section 2.0, two serious problems were encountered at the outset of the USACE data review: (1) peak resolution on the USACE sample chromatograms was poor; and (2) Aroclor standard chromatograms run under the sample analysis conditions were unavailable. The resolution problem was improved by applying a one-dimensional reduction to the chromatograms; specifically, the vertical dimension of each chromatogram was essentially unchanged while the horizontal dimension was reduced. This reduction treatment produced chromatograms similar to those that would have been generated if a slower recorder speed had been used during data acquisition. The resulting improvement in peak resolution is illustrated in Exhibits 1 and 2

Shimadzu 221-25412 503001A 064

Shimadzu 221-25412 503001A

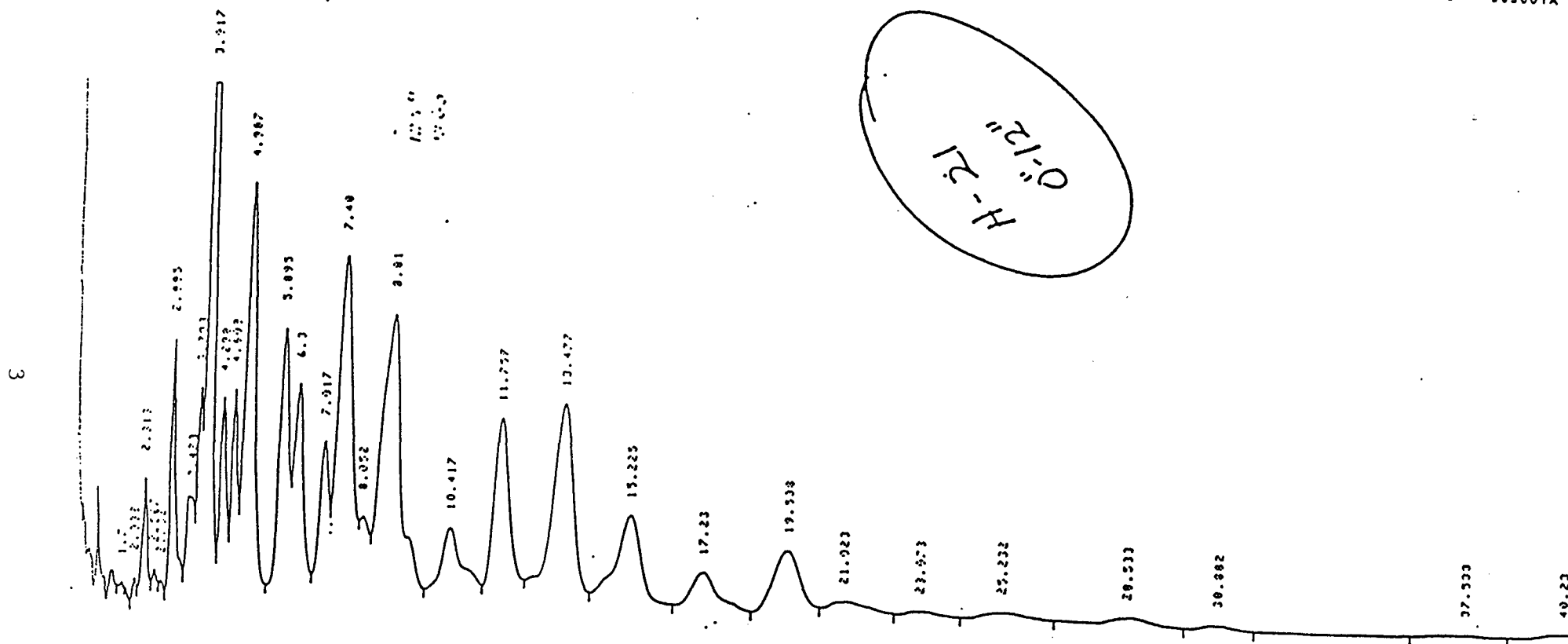


Exhibit 1. "As Received" Chromatogram for Task 2 Sample H-21 (0-12")



a)

b)

c)

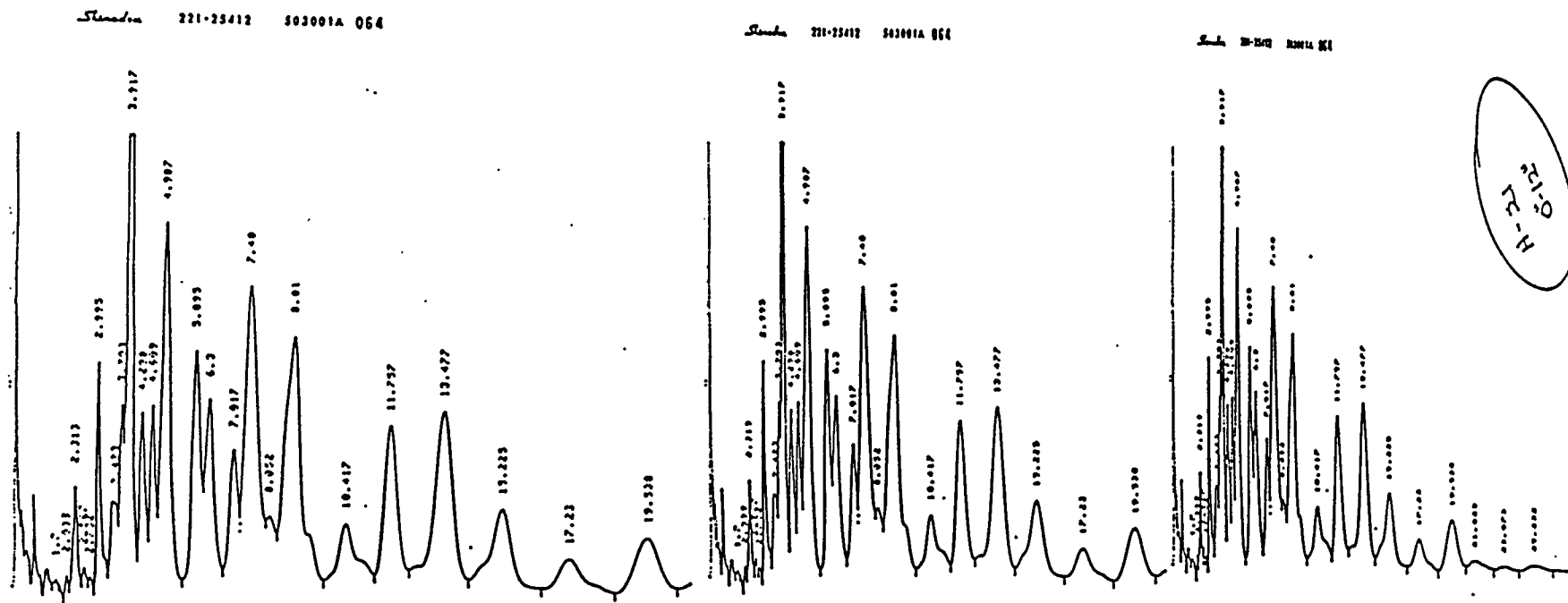


Exhibit 2. Illustration of Resolution Enhancement of Two Successive Reductions (b & c)

for sample H-21 (0-12"). Exhibit 1 is the "as received" chromatogram; the chromatographic resolution enhancement of two successive reduction treatments is shown in Exhibit 2 (b and c).

According to the draft Chemical Laboratory QA/QC Program, Appendix E, of the USACE Report (1986), the PCBs were run using a 1.5% SP-2250/1.95% SP-2401 mixed phase column at a temperature of 200°C. However, the time required for an analytical run of Aroclor 1260 was in excess of 40 minutes [See chromatogram (a) in Exhibit 3]. As illustrated by chromatogram (b) of Exhibit 3, the normal time required for an analysis run of Aroclor 1260 under the conditions prescribed by USACE is less than 24 minutes. Retention times are directly related to the oven temperature of the chromatograph and, to a lesser extent, the carrier gas flow. It would appear that one or both of these parameters was somewhat out of adjustment. By referring to Exhibit 3, it can be seen that the "resolution enhanced" USACE chromatogram (c) has resolution comparable to chromatogram (b) which is an illustration taken from EPA Method 8080 (1986).

The unavailability of standard chromatograms run with the USACE samples posed a more difficult problem. Significant and sometimes extensive Aroclor pattern alterations have been observed in sediment samples taken from the Acushnet River upper estuary (Y & A Project NMF-3003 Task 7). The primary cause of these pattern alterations is anaerobic PCB degradation. Since PCB degradation is evidenced by alterations in the GC/EC patterns of Aroclors, unaltered chromatograms of Aroclor standards are needed for comparisons before PCB transformation evaluations can be made.

The "resolution enhancement" treatment described above was applied to all USACE chromatograms prior to performing detailed evaluations. Not only is there a close match between the "resolution enhanced" USACE sample chromatogram and the EPA Method 8080 chromatogram for Aroclor 1260 (Exhibit 3), an equally close resemblance was observed between the USACE sample chromatograms and the packed column chromatograms from the special research project (Y&A Project NMF-3003 Task 7). This striking similarity is illustrated in Exhibit 4. The chromatogram (a) for Task 7 sample NBH-105 is

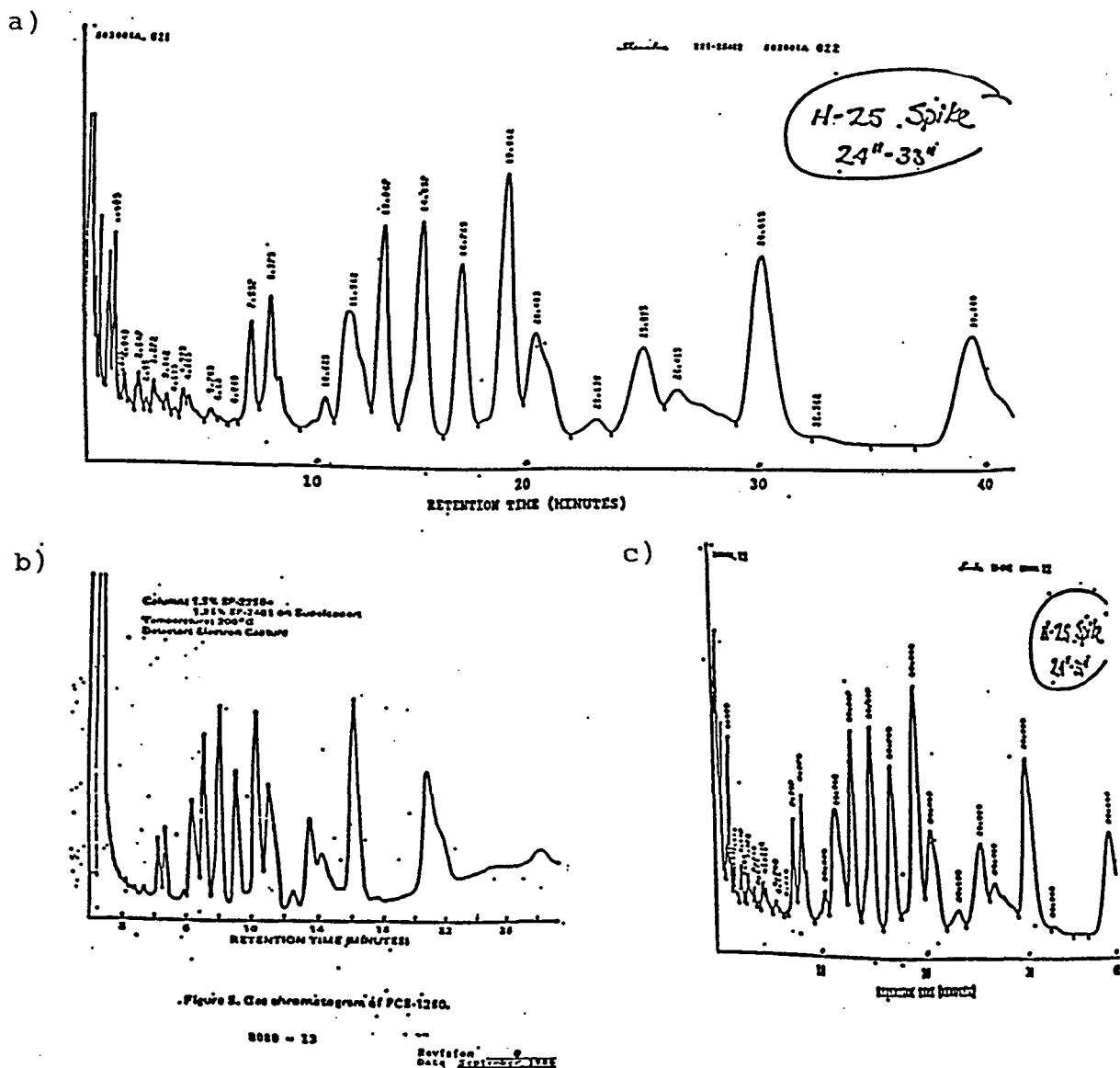


Exhibit 3. Chromatograms Illustrating a) "As Received" USACE Analysis Run, b) Figure 5 from EPA Method 8080, and c) "Resolution Enhanced" USACE Sample H-25 Spike (24" - 33")

1 26 RUN 41 STARTED 02:14.0 88/03/26 PCB BME PROJ 3UL  
 METHOD 22 03740-D HP LAST EDITED 17:15.1 03.05 54  
 .54 C-10 0.5 NBH-105-50 .2/25/88 EE 4312 11g(F) 1000 BME

2.36  
 2.40  
 2.43  
 2.47  
 4.43  
 4.77  
 5.81  
 6.55  
 6.94  
 7.73  
 9.70  
 9.91  
 11.16  
 14.25  
 14.37

1  
 1000 BME

Packed Column GC/EC Chromatogram  
 Sample NBH-105

06/03/26 11140144 Pix2-44 Run-1- 9965A(1.10) LAdm.

Mass spectrum plot showing relative intensity versus mass-to-charge ratio (m/z). The x-axis ranges from 0 to 22.0. The y-axis represents relative intensity. The base peak is at m/z 11.392. Other significant peaks are labeled with their m/z values.

Mass spectrum data points (m/z):

m/z
1.3592
1.5187
1.5187
2.203
3.339
4.3
5.792
6.917
7.417
7.925
8.717
9.142
10.342
11.392
12.317
12.263
13.023
17.1
19.206
20.700
22.0

Handwritten notes:

- 124.2
- 155.1

Handwritten label in a circle:

M-6-2  
0°-24°

7

virtually identical to the chromatogram (b) for sample M-6-2 (0" - 24") from the USACE study (Task 2).

Because of the similarity between the chromatograms for the samples from these two studies, the Task 7 Aroclor standards were used for the evaluation of pattern alterations in the USACE samples (Task 2) in the absence of the standards actually run with these samples.

#### 4.0 EVALUATION OF USACE CHROMATOGRAMS

##### 4.1 Analytical Methodology

The analytical methodology used for the study was taken from EPA publication SW-846 (1982). Specifically, Method 3540 for extraction and Method 8080 for PCB analysis were reported followed with two minor exceptions, which were noted. Both the methodologies and the instrumentation employed were considered state-of-the-art at the time the samples were analyzed. These procedures, performed by experienced analysts, should yield valid analytical data.

##### 4.2 Identification of PCBs in USACE Samples

The results reported by USACE for the Task 2 samples are expressed as "Total PCBs," with no indication as to which Aroclors were determined to be present. Based on notes written on the available chromatograms and peak assignments from the integrator output, however, there are indications that the laboratory identified Aroclors 1242, 1254, and sometimes 1260 in the samples. Also, the USACE draft QA/QC Plan indicated that the chromatograph would be calibrated with standards of the following Aroclors: 1016, 1242, 1254, and 1260.

Aroclor 1016 and/or 1242, as well as Aroclor 1254, are present in the samples. Because of their compositional similarities, it is difficult, if not impossible, to distinguish between Aroclor 1016 and Aroclor 1242 in a packed column chromatogram when Aroclor 1254 is also present in the sample. To illustrate, packed column GC/EC chromatograms of Aroclor 1016, Aroclor 1242, and Aroclor 1254 standards are shown in Exhibit 5. The only difference in the chromatograms of Aroclor 1016 and Aroclor 1242 occurs beyond peak retention

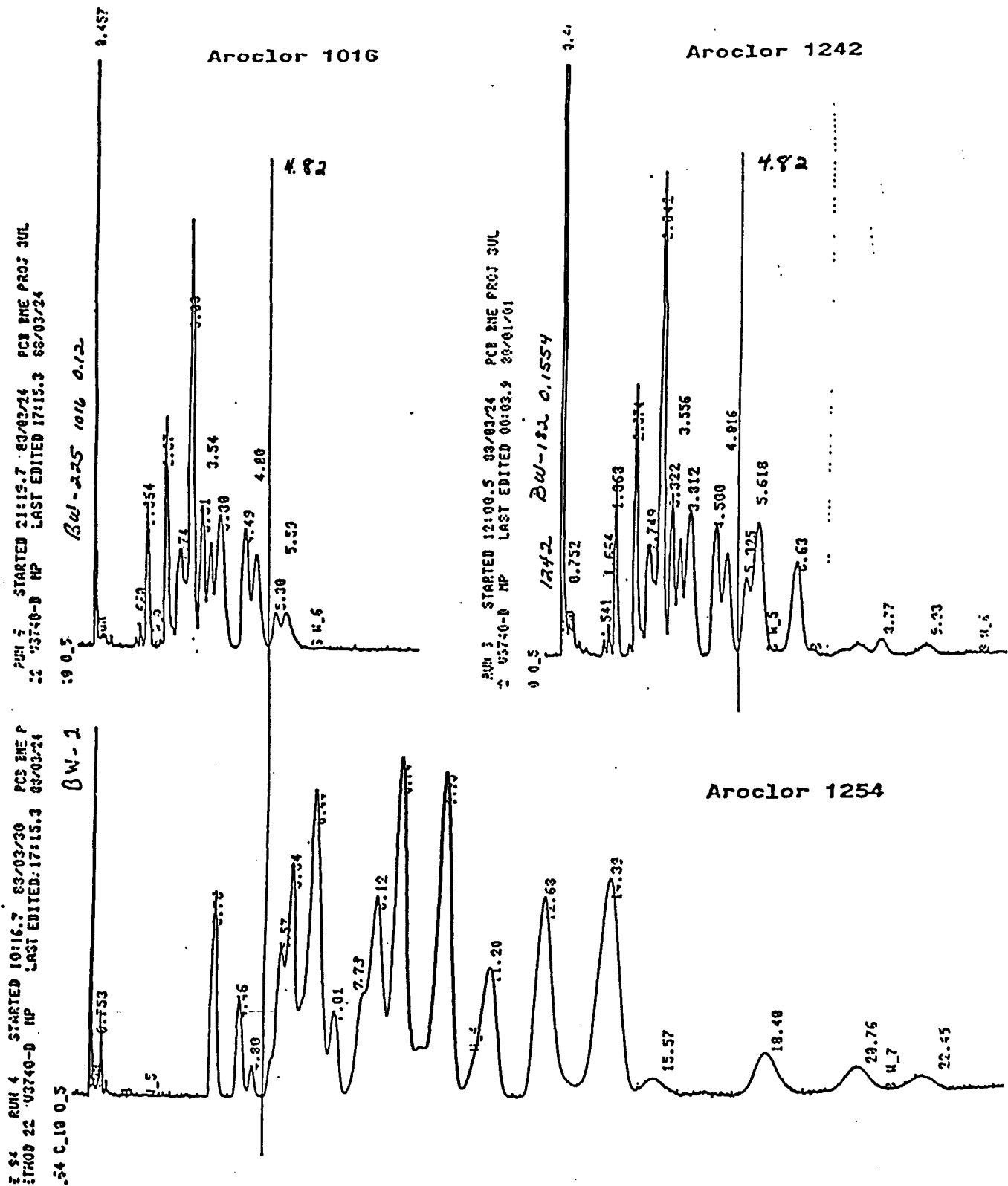


Exhibit 5. Standard Chromatograms - Aroclor 1016, Aroclor 1242, and Aroclor 1254

time 4.82 minutes. Since peak overlap from Aroclor 1254 begins to occur at retention time 3.76 minutes, the pattern difference between Aroclor 1016 and Aroclor 1242 is obscured by the "additive effect" of the peaks from Aroclor 1254 when it is present in a sample which also contains Aroclor 1016 and/or Aroclor 1242. Therefore, the notation Aroclor 1016/1242 will be used throughout this document.

The chromatographic patterns of Aroclor 1016/1242 and Aroclor 1254 exhibit significant and frequently extensive alterations in the majority of the USACE samples. Chromatographic pattern alterations will be discussed further in Section 4.4 of this report.

In addition to Aroclor 1016/1242 and Aroclor 1254, Aroclor 1260 is clearly present in four sample chromatograms and a trace amount exists in eight others. Chromatograms of three sample runs containing Aroclor 1260 are shown in Exhibit 6, with an Aroclor 1260 standard for comparison. The unaltered pattern of the Aroclor 1260 in these sample runs suggests that it was not present in the environmental samples. Rather, it more likely was introduced into the samples at the laboratory, possibly as a blind spike for QA/QC purposes or as carry-over contamination from a QA/QC spiked sample. Contamination carry-over from a previous sample is not uncommon when an automatic sampler is used in an unattended mode. Although there is a built-in wash cycle between samples, carry-over can still occur when the previous sample contains significant concentrations of Aroclors. Since the use of an automated GC for PCB analysis was new to the USACE laboratory, the analysts may not have been aware of the potential for carry-over contamination. Unfortunately, the analysis date and the analytical run sequence were not made available to YAI. As a consequence, this contamination possibility cannot be fully evaluated in this report.

Aroclor 1260 was apparently used by the laboratory as a "spiking agent" as part of the QA/QC program. Exhibit 7 illustrates the results of this "spiking" procedure, using sample H-25 (24"-33") as an example. Comparison of the spiked sample chromatogram with the Aroclor 1260 standard chromatogram further substantiates the conclusion that the Aroclor 1260 in these samples was introduced at the laboratory. Since Aroclor 1260 is known to undergo anaerobic

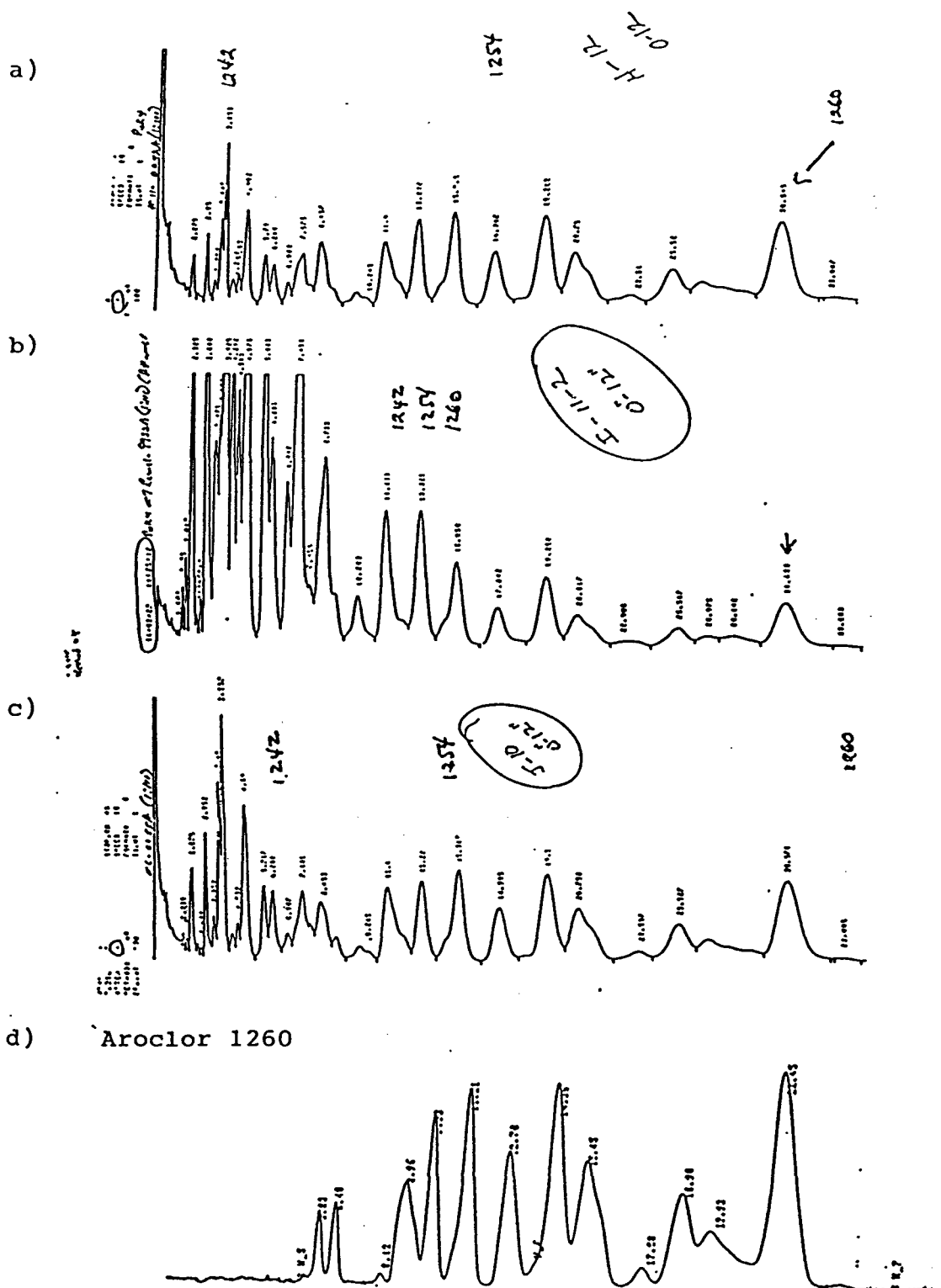


Exhibit 6. Chromatograms for Three Task 2 Samples (a-c) and Aroclor 1260 Standard (d)





dechlorination in sediments, some evidence of PCB transformation in the USACE Task 2 samples (Exhibit 6) would be expected if it had been environmentally exposed.

#### 4.3 Quantitation of PCBs

The quantitation procedure used by the laboratory was not specified in the USACE report issued in June, 1986. According to the draft QA/QC plan, quantitation was to be performed via computerized peak-by-peak relative retention time and area comparisons. There are indications, based on the integrator output data (Exhibit 8), that a procedure similar to the Webb-McCall (1973) approach to quantitation of PCBs by peak area was used. An example of peak assignments for quantitation purposes is shown in Exhibit 9 for sample H-21 (0"-12"). The distribution of peak assignments for standards of Aroclor 1016, 1242, 1254, and 1260 used by the laboratory, are illustrated in Exhibit 10. For the purpose of this study, a more appropriate assignment would have been to include peaks 18 through 21 in the Aroclor 1254 quantitation.

Two problems were observed relating to the quantitation of PCBs in the USACE samples:

- 1) di- and trichlorobiphenyls formed as the result of reductive dechlorination were not quantitated and are not, therefore, included in the total PCB data, and
- 2) sulfur interference, present in a number of samples, was not always excluded from the PCB quantitation.

As a consequence, the total PCB data are impacted by a negative bias due to the first problem; a positive bias results from the second problem. The magnitude of the negative bias associated with the first problem is directly related to the amount of dechlorination which has occurred in the sample. For samples showing slight to moderate transformations, the impact is minimal.

However, for samples showing advanced transformation in the Aroclor 1016/1242 region, as illustrated by Exhibit 11, the under reporting is approximately 30%. The overestimation of PCB due to the inclusion of sulfur in the total PCB calculation for this same sample is approximately 18%. Because of the inconsistent manner in which the sulfur interference was handled, a

43.807

CHROMATOPAC C-R3A  
 SAMPLE NO 0 H-21 (0"-12")  
 REPORT NO (784)

FILE 0  
 METHOD 64  
 SAMPLE WT 100

PKNO	TIME	AREA	HK	CONC	NAME
1	1.7	5643			
2	2.038	39706		5.3276	1242
3	2.313	301704	V	25.5923	1242
4	2.567	73342	V		
5	2.732	48773	V		
6	2.995	630854	V	50.181	1242
7	3.423	392410	V	29.4566	1242
8	3.703	460159	V		
9	3.917	2303511	V	183.5694	1242
10	4.298	652042	V	51.5728	1242
11	4.608	612573	V	53.0896	1242
12	4.987	1973133	V	198.9589	1242
13	5.895	1320028	V	103.7284	1242
14	6.3	1048206	V	78.6465	1242
15	7.017	739740	V	38.356	1242
16	7.48	2439340	V	121.4543	1254
17	8.052	415195	V		
18	8.81	2838461	V	145.5977	1254
19	10.417	1026112	V	23.6061	1254
20	11.757	1567983	V		
21	13.477	2281276	V	93.0173	1260
22	15.225	1374638	V	46.7581	1260
23	17.23	722777	V	24.6072	1260
24	19.538	969583	V	34.5533	1260
25	21.023	415640	V	10.317	1260
26	23.073	247640	V		
27	25.232	327199	V	8.8309	1260
28	28.533	327958	V		
29	30.882	89342	V	2.345	1260
30	37.533	49269	V		
31	40.23	107161	V		
32	43.807	54216	V		

TOTAL 25855602

(1368.1881)

Exhibit 8. Integrator Output for Sample H-21 (0"-12")

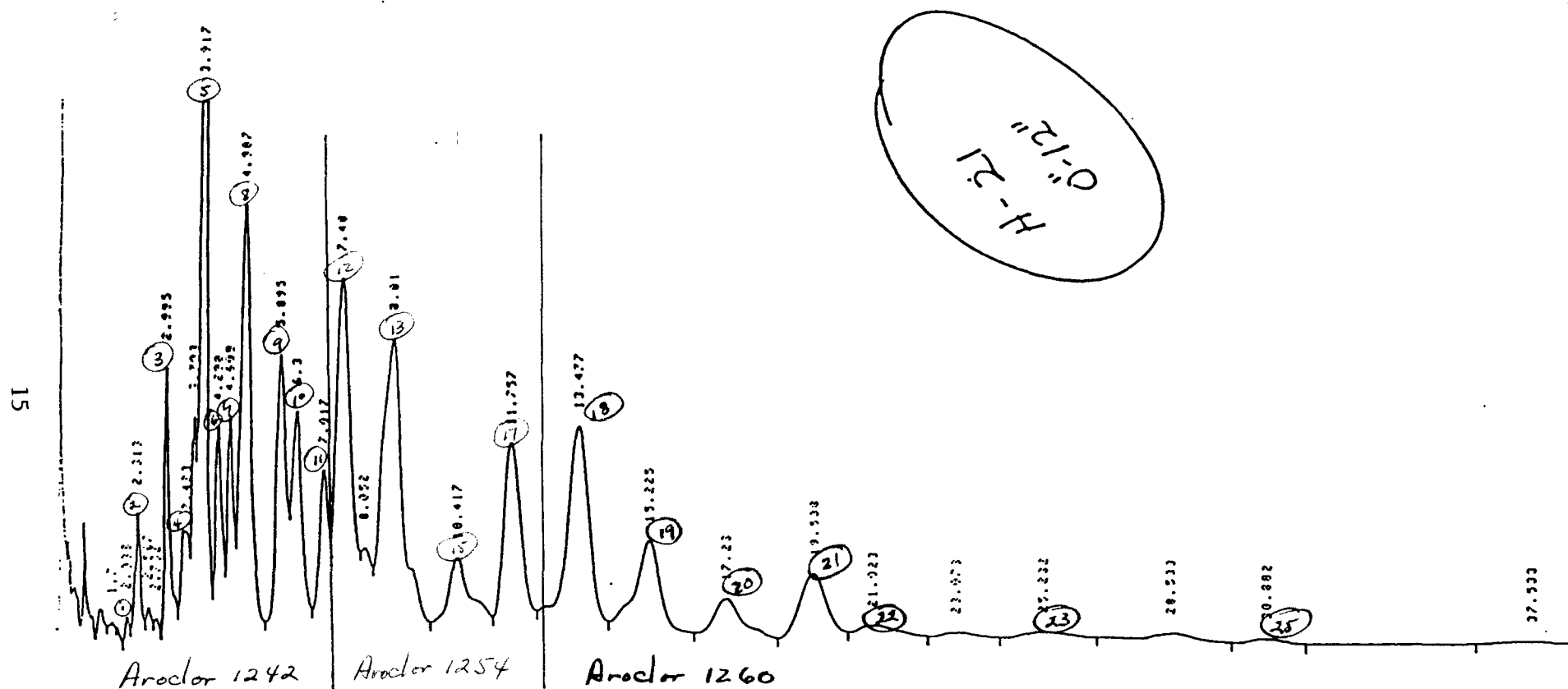


Exhibit 9. Peak Assignments for Aroclor Quantitations of Task 2 Sample

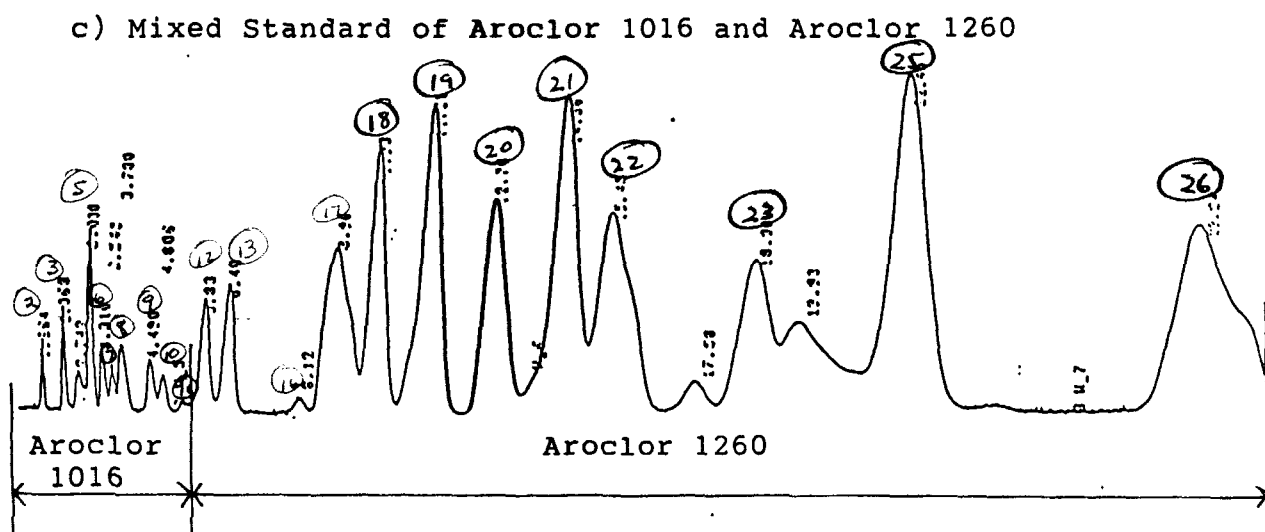
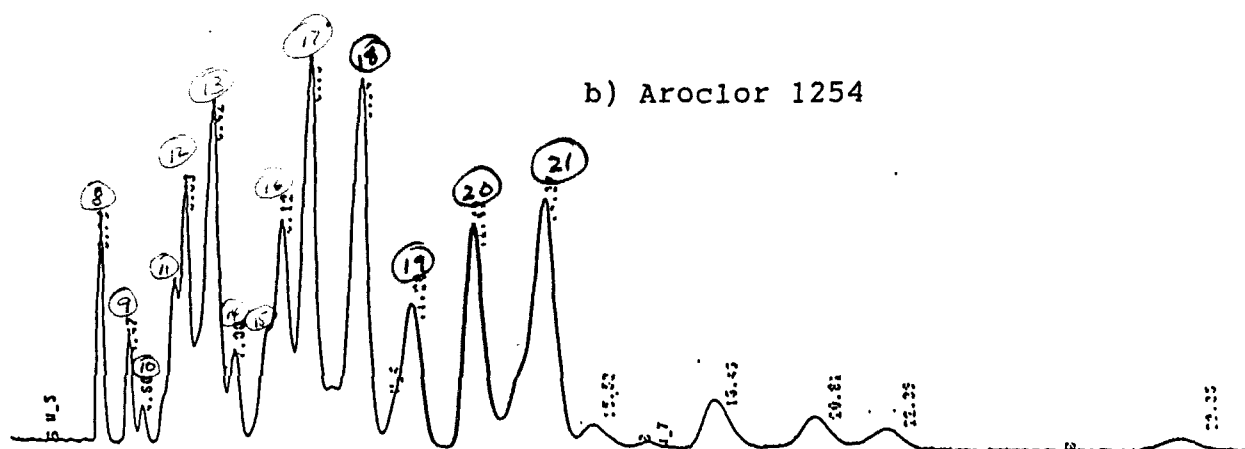
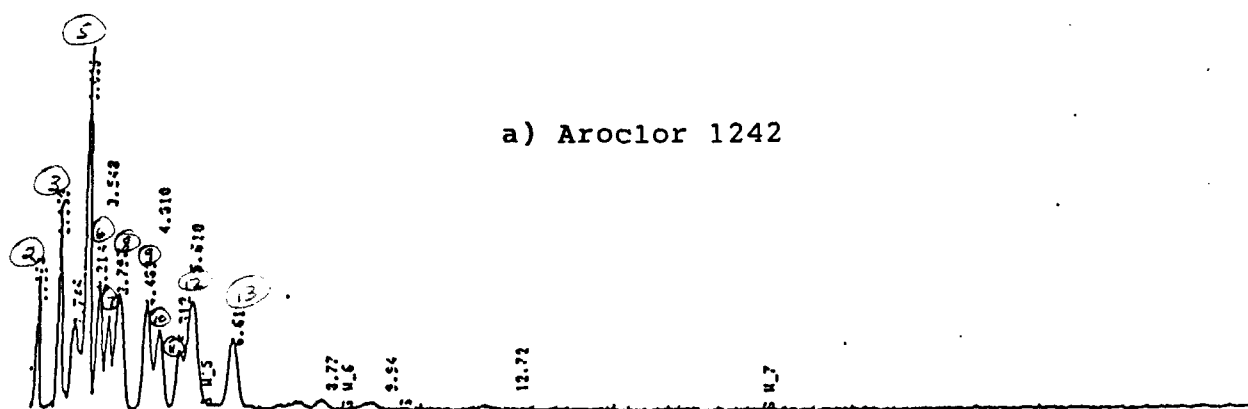
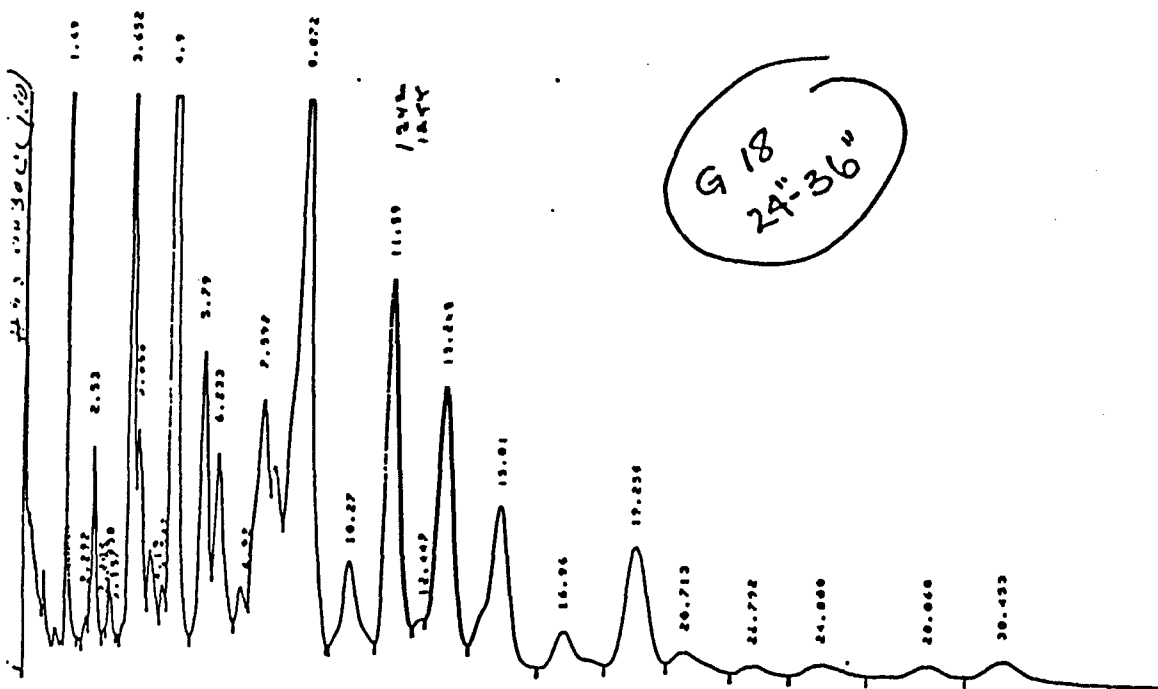


Exhibit 10. USACE Peak Assignments for Quantitation of Aroclors 1016, 1242, 1254, and 1260



CHROMATOPAC C-R3A  
SAMPLE NO 8  
REPORT NO 871

FILE 0  
METHOD 64  
SAMPLE WT 100

PKNO	TIME	AREA	HK	IDNO	CONC	NAME
1	1.69	795939				
2	2.292	33833		2	3.294	1242
3	2.53	342797	V			
4	2.808	16204	V			
5	2.958	98374	V	3	7.841	1242
6	3.157	5609	V			
7	3.432	1312787	V			
8	3.868	489422	V	5	39.0026	1242
9	4.19	245171	V			
10	4.542	109112	V	7	9.4564	1242
11	4.9	2480286	V	8	250.0971	1242
12	5.79	929993		9	73.0794	1242
13	6.233	648174	V	10	48.0321	1242
14	6.92	56813		11	2.9458	1242
15	7.592	570937		12	28.4268	1254
16	8.672	3098721		13	158.9476	1254
17	10.27	587393		15	13.5132	1254
18	11.59	2221471	V	17	49.494	1254
19	12.447	170289	V			
20	13.263	2051690	V	18	83.6561	1260
21	15.01	1445422	V	19	49.1658	1260
22	16.96	347064		20	11.8159	1260
23	19.253	1189700	V	21	42.3976	1260
24	20.713	234783	V	22	5.8278	1260
25	22.792	71253				
26	24.808	162417				
27	28.068	232213	V			
28	30.453	366544	V	25	9.6206	1260
29	39.652	240210		26	8.2686	1260
TOTAL		20551212			824.9822	

Exhibit 11. Sulfur Interference in Sample G-18 (24"-36")

generalized estimation of the magnitude of this bias cannot be made. This problem is discussed in more detail in Section 4.3.2.

#### 4.3.1 Quantitation Problem One.

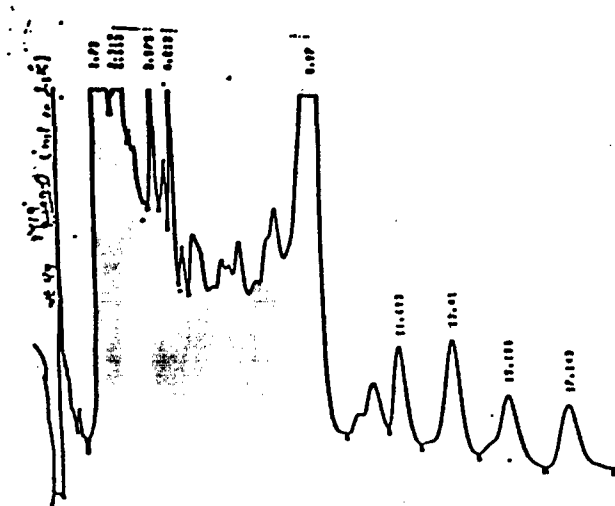
The analytical methodology used (EPA Method 8080) does not provide a means for quantitating PCB congeners in the samples which are not present in the Aroclor standards. As a consequence, di- and trichlorobiphenyls formed as the result of reductive dechlorination have not been quantitated and are not included in the total PCB data. This quantitation need is outside the scope of the EPA Method 8080 requirements. Methods such as EPA Method 680, the determination of PCB homologs by GC/MS, can be used to determine the total PCB content of samples in which these processes occur. It should be noted, however, that this methodology was not available at the time this study was conducted.

#### 4.3.2 Quantitation Problem Two.

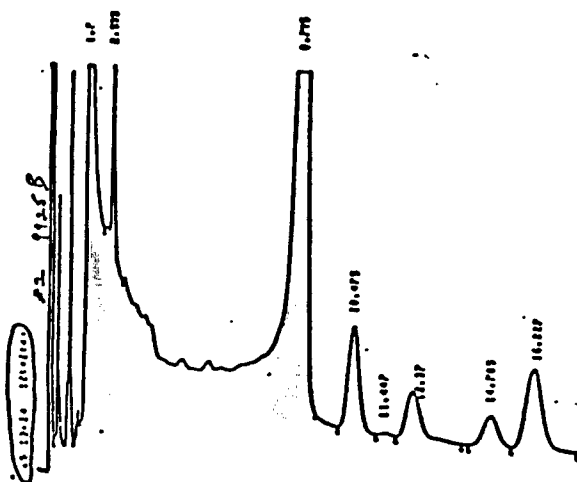
Although the electron capture GC detector is a chlorine sensitive detector, it can respond to certain non-PCB compounds. Consequently, when non-PCB interferences are present above detectable levels, they can cause pattern alterations and lead to false positive results. Sulfur is a common contaminant in sediment samples. Its presence, however, is easily recognized when it is present at high concentrations because it produces a uniquely characteristic chromatographic pattern. Exhibit 12 illustrates sulfur interference patterns observed in the USACE samples. The sulfur concentration in the samples decreases progressively from chromatograms (a) through (e). The problem is easily recognized in chromatograms (a) and (b). As the sulfur concentration decreases and the PCB concentration increases, it is much more difficult to recognize the sulfur interference. The three samples shown in Exhibit 13 all have sulfur interference (color-coded green). This interference was included in PCB area quantitations because it was not recognized by the USACE analysts.

The analytical procedure reportedly used in this study (EPA Method 8080) prescribes that a sulfur cleanup procedure (EPA Method 3660) be used to eliminate sulfur interferences in the sample extracts. Use of this clean-up

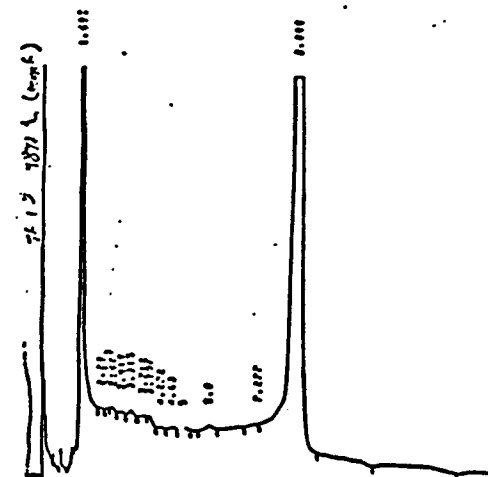
a)



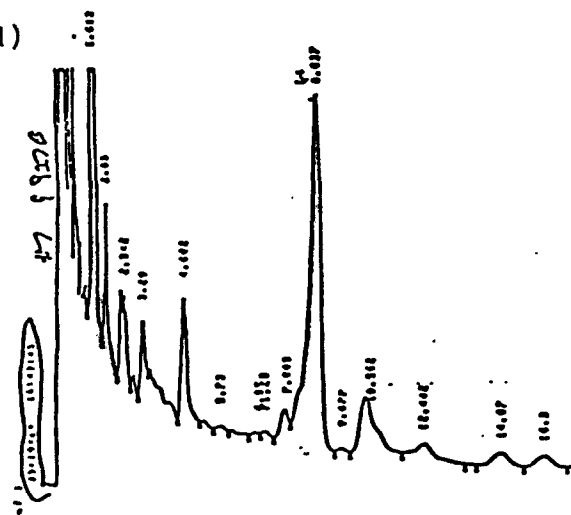
b)



c)



d)



e)

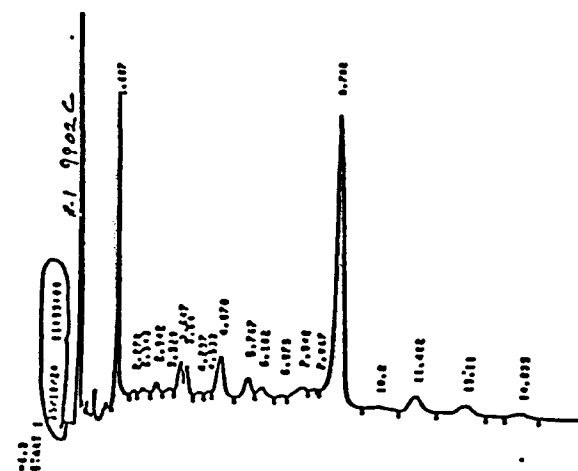
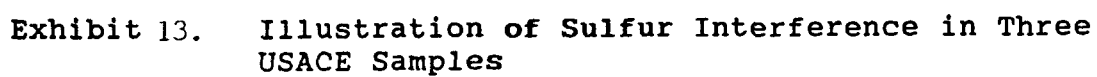


Exhibit 12. Sulfur Interference Patterns Observed in USACE Chromatograms



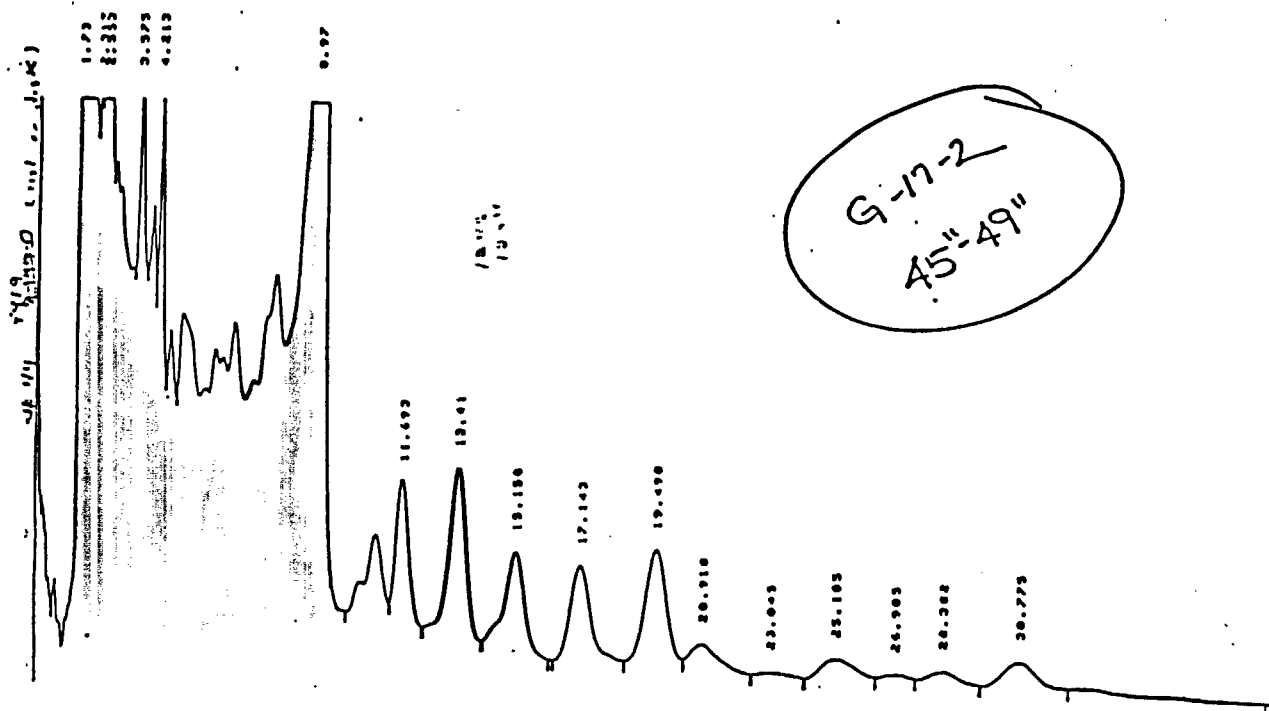


procedure is very effective and sulfur interferences can almost always be completely eliminated when it is used.

Although the draft QA/QC plan stated that elemental sulfur would be removed as necessary via activated copper prior to analysis, the required clean-up apparently was not performed. Further, the problem associated with the sulfur interference in the samples was handled inconsistently. The peak which occurs at RT approximately 1.7 minutes had no impact on the data since it occurs prior to the first peak of Aroclor 1242, and it was not included in the integrated area total. The inconsistency centers around the peak at RT approximately 8.8 minutes. As Exhibit 14 shows, there is no problem although sulfur is the main component of the sample. There is no concentration contribution calculated for either peak (RTs 1.73 or 8.97). The same thing holds true for the Sample I-15 (24"-36") chromatogram presented in Exhibit 15. For sample I-9-1 (22"-29"), shown in Exhibit 16, a concentration contribution was calculated, but it was recognized by the analyst and subtracted from the concentration total. However, in the case of samples G-18 (24"-36") and M-27-1 (0"-16") [Exhibits 11 and 17, respectively], significant concentrations from the peaks at RTs 8.87 and 8.84 are included in the concentration totals for each chromatogram. The inconsistency is further illustrated by Exhibits 18 and 19. When sample I-9-1 (22"-29") was initially analyzed, the sulfur interference was recognized by the analyst, and a subtraction was made for its contribution (Exhibit 16). However, as can be seen in Exhibit 18, the interference was not taken into account when the sample was rerun as a QA/QC spike (Exhibit 20). Because of the inconsistency in the manner by which the sulfur interference was handled, no attempt was made by YAI to quantitatively estimate the extent of this positive bias on the total PCB results reported by the laboratory.

#### 4.4 Pattern Alterations in USACE Samples

Frequently PCB alteration processes produce subtle chromatographic pattern changes which are difficult to detect unless the chromatogram is of high quality. It is extremely important that the full pattern be displayed and that all peaks remain "on-scale," with the most intense peaks giving between 90 and 95% full-scale deflection. For the most part, the USACE samples were diluted



CHROMATOPAC C-R3A  
 SAMPLE NO 0  
 REPORT NO 794

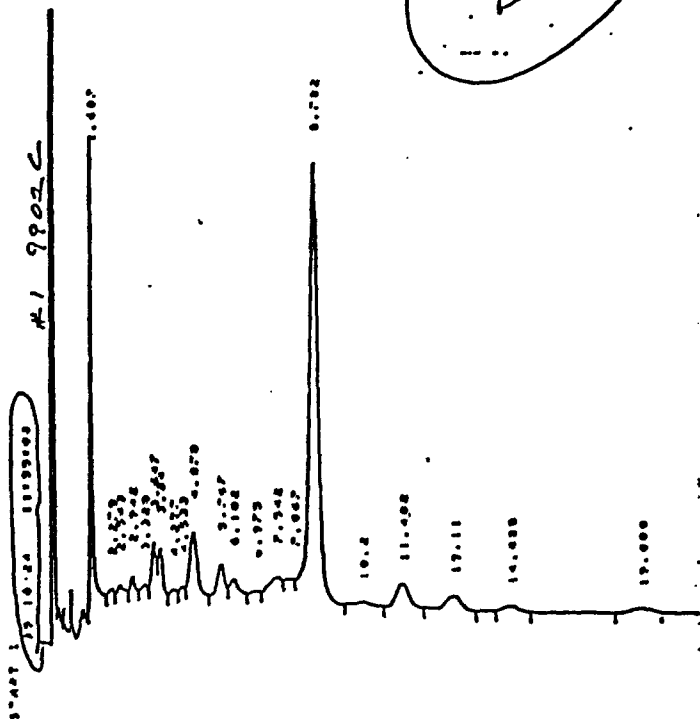
FILE 0  
 METHOD 64  
 SAMPLE WT 100

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.73	11363740	S E			
2	2.317	19735	T	2	1.674	1242
3	2.553	1260234	V			
4	3.575	369523		4	27.7307	1242
5	4.213	422864		6	33.4462	1242
6	6.97	10743556				
7	11.693	671869		17	14.9691	1254
8	13.41	1187650		18	48.4255	1260
9	15.158	806259		19	27.4248	1260
10	17.143	838678		20	28.5531	1260
11	19.493	1118805	V	21	39.8711	1260
12	20.918	300627	V	22	7.4621	1260
13	23.045	28059				
14	25.105	269243				
15	26.905	78636	V	24	3.0509	1260
16	28.382	143552	V			
17	30.775	311636		25	8.1795	1260
18	40.1	372109		26	12.8089	1260
TOTAL		38386768			253.6039	

Exhibit 14. Sulfur Interference in Sample G-17-2 (45"-49")

Simula 211-25412 502001A 135

I-15  
24"-36"



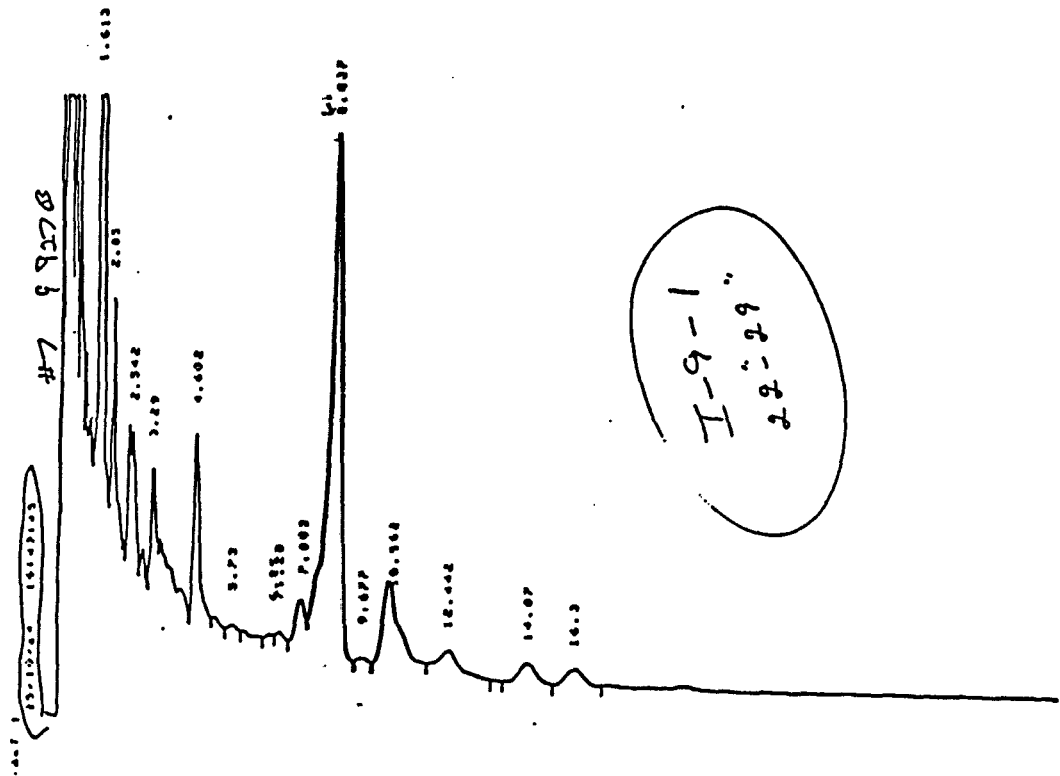
C-PROGRAM 1 MEMORIZED

C-1000-SPAC C-234  
SAMPLE NO 0  
REPORT NO 534

FILE 0  
RE 7 64  
SA MT 160

PAGE	TIME	AREA	PK	ICNO	LN	NAME
1	1.687	564869				
2	1.779	67892	V	1	2.8294	1242
3	1.943	118109	V			
4	2.942	111269	V	2	3.3434	1242
5	2.928	108654	V			
6	3.647	161562	V			
7	3.34	156517	V	4	4.5675	1242
8	4.237	94997	V	5	1.7419	1242
9	4.533	73719	V	6	2.6755	1242
10	4.878	353644	V	7	11.3235	1242
11	5.767	229836	V	8	6.3625	1242
12	6.192	194018	V	9	5.7726	1242
13	6.875	114523	V	10	6.2695	1242
14	7.542	259293	V			
15	7.867	151323	V			
16	8.782	1944014	V			
17	10.2	129859	V	14	2.8176	1254
18	11.402	199992	V	16	2.1316	1254
19	13.11	130688	V	17	3.0156	1254
20	14.935	31997		19	3.333	1254
21	19.000	46025		20	6.15	1260
TOTAL		3219713			18:	

Exhibit 15. Sulfur Interference in Sample I-15 (24"-36")



CHROMATOGRAM ( 3 ) MEMORIZED

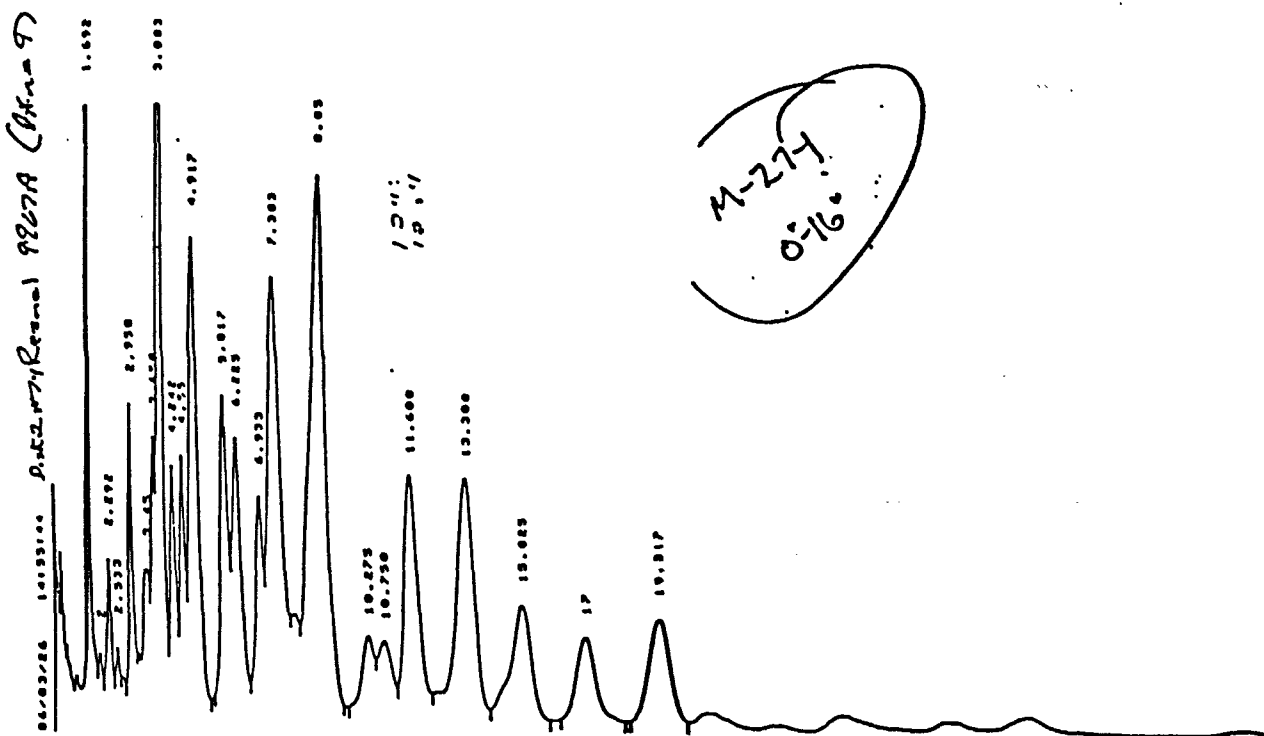
CHROMATOPAC C-R3A  
SAMPLE NO 8  
REPORT NO 343

FILE 0  
M. MOD 64  
SAMPLE WT 100

PKNO	TIME	AREA	NK	IDNO	CONC	NAME
1	1.613	1597242				
2	2.05	289322				
3	2.342	366634				
4	3.29	164573				
5	4.602	454386				
6	5.73	14254		8	9.395	1242
7	6.85	16767		10	0.9177	1242
8	7.128	23229	V	11	0.424	1242
9	7.803	177572				
10	8.837	2631352	V	13	38.1519	1254
11	9.677	12914				
12	10.562	425117		15	12.414	1254
13	12.442	213256	V			
14	14.07	130593		18	2.5848	1254
15	16.3	103485		19	2.2261	1260
TOTAL		6822891			57.318	

57.3  
38.2  
19.1

Exhibit 16. Sulfur Interference in Sample I-9-1 (22"-29")



PARAC 16-02 PAC C-23A  
 REPORT NO 70  
 225

FILE 0  
 METHOD 64  
 SAMPLE NT 100

PKNO	TIME	AREA	HK	IDNO	CONC	NAME
1	1.692	2435516				
2	1.999	765225		1	10.2677	1242
3	2.203	721364		2	61.2072	1242
4	2.533	122291				
5	2.958	1027874		3	145.3972	1242
6	3.443	1453109	V	4	109.0789	1242
7	3.650	1775059	V			
8	3.877	8164459	V	5	652.2266	1242
9	4.242	2107023	V	6	169.0266	1242
10	4.548	2143881	V	7	185.8029	1242
11	4.913	6535850	V	8	659.0358	1242
12	5.317	4034176	V	9	317.0072	1242
13	5.823	3420023	V	10	256.6032	1242
14	6.927	2916132		11	104.2266	1242
15	7.303	7077211	V	12	352.373	1254
16	8.843	12264264		13	629.6982	1254
17	9.272	1353783		15	31.1443	1254
18	9.763	1486195	V	16	41.2573	1254
19	11.602	5320051	V	17	118.5298	1254
20	13.303	6712913	V	18	273.714	1260
21	15.022	3533909		19	120.2853	1260
22	16.997	2581495		20	87.8879	1260
23	19.315	3586099		21	127.7986	1260
TOTAL		80843374			4451.2807	

Exhibit 17. Sulfur Interference in Sample M-27-1 (0-16")

C-ROHATOGRAM 5 MEMORIZED

CHROMATOPAC C-R3A

SAMPLE NO 0 I-9-1 (22"-29") Spike

REPORT NO 502

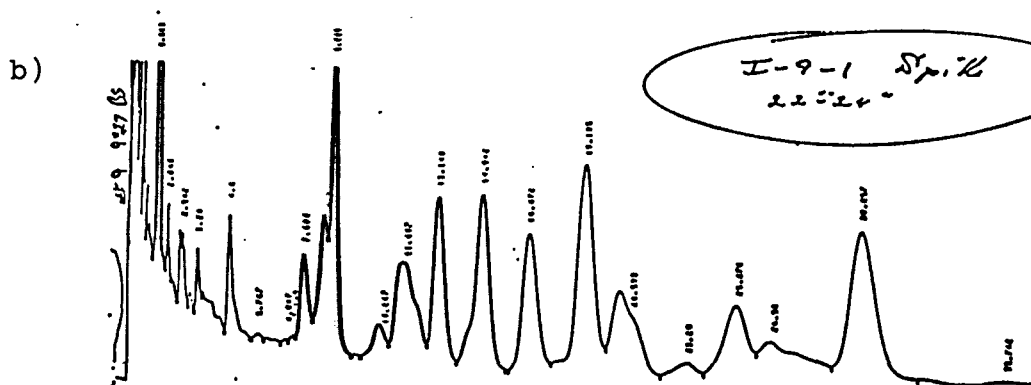
FILE 0

METHOD 64

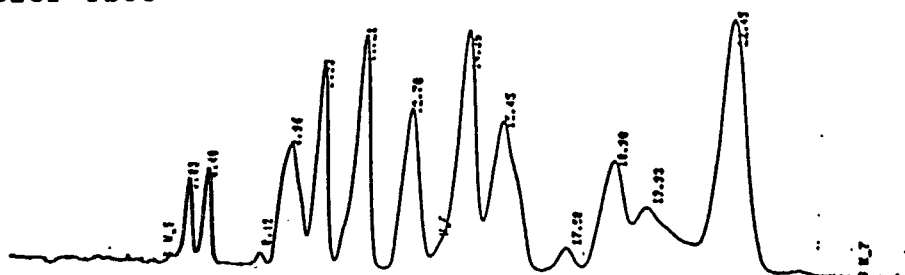
SAMPLE WT 100

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	1.613	1411245				
2	2.048	142338				
3	2.542	378706				
4	3.28	168419				
5	4.6	651090				
6	5.767	23834		8	0.6605	1242
7	6.347	17916		10	0.9808	1242
8	7.165	52273	V	11	1.414	1242
9	7.608	810351	V			
10	8.413	1265667	V	12	30.9559	1254
11	8.828	2323019	V	13	33.6788	1254
12	10.667	440581		15	8.7494	1254
13	11.697	2185201	V			
14	13.148	1999939	V	17	46.1485	1254
15	14.942	2687366		18	53.1905	1254
16	16.872	2329824		19	50.1175	1260
17	19.185	4082068	V	20	85.9099	1260
18	20.593	2245584	V	21	94.0741	1260
19	23.28	259589				
20	25.27	1844424	V	23	50.3641	1260
21	27.27	1710270	V	24	129.1913	1260
22	30.257	4105642	V			
23	35.742	121130				
24	39.378	4416322	V			
TOTAL		35672788			585.4351	

Exhibit 18. Integrator Output for Sample I-9-1 (22"-29")  
Spike



c) Aroclor 1260

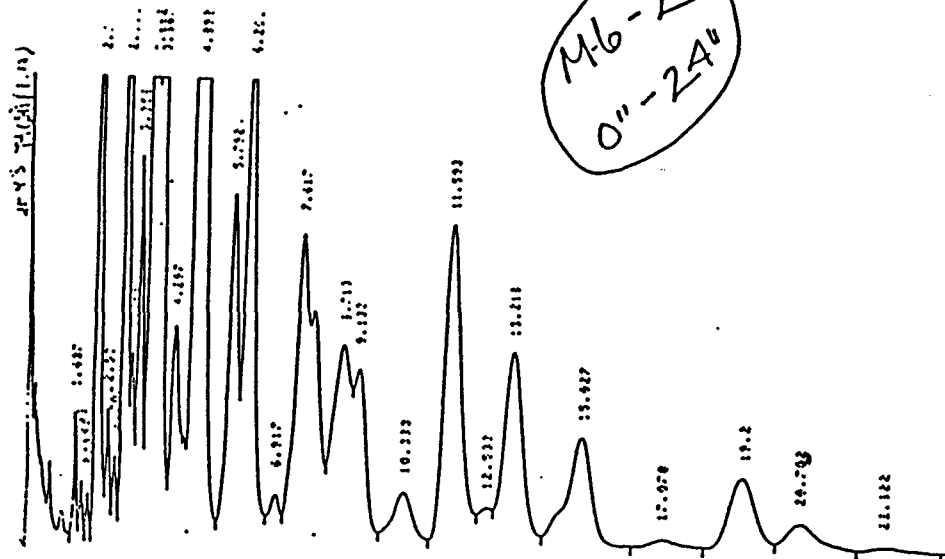


27



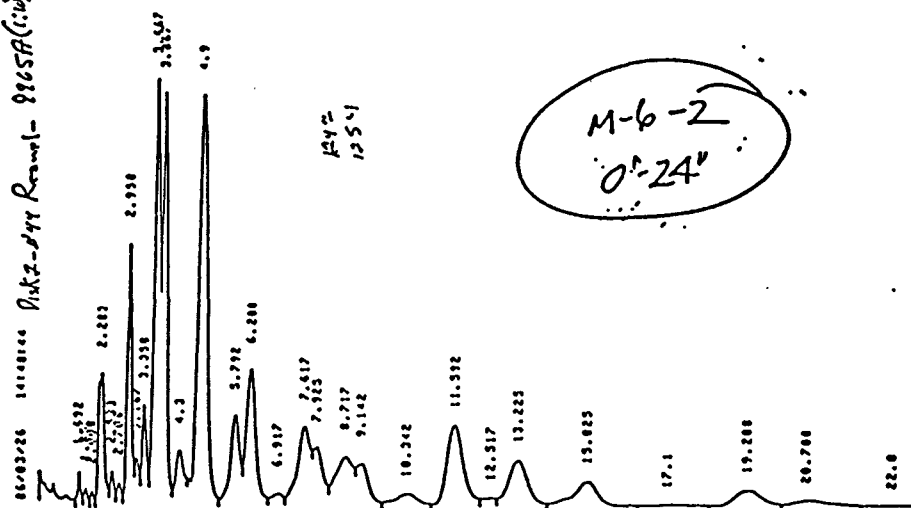
*Medusa*

M-6-2  
0"-24"



86-0326 1410144 NK2-044 Rempt- 8965A(1.0) (Athen:

M-6-2  
01-24"



28

and re-analyzed when high PCB concentrations were encountered (see Exhibit 20). Although the desired situation where all peaks remain "on scale" was not always met, the re-analysis chromatograms were invaluable in assessing pattern alterations in the USACE samples.

Four pattern alteration sources were identified from the review of the "resolution enhanced" USACE chromatograms:

1. The presence of more than one Aroclor in the samples, and widely varied ratios of Aroclor 1016/1242 to Aroclor 1254;
2. The presence of sulfur, a non-PCB interference;
3. The partial loss of lower chlorinated congeners (di- and certain trichlorobiphenyls), due to environmental aging losses;
4. Aroclor degradation in 97% of the sediments.

The first two sources were discussed in Sections 4.2 and 4.3, respectively. Sources 3 and 4 will be covered in the following sections.

#### 4.4.1 Environmental Aging or "Weathering."

Pattern alterations due to environmental aging or "weathering" occur because Aroclors do not behave as a homogeneous substance. Differences in volatility and water solubility of the individual PCBs tend to fractionate the residue. A "weathered" sample has undergone modification with respect to the proportions of individual PCB congeners present. Loss of more volatile or soluble congeners yields a residue which demonstrates low-end drop-off and, usually, high-end enhancement of peaks. Numerous USACE samples demonstrate low-end drop-off in the Aroclor 1016/1242 region of the chromatograms.

#### 4.4.2 Anaerobic Degradation.

The most significant Aroclor pattern alteration observed in USACE sediment samples is that due to anaerobic dechlorination. The congener distribution patterns exhibited by the samples show evidence of the occurrence of anaerobic biotransformations. New peaks are present in the patterns as well

as "high-end" drop-off due to the degradation of higher chlorinated PCBs. Peak enhancements, reductions and disappearances have also occurred. Anaerobic alteration patterns in sediment samples are distinctively different from those occurring as the result of extractive losses of the more soluble congeners of Aroclors. As stated earlier, evidence of anaerobic degradation is seen at approximately 97% of the USACE sampling sites.

## 5.0 DISCUSSION OF RESULTS

### 5.1 Comparison of Task 2 and Task 7 Data

The USACE study (Task 2) was a more extensive program involving many more samples than the special research investigation described in the Task 7 report. The harbor area sampled was larger and collections were made to greater depths at the sampling sites. An example of sample compositional variability with depth for a USACE sampling site (G-17-2) is shown in Exhibit 21. The PCB concentration in chromatogram (a) was so high that re-analysis at a dilution was necessary [chromatogram (b)]. Evidence of Aroclor 1254 degradation is seen in both chromatograms (b) and (c). Chromatogram (d) shows a significant sulfur interference which completely masks the Aroclor 1016/1242 region. The compositional distribution for this sample is typical of the entire study area where the highest PCB concentrations are found in the upper stratum (0"-12") and the highest sulfur concentrations occur in the deeper samples (>12").

Even though the USACE study (Task 2) and the Task 7 investigation differ in scope, the two studies complement each other and together provide an indication as to the status of PCBs in the sediments of the upper estuary of the Acushnet River, from the Coggeshall Street Bridge north to the mouth of the river.

The anaerobic dechlorination patterns seen in the USACE samples closely resemble the patterns observed in the Task 7 samples. The correlation between sample patterns from the two studies is shown in Exhibits 22-24.

Progressive transformation of both Aroclor 1016/1242 and Aroclor 1254 was observed in the USACE samples. For a more detailed discussion of Aroclor pattern alterations in general and anaerobic biotransformations in NBH

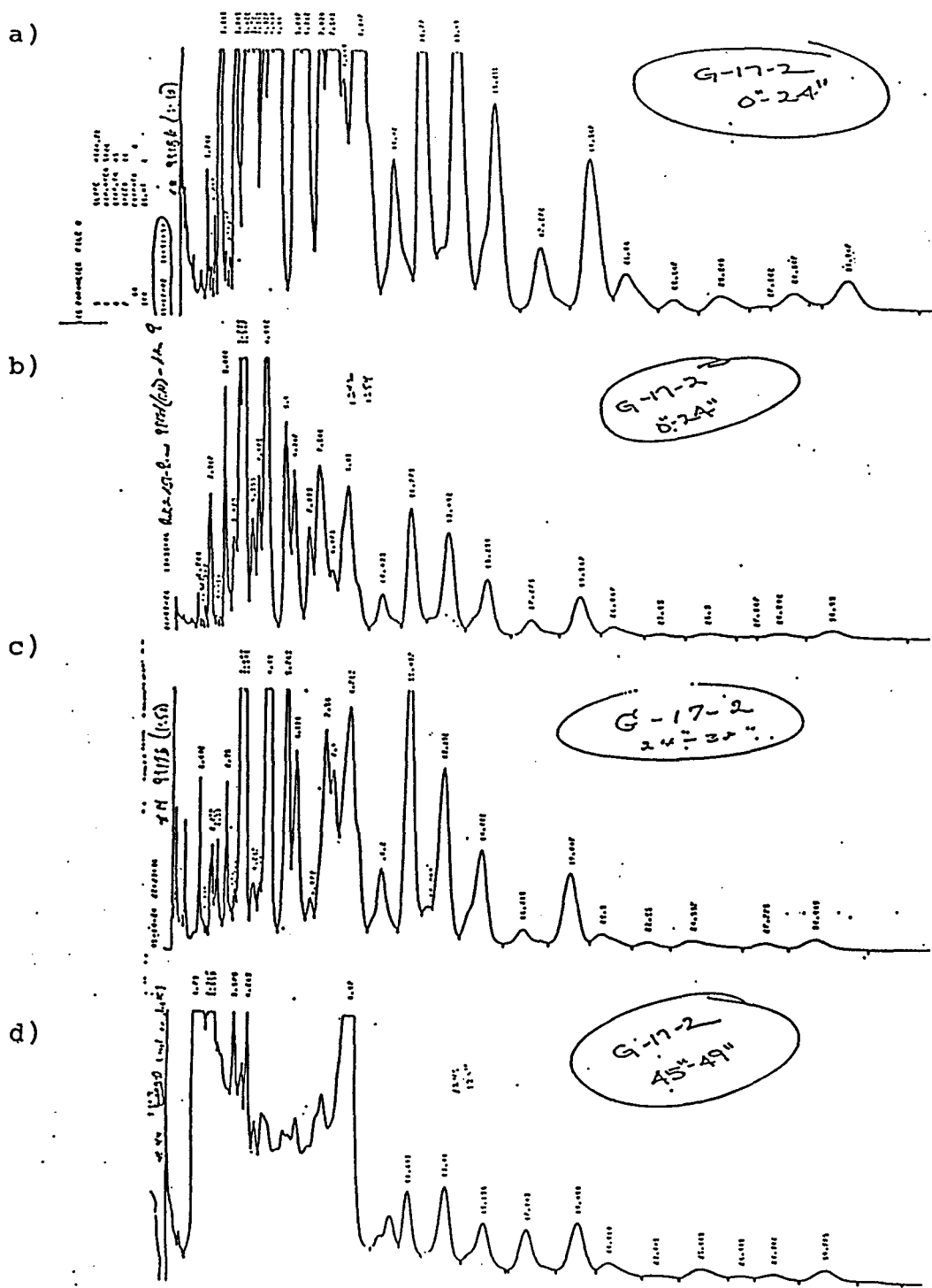


Exhibit 21. Example of Compositional Variation with Depth at Site G-17-2





UN 21 STARTED 11:04.4 83/03/25 PCB ONE PKUJ JUL  
: 03740-D MP LAST EDITED 17:15.9 88/03/24

10.5 NBH-110-50-02, 3-25-88 1" 11375 100.000

NBH-110-02

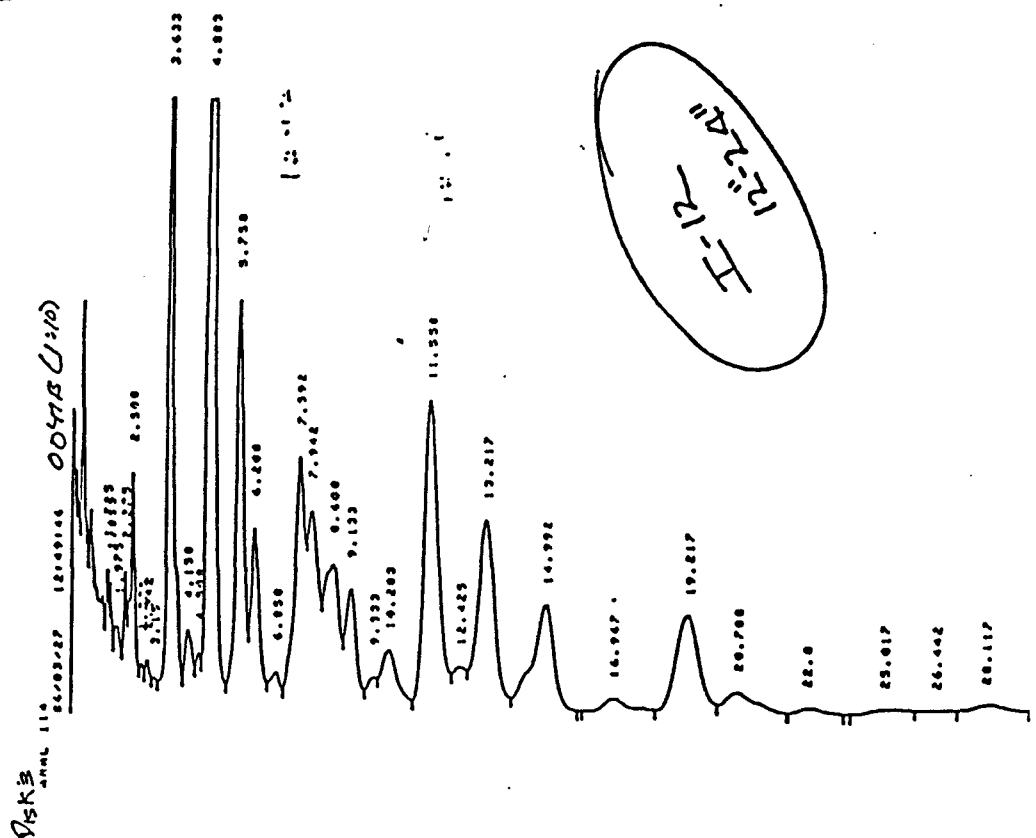


Exhibit 24. Comparison of Task 7 Sample NBH-110-02 and Task 2 Sample I-12 (12\"-24\")

sediments in particular, the reader is referred to the YAI final reports for Task 11 and Task 7, respectively. As was the case for Task 7, one Task 2 sampling site (J-7) showed little if any evidence of PCB transformations (see Exhibit 25). Both of these sites contained the highest concentrations of PCBs found in the respective studies, 76,100 ppm for J-7 (Task 2) and 130,000 ppm, for NBH-112-02.

A number of USACE samples, especially those taken at depths below 12 inches, appear to show a more advanced Aroclor 1254 degradation than was observed in any of the Task 7 samples. The chromatograms for three of these samples are shown in Exhibit 26. The tri-, tetra-, and pentachlorobiphenyls are reduced significantly in these samples while the occurrence of the very early eluting peaks suggests the presence of biphenyl and monochlorobiphenyls. The classification of the PCB transformations observed in the USACE samples is presented in the Task 10 final report.

## 5.2 Quality Assurance/Quality Control (QA/QC) Evaluation

The intended use of the final data determines the level of QA/QC effort which must be an integral part of a project. The magnitude of the effort put into the project as well as designation of the New Bedford Harbor as a Superfund site should have justified and required the preparation of a site specific Quality Assurance Project Plan (QAPP) covering both the field and laboratory aspects of the project. The only known formalized document prepared for the project was the draft QA/QC plan contained in Appendix E of the USACE project report (Condiak, 1986). The draft QA/QC plan was a good start, but did not qualify as a formalized QAPP. A detailed and properly implemented QAPP would have resulted in higher overall quality of the analytical data with reduced QA/QC effort.

The laboratory QA/QC plan contained the necessary elements required for documenting the quality of data:

- o spike recoveries and the analysis of standard reference materials to establish the accuracy of the data,
- o replicate samples to measure precision, and





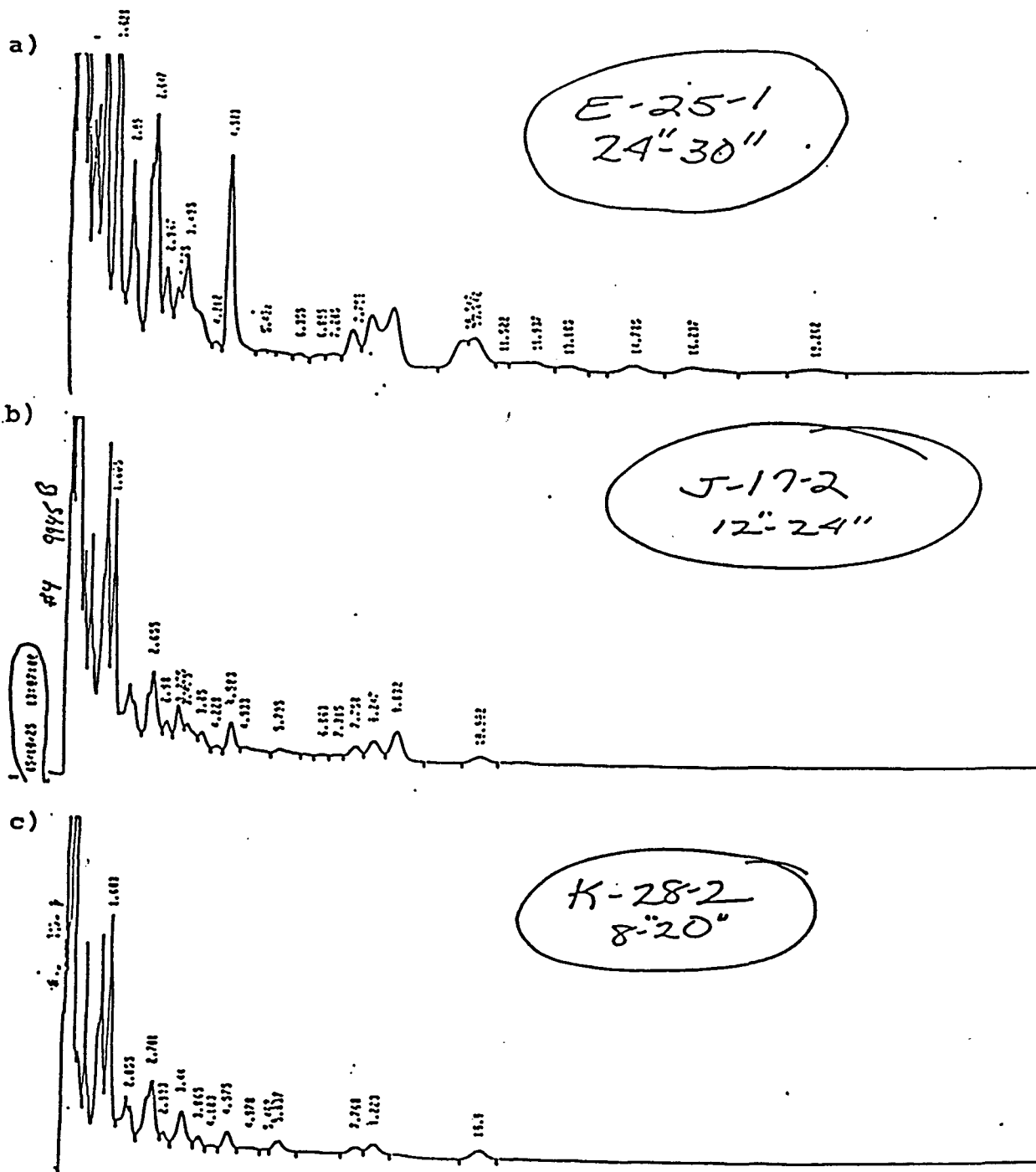


Exhibit 26. Chromatograms Illustrating Advanced Aroclor 1254 Degradation

- o a split sampling program with an outside laboratory for collaborative testing.

However, the overall use of QA/QC samples was excessive. A total of 51 QA/QC samples were utilized for the project of 86 samples analyzed for PCBs--a 59% effort. Notwithstanding, the mere use of QA/QC samples does not constitute a successful QA/QC effort. This is illustrated by the USACE control samples. Ideally, control samples for PCB projects should be completely free from electron-capture responsive components. When "clean" control samples are used, they serve as excellent process blanks for the entire system--from sample collection through final analysis. Unfortunately this was not the case for this study. In fact, the chromatogram for Control 1 (Exhibit 27) suggests the presence of degraded Aroclor 1260. As a consequence, the analysis of the 11 control samples served no useful purpose.

The two areas where this program appeared most deficient were data validation and the lack of use of written standard operating procedures which would have documented the analysis protocol to be followed. Had a written protocol required the use of the clean-up for sulfur, the false positive data would not have occurred. Additionally, an effective data validation scheme would have detected the presence of sulfur in the chromatograms and necessary corrective action could have been taken. In spite of these deficiencies, a data validation review of the chromatograms should have detected the significant Aroclor pattern alterations which were clearly evident.

The analysis of the EPA standard reference materials produced acceptable results and the percent recoveries of the Aroclor 1260 spikes were reasonable for samples of this type. However, these accuracy assessments have very little direct bearing on the accuracy of the actual samples. The pattern alterations which gave rise to the quantitative bias of the samples (the presence of new PCB congeners and the sulfur interferences) were not present in the EPA standard reference materials. The sulfur interference only affected one minor peak of Aroclor 1260, and the new congener peaks occurred prior to the Aroclor 1260 pattern. For these reasons, Aroclor 1260 was a poor choice as a spiking compound for the study.

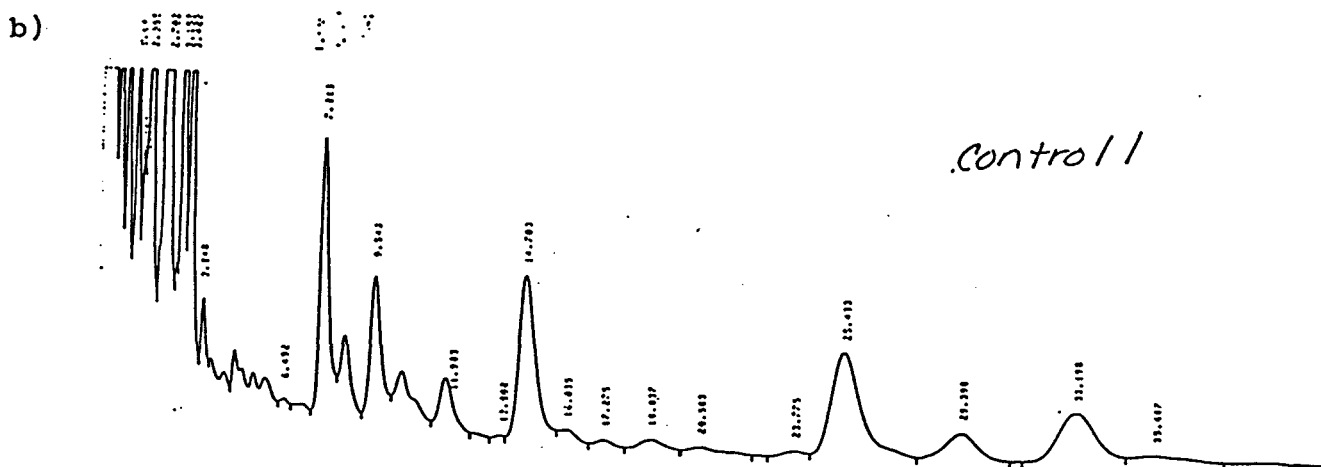
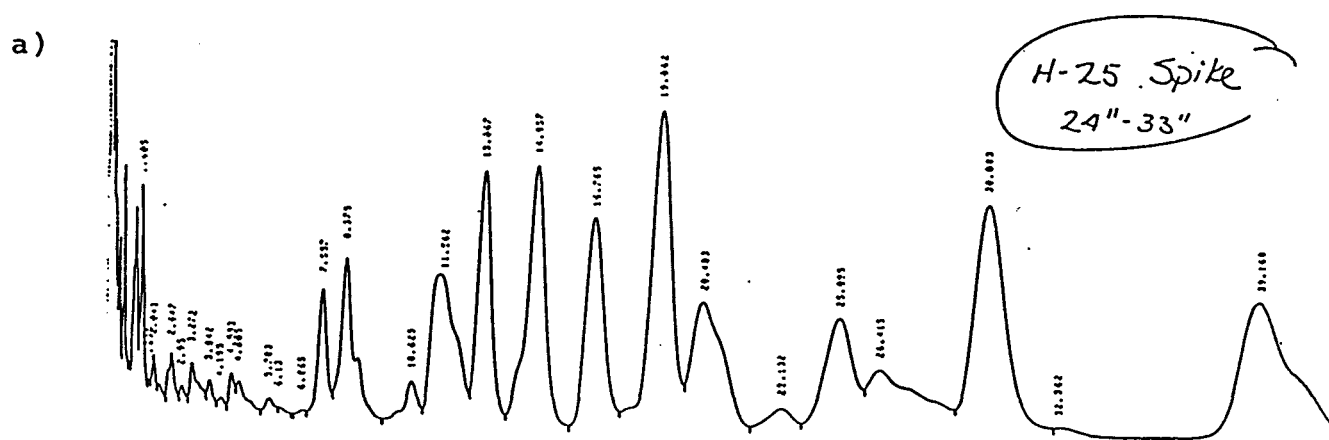


Exhibit 27. Chromatograms of Sample H-25 (24"-33") with Aroclor 1260 Spike (a) and USACE Control 1 Sample (b)

It is not clear from the write-up in the draft QA/QC plan if the sample replicates are true sample splits or aliquots of the same extract. However, since the split samples for confirmation analyses were true sample splits, the assumption is made that the internal duplicate and spike samples represented separate 5-gram aliquots of the samples. Both the inter- and intra-laboratory replicate data are reasonable for sediment samples, but a statistical analysis of the results would be helpful. From the standpoint of data completeness, useable chromatograms were produced for 91% of the samples. Interferences precluded the generation of valid data for 8 samples. Three of the 8 samples showed poor chromatography. The other five samples had excessive sulfur interferences. In summary, the overall quality of the data is adequate for contamination assessment purposes; but the quantitations should be considered as estimates only.

## 6.0 OVERALL ASSESSMENT

The data evaluation has shown the following:

1. The analytical methodology proposed for use in the study was appropriate as was the instrumentation employed. The quality of the data suffered, however, because the prescribed sample clean-up for sulfur removal was not used.
2. Peak resolution of the chromatograms was poor. This situation should not have had a negative impact on data quality, however, since both the standards and the samples should have been run under identical analysis conditions.
3. Poor peak resolution of the original chromatograms presented a problem as it related to the pattern alteration evaluation, especially since the corresponding standards were not available.
4. The predominant PCBs present in the samples are Aroclor 1016/1242 and Aroclor 1254.
5. Aroclor 1260 was found in four samples which came from three different sampling sites. In addition, trace levels of Aroclor 1260 were observed in eight additional samples. Since there is no evidence of alteration of the Aroclor 1260 pattern, laboratory contamination is suspected as the source of Aroclor 1260 in these samples.

6. PCB quantitation was impacted by two problems. First, the quantitation of the new congeners formed during biotransformation (which are not present in commercial Aroclor mixtures) is beyond the scope of analytical method (EPA Method 8080). Therefore, these PCBs were not included in the total PCB data. When new congeners are present in the samples, the data are biased low. Second, a positive bias exists in the data for some of the samples due to the presence of sulfur.
7. The QA/QC protocol apparently was not followed as it related to the clean-up of samples extracts for the removal of sulfur. As a consequence, sulfur interference was present in 60 of the 85 sample chromatograms (70%).
8. Chromatographic pattern alterations arising from one or more of the following sources were present in the chromatograms:
  - o the presence of Aroclor mixtures with wide variations in mixture ratios;
  - o non-PCB interference due to the presence of sulfur in 70% of the samples;
  - o partial loss of lower chlorinated congeners resulting from environmental "weathering" losses; and,
  - o changes in congener distributions as the result of anaerobic dechlorination of PCBs.

New peaks are present in the patterns as well as "high-end" drop-off due to the degradation of higher chlorinated PCBs. Peak enhancements, reductions, and disappearances have also occurred.
9. The most significant Aroclor pattern alteration observed in USACE sediment samples is that due to anaerobic dechlorination. Evidence of PCB transformation is seen at approximately 97% of the USACE sampling sites.

## 7.0 SUMMARY

By utilizing the "resolution enhanced" USACE chromatograms, an analytical data evaluation was performed which has identified the Aroclors present in the samples, determined the sources of alteration patterns observed, and demonstrated the presence of anaerobic degradation in the sediments. Although PCB transformations were obvious in the majority of the samples, they apparently were not recognized by the USACE analysts.

There were sufficient problems with the PCB determinations that the quantitative data should be considered as estimates of the total PCB content of the samples. In the opinion of the author, however, there is every indication that the data are adequate for contamination assessment and that the study provides much useful information.

## REFERENCES

1. Condike, B. J., New Bedford Harbor Superfund Site Acushnet River Estuary Study, U. S. Army Corps of Engineers, New England Division, MWQL, Hubbardston, MA (1986).
2. Method 680, "Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry," EMSL, U. S. Environmental Protection Agency: Cincinnati, OH (1985).
3. Method 8080, "Organochlorine Pesticides and PCBs," Test Methods for Evaluating Solid Waste, SW-846, 2nd Ed., U. S. Environmental Protection Agency, Office of Solid Waste and Emergency Response: Washington, DC (1982) and 3rd Ed. (1986).
4. Webb, R. G., and McCall, A. C., J. Chromatogr. Sci 11: 366-373 (1973).



APPENDIX A  
TERMS AND ABBREVIATIONS

## TABLE A-1. TERMS

"Additive Effect": To heighten or increase the intensity of a peak in a chromatogram (enhancement).

Anaerobe: A microorganism that flourishes without free oxygen.

Anaerobic microbial (bio)degradation: The reduction of a chemical component from a higher to a lower type by the action of anaerobic microbes.

Anaerobic biotransformations: Changes brought about as the result of the action of anaerobic bacteria.

Anaerobic dechlorination: A specific PCB microbial degradation process whereby chlorine is selectively removed from a congener as the result of anaerobic microbial actions.

Aroclor: Trade name (Monsanto) for a series of commercial PCB and polychlorinated terphenyl mixtures marketed in the United States.

Aroclor degradation: A reductive modification with respect to the proportions of the individual PCB congeners present in the specific Aroclor.

Aroclor transformation: Any change (either reduction or enhancement) in the unique characteristic of the composition of a specific Aroclor.

Chromatogram: A tracing of the detector output from a chromatograph which consists of a series of peaks with time.

Chromatographic pattern alteration: Any change or modification which occurs in the chromatogram produced by a known reference material (e.g., a specific Aroclor).

Congener: One of the 209 PCBs or other group of compounds, not necessarily the same homolog.

Degrade: To reduce from a higher to a lower type.

Enhance: To heighten or increase in intensity.

Environmental aging (weathering): The process whereby the Aroclor(s) present in an environmental sample undergoes modification with respect to the proportions of individual PCB congeners present as the result of partial vaporization, adsorption onto surfaces, and/or extraction into water. True molecular solution in water is shown (on chromatograms) as the non-selective loss of the more volatile and more water-soluble congeners from the Aroclors in the sediments.

TABLE A-1. TERMS (continued)

"High-end drop-off": The pattern alteration observed when higher chlorinated PCB congeners (usually penta- and hexa-) undergo anaerobic dechlorination.

High resolution gas-liquid chromatography: Gas chromatography with a capillary column.

Homolog: One of the 10 degrees of chlorination of PCBs ( $C_{12}H_9Cl$  through  $C_{12}Cl_{10}$ ) or other group of compounds varying by systematic addition of a substituent.

Isomer: Any PCB or other compound which has the same molecular formula, different positional substitutions. 2,2'-Dichlorobiphenyl and 2,3-dichlorobiphenyl are isomeric; 4-chlorobiphenyl and 2,3,4-trichlorobiphenyl are not.

"Low-end drop-off": The pattern alteration observed when lower chlorinated PCB congeners are removed from samples by weathering.

Part per million (ppm): One part in  $10^6$ .

Pattern alterations: Changes in a characteristic chromatographic pattern. The effect of the changes will be reflected by peak enhancements, reductions, or both. (See chromatographic pattern alterations.)

Polychlorinated biphenyl (PCB): One of 209 individual compounds having the molecular formula  $C_{12}H_nCl_{10-n}$ , where  $n = 0-9$ . This definition includes monochlorobiphenyls, but not biphenyl.

PCB degradation: A conversion whereby a PCB congener of a higher chlorine content is reduced (converted) to one of a lower chlorine content.

PCB transformation: Any change whereby a PCB congener is converted into another compound.

Qualitative: Having to do with establishing the presence or identify of a compound.

Quantitative: Having to do with measuring the amount of concentration of a compound in a sample.

Retention time: Time between injection and detection of a compound on a chromatographic system under specified conditions, expressed in seconds or minutes.

TABLE A-1. TERMS (continued)

Transformation: Any change which gives a different appearance.

Weathering: A process which gives a compositional change in an Aroclor residue  
(see environmental aging).

TABLE A-2. ABBREVIATIONS

Balsam	Balsam Environmental Consultants, Inc.
EPA	(U.S.) Environmental Protection Agency
GC	Gas-liquid chromatography (column type unspecified)
GC/EC	Gas chromatography/electron capture
GC/MS	Gas-liquid chromatography/mass spectrometry (ionization mode unspecified)
NBH	New Bedford Harbor
PCB	Polychlorinated biphenyl
ppm	Parts per million ( $10^{-6}$ )
RT	Retention time
USACE	(U.S.) Army Corps of Engineers
YAI	Yoakum & Associates, Inc.

APPENDIX III

TASK 3

*Yoakum & Associates, Inc.*

ENVIRONMENTAL CONSULTANTS

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**EVALUATION OF PCB ANALYTICAL DATA FOR SAMPLES ANALYZED  
BY CAMBRIDGE ANALYTICAL ASSOCIATES (CAA) - EPA CASE #5058**

**Prepared for:**

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**Prepared by:**

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Lenoir City, Tennessee 37771**

**September 8, 1989**

**Y & A Project NMF-3003 Task 3**

**DRAFT**

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**EVALUATION OF PCB ANALYTICAL DATA FOR SAMPLES  
ANALYZED BY CAMBRIDGE ANALYTICAL ASSOCIATES (CAA) -  
EPA CASE #5058**

**Y & A PROJECT NMF-3003 TASK 3**

**1.0 TASK 3 BACKGROUND**

Environmental Protection Agency (EPA) Case #5058 consisted of 85 Acushnet River upper estuary samples collected by the U. S. Army Corps of Engineers (USACE) and analyzed for Hazardous Substance List (HSL) Organic and Inorganic Compounds by four EPA contract laboratories.

Task 3 covers the evaluation of the PCB analytical data for 15 of the Case #5058 samples which were analyzed by Cambridge Analytical Associates (CAA). These soil samples were collected from 14 sites in the wetlands area of the upper estuary (see Exhibit 3-1). Thirteen of the samples were 0-12" collections. Two samples (AD587 and AD597) were from the 12"-24" stratum.

**2.0 DATA EVALUATION**

**2.1 Pattern Alterations in CAA Samples**

No evidence of PCB biotransformation was seen in any of the soil samples. This is not surprising since the PCB degradation seen in the Task 2 USACE samples occurs as the result of anaerobic dechlorination which has been observed only in sediment samples.

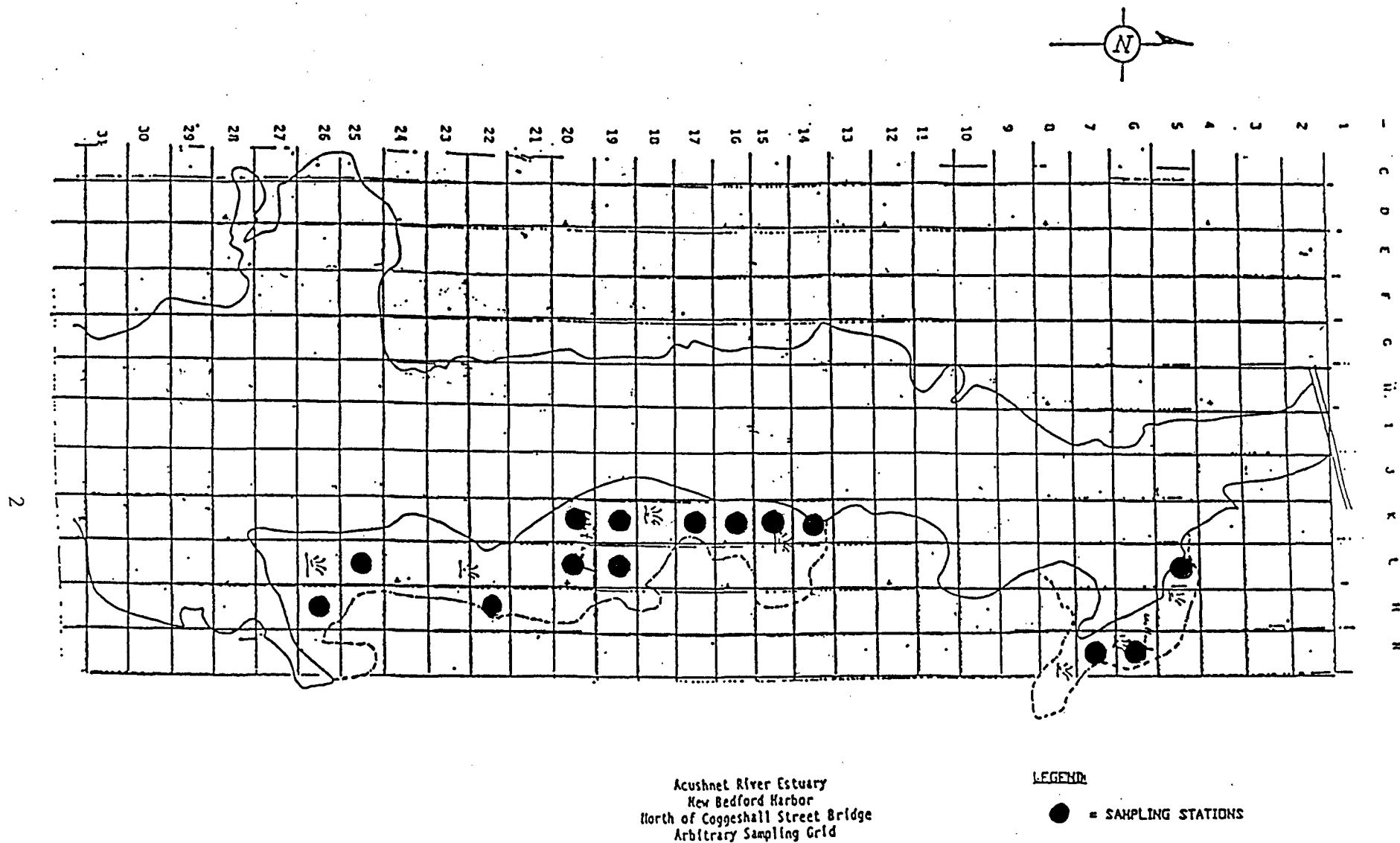


Exhibit 3-1. Location of Samples Analyzed by CAA - EPA Case #5058

Pattern alteration as the result of the environmental aging of Aroclor 1016/1242 was observed in all but one of the samples (AD586) where PCBs were detected. Environmental aging, or "weathering," is defined as the process whereby the Aroclor(s) present in an environmental sample undergoes modification with respect to the proportions of individual PCB congeners present as the result of partial vaporization, adsorption onto surfaces, and/or extraction into water. The Aroclor pattern alterations which occur as the result of weathering are distinctively different from those which result from anaerobic PCB degradation.

During weathering, Aroclors 1016 and 1242 experience a non-selective loss of the more volatile or soluble congeners, yielding a residue which demonstrates low-end drop-off and, usually, a high-end enhancement of peaks. As a result, the pattern of the weathered Aroclor residue resembles the pattern of Aroclor 1248, the next higher chlorinated Aroclor in the percent chlorination sequence. This phenomenon is demonstrated in Exhibit 3-2. Chromatogram (a) is a standard of Aroclor 1016. A severely weathered Aroclor 1016 residue is shown in chromatogram (b). This chromatogram (b) has a congener distribution in the tri- and tetrachlorobiphenyl region which is very similar to that of chromatogram (c), which is an Aroclor 1248 standard.

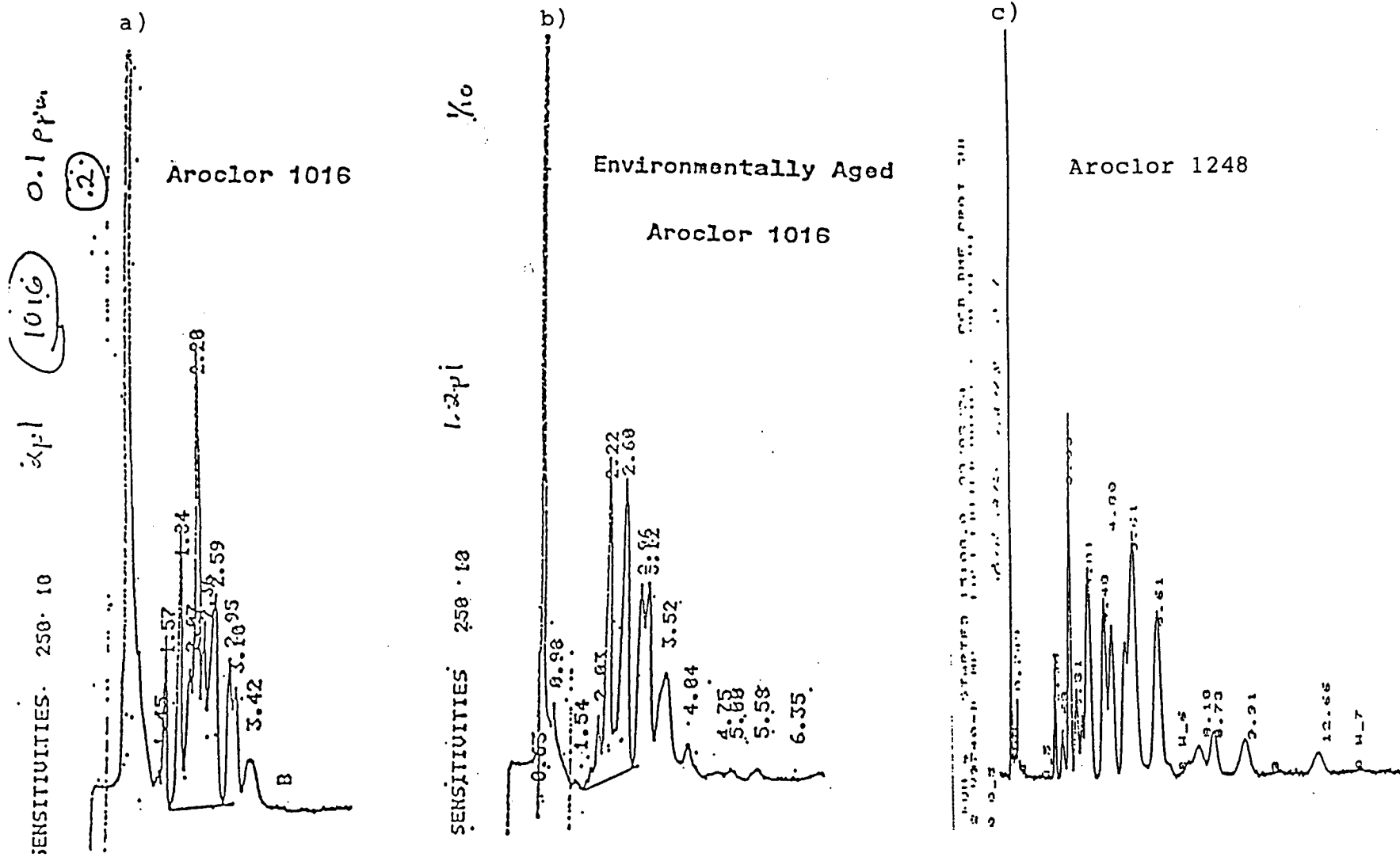


Exhibit 3-2. Demonstration of Pattern Alteration Due to Weathering

There was no evidence of Aroclor 1254 pattern alteration from either weathering or biotransformation in any of the PCB-containing samples.

## 2.2 Identification and Quantitation of Aroclors

Chromatogram (a) of Exhibit 3-3 illustrates very slight pattern alteration for Aroclor 1016/1242 and no alteration for Aroclor 1254. A mixed standard containing a 1.78 ratio of Aroclor 1242 to Aroclor 1254 is shown in chromatogram (b) for comparison. This sample (AD595) was identified by CAA as containing Aroclor 1242 and Aroclor 1254.

The weathering of Aroclor 1016/1242 was more advanced in the balance of the samples where PCBs were detected. As can be seen in Exhibit 3-4, the weathering of these samples is not as advanced as that of the environmentally aged Aroclor 1016 in chromatogram (a), but the three samples (chromatograms b, c, and d) do closely resemble the Aroclor 1248 standard. The samples were identified by CAA as containing Aroclor 1248 as well as Aroclor 1254. Since no new congeners occurred in these samples as the result of weathering (as opposed to the occurrence of new congeners in biotransformed samples), the use of Aroclor 1248 for the quantitation of these samples will yield valid quantitative results because there is no exclusion of PCB peaks from the area quantitations.



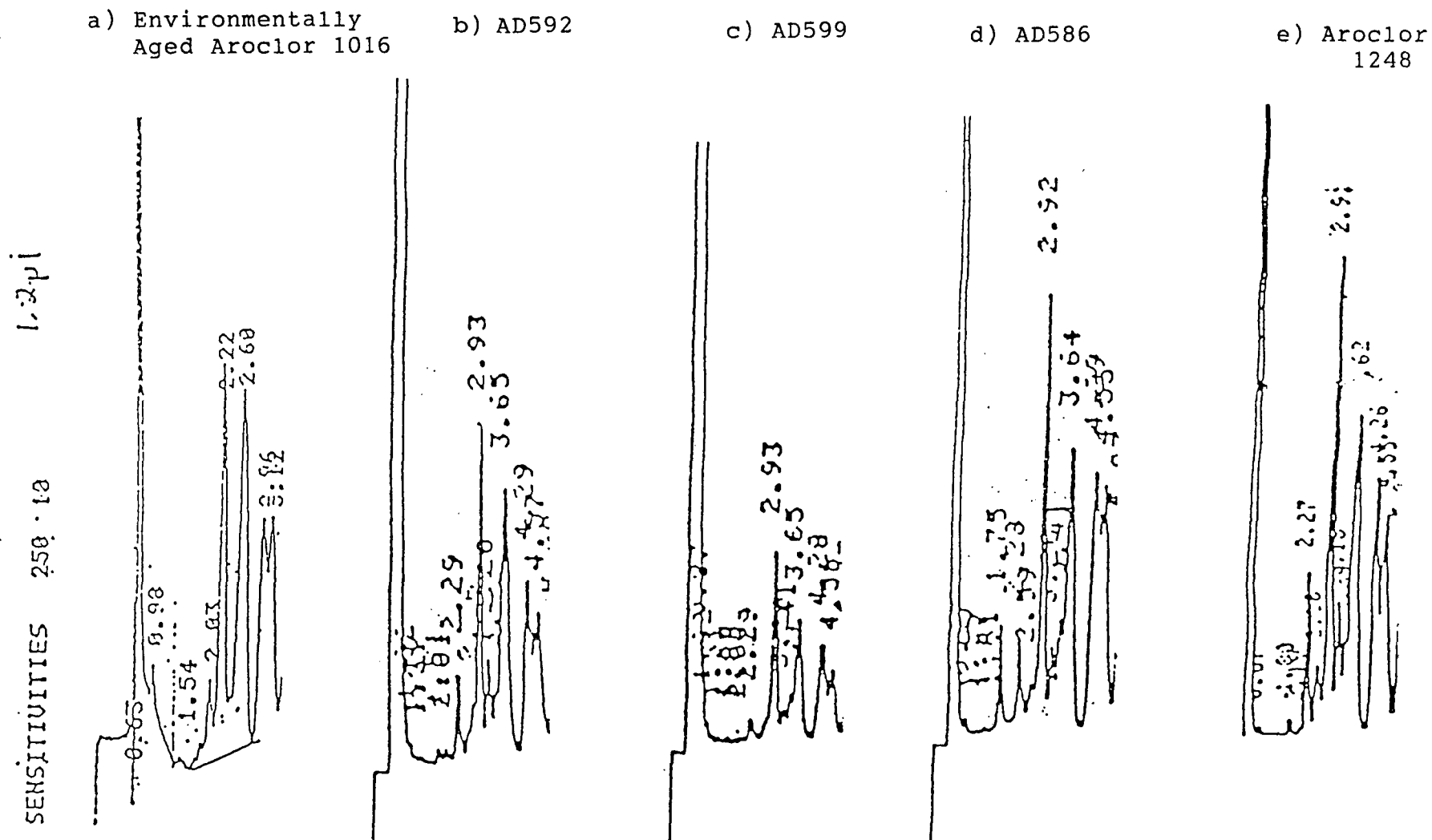


Exhibit 3-4. Comparison of Environmentally Aged Aroclor 1016/1242 and Aroclor 1248 Standard



One sample, AD586, appeared to contain Aroclor 1248 and Aroclor 1254. The chromatogram of this sample is shown in Exhibit 3-5 with the chromatograms of two mixed Aroclor standards. Chromatogram (a) is a mixture of 2 parts Aroclor 1248 and 3 parts Aroclor 1254. Chromatogram (b) is sample AD586, and chromatogram (c) is a mixed standard of one part Aroclor 1242 and one part Aroclor 1254. As can be seen, the best match occurs with the sample and mixed standard of Aroclor 1248 and Aroclor 1254. This is most evident for the peak in the sample at retention time (RT) 11.93. Aroclor 1248 makes a contribution at this retention time while Aroclor 1242 does not. The ratio of the peaks at RTs 10.54, 11.93, and 13.49 indicate the presence of Aroclor 1248, not Aroclor 1016/1242, in this sample. For all other samples, the ratios between the peaks at these retention times correspond to the ratios shown in the Aroclor 1242/1254 mixed standard (see example in Exhibit 3-6).

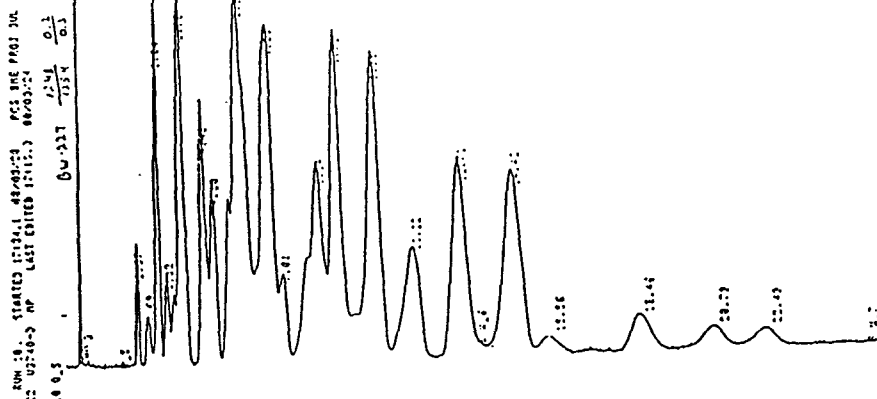
### 3.0 OVERALL ASSESSMENT

The data package was complete, the analytical and QA/QC protocols were followed and the data quality is excellent.

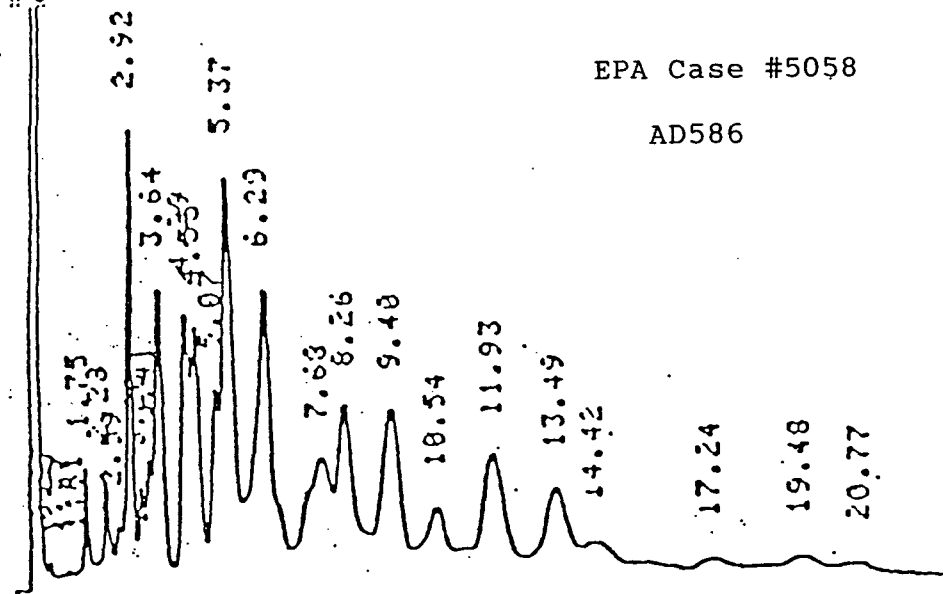
### 4.0 SUMMARY

No evidence of PCB biotransformation was seen in any of the Task 3 samples. These samples, collected from salt marsh

a) Aroclor 1248/1254



b) EPA Case #5058  
AD586



c) Aroclor 1242/1254

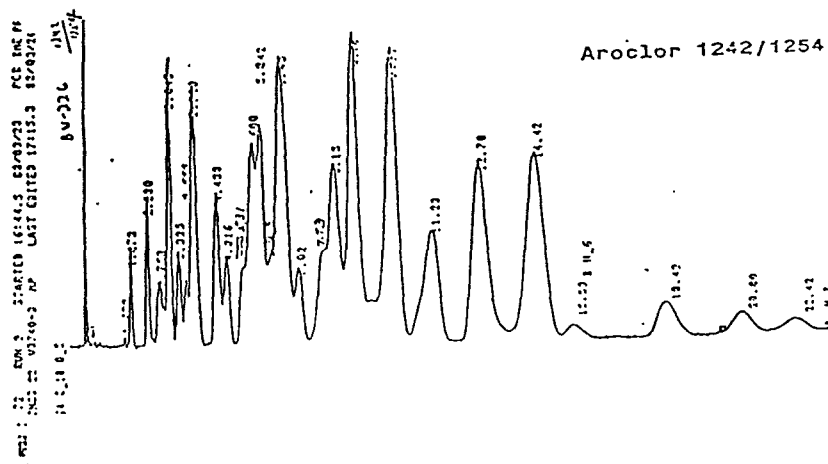
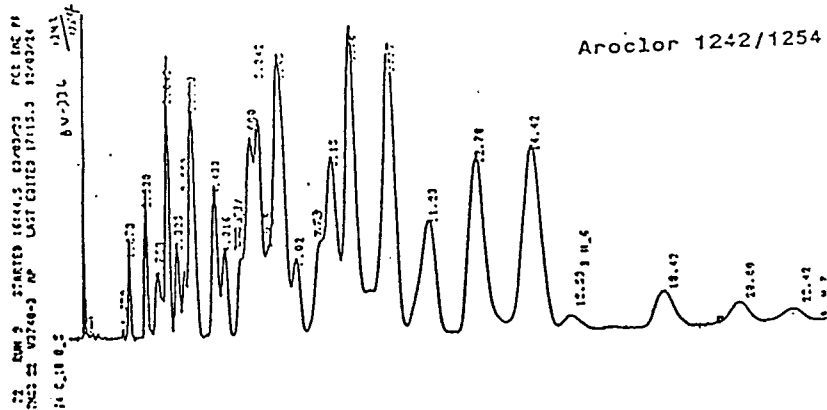


Exhibit 3-5. Comparison of Sample AD586 with Mixed Standards of Aroclor 1248/1254 and Aroclor 1242/1254

a)



wetlands, are classified as soils and as such represent a different segment of the environmental ecosystem. The PCB transformation process associated with soils is that of simple evaporation from the soil surface. The biotransformation process, seen in Task 2 USACE samples, occurs as the result of anaerobic dechlorination which has been observed only in sediment samples.

Chromatographic pattern alterations associated with the weathering of Aroclor 1016/1242 were present. However, an indication of Aroclor 1254 pattern alteration was observed in only one sample (AD586) from the sample set.

**APPENDIX A**

**TERMS AND ABBREVIATIONS**

Table A-1. TERMS

"Additive Effect": To heighten or increase the intensity of a peak in a chromatogram (enhancement).

Anaerobe: A microorganism that flourishes without free oxygen.

Anaerobic microbial (bio)degradation: The reduction of a chemical component from a higher to a lower type by the action of anaerobic microbes.

Anaerobic biotransformations: Changes brought about as the result of the action of anaerobic bacteria.

Anaerobic dechlorination: A specific PCB microbial degradation process whereby chlorine is selectively removed from a congener as the result of anaerobic microbial actions.

Aroclor: Trade name (Monsanto) for a series of commercial PCB and polychlorinated terphenyl mixtures marketed in the United States.

Aroclor degradation: A reductive modification with respect to the proportions of the individual PCB congeners present in the specific Aroclor.

Aroclor transformation: Any change (either reduction or enhancement) in the unique characteristic of the composition of a specific Aroclor.

Chromatogram: A tracing of the detector output from a chromatograph which consists of a series of peaks observed over time.

Chromatographic pattern alteration: Any change or modification which occurs in the chromatogram produced by a known reference material (e.g., a specific Aroclor).

Congener: One of the 209 PCBs or other group of compounds, not necessarily the same homolog.

Degrade: To reduce from a higher to a lower type.

Enhance: To heighten or increase in intensity.

Table A-1. TERMS (Cont'd)

Environmental aging (weathering): The process whereby the Aroclor(s) present in an environmental sample undergoes modification with respect to the proportions of individual PCB congeners present as the result of partial vaporization, adsorption onto surfaces, and/or extraction into water. True molecular solution in water is shown (on chromatograms) as the non-selective loss of the more volatile and more water-soluble congeners from the Aroclors in the sediments.

"High-end drop-off": The pattern alteration observed when higher chlorinated PCB congeners (usually penta- and hexa-) undergo anaerobic dechlorination.

High resolution gas-liquid chromatography: Gas chromatography with a capillary column.

Homolog: One of the 10 degrees of chlorination of PCBs ( $C_{12}H_9Cl$  through  $C_{12}Cl_{10}$ ) or other group of compounds varying by systematic addition of a substituent.

Isomer: Any PCB or other compound which has the same molecular formula, but different positional substitutions. 2,2'-Dichlorobiphenyl and 2,3-dichlorobiphenyl are isomeric; 4-chlorobiphenyl and 2,3,4-trichlorobiphenyl are not.

"Low-end drop-off": The pattern alteration observed when lower chlorinated PCB congeners are removed from samples by weathering.

Part per million (ppm): One part in 10<sup>6</sup>.

Pattern alterations: Changes in a characteristic chromatographic pattern. The effect of the changes will be reflected by peak enhancements, reductions, or both. (See chromatographic pattern alterations.)

Polychlorinated biphenyl (PCB): One of 209 individual compounds having the molecular formula  $C_{12}H_nCl_{10-n}$ , where  $n = 0-9$ . This definition includes monochlorobiphenyls, but not biphenyl.

PCB degradation: A conversion whereby a PCB congener of a higher chlorine content is reduced (converted) to one of a lower chlorine content.

PCB transformation: Any change whereby a PCB congener is converted into another compound.

Table A-1. TERMS (Cont'd)

Qualitative: Having to do with establishing the presence or identity of a compound.

Quantitative: Having to do with measuring the amount or concentration of a compound in a sample.

Retention time: Time between injection and detection of a compound on a chromatographic system under specified conditions, expressed in seconds or minutes.

Transformation: Any change which gives a different appearance.

Weathering: A process which gives a compositional change in an Aroclor residue (see environmental aging).



Table A-2. ABBREVIATIONS

BEC	Balsam Environmental Consultants, Inc.
CAA	Cambridge Analytical Associates
EPA	(U.S.) Environmental Protection Agency
GC	Gas-liquid chromatography (column type unspecified)
GC/EC	Gas chromatography/electron capture
GC/MS	Gas-liquid chromatography/mass spectrometry (ionization mode unspecified)
HSL	Hazardous Substance List
NBH	New Bedford Harbor
PCB	Polychlorinated biphenyl
ppm	Parts per million ( $10^{-6}$ )
QA/QC	Quality Assurance/Quality Control
RT	Retention time
USACE	(U.S.) Army Corps of Engineers
YAI	Yoakum & Associates, Inc.

APPENDIX IV

TASK 7

SPECIAL RESEARCH REPORT  
EVALUATION OF PCB  
TRANSFORMATIONS  
IN NEW BEDFORD HARBOR SEDIMENTS

Prepared for:

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Prepared by:

YOAKUM & ASSOCIATES, INC.  
Lenoir City, Tennessee 37771

October 16, 1989

Y & A Project NMF-3003 Task 7

DRAFT

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## APPENDICES

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- Appendix B. ITAS Certificates of Analysis



## TERMS

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Chromatographic pattern alteration: Any change or modification which occurs in the chromatogram produced by a known reference material (e.g., a specific Aroclor).

Congener: One of the 209 PCBs or other group of compounds, not necessarily the same homolog.

Congener selectivity pattern: The sequence whereby specific PCB congeners undergo anaerobic dechlorination.

Degrade: To reduce from a higher to a lower type.

Enhance: To heighten or increase in intensity.

## TERMS

Environmental aging (weathering): The process whereby the Aroclor(s) present in an environmental sample undergoes modification with respect to the proportions of individual PCB congeners present as the result of partial vaporization, adsorption onto surfaces, and/or extraction into water. True molecular solution in water is shown (on chromatograms) as the non-selective loss of the more volatile and more water-soluble congeners from the Aroclors in the sediments.

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PCB degradation: A conversion whereby a PCB congener of a higher chlorine content is reduced (converted) to one of a lower chlorine content.

PCB transformation: Any change whereby a PCB congener is converted into another compound.

Reductive dechlorination: Selective removal of chlorine from PCB congeners in an atmosphere without free oxygen.

## TERMS

Retention time: Time between injection and detection of a compound on a chromatographic system under specified conditions, expressed in seconds or minutes.

Surrogate: Non-analyte compounds intentionally added to the sample (for QC purposes) to monitor the performance of the extraction, cleanup, and analytical system as well as the effectiveness of the method.

Transformation: Any change which gives a different appearance.

Weathering: A process which gives a compositional change in an Aroclor residue (see environmental aging).

## ABBREVIATIONS

ACOE	(U.S.) Army Corps of Engineers
Balsam	Balsam Environmental Consultants, Inc.
DBC	Dibutylchlorendate
EPA	(U.S.) Environmental Protection Agency
GC	Gas-liquid chromatography (column type unspecified)
GC/EC	Gas chromatography/electron capture
GC/MS	Gas-liquid chromatography/mass spectrometry (ionization mode unspecified)
HRGC	High resolution gas-liquid chromatography
ITAS	International Technology Corporation, Analytical Services
NBH	New Bedford Harbor
PCB	Polychlorinated biphenyl
ppm	Parts per million ( $10^{-6}$ )
RIC	Reconstructed ion chromatogram (in GC/MS)
RT	Retention time

SPECIAL RESEARCH REPORT  
EVALUATION OF PCB  
TRANSFORMATIONS  
IN NEW BEDFORD HARBOR SEDIMENTS  
(Y & A Project NMF-3003 Task 7)

## 1.0 INTRODUCTION

This report presents the initial results of a special investigation to evaluate PCB transformations in New Bedford Harbor (NBH) sediment samples. The samples were collected by Balsam Environmental Consultants, Inc. (Balsam), and analyzed by IT Analytical Services (ITAS, Knoxville, Tennessee laboratory). Data evaluations were performed by YOAKUM & ASSOCIATES, INC. (YAI).

### 1.1 Background

During the review by YAI of reports and analytical data pertaining to the New Bedford Harbor project, it became apparent that, in all probability, PCB transformations were occurring in the NBH sediments. This supposition was based on YAI experience with Aroclor transformations in PCB contaminated sediments at a number of sites throughout the country. Two information sources indicated probable PCB transformations:

- 1) the reported presence by a number of laboratories of Aroclor 1248 in NBH sediment samples, and
- 2) Brown personal communication (1986 data) concerning NBH sediments.

Because of PCB and heavy metals contamination, the NBH area has been designated by EPA as a Superfund site. In the 10-year period just prior to 1983, approximately 3700 PCB analyses were performed by more than 20 different analytical laboratories on NBH samples to determine the extent of the PCB pollution problem. The analysis of estuarine sediments accounted for more than 50% of these data. According to Alford-Stevens, Budde, and Bellar (1985) of EPA, standardized procedures were not used for the PCB determinations. Instead, each laboratory produced data acquired with its favorite procedure for PCB extraction, enrichment, detection and measurement. As a consequence, many samples were analyzed with much variability and

inconsistency in the results. This is especially true for the identification of the Aroclor(s) present in the samples.

A review of past purchasing and inventory records indicated that the PCBs used by electrical capacitor manufacturing facilities located adjacent to NBH were Aroclors 1254, 1242, and 1016. There is no similar evidence of use of Aroclor 1248 at these facilities. However, Aroclor 1248 was reported to be present in approximately 25% of the inner harbor sediment samples contained in the Acushnet Estuary Data Base (Metcalf & Eddy, 1983). In addition, data generated in 1987 to support a Balsam sediment sampling program reported the presence of Aroclors 1248 and 1254 in upper estuary sediments. Oddly, the laboratory reportedly observed no Aroclor 1242 or Aroclor 1016 in any of the samples.

When Aroclor 1248 is reported to be present in samples, but cannot be implicated as a primary PCB contamination source, chromatographic pattern alterations due to PCB transformations in other Aroclors are usually indicated. This is especially true when Aroclor 1016/1242 and Aroclor 1254 are present as mixtures in sediment samples (as is the case for upper harbor samples). Three sediment samples from New Bedford Harbor (one inner harbor and two outer harbor) were analyzed for PCBs in a collaborative study sponsored by EPA (Alford-Stevens, 1985). Six laboratories analyzed the samples using packed column GC/EC, and four used capillary column GC/MS. All 10 laboratories identified the Aroclors present in the samples as mixtures of either 1016 and/or 1242 and 1254. It is significant that the presence of Aroclor 1248 in the samples was not reported by any of the participants, all of whom were considered by EPA to be experts in the field of PCB analysis. For this reason, it appears that a number of the laboratories involved in the NBH project lacked the expertise to make Aroclor identifications which are fully reliable.

In sediment samples, anaerobic microbial degradation of Aroclor 1254 as well as environmental aging (evaporative and/or solubility losses) of Aroclor 1016/1242 can produce pattern alterations which, to the casual or inexperienced observer, resemble Aroclor 1248. Since the anaerobic degradation of New Bedford Harbor sediment samples had been reported by Brown (1986), the decision was made to design a special research project to determine if PCB degradation was responsible for the pattern alterations observed in the NBH sediment samples.

## 1.2 Project Design and Scope

The Project was designed to answer (if possible) a number of questions pertaining to New Bedford harbor sediment samples, including

1. what Aroclors are present,
2. are discrete alteration patterns observed,
3. is there evidence of anaerobic PCB degradation, and
4. what is the congener selectivity pattern(s) for the reductive dechlorination processes.

An additional purpose of the project was to generate superior quality packed column GC/EC chromatograms of NBH sediment samples. The need for reference chromatograms became apparent during the review of chromatograms from the U. S. Army Corps of Engineers (USACE) study (Task 2) and EPA Case 5058 (Task 3).

The initial phase of the project was two-fold:

1. the identification of the Aroclors present, and
2. the evaluation of PCB transformations.

In the event that significant PCB transformations were found, a second phase of the project was planned which would identify the specific PCB congeners involved and determine the most probable path of the transformation process. This report covers the first phase of the investigation.

## 2.0 EXPERIMENTAL

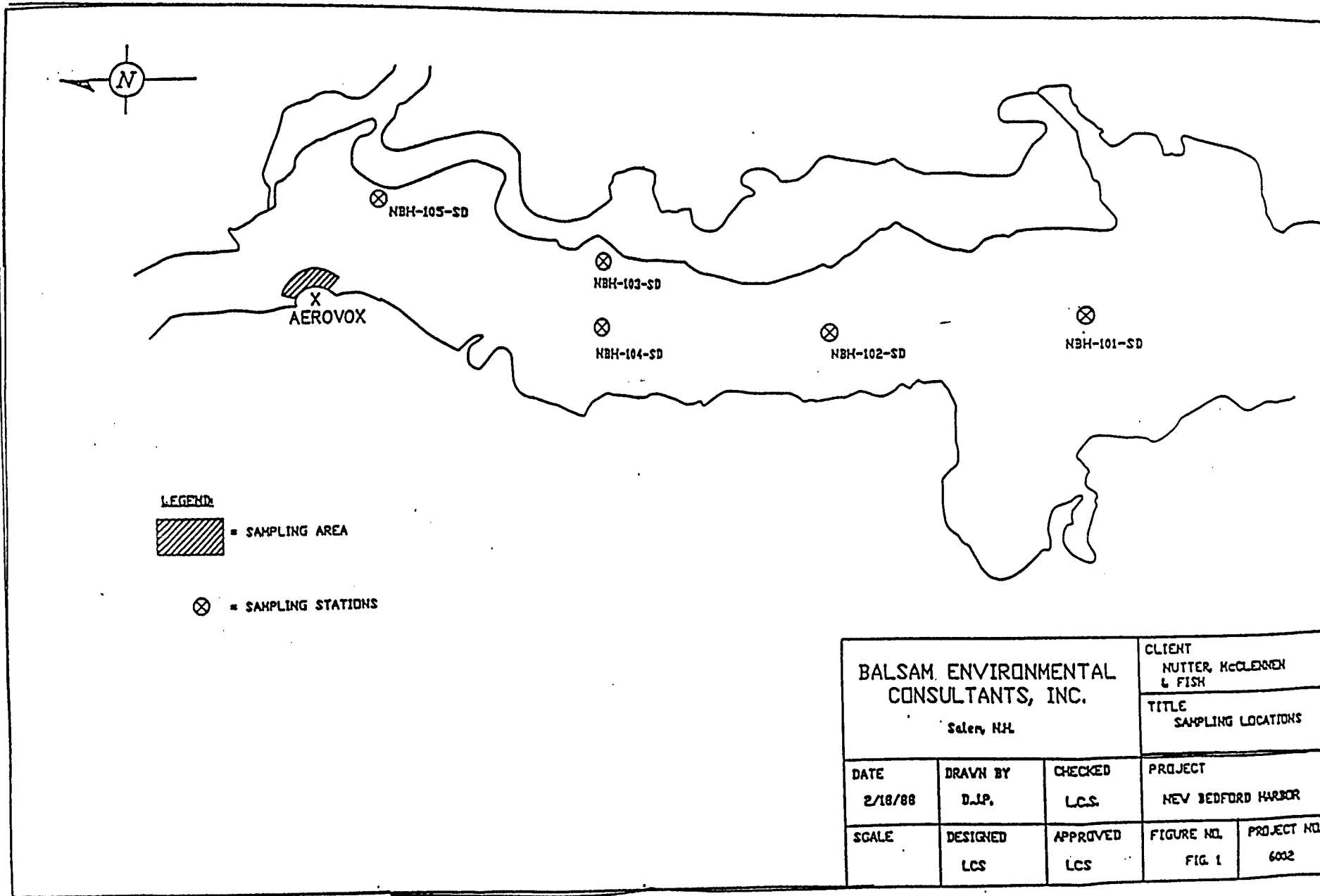
### 2.1 Sample Collections

Fourteen sediment samples from the upper Acushnet River Estuary region of New Bedford Harbor were used in this investigation. The approximate locations of five of the sampling stations are shown in Figure 1. The balance of the samples were collected in the vicinity of the Aerovox facility.

### 2.2 Sample Analysis

The analytical methodology used in the investigation was that prescribed by EPA publication SW-846, 3rd Edition (1986). All samples were analyzed for PCBs, pH, oil and grease, and moisture.

Samples were thawed and thoroughly homogenized prior to the removal of aliquots for the determination of parameters which required an "as received"





sample. The sediments were then air dried, thoroughly homogenized, and screened prior to extraction and cleanup.

PCBs were determined using both packed column GC/EC and capillary column GC/EC. The packed column used (Supelcoport coated with 1.5% SP2250/1.95% SP2401) is the primary quantitation column prescribed by the EPA contract laboratory program (CLP) protocol (1985). Since the packed column GC/EC chromatograms were to be used as references in classifying the USACE and EPA Case 5058 and Case 5151 chromatograms (Task 10), the DBC (dibutylchloroendate) surrogate was not included in the sample extracts. The capillary column used was the CLP protocol confirmation column, a megabore DB-5 column. The DBC surrogate is present in the samples analyzed by capillary column.

## 2.3 Analytical Results

### 2.3.1 PCB Data

Aroclor identifications and quantitations of PCBs were performed by the analytical contractor (ITAS) according to the guidelines in EPA Method 8080. Evidence of pattern alteration, when present, was noted. According to the method, PCBs are identified and quantitated by comparison to one or more of the Aroclor standards, depending on the chromatographic pattern of the residue. A choice must be made by the analyst as to which Aroclor or mixture of Aroclors will produce a chromatogram most similar to that of the sample. This may also involve a judgment about what proportion of the different Aroclors to combine to produce the appropriate reference material. Only those peaks in the samples that can be attributed to chlorobiphenyls should be used in the quantitation. The peaks chosen for inclusion in the quantitation determination for the sample must also be present in the chromatogram of the reference material (Aroclor) standards. PCB data for the samples are contained in Table 1. Based on a review of the total Aroclor concentration data set presented in Table 1, it appears that the result for sample NBH-112-2, 130 ppm, is an outlier. The chromatograms for both the packed column and capillary column GC/EC runs are appended (Appendix A). The certificates of analysis issued by the laboratory are contained in Appendix B.

Samples were thawed and thoroughly homogenized prior to the removal of aliquots for the determination of parameters which required an "as received" sample. The sediments were then air dried, thoroughly homogenized, and screened prior to extraction and cleanup.

PCBs were determined using both packed column GC/EC and capillary column GC/EC. The packed column used (Supelcoport coated with 1.5% SP2250/1.95% SP2401) is the primary quantitation column prescribed by the EPA contract laboratory program (CLP) protocol (1985). Since the packed column GC/EC chromatograms were to be used as references in classifying the USACE and EPA Case 5058 and Case 5151 chromatograms (Task 10), the DBC (dibutylchlorodate) surrogate was not included in the sample extracts. The capillary column used was the CLP protocol confirmation column, a megabore DB-5 column. The DBC surrogate is present in the samples analyzed by capillary column.

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Table 1. Analytical Results - PCBs  
(concentration units are mg/kg, ppm, dry basis)

Sample	Aroclor 1016/1242	Aroclor 1254	Total Aroclors	Ratio 1016/1242 to 1254
NBH-101	4.0*	5.6*	9.6	0.71
NBH-101	520.*	300.*	820.	1.73
NBH-103	19.0*	28.*	47.	0.66
NBH-104	200.*	160.*	360.	1.23
NBH-105	760.*	360.*	1,100.	2.11
NBH-106	660.*	300.*	960.	2.20
NBH-110-01	3,200.*	4,400.*	7,600	0.73
NBH-110-02	<5,000.**	11,000.*	11,000	(<0.45)
NBH-111-02	13,000.*	15,000.*	28,000.	0.89
NBH-111-02	6,800.*	32,000.*	39,000.	0.21
NBH-112-01	19,000.	11,000.*	30,000.	1.63
NBH-112-02	80,000.*	48,000.*	130,000.	1.67
NBH-113-01	160.*	340.*	500.	0.48
NBH-113-02	<48.**	180.*	180.	(<0.27)

\*Sample exhibits alteration of standard Aroclor pattern.

\*\*Higher detection limit due to interference.

### 2.3.2 Other Parameters

The analytical results for pH, oil and grease and moisture are presented in Table 2. Laboratory certificates of analysis can be found in Appendix B.

## 3.0 DATA EVALUATION

### 3.1 Packed Column GC/EC Chromatograms

#### 3.1.1 Overview

Significant and sometimes extensive Aroclor pattern alterations appear in all of the chromatograms. Pattern alteration indicating the presence of more than one Aroclor in the samples is evident; in addition, wide pattern variations due to changes in the Aroclor 1016/1242 to Aroclor 1254 mixture ratio are apparent. The partial loss of lower chlorinated congeners (di- and certain trichlorobiphenyls) is also indicative of environmental aging losses. Finally, alterations in the lower-chlorinated peak distributions and the presence of significant reductions of the higher-chlorinated congeners (mainly penta- and hexachlorobiphenyls) in approximately 93% (13 of 14) of the samples also indicates degradation of the Aroclors in the sediments. Samples exhibiting advanced Aroclor 1254 degradation also show significant, wide distribution variations among the tri- and tetrachlorobiphenyl congeners including reduction of some, enhancements for others, as well as the appearance of completely new congeners.

#### 3.1.2 Pattern Alteration Sources

The chromatograms of the NBH sediments were carefully studied to identify possible causes of the observed alterations.

##### 3.1.2.1 Aroclor Mixtures in the Samples

Aroclor 1016 and/or Aroclor 1242 as well as Aroclor 1254 were detected in all the samples. Because of compositional similarities between Aroclor 1242 and Aroclor 1016, it is difficult, if not impossible, to distinguish between Aroclor 1016 and/or Aroclor 1242 in a sample if Aroclor 1254 is also present in that sample. Packed column GC/EC chromatograms of Aroclor 1016, Aroclor 1242, and Aroclor 1254 standards are shown in Figure 2. The differences in the

Table 2. Analytical Results - Other Parameters  
(concentration units are mg/kg, ppm, dry basis)

Sample	pH (standard units)	Oil & Grease (mg/kg)	<u>Moisture</u>	
			*As Received* (% by weight)	After Air Drying (% by weight)
NBH-101	7.80	760.	17.8	0.55
NBH-102	7.79	11,000.	67.8	3.00
NBH-103	6.68	1,100.	51.4	0.50
NBH-104	7.19	1,600.	57.0	1.04
NBH-105	7.39	3,000.	57.7	1.24
NBH-106	7.46	4,500.	57.0	1.65
NBH-110-01	7.19	15,000.	53.9	2.82
NBH-110-02	6.70	17,000.	71.4	3.70
NBH-111-01	6.62	15,000.	64.7	3.22
NBH-111-02	6.44	19,000.	74.0	3.52
NBH-112-01	6.63	22,000.	59.5	3.98
NBH-112-02	6.65	41,000.	65.7	5.49
NBH-113-01	6.97	8,900.	70.9	2.71
NBH-113-02	7.03	11,000.	72.9	2.74

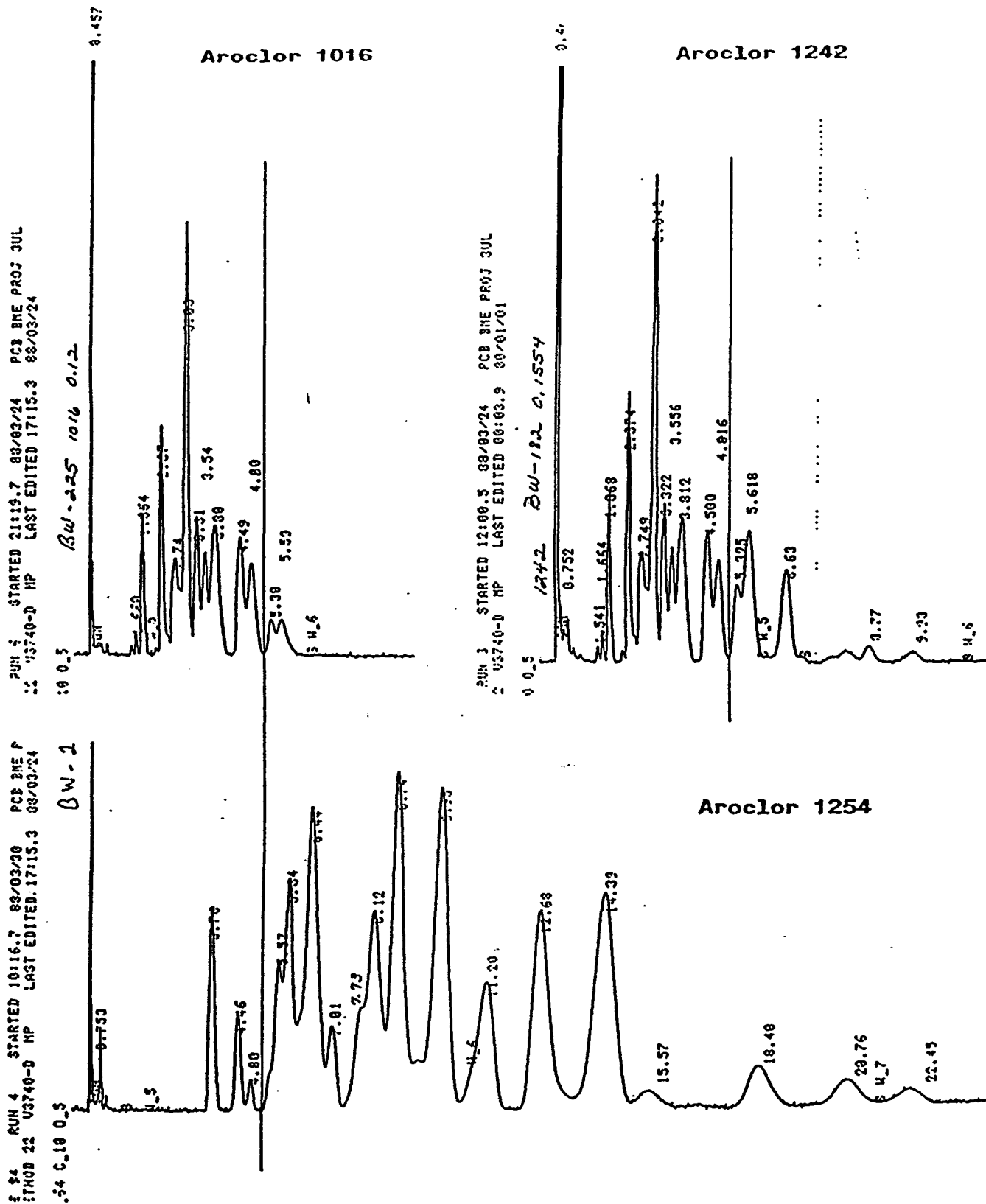


Figure 2. Standard Chromatograms - Aroclor 1016, Aroclor 1242, and Aroclor 1254

chromatograms of Aroclor 1016 and Aroclor 1242 all occur beyond peak retention time 4.82 minutes. Since peak overlap from Aroclor 1254 begins to occur at retention time 3.763 minutes, the pattern difference between Aroclor 1016 and Aroclor 1242 is obscured by the "additive effect" of the peaks from Aroclor 1254 when it is present in a sample which also contains Aroclor 1016 and/or Aroclor 1242.

A comparison of the chromatograms in Figure 3 clearly shows that even without the complication of environmental aging or Aroclor degradation, it is impossible to distinguish between the Aroclor 1242/Aroclor 1254 mixture and the Aroclor 1016 /Aroclor 1254 mixture based only on packed column GC/EC patterns. Therefore, this report will identify the sediment Aroclors as 1016/1242 and 1254 based on the packed column GC/EC data.

When two or more Aroclors are mixed together, the alteration to the GC pattern is an additive or enhancement effect on peaks. Strikingly different patterns can result just from varying the ratio of Aroclors in the mixture. This is illustrated in Figure 4 where the (a) chromatogram results from an Aroclor 1242/Aroclor 1254 mixture ratio of 1.78 and (b) is an Aroclor 1242/Aroclor 1254 mixture ratio of 0.35. The comparison of the patterns for the Aroclor 1242/Aroclor 1254 mixture ratio is 1.78 standard and New Bedford Harbor sediment sample NBH-112-02 in Figure 5 illustrates a near perfect pattern match. No apparent Aroclor degradation can be discerned from this GC/EC chromatogram.

#### 3.1.2.2 Non-PCB Compound Interference

The electron capture GC detector is a chlorine sensitive detector, but it also can respond to certain non-PCB compounds. Consequently, non-PCB interferences, when present above detectable levels, can cause pattern alterations. The most common non-PCB interferences occur in biological samples and are due to the presence of chlorinated pesticides and/or their metabolites. In addition, pattern alterations due to the presence of non-halogen containing compound interferences can occur. Phthalate esters and polynuclear aromatic compounds including anthracene, fluoranthene, and pyrene have been identified in the chromatograms of Aroclor-contaminated sediments taken from other PCB spill site locations.

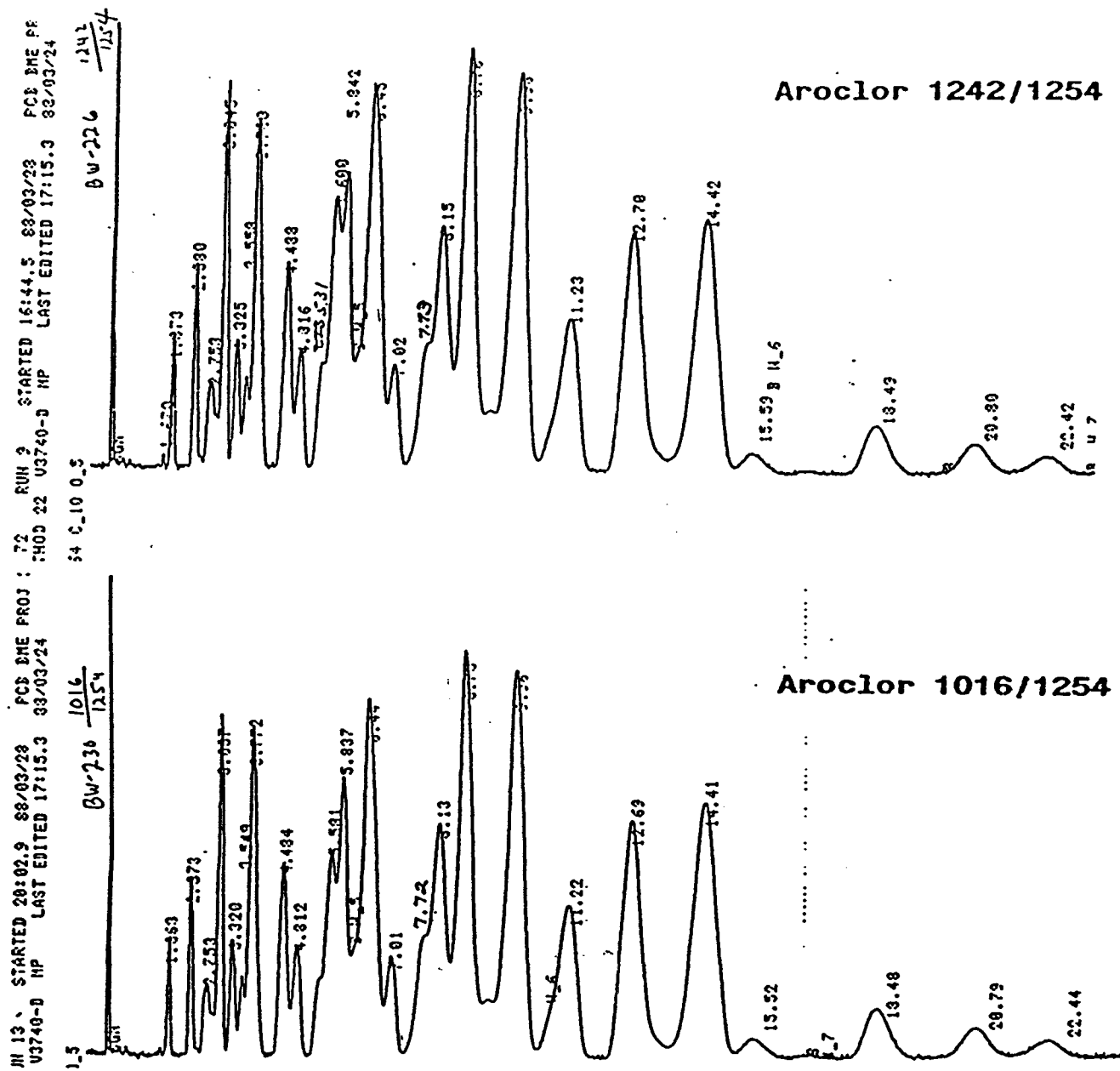


Figure 3.

Comparison of Chromatograms for  
 Aroclor 1242/1254 and Aroclor 1016/1254  
 Mixtures



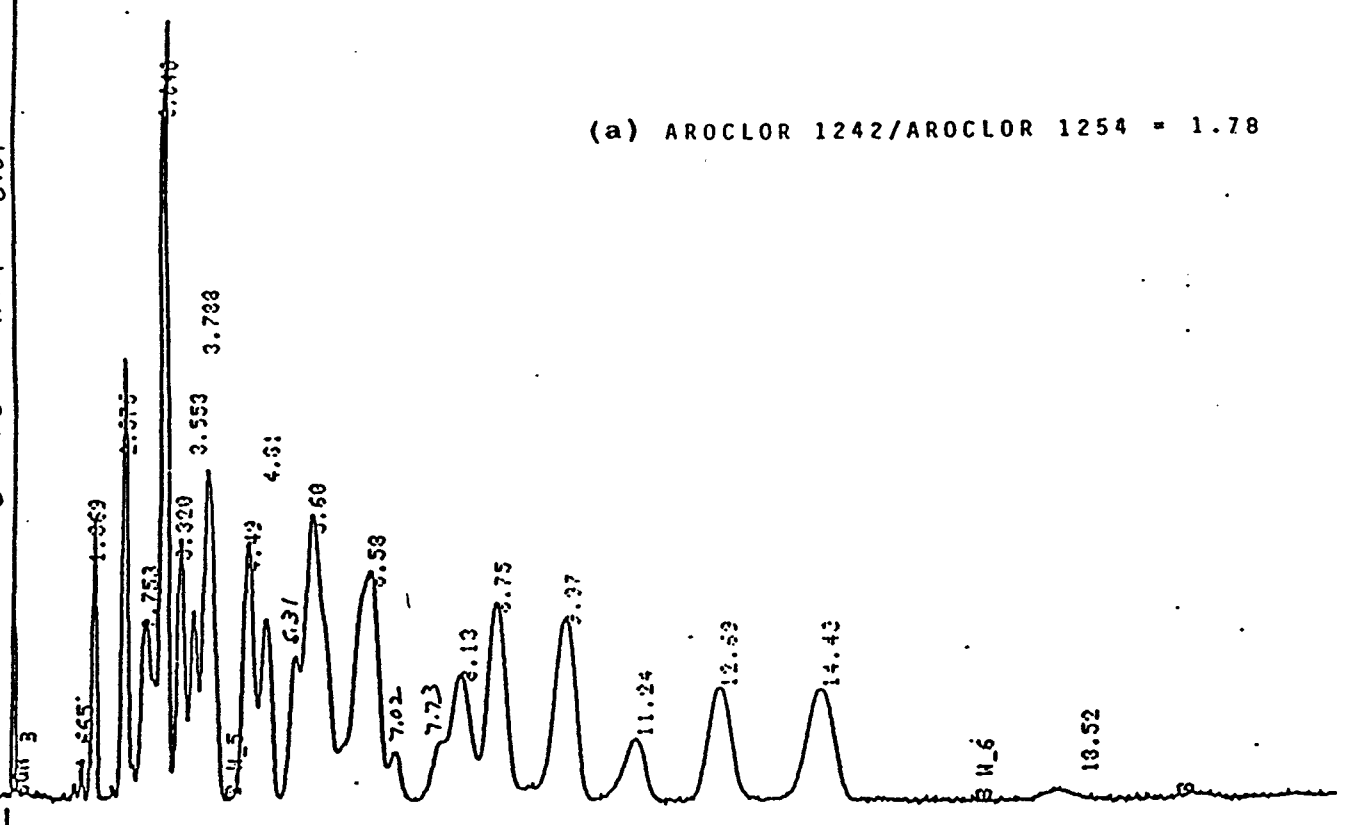
2.2 RUN 3 STARTED 16:44.5 88/03/26 PCB BME 880J 34.17 STARTED 15:53.7 88/03/23 PCB 2HE PROJ JUL  
 3409 02 U3740-D HP LAST EDITED 17:15.3 88/03/24 J3740-D HP LAST EDITED 17:15.3 88/03/24

0.16  
 1242  
 1254  
 0.09  
 BME 40786

BW-231

0.10 0.5  
 1242  
 1254  
 BW-226

(a) AROCLOR 1242/AROCLOR 1254 = 1.78



(b) AROCLOR 1242/AROCLOR 1254 = 0.35

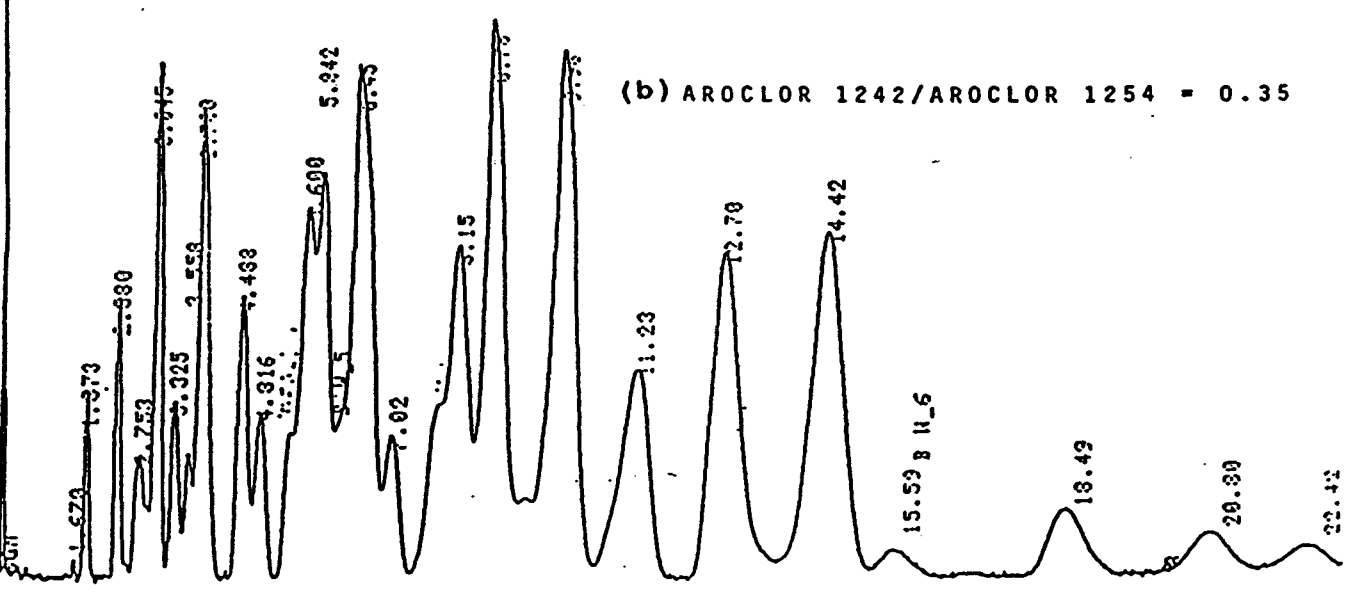


Figure 4. Comparison of Pattern Alterations Resulting from Two Different Aroclor 1242/1254 Mixtures

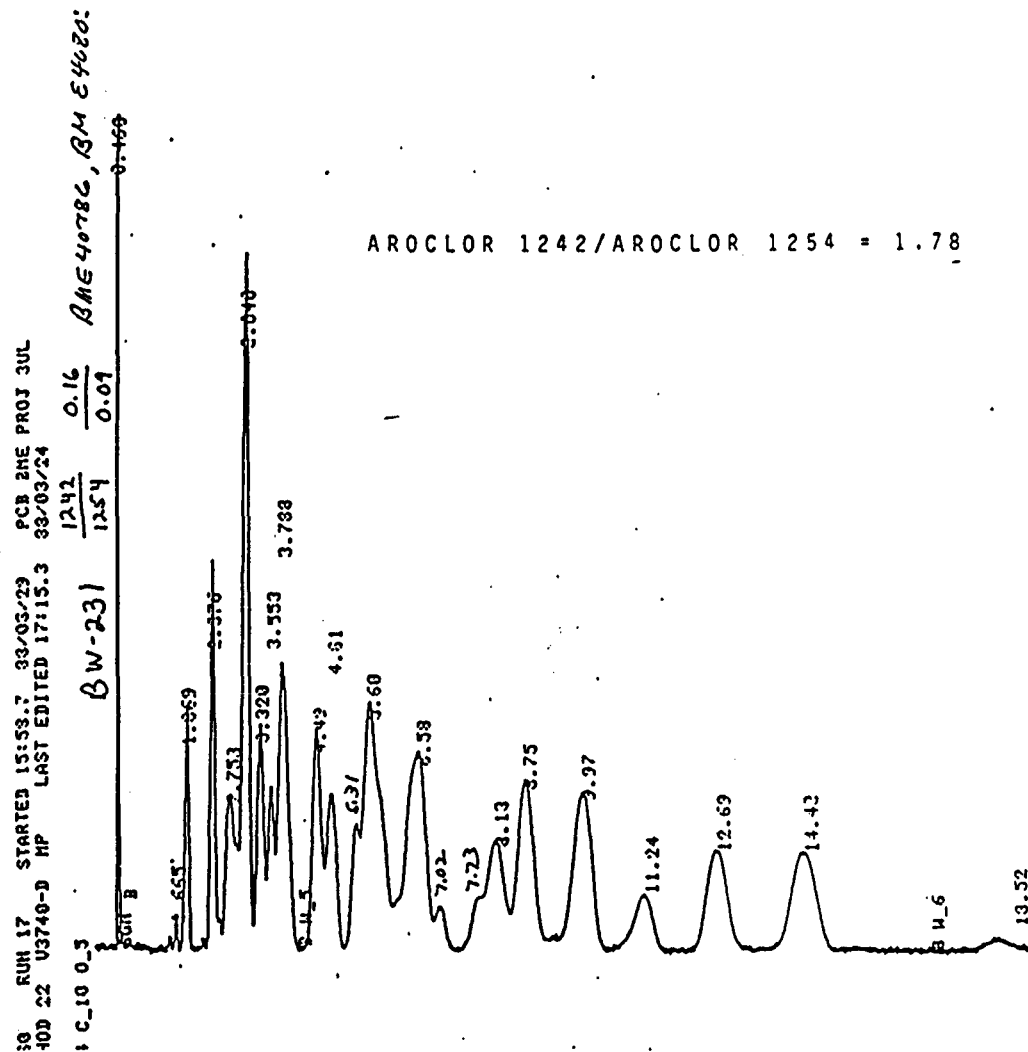
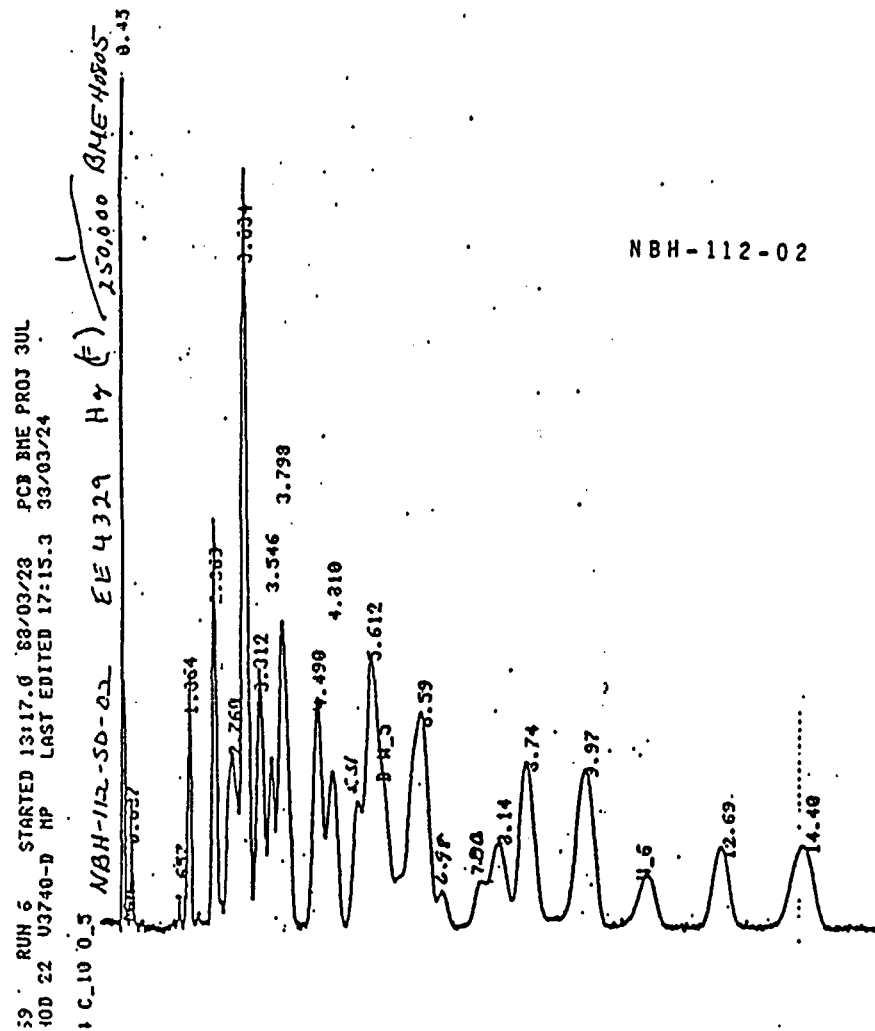


Figure 5. Comparison of Patterns for Sample NBH-112-02 and 1.78 Ratio Aroclor 1242/1254 Standard

Pattern alterations due to the presence of non-PCB interferences of the type discussed in the preceding paragraph are especially significant in the Aroclor 1248 region of the chromatogram. Potential co-elution problems which can occur are shown in the reconstructed ion chromatogram of a GC/MS standard of Aroclor 1248 (Figure 6). The presence of these kinds of interferences can contribute to the misidentification of Aroclor 1248 in samples.

Pattern alterations due to the presence of non-PCB interferences were not discernible in the packed column GC/EC chromatograms of the NBH sediment samples used for this investigation.

#### 3.1.2.3 Environmental Aging or "Weathering"

The occurrence of environmental aging in environmental samples is demonstrated by alterations in the standard Aroclor pattern. When alterations of this type do occur, they are due to the fact that Aroclors do not behave as a homogeneous substance. Differences in volatility and water solubility of the individual PCBs tend to fractionate the residue. A "weathered" sample has undergone modification with respect to the proportions of individual PCB congeners present as the result of partial vaporization, adsorption onto surfaces, and/or extraction into water. Loss of more volatile or soluble congeners yields a residue which demonstrates low-end drop-off and, usually, a high-end enhancement of peaks. An environmentally aged sample of Aroclor 1016 is illustrated in Figure 7. This pattern shows both significant low-end drop-off and high-end enhancement of peaks.

Although environmental aging is well known and widespread in environmental samples, no chromatograms were observed in this study which exhibited this phenomenon exclusively; namely, low-end drop-off and high-end enhancement of peaks. Preferential dissolution of the more soluble PCB congeners from the sediments has undoubtedly occurred, but it is less obvious than the anaerobic dechlorination exhibited by the samples.

#### 3.1.2.4 Anaerobic Degradation

The most significant alteration which has occurred in NBH sediment samples is that due to anaerobic dechlorination. The chromatograms of samples undergoing anaerobic biotransformations frequently demonstrate the presence of new peaks in the pattern as well as "high-end" drop-off due to the degradation

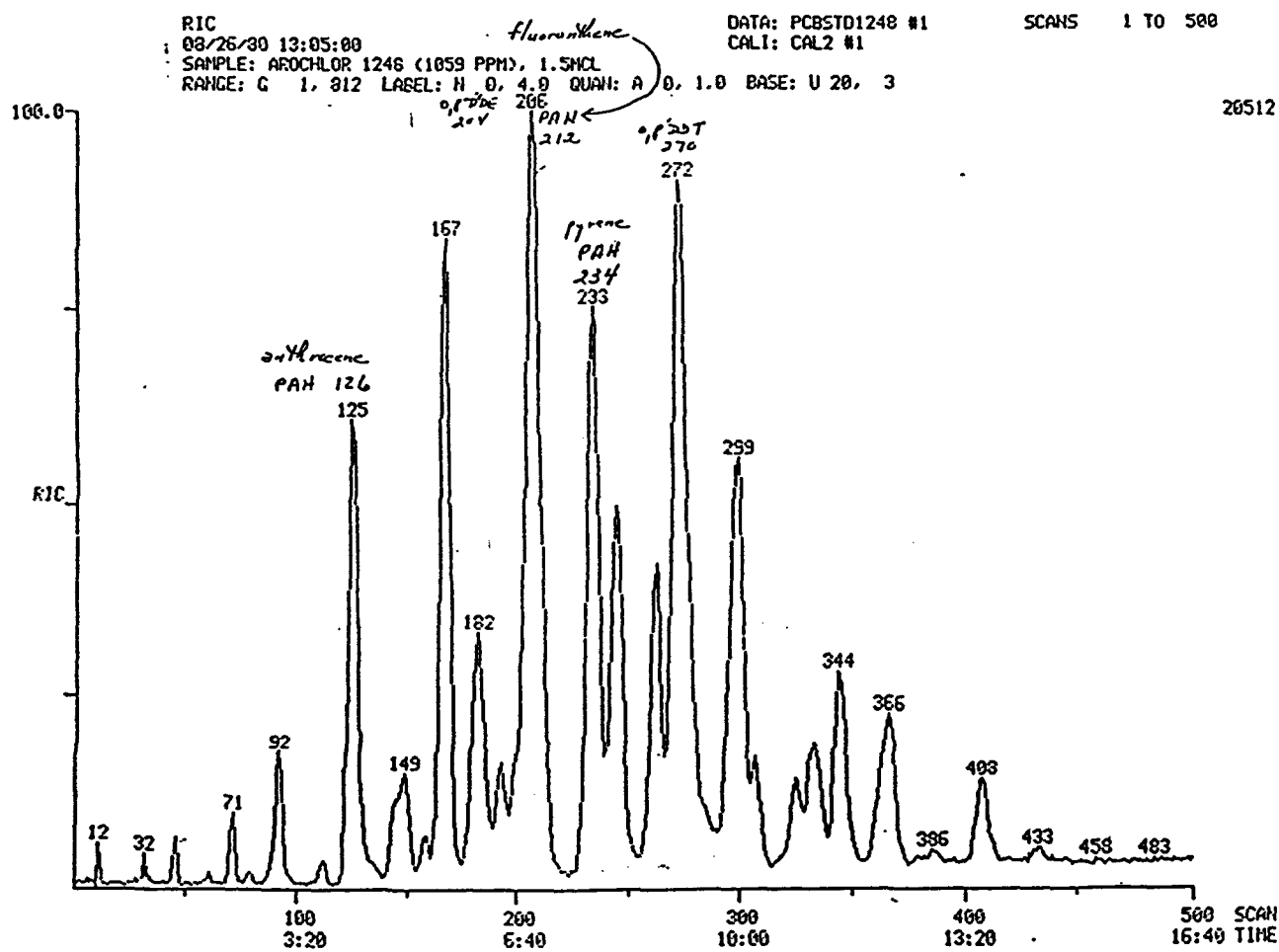


Figure 6. RIC of Aroclor 1248 with Non-PCB Interferences Shown

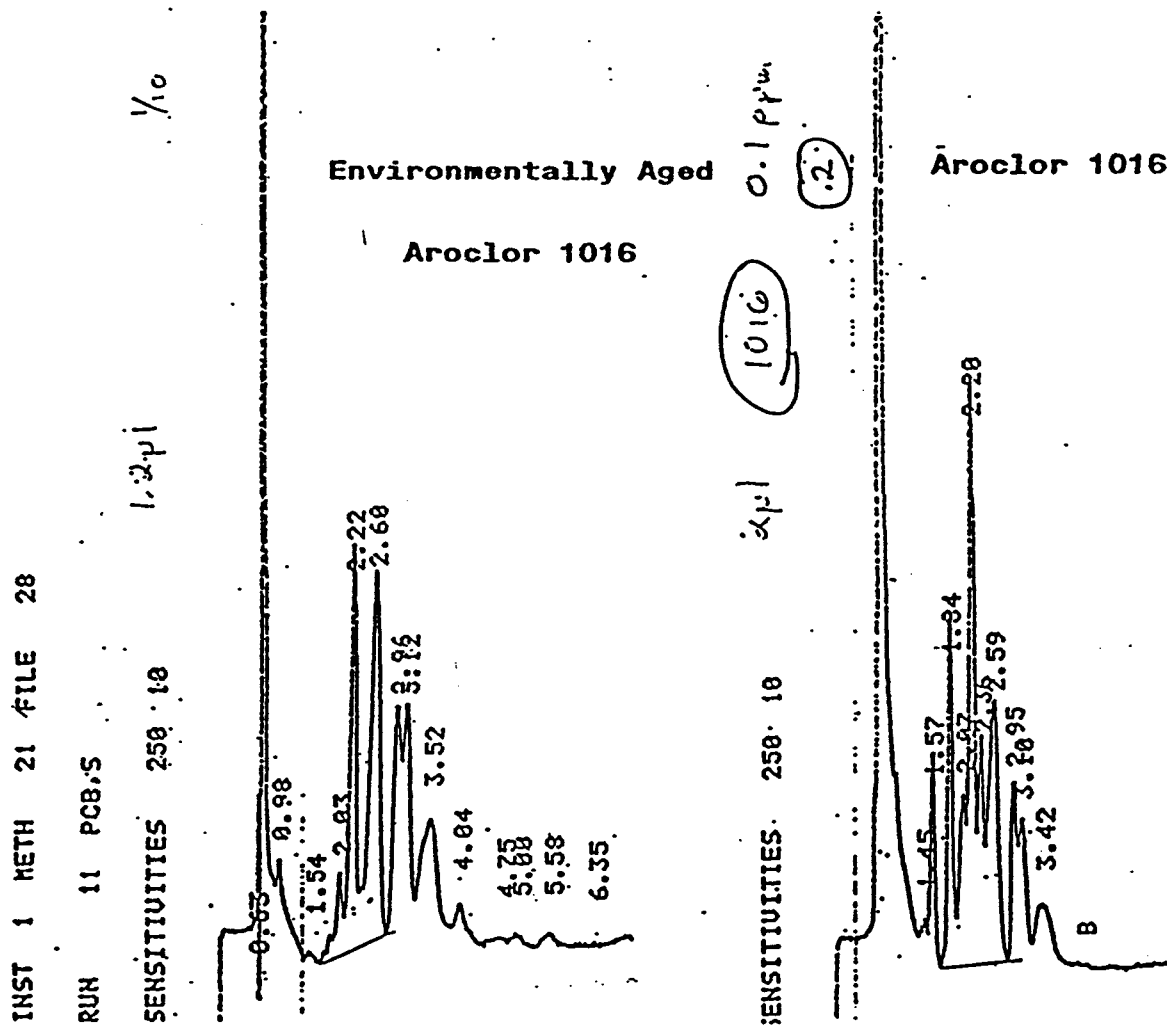


Figure 7. Environmentally Aged Aroclor 1016

of higher chlorinated PCBs. Peak enhancements, reductions, and even disappearances also occur. Alteration patterns resulting from anaerobic dechlorination in sediment samples are distinctively different from those found in weathered samples which have undergone alterations as the result of partial vaporization, adsorption on to surfaces, and/or extraction into water. As stated earlier, evidence of anaerobic degradation is seen in approximately 93% of the samples studied.

### 3.1.3 Observed Transformation of Aroclors 1016/1242 and 1254

#### 3.1.3.1 Aroclor 1016/1242

Pattern alterations in the Aroclor 1016/1242 region of the chromatograms are complicated by the contribution from peaks resulting from Aroclor 1254 degradation. New peaks or an increase in intensity of peaks normally present in Aroclor 1016/1242 cannot be unerringly assigned to either Aroclor 1016/1242 or Aroclor 1254 based on the data currently available. However, a reduction in intensity or the disappearance of a peak normally represent in Aroclor 1016/1242 can be attributed to the transformation of Aroclor 1016/1242. Progressive Aroclor 1016/1242 transformation is illustrated in Figure 8. Transformation increases from none (a) to advanced (g). The normal Aroclor 1016/1242 identifier peaks are at retention times 1.86, 2.37, and 3.03 and are color coded yellow. New peaks can be observed at retention times 1.35, 2.04, and 2.87 (color coded green). The preliminary indication, based on capillary column GC/EC data, is that these new peaks are due to mono-, di-, and trichlorobiphenyls, respectively. However, positive identification of the compounds responsible for the new peaks will require definitive analysis by GC/MS in Phase 2 of this investigation. The peaks at 2.87 and 3.80 are known to be transformation products formed during the degradation of Aroclor 1254 and/or Aroclor 1260. The disappearance of the peaks at RTs 3.32 and 3.55 are indicative of Aroclor 1016/1242 degradation while the appearance of the new peak at RT 3.37 results from Aroclor 1254 dechlorination. Peak 380 is composed primarily of 2,2', 5,5'- and 2,2', 4,5'- tetrachlorobiphenyl (color coded orange). This peak is normally present in both 1016/1242 and 1254, but it is significantly enhanced by the anaerobic dechlorination of Aroclor 1254 and Aroclor 1260. The peak at RT 4.81, which is mainly 2,3',4',6-tetrachlorobiphenyl,

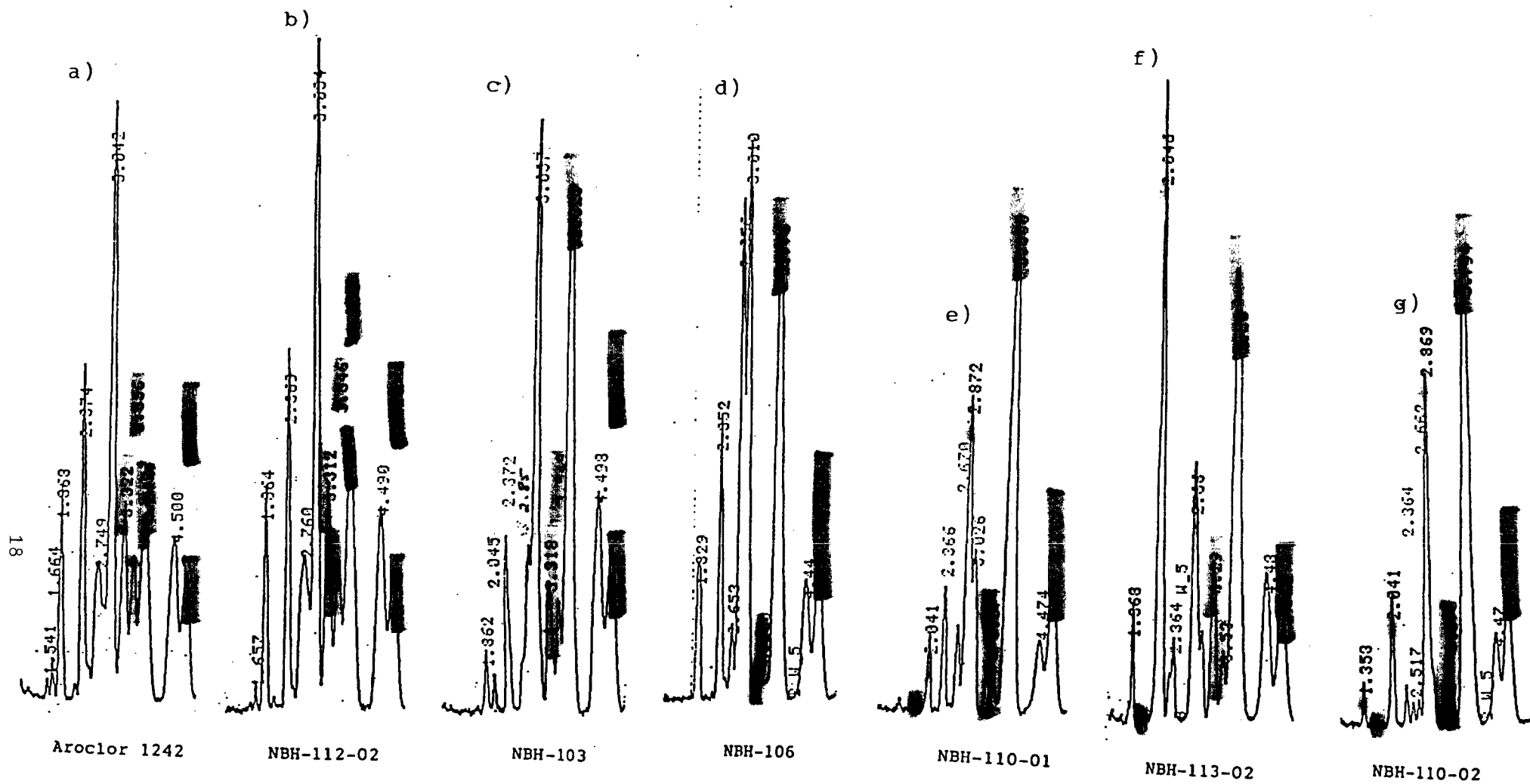


Figure 8. Progressive Aroclor 1016/1242 Transformation

does not appear to be significantly formed or destroyed during the early stages of transformation and has been used by some researchers as an Aroclor 1016/1242 indicator peak (color coded pink).

Transformation indicator peaks for Aroclor 1016/1242 as well as Aroclor 1254 are summarized in Table 3.

### 3.1.3.2 Aroclor 1254

Pattern alterations in the Aroclor 1254 region of the chromatograms demonstrate peak enhancements, reductions, and even disappearances. This alteration pattern is associated with the anaerobic dechlorination of Aroclors.

Progressive Aroclor 1254 transformation is illustrated in Figure 9. Transformation increases from none (a & b) to advanced (f). The normal Aroclor 1254 identifier peaks are located at retention times 9.97, 11.20, and 14.39 and are color coded yellow. These peaks undergo a gradual reduction in intensity as the transformation progresses. The peak at 3.80 (color coded orange) exhibits obvious enhancement throughout the sequence.

The progress of the transformation is easily followed by observing the dramatic decreases and ultimate disappearance of the peaks at RTs 8.15 and 12.70 (color coded blue). Changes in the peak at 8.76 are the least obvious, and for that reason, it serves as the Aroclor 1254 indicator peak (color coded pink).

Certain trichlorobiphenyls, which are not normally present in Aroclor 1016/1242 or Aroclor 1254, are known to be formed during the anaerobic dechlorination of Aroclor 1254. The presence of these trichlorobiphenyls is indicated by the new peak shown at RT 2.87 (color coded green).

The portion of the chromatograms between retention times 5.60 through 7.02 has been designated the transition region in Table 3 and is enclosed in red lines on Figure 9. In the initial stages of the Aroclor 1254 dechlorination, the peaks in this region are enhanced as illustrated by Sample NBH 111-02 (d). As dechlorination progresses (Samples NBH 104 and NBH 106, e and f, respectively), the peaks decrease and the pattern changes. The initial peak enhancement due to the dechlorination alteration process, in the area between retention times 3.80 and 7.02, is frequently mistaken as being due to the presence of Aroclor 1248 in the samples.



Table 3. Transformation Indicator Peaks for Aroclor 1016/1242 and Aroclor 1254

Aroclor 1242 (and/or Aroclor 1016)

<u>Description</u>	<u>Retention Time (Minutes)</u>
New Peaks	1.35, 2.04, 2.87, 3.37
Enhanced Peak	3.80
Decreased Peaks	1.86, 2.37, 3.03, 3.32, 3.55
Missing Peak	1.86, 3.32, 3.55
Indicator Peak	4.81

Aroclor 1254

<u>Description</u>	<u>Retention Time (Minutes)</u>
New Peak	2.87
Enhanced Peak	3.80
Transition Region	RTs 5.60 through 7.02
Decreased Peaks	9.97, 11.20, 14.39
Missing Peaks	8.15, 12.70
Indicator Peak	8.76

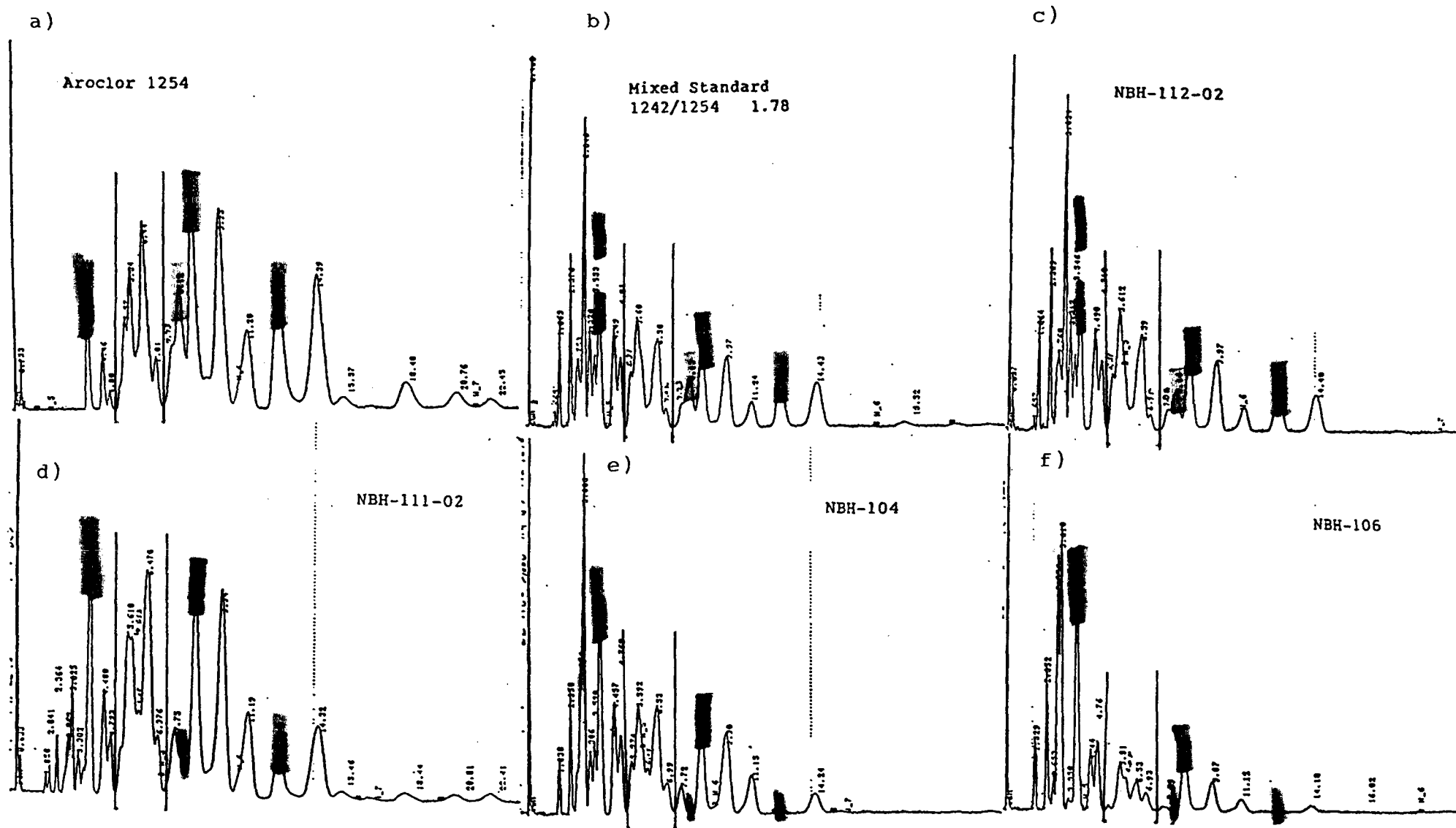


Figure 9. Progressive Aroclor 1254 Transformation

#### 3.1.4 Summary

Evaluations of the packed column GC/EC chromatograms indicate that Aroclor pattern alterations have occurred as the result of two different processes:

- o environmental aging, and
- o PCB transformations resulting from anaerobic degradation.

One analysis difficulty was encountered. Current EPA methodology (Method 8080) does not provide a means for quantitating PCB congeners in the samples which are not present in the Aroclor standards. As a consequence, di- and trichlorobiphenyls formed as a result of reductive dechlorination have not been quantitated and are not included in the total PCB data. This quantitation requirement is outside the scope of the EPA Method 8080. Methods such as EPA Method 680, the determination of PCB homologs by GC/MS, can be used for determining the total PCB content of samples in which these processes occur.

#### 3.2 Classification of Pattern Alterations Observed in the Packed Column GC/EC Chromatograms

The two principal causes of the pattern alterations observed were

- o changes due to the ratio of Aroclor 1016/1242 to Aroclor 1254 in the samples, and
- o changes due to compositional alteration of the PCB congeners present.

Since their impacts operate independently of one another, a consistent, uniquely distinct pattern was not observed in all the samples. Nonetheless, when the compositional ratio changes are discounted, a qualitative classification of the Aroclor transformations is possible.

3.2.1 Aroclor Transformation Observations. The following definitions apply to the sample evaluations:

1. Moderate alteration for Aroclor 1016/1242, sample shows "low-end" congener reduction.
2. Advanced alteration of Aroclor 1016/1242, sample exhibits significant reductions or the complete absence of the three normal pattern indicator peaks.

3. Moderate alteration of Aroclor 1254, pattern demonstrates "high-end" congener reduction and enhancement of peaks in the transition region.
4. Advanced alteration of Aroclor 1254, sample shows complete absence of peaks at RTs 8.15 and 12.70, significant reduction of "high-end" congeners as well as transition region peaks, and a new peak at RT 2.87 is present.

The Aroclor transformations demonstrated by the samples are tabulated according to these classifications in Table 4.

### 3.2.2 Examples of Classification Patterns

The pattern alterations shown in Figures 10 through 13 illustrate the following:

Figure 10. Sample NBH-101: Moderate alterations for both Aroclor 1016/1242 and Aroclor 1254.

Figure 11. Sample NBH-105: Moderate alteration for Aroclor 1016/1242 and advanced alteration for Aroclor 1254.

Figure 12. Sample NBH-113-02: Advance alteration for Aroclor 1016/1242 and slight alteration for Aroclor 1254.

Figure 13. Sample NBH-110-02: Advanced alteration for both Aroclor 1016/1242 and Aroclor 1254.

## 3.3 Capillary Column GC/EC Chromatograms

### 3.3.1 Overview

In recent years capillary columns have been developed for use in gas chromatography. Since the separation of individual PCB congeners is much more effective with these columns than with packed columns, the technique is called high resolution gas chromatography (HRGC). When the technique is properly used, substantially more resolution and information are provided by a capillary column chromatogram than by a packed column chromatogram.

One goal of this investigation was to determine the congener selectivity pattern(s) for the reductive dechlorination process. Before this can be accomplished, the identity of the individual PCB congeners present in the samples must be known. Capillary column GE/EC was used in an effort to

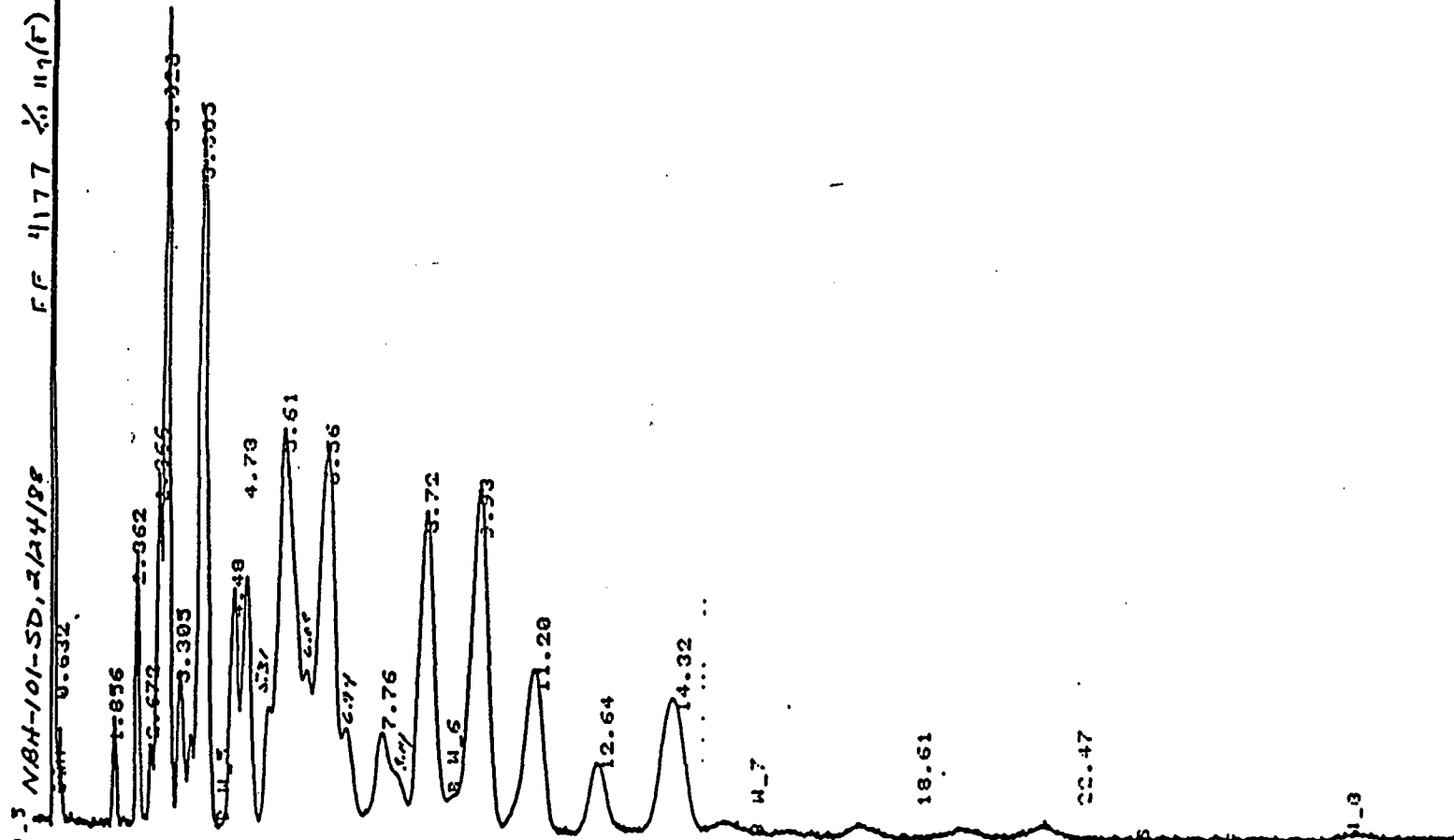
Table 4. Aroclor Transformation Demonstrated by NBH Samples

Sample	Ratio <u>1016 and/or 1242</u> 1254	<u>Transformation<sup>^</sup></u>	
		Aroclor 1016/1242	Aroclor 1254
NBH-101	0.71	M	M
NBH-102	1.73	S	S
NBH-103	0.66	M	M to A
NBH-104	1.23	S	M to A
NBH-105	2.11	M	A
NBH-106	2.20	M	A
NBH-110-01	0.73	A	A
NBH-110-02	(<0.45)	A	A
NBH-111-01	0.89	M	M to A
NBH-111-02	0.21	M	M
NBH-112-01	1.63	None	S
NBH-112-02	1.67	None	None
NBH-113-01	0.48	A	M
NBH-113-02	(<0.27)	A	S

<sup>^</sup>Transformation Key  
 S = Slight  
 M = Moderate  
 A = Advanced

JUN 36  
 11:40-D  
 STARTED 23:06.9 88/03/25  
 LAST EDITED 17:15.3  
 MP  
 PCB BME PROJ 3UL  
 88/03/24

3 N84-101-SD, 2/24/88 FF 4177 117(F)



Packed Column GC/EC Chromatogram for  
Sample NBH-101

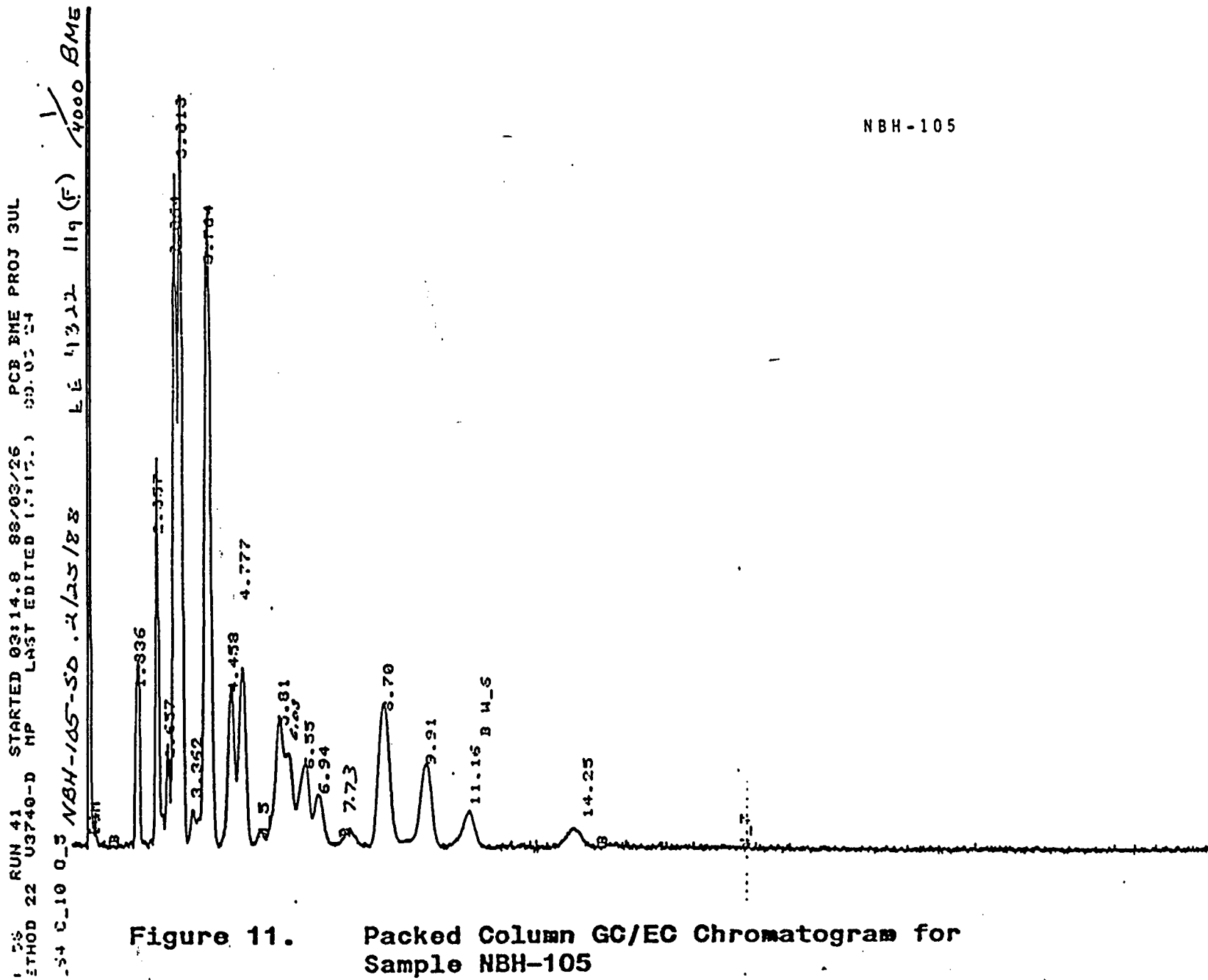
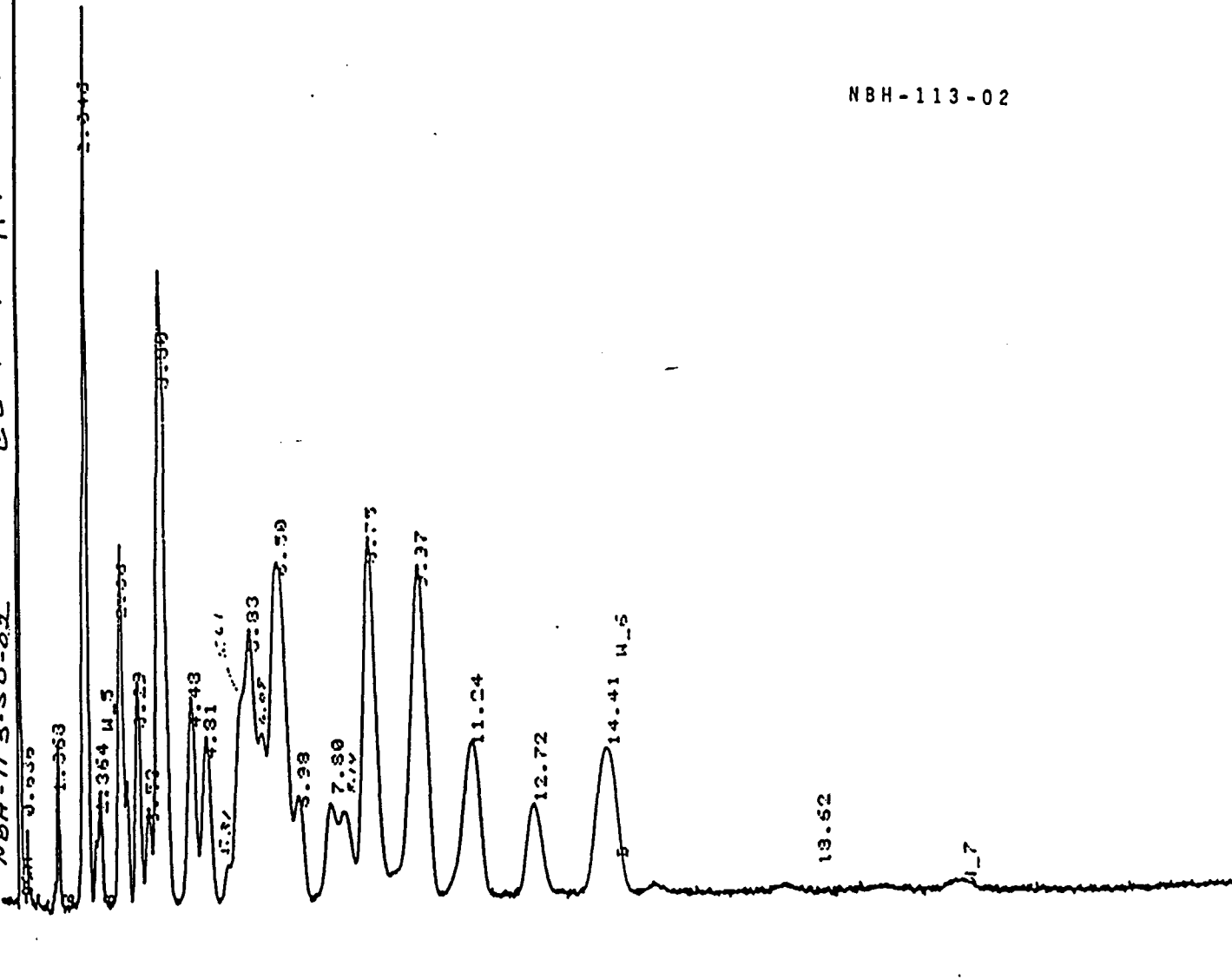


Figure 11.

Packed Column GC/EC Chromatogram for Sample NBH-105

[illegible]

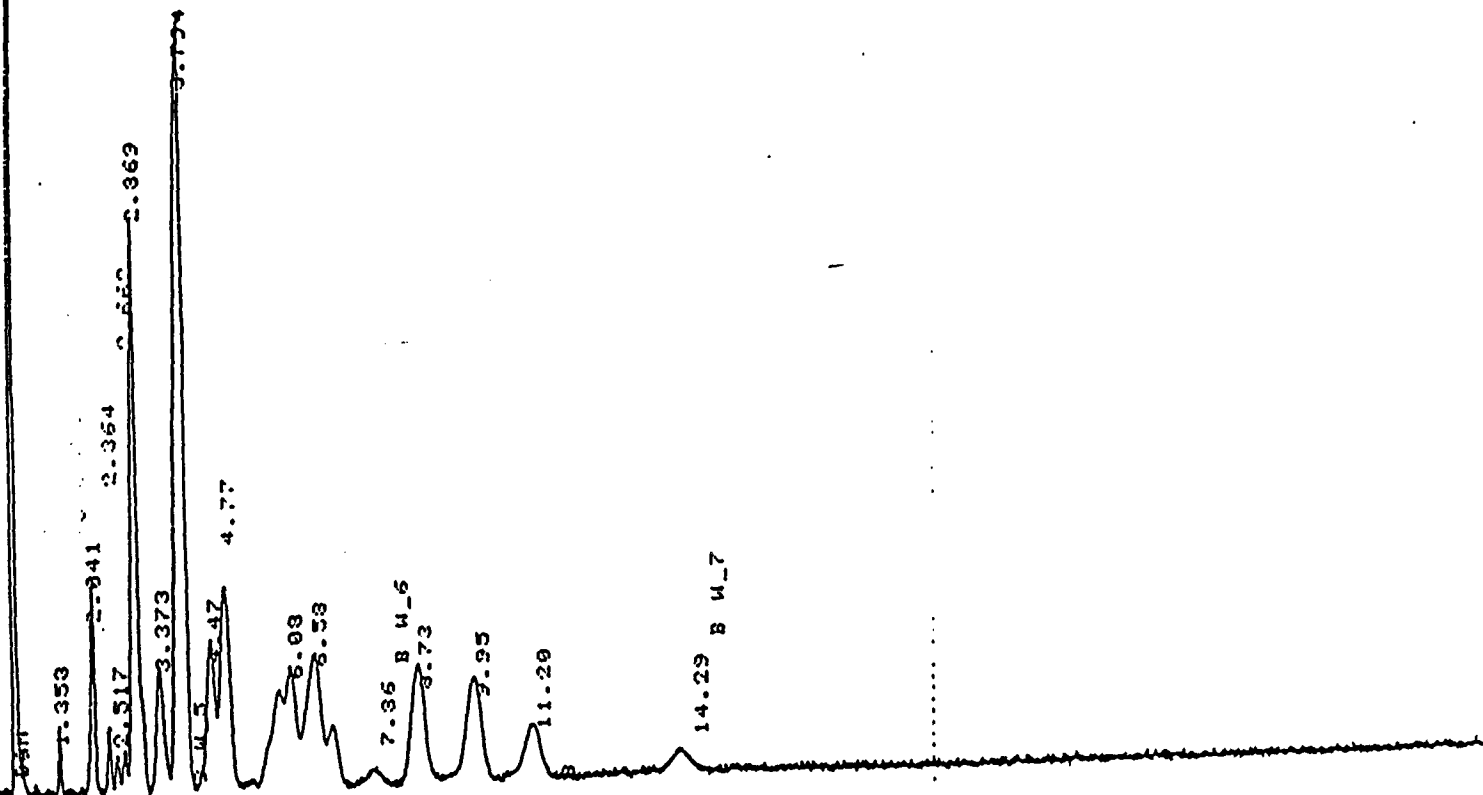
**Figure 12. Packed Column GC/EC Chromatogram for Sample NBH-113-02**

N B H - 1 1 3 - 0 2



PUN 21 STARTED 11:04.4 03/03/23 PC3 BME PROJ 3UL  
 D 22 03740-D MP LAST EDITED 17:15.2 08/08/24

0.10 0.5 NBH-110-50-02, 0.25-22 11 11 375 100.000 H<sub>1</sub>(F) BME



NBH-110-02

Figure 13. Packed Column GC/EC Chromatogram for Sample NBH-110-02

acquire these data. Although the separation of the individual PCB congeners was substantially improved over the packed column chromatogram, co-elution of some congeners was apparent and confirmation of compound identity will require the use of GC/MS (Phase 2 of this study).

### 3.3.2 Visual Inspection of DB-5 Capillary Column Chromatograms

Visual inspection of the DB-5 capillary column chromatograms revealed a variety of patterns which could be correlated with the packed column alteration patterns. Although congener identifications were not known for the capillary column peaks, comparison of the samples with the Aroclor 1016/1242 and Aroclor 1254 standards revealed significant alterations in the congener distributions found in the samples.

Four DB-5 capillary column chromatograms are shown in Figure 14. Sample NBH-104 represents the prevalent pattern seen in the samples. Sample NBH-105 resembles closely the pattern characterized in the Brown (1986) investigation. Samples NBH-110-02 and NBH-113-01 show significant, new alterations.

The complexity of the changes occurring in a portion of the so-called "transition region" of the packed column chromatograms (Section 3.1.3.2 and Figure 9) is illustrated by Figure 15. Transition stages involving differential formation rates are shown by the enhanced peaks occurring at RTs 16.80 and 16.98 (color-coded orange). The indicator peak which is essentially unaffected by anaerobic dechlorination through the stages represented, is color-coded pink (RT 18.13). The peak at RT 18.85 (color-coded green) does not occur in the Aroclor standard which contains equal amounts of Aroclors 1016, 1242, and 1254. The intensity of this new peak increases to a maximum between b) and d) and then decreases as the dechlorination progresses to more advanced stages e) through g). The disappearance of a congener(s) is illustrated by the peak at RT 19.20 (color-coded blue). Once the identification of the PCB congeners giving rise to the illustrated peaks is known, estimations can be made for the extent of dechlorination and possibly for other critical parameters as well. The identity of the components will be determined by GC/MS during the second phase of this investigation.

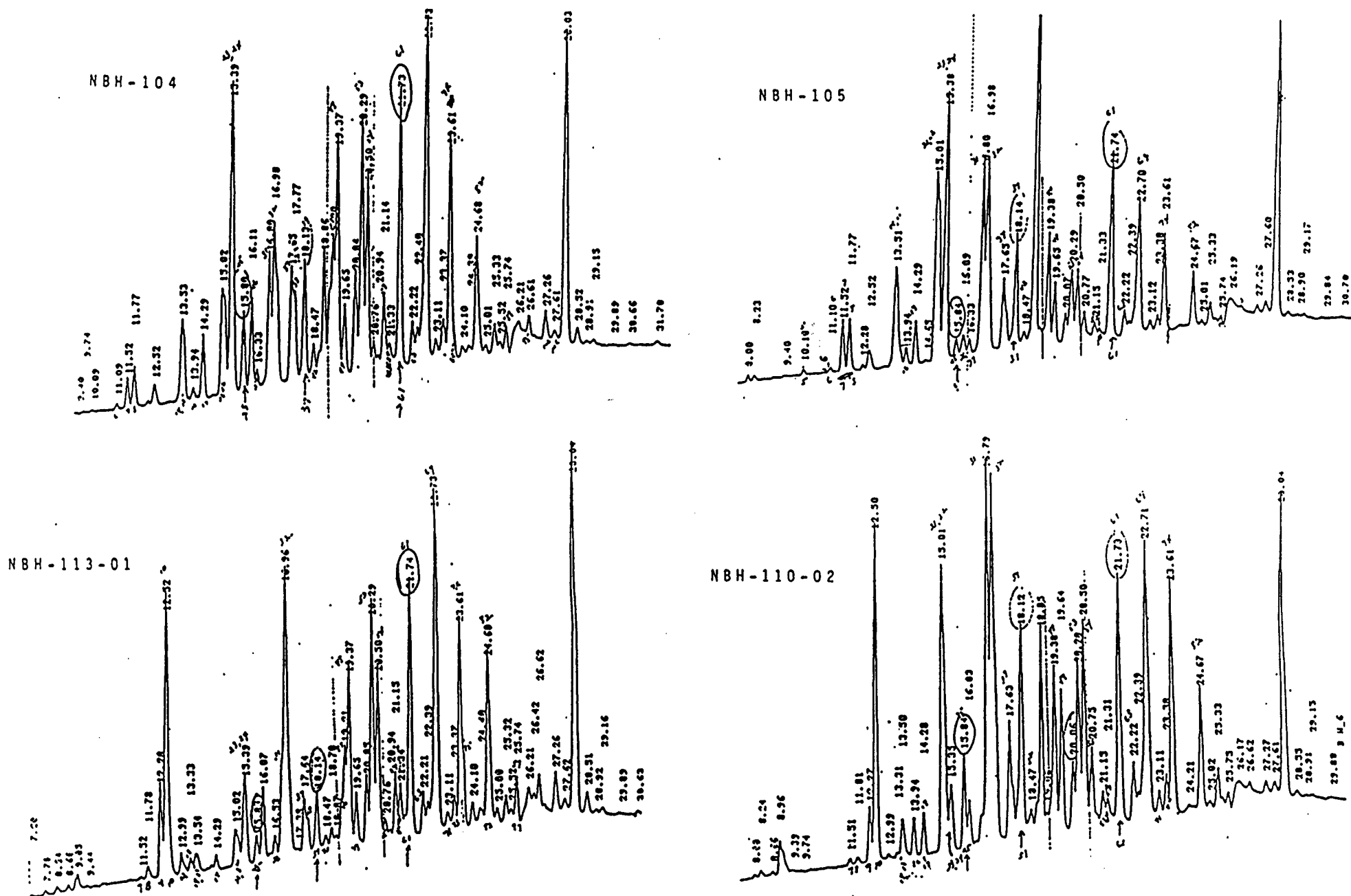


Figure 14. Representative Capillary Column GC/EC Chromatograms for NBH Samples

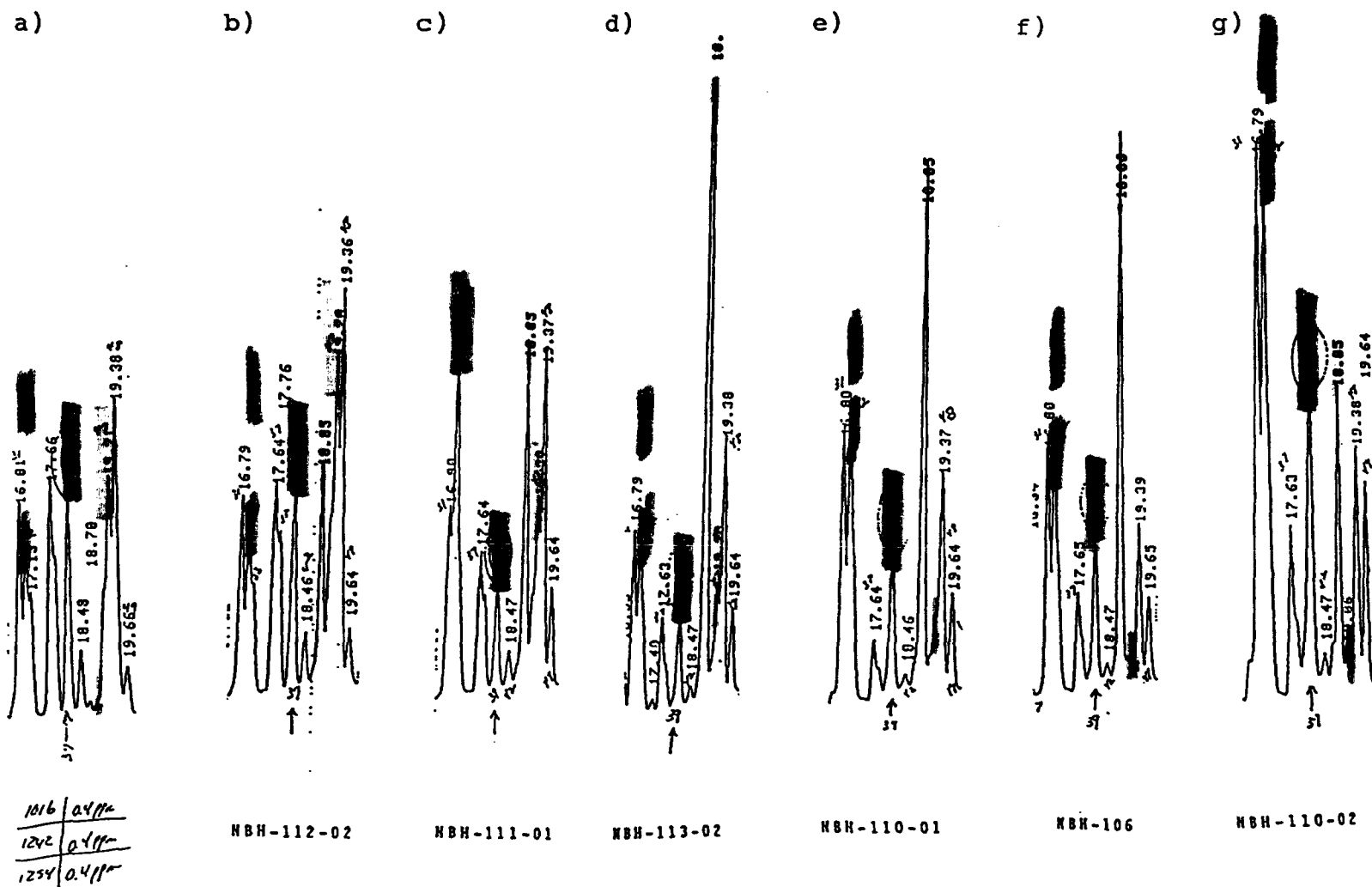


FIGURE 15. Reductive Dechlorination Changes Occurring in the Transition Region of Capillary Column GC/EC Chromatograms

### 3.3.3 Comparison of DB-1 and DB-5 Capillary Column Chromatograms

As a means of relating the study results to the work performed by Brown (1986) on NBH sediment samples, an effort was made to correlate the DB-5 capillary peaks with the 18 distinguishable peaks observed by Brown on a DB-1 capillary column. The effort was successful, for the most part, as the peak elution sequences for the Aroclor 1016, 1242, and Aroclor 1254 standards on DB-5 closely paralleled those on DB-1. However, congener co-elution problems were identified with both columns.

### 3.3.4 Summary

There is substantial evidence in the data to indicate the occurrence of anaerobic dechlorination of PCBs in the NBH sediments. However, the extent of the transformation and the source of the new congeners cannot be fully determined from the present data. Structure-dependent selectivities leading to the transformations cannot be identified until the identities of the PCB congeners in the samples are known.

## 4.0 DISCUSSION OF RESULTS

### 4.1 Study Findings

Three questions pertaining to NBH sediment samples have been answered by this investigation. In addition, reference packed column GC/EC chromatograms have been generated which exemplify Aroclor transformation patterns occurring in the upper estuary sediments.

#### 4.1.1 Aroclor Identification

This study has shown that Aroclor 1016/1242 and Aroclor 1254 are present in the NBH sediment samples. Over 90% of the chromatograms showed Aroclor transformation patterns.

The progressive anaerobic dechlorination of the higher chlorinated biphenyls present in Aroclor 1254 appears to have a cascading effect on the Aroclor alteration pattern. The first step in the process results in a decrease in the penta- and hexachlorobiphenyl region of the pattern with a corresponding increase in the tri- and tetrachlorobiphenyl area. Further dechlorination yields increases in mono- and dichlorobiphenyls and decreases in certain tri- and

tetrachlorobiphenyls. The NBH sediments appear to demonstrate different stages of the Aroclor 1254 degradation process. In addition, Aroclor 1016/1242 degradation is apparently occurring in a number of the samples.

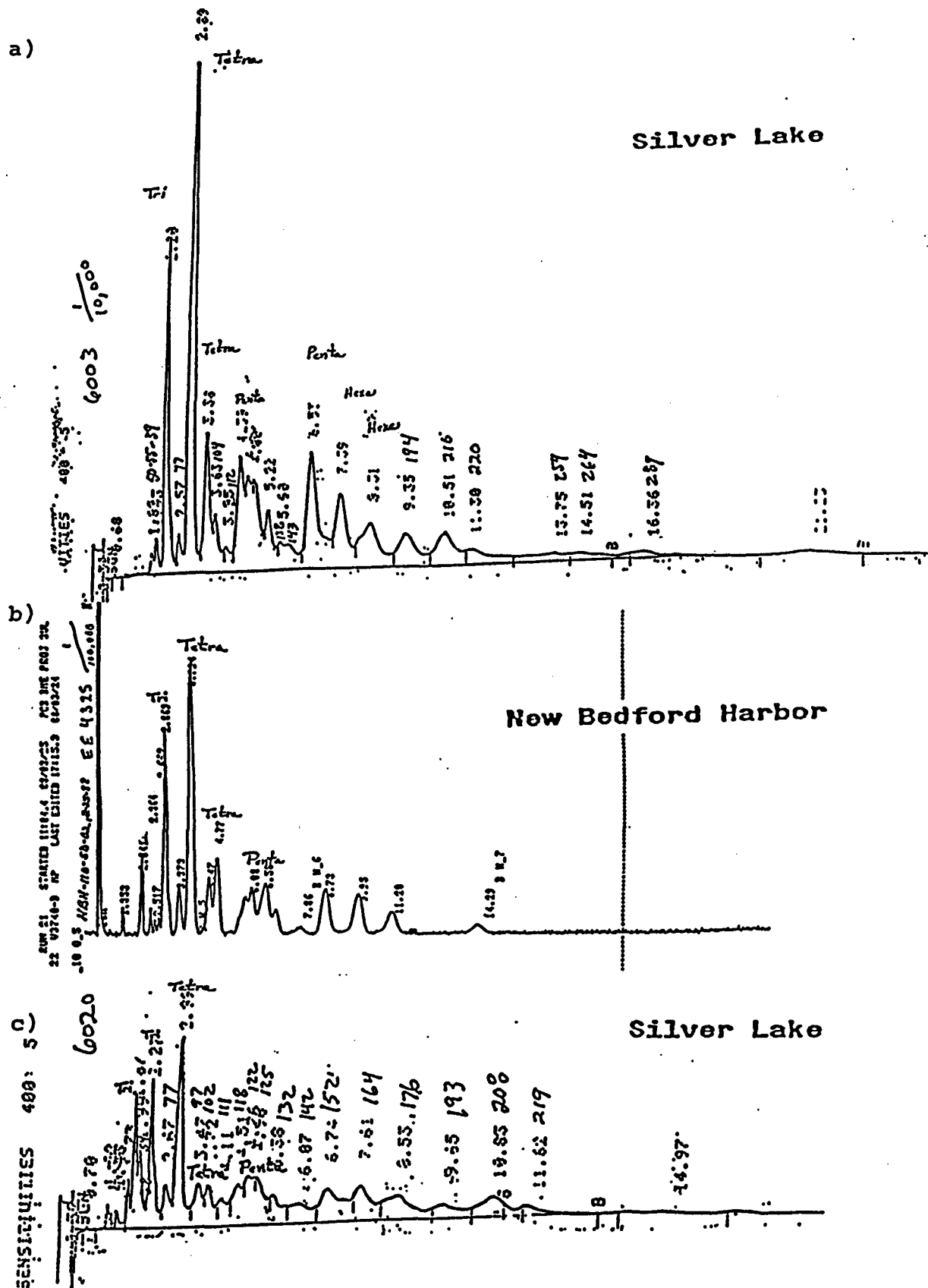
The tetrachlorobiphenyl region of the chromatograms is subject to additive effects from the "high-end" enhancement of Aroclor 1016/1242 which has undergone pattern alteration due to preferential solubilization of the di- and trichlorinated congeners. The peak enhancements in the tri- and tetrachlorobiphenyl regions, due to the initial dechlorination of Aroclor 1254, coupled with the environmental aging of Aroclor 1016/1242 have produced Aroclor pattern alterations which resemble Aroclor 1248. It appears that some laboratories have misinterpreted the altered patterns described above as indicating the presence of Aroclor 1248 in the sediments.

#### 4.1.2 Aroclor Alteration Patterns

Aroclor alteration patterns were observed in both the packed column and capillary column chromatograms. Four rather distinctive alteration patterns were identified, as illustrated in Figures 10 through 14. The packed column chromatograms of the NBH sediments which represent advanced Aroclor transformations bear a striking resemblance to the patterns observed in sediments from other PCB spill sites (See Figure 16). The Silver Lake samples (a & c) were confirmed by GC/MS to contain Aroclor 1254 and a lesser amount of Aroclor 1260. However, many di-, tri, and tetrachlorobiphenyls were present which did not match the normal patterns of Aroclor 1254 and 1260 (Yoakum, 1982). The NBH sediment transformation pattern is illustrated by Sample NBH-110-02 (b) in Figure 16.

#### 4.1.3 Anaerobic Degradation in NBH Sediments

The most significant Aroclor pattern alteration observed in NBH sediment samples was that due to anaerobic dechlorination. This phenomenon was demonstrated by both the packed column and capillary column chromatograms. The congener distribution patterns exhibited by the samples show evidence of the occurrence of anaerobic biotransformations. New peaks are present in the patterns as well as "high-end" drop-off due to the degradation of higher chlorinated PCBs. Peak enhancements, reductions and disappearances have also occurred. Anaerobic alteration patterns in sediment samples are distinctively



**FIGURE 16. Comparison of Chromatograms Showing Advanced Aroclor Transformations in Sediments from New Bedford Harbor and Silver Lake**

different from those occurring as the result of extractive losses of the more soluble congeners of Aroclors.

Some of the degradation patterns of the NBH sediment samples appear to be more complex than those observed at other sites where anaerobic dechlorination has been studied. This is probably due to the simultaneous dechlorination of both Aroclor 1016/1242 and Aroclor 1254.

#### 4.2 Comparison of Study Findings with Brown (1986) Observations

Both studies conclude that anaerobic dechlorination is evident. Brown has identified Aroclor 1242 and Aroclor 1254 in the samples. Based on the capillary column data for the Task 7 samples, a distinction between Aroclor 1016 and Aroclor 1242 could not be made. The Task 7 conclusion is, therefore, that either Aroclor 1016 and/or Aroclor 1242 is present together with Aroclor 1254.

##### 4.2.1 Aroclor Identifications

Brown (1986) concluded that the samples resembled Aroclor 1242-1254 mixtures that had been subjected to either or both of two types of pattern alteration: a general, non-selective loss of peaks with short retention times; and the unusual congener distribution patterns previously seen at other PCB spill sites.

A procedure, utilizing capillary column indicator peaks for Aroclor 1242 (peak 39) and Aroclor 1254 (peak 61), was used to calculate the original Aroclor ratios and solubilization losses. A similar procedure, based on the disappearance rates of peaks 25 and 50 (relative to the Aroclor 1242 indicator peak 39) was used to measure admixed Aroclor 1016 in the samples. An attempt was made to apply this approach to the Task 7 samples. Limited success was achieved with the procedures for the measurement of admixed Aroclor 1016 using standard mixtures of Aroclors. However, the procedure could not be applied successfully to the actual samples. This appears to be due, at least in part, to congener resolution differences between the DB-1 and DB-5 columns in the vicinity of peak 50 in the capillary chromatogram. Either peaks 50 and 51 are co-eluting, or there is some formation of one or more of the components of peak 50 during the transformation process.



#### 4.2.2 Anaerobic Dechlorination Patterns

During his investigation of anaerobic PCB alterations in sediment samples, Brown (1984, 1987) has assigned letter designations to patterns seen consistently enough to suggest their individuality. According to Brown (1986) the pattern observed in New Bedford Harbor sediments was somewhat intermediate between, but clearly distinct from, those seen in sediments from the upper Hudson River (Pattern B) and Silver Lake (Pattern F). He concluded that the New Bedford process was a new type of alteration and designated it Pattern H. A second, slightly different pattern was designated Pattern H'.

The Aroclor alteration patterns observed in this study fall into three basic categories:

- o a pattern essentially corresponding to Pattern H,
- o a pattern resembling Pattern H but showing less transformation,
- o a pattern showing new peaks and additional transformations not seen in Pattern H.

More data is needed before a pattern of positional selectivity can be established for the transformations observed in this study. The initial indications are that the different alteration patterns observed in fact represent different stages of the same process, rather than different & unrelated transformation patterns.

#### 4.3 Conclusions

The following conclusions are drawn from the investigation:

1. The NBH sediments contain mixtures of Aroclor 1016/1242 and Aroclor 1254.
2. The total Aroclor content of the samples range from 9.6 to 130,000 ppm.
3. Reference packed column GC/EC chromatograms are now available which are representative of the Aroclor pattern alterations observed in the NBH sediments.
4. Three stages (or levels) of pattern alterations were observed.
5. Anaerobic PCB degradation is evident in over 90% of the samples.
6. The most pronounced degradation was observed in samples from the Aerovox facility sampling area and sampling station NBH-105.

## 5.0 RECOMMENDATIONS

Since significant PCB transformations were found in the sediment samples, the recommendation is made that the second phase of the project be conducted. The identification of the specific PCB congeners involved in all stages of the degradation must be determined before the most probable path of the PCB transformation process can be ascertained.

In addition, the recommendation is made to analyze representative samples by EPA Method 680 to determine the homolog distributions compared to Aroclor standards and standard mixes.

## REFERENCES

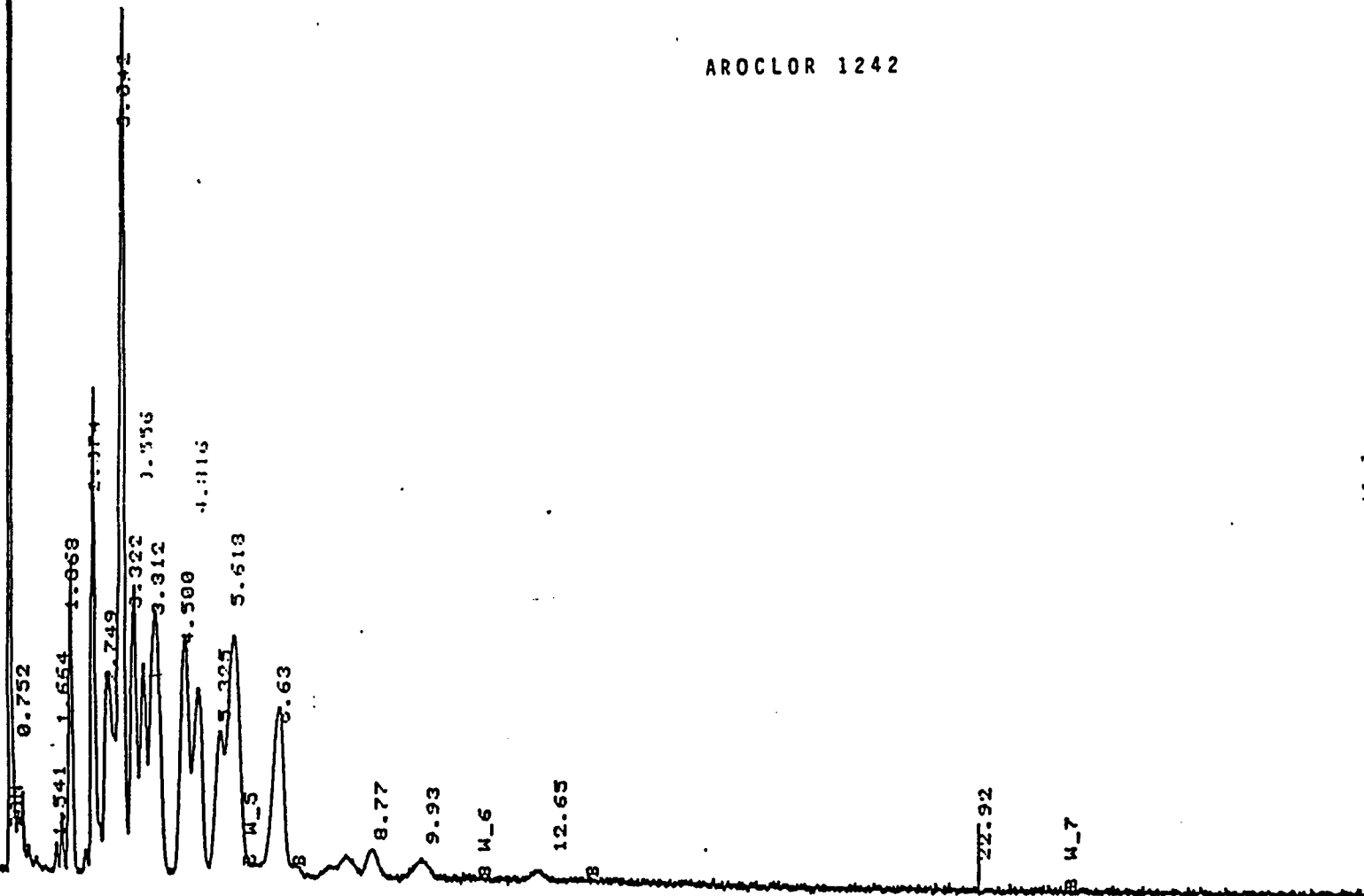
1. Alford-Stevens, A. L., Budde, W. L., and Bellar, T. A., Anal. Chem. 57: 2452-2457 (1985).
2. Brown, J. F. Jr., et al., Northeast Environ Sc. 3: 167-179 (1984).
3. Brown, J. F. Jr., et al., Science 236: 709-712 (1987).
4. Contract Laboratory Program (CLP) Protocol, U.S. Environmental Protection Agency, Statement of Work (7/85).
5. Metcalf & Eddy Engineers, Acushnet Estuary PCBs, Data management Final Report - for EPA Region 1: Boston, MA (1983).
6. Method 680, "Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry," EMSL, U. S. Environmental Protection Agency: Cincinnati, OH (1985).
7. Method 8080, "Organochlorine Pesticides and PCBs," Test Methods for Evaluating Solid Waste, SW-846, 3rd Ed., U. S. Environmental Protection Agency, Office of Solid Waste and Emergency Response: Washington, DC (1986).
8. Yoakum, A. M., Housatonic River Study - Final Report, Stewart Laboratories, Inc., Knoxville, TN (1982).

**APPENDIX A-1**  
**PACKED COLUMN CHROMATOGRAMS**

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MTHOD 22 U3740-D MP LAST EDITED 00:03.9 80/01/01

0.54 C\_10 0.5

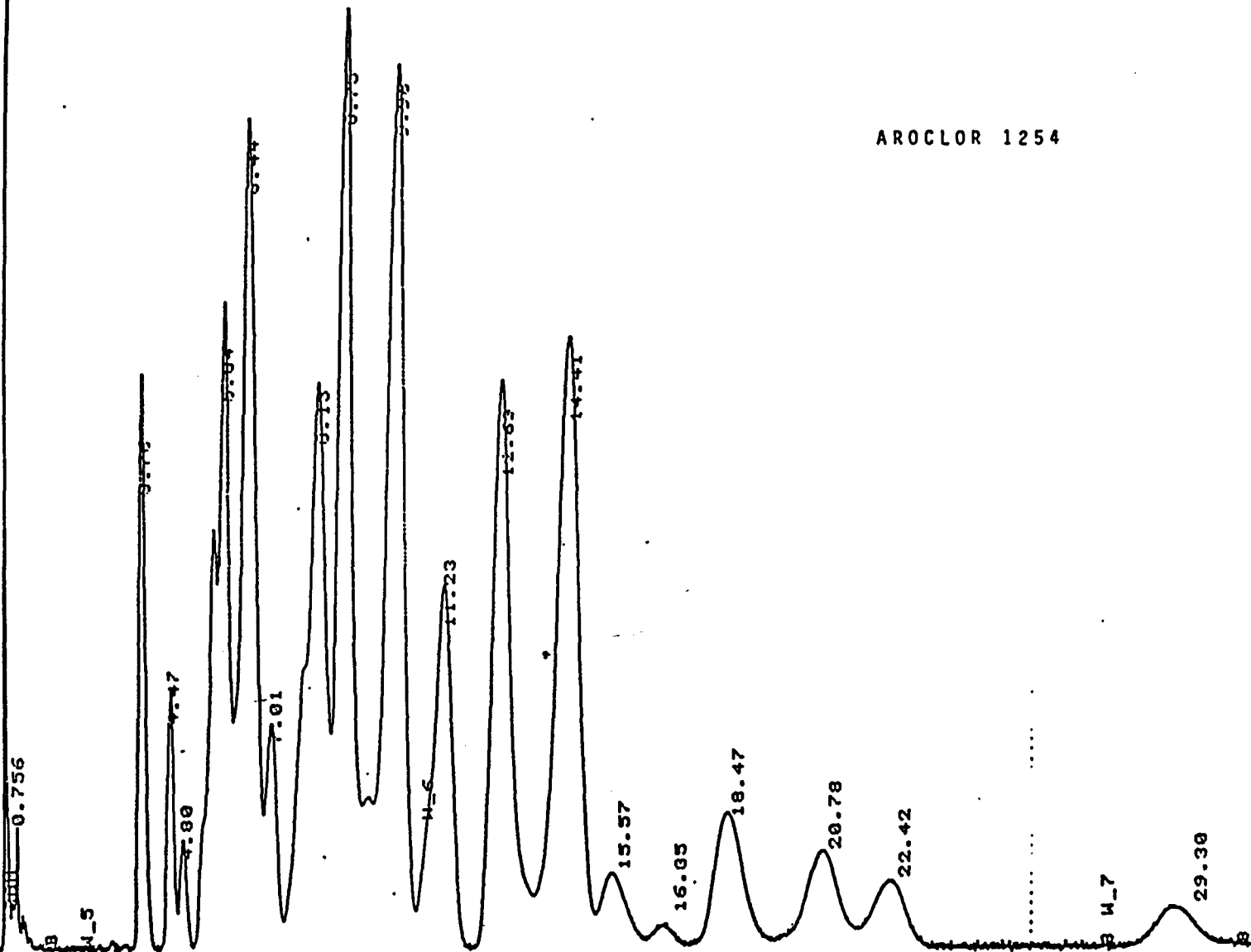
1242 BW-182 0.15



AROCLOR 1242

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0D C2 V3740-D MP LAST EDITED 17:13.3 88/03/24

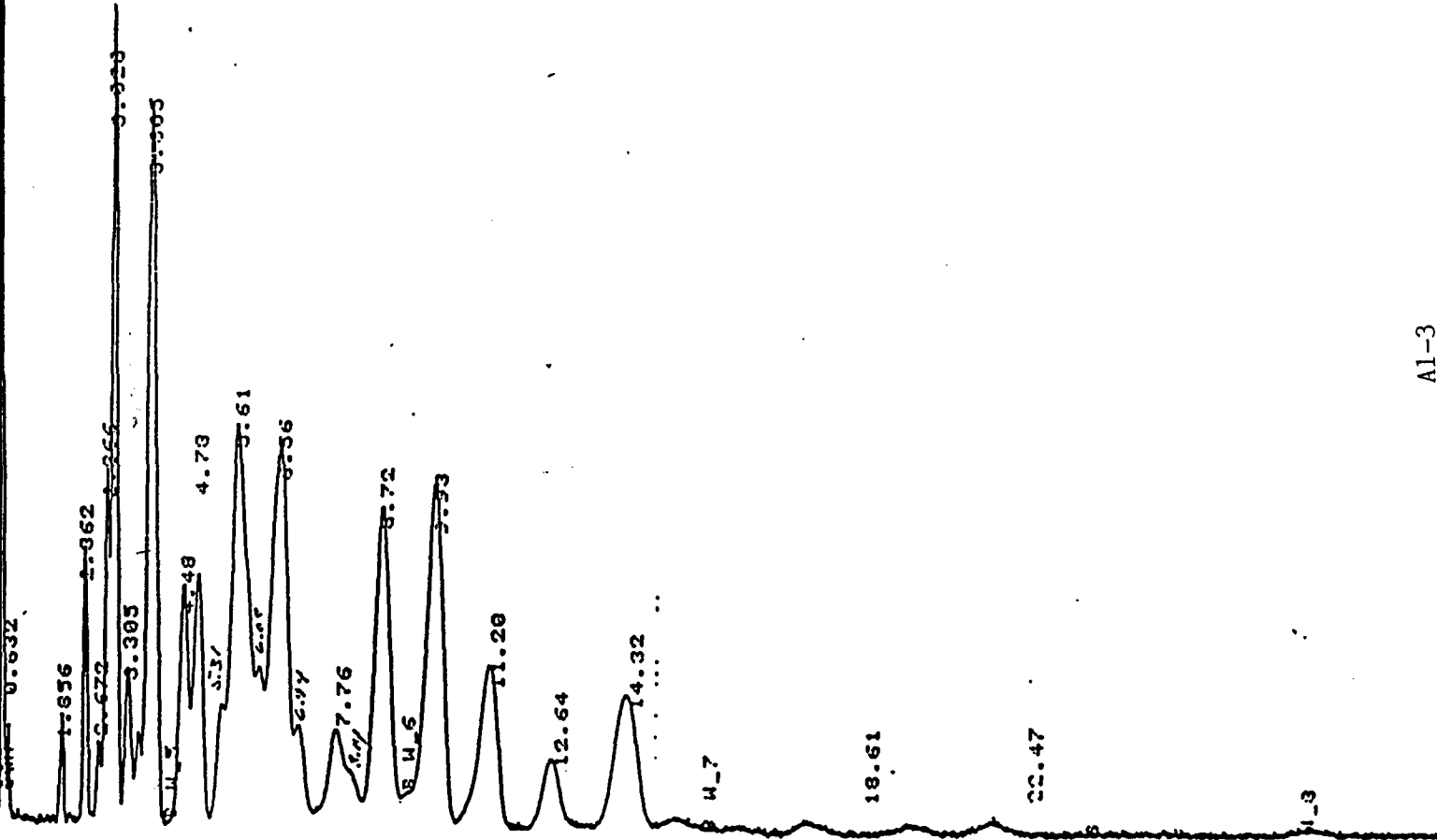
0.10 0.5 BW-176 1254 0.5



AROC LOR 1254

11 36 STARTED 23:05.8 88/03/25 PCB BME PROJ 3UL  
11 40-D MP LAST EDITED 17:15.3 88/03/24

1.3 NBH-101-SD, 2/24/88 FF 4177 1/11(F)

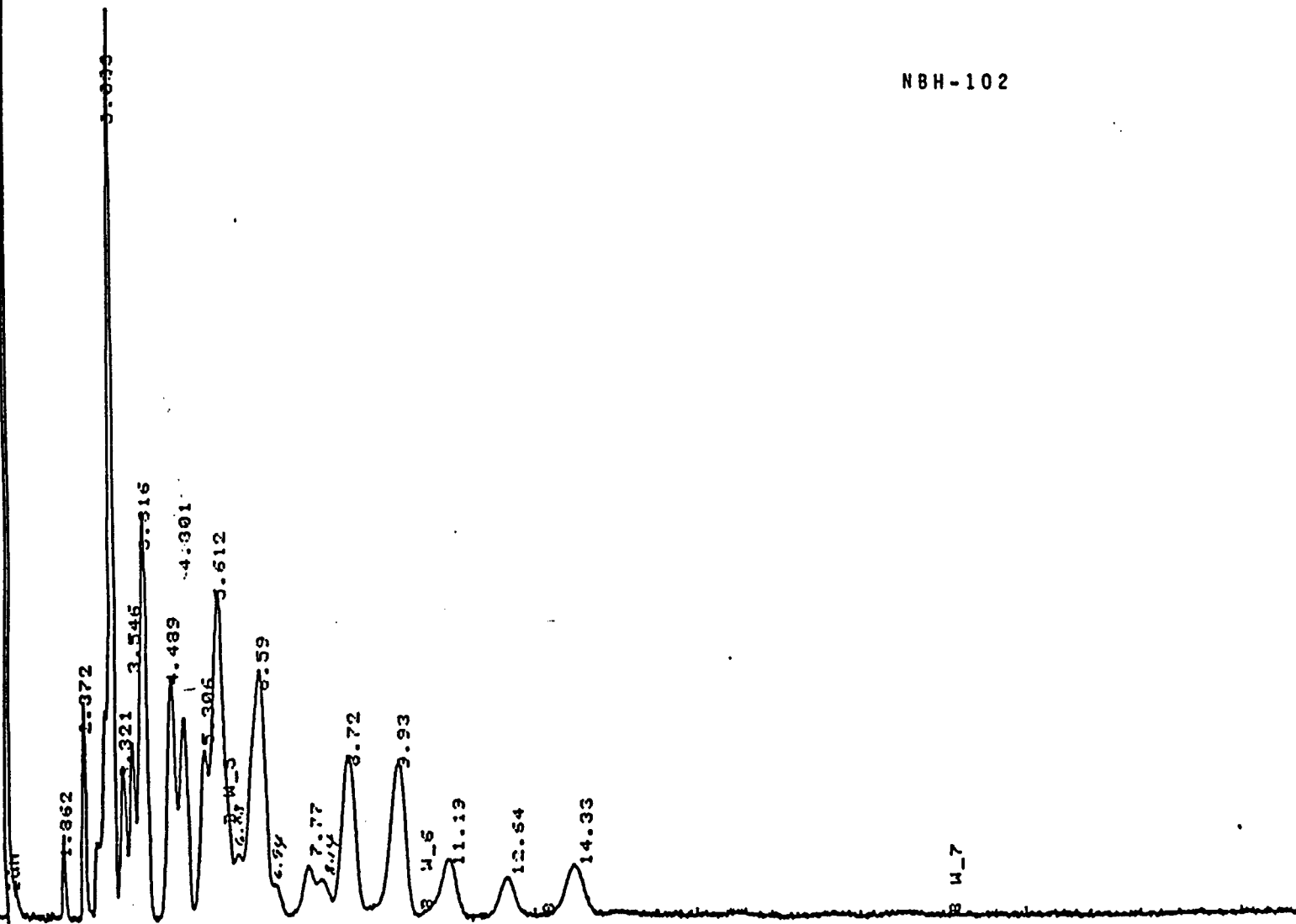


NBH-101

• 051

RUN 13 STARTED 08:05.3 88/03/05 PCR DME P007 JUL  
CC 03740-D MP LAST EDITED 17:15.3 88/03/24

-10 0.5 NBH-102-50.2-24.88 DME-40786 EE 4170 1000 H<sub>1</sub>(F)

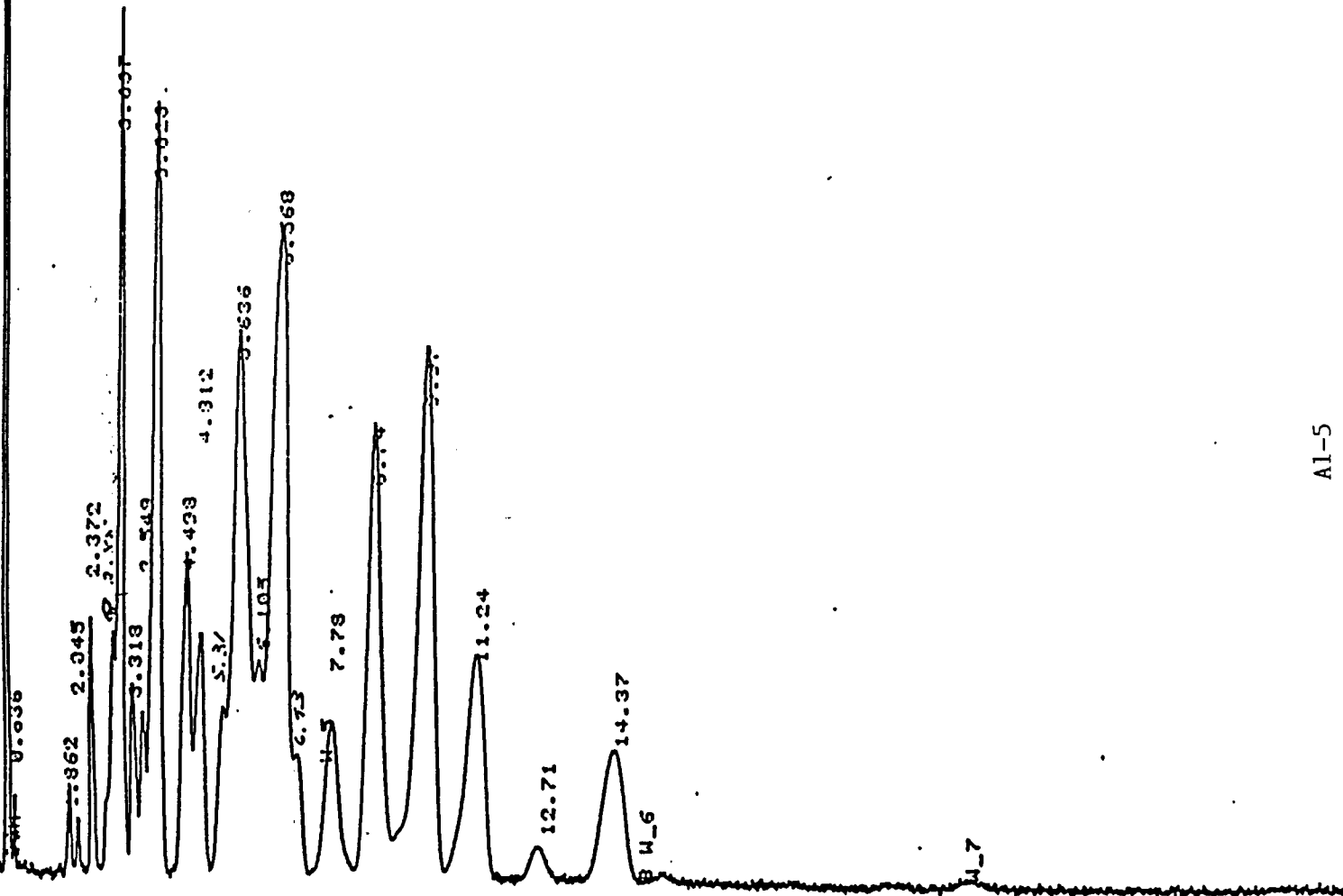


NBH-102



NO RUN 7 STARTED 14:06.6 88-03/28 PCB EME PROJ SUL  
100 22 U3740-D MP LAST EDITED 17:13.3 88-03-24

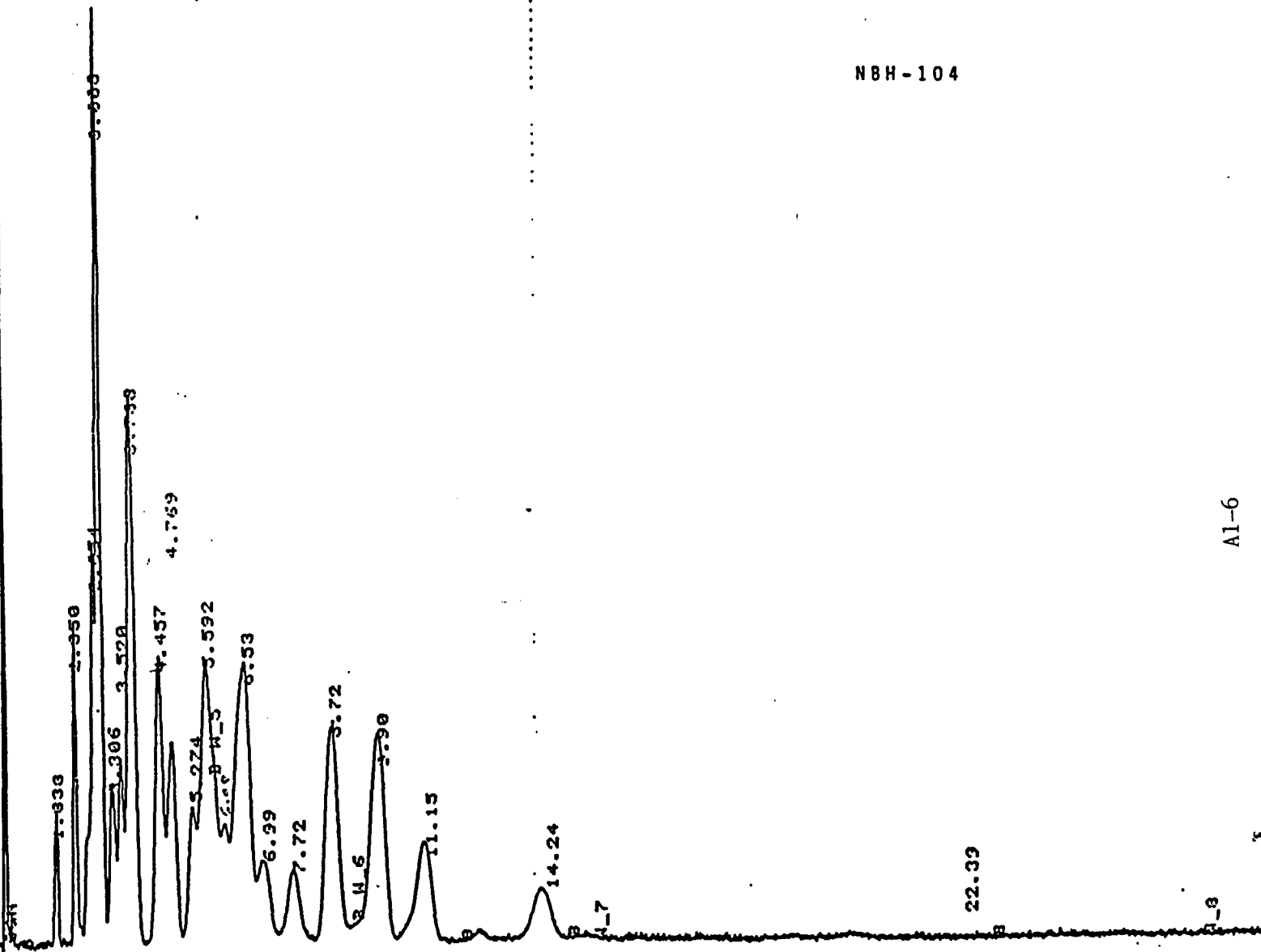
10-10 0-5 NBH-103-SD.2/24/88 EE 4179 AT H9 (F) 100%



NBH-103

RUN 46 STARTED 07:22.9 08/03/26 FLE BME PROJ 3UL  
U 000 U3740-D MP LAST EDITED 17:15.3 08/03/24

C-10 0.5 NBH-104-SD, 2/24/88 17:41:00 1/1000 Hg (F) BMF 40786 0.15



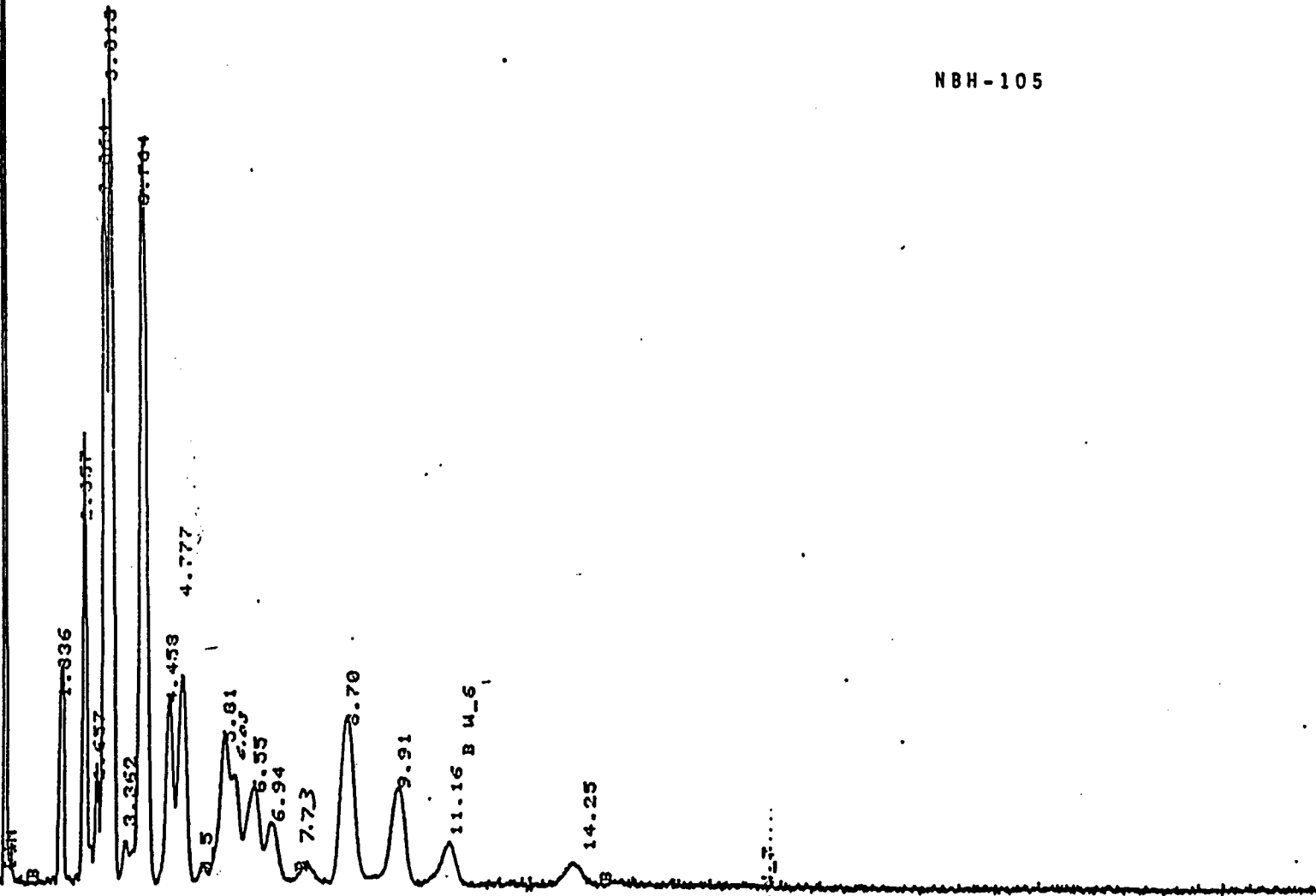
NBH-104

METHOD 22 U3740-D NP LAST EDITED 17:15:30 03.03.24  
 RUN 41 STARTED 03:14:08 88/03/26 PCB BME PROJ 3UL

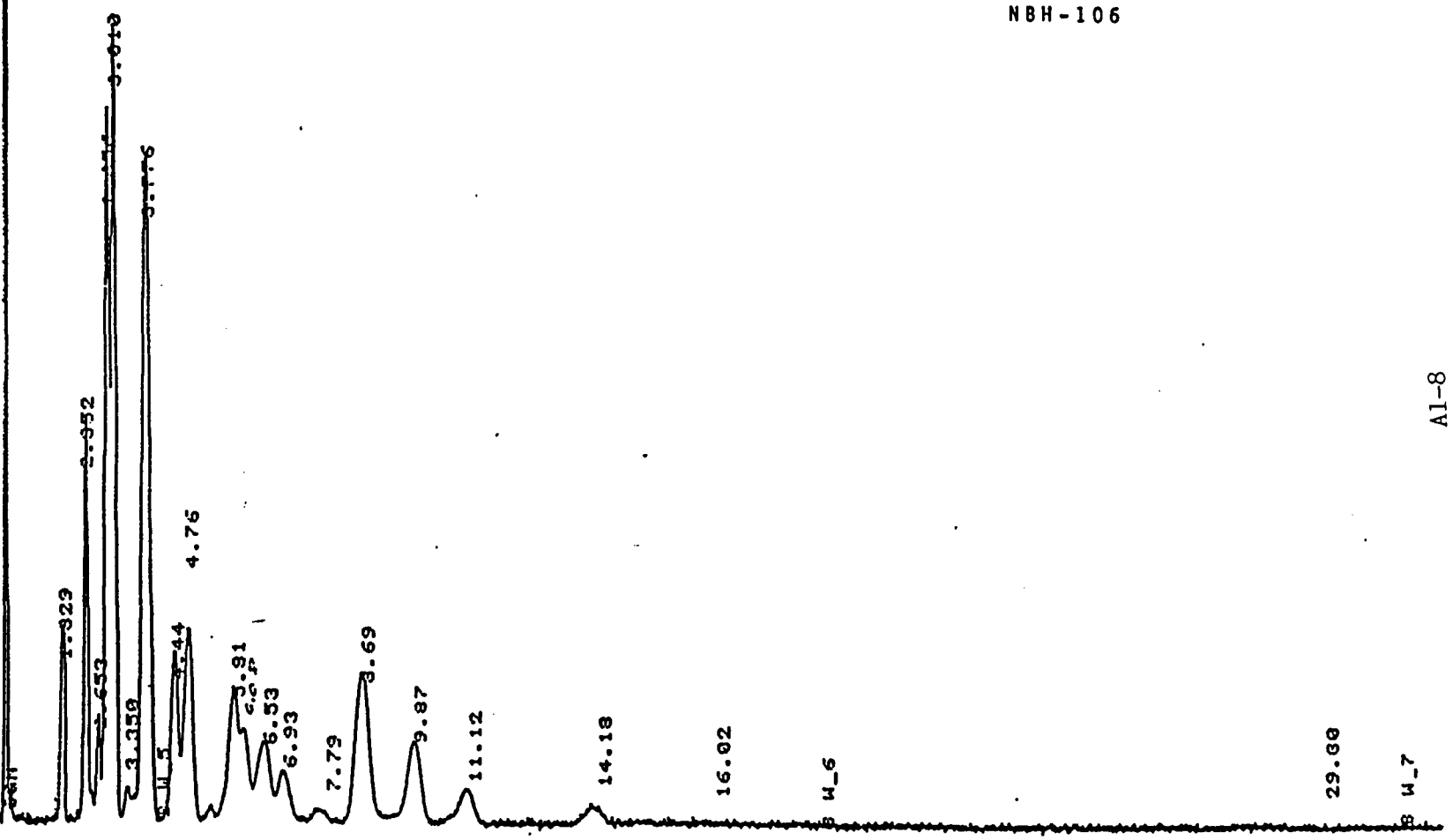
44-38861-1000

1 28 RUN 41 STARTED 03:14.8 88/03/26  
ETHOD 22 U3740-D NP LAST EDITED 1:17.)

-54 C-10 0-5 NBH-105-SB .2/25/88 L E 113.2 119 (F)  $\frac{1}{4000 \text{ BME}}$

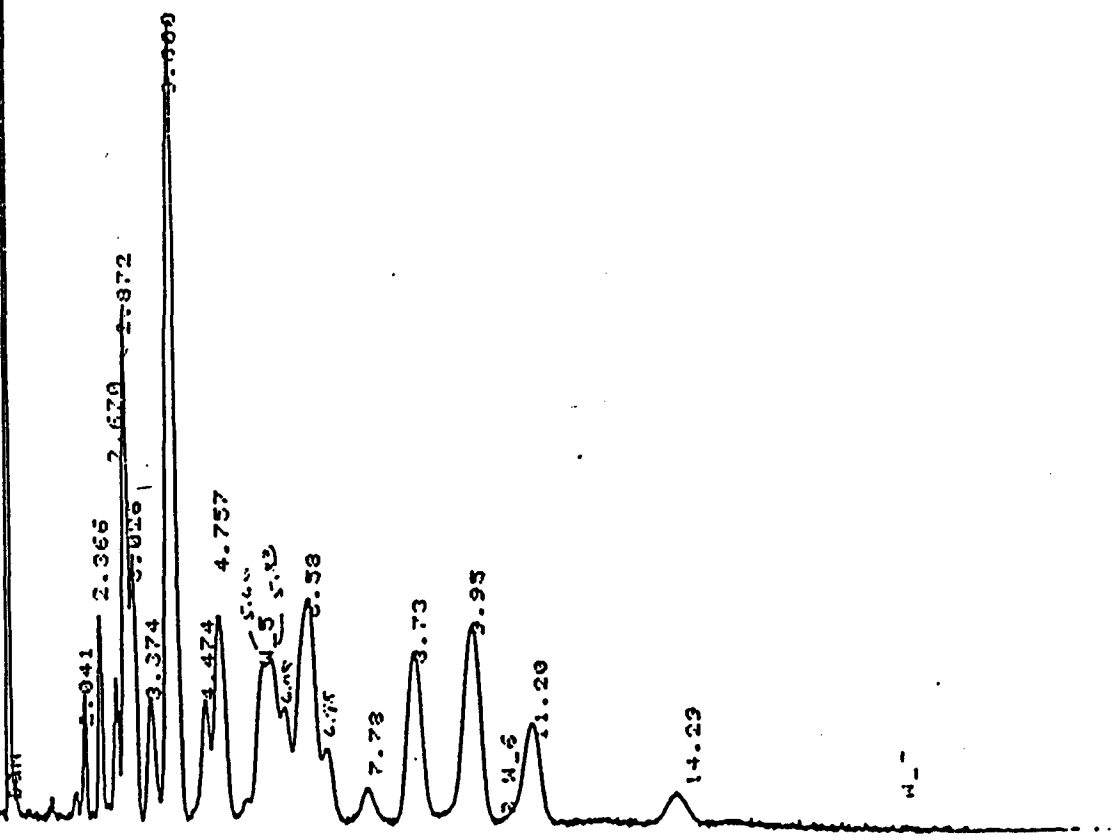


0.10 0.3 NBH-106-SD, 1/25/88  
 LAST EDITED 17:15:3 88/03/24  
 FE 432.3 Hg(F) 1/4000 BME



NBH-106

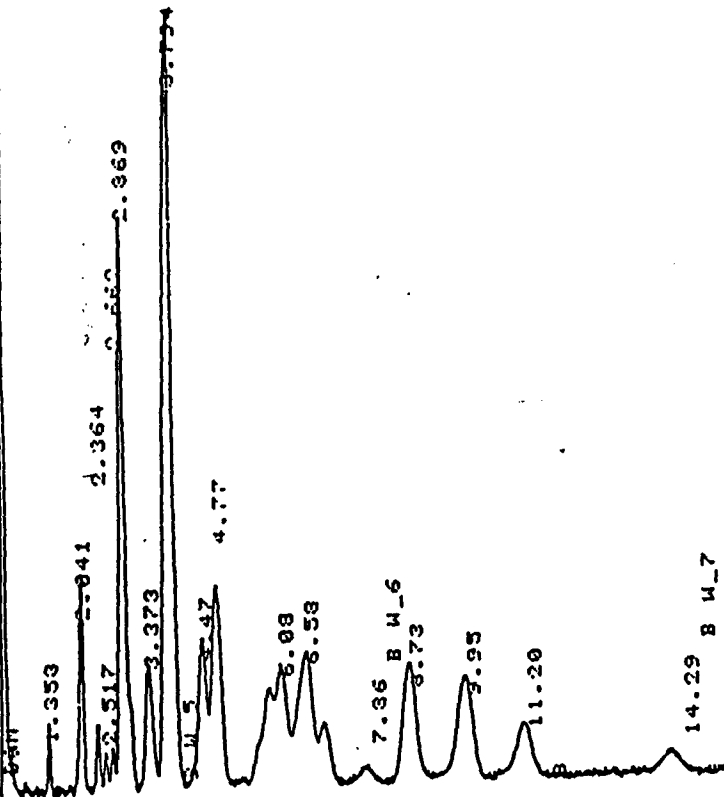
JUN 22 STARTED 11:54.0 88-03-23 PCB SMC PROJ JUL  
 11:40-0 MF LAST EDITED 17:15.3 88-03-24  
 0.5 NBH-110-5D-01 2-25-88 1.0 1321 114.000 H9(F) Bx



NBH-110-01

1 RUN 01 STARTED 11:04.4 23/03/25 PC3 BME PROJ 3UL  
00 22 03740-D MP LAST EXITED 17:15.3 28/03/24

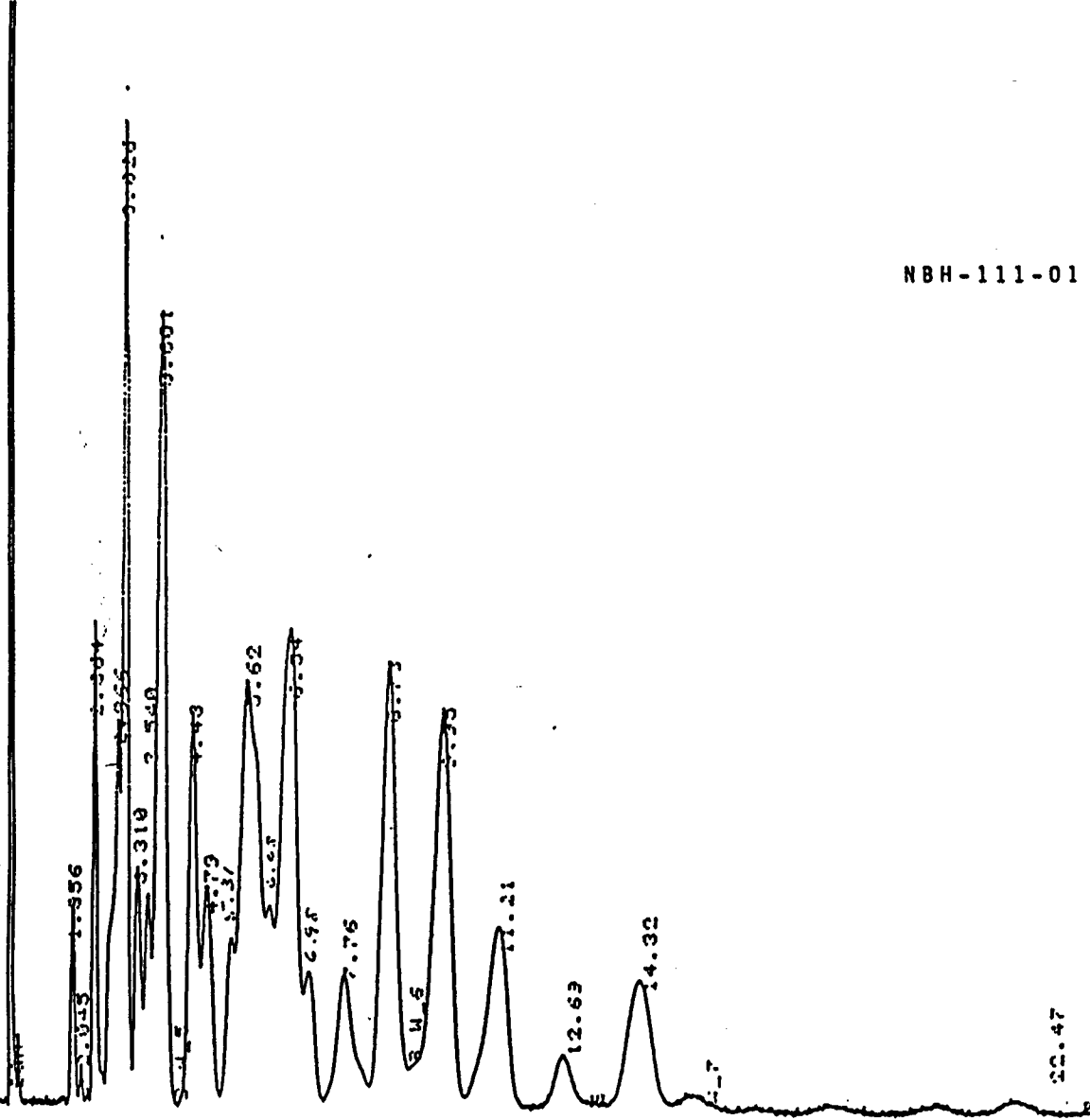
1 0\_10 0\_5 NBH-110-50-02, 0.25-PR 1 1 1375 100.000 H<sub>2</sub>(F) BME



NBH-110-02

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01 40-D MP LAST EDITED 17:13.3 88/03/24

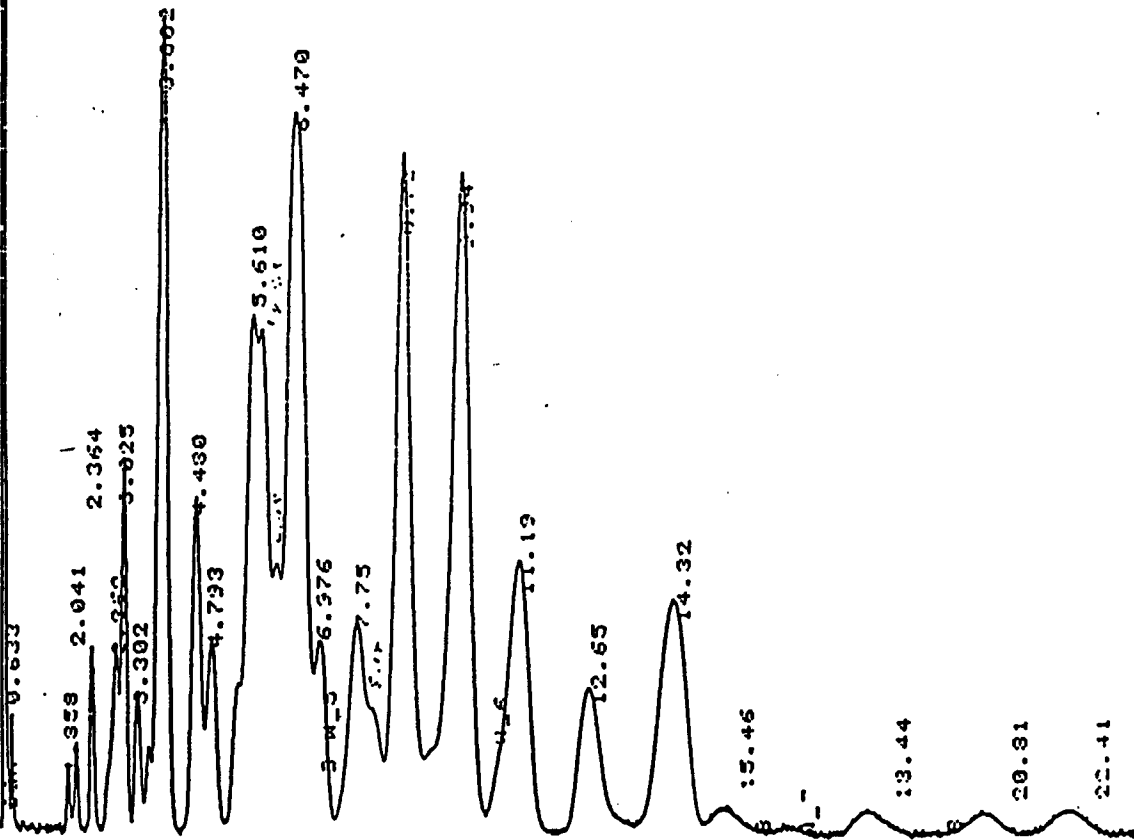
01 5 NBH-11-50-01, 2.2538 66 4326 1/50,000 1/5(r)



NBH-111-01

RUN 25 STARTED 22:17.1 88/03/25 PCB BME PROJ JUL  
2 00740-D MP LAST EDITED 17:15.3 88/03/24

3 3-5 NBH-111-50-01, 2-25-88 664327 50,000 Hz(F)

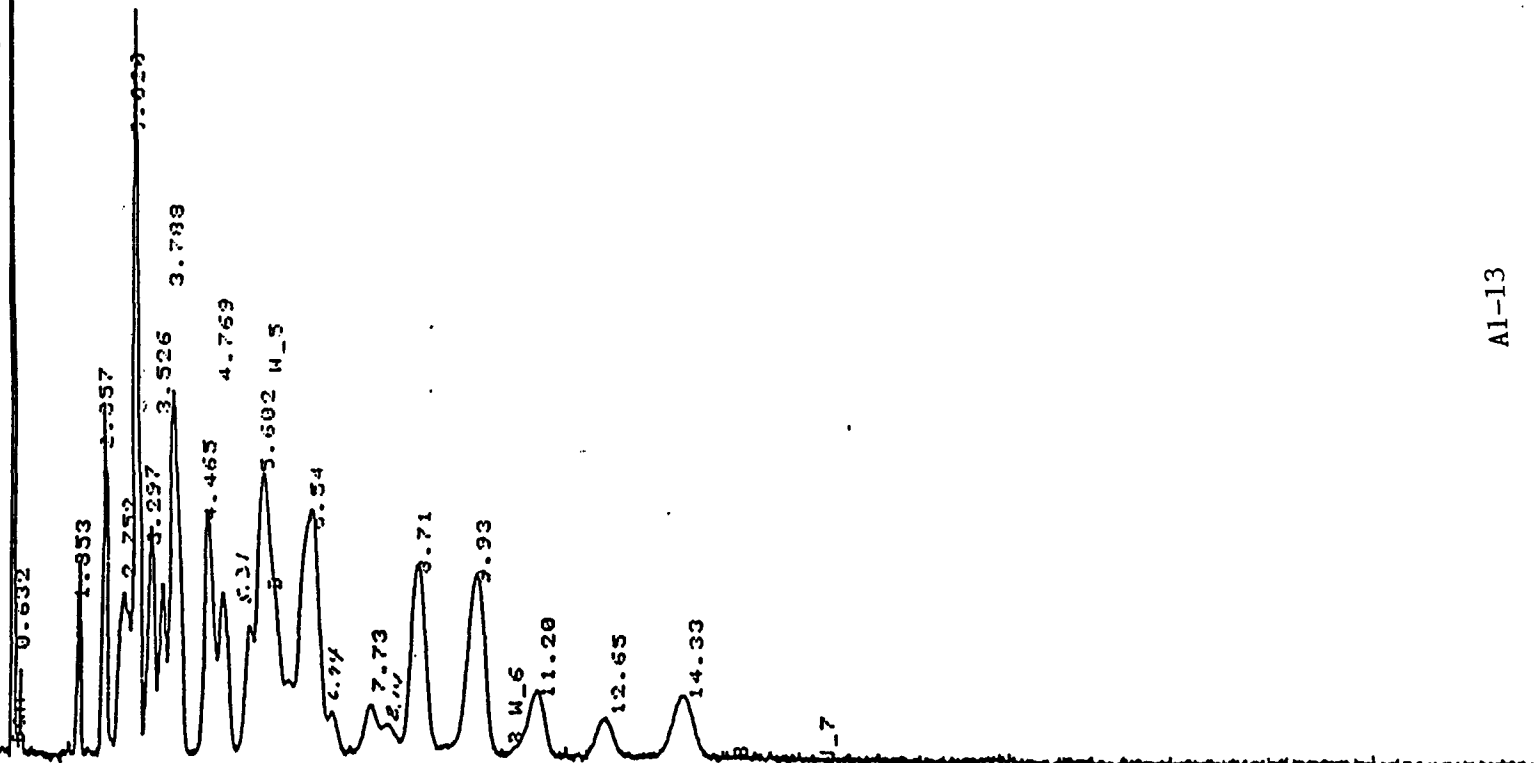


NBH-111-02



PUL 11 STARTED 00:32.3 88/03/23 PUL BME PROJ 3UL  
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.. 0.5 BME40805 EC4328 1100.000 Hz (F) NBN-112-50

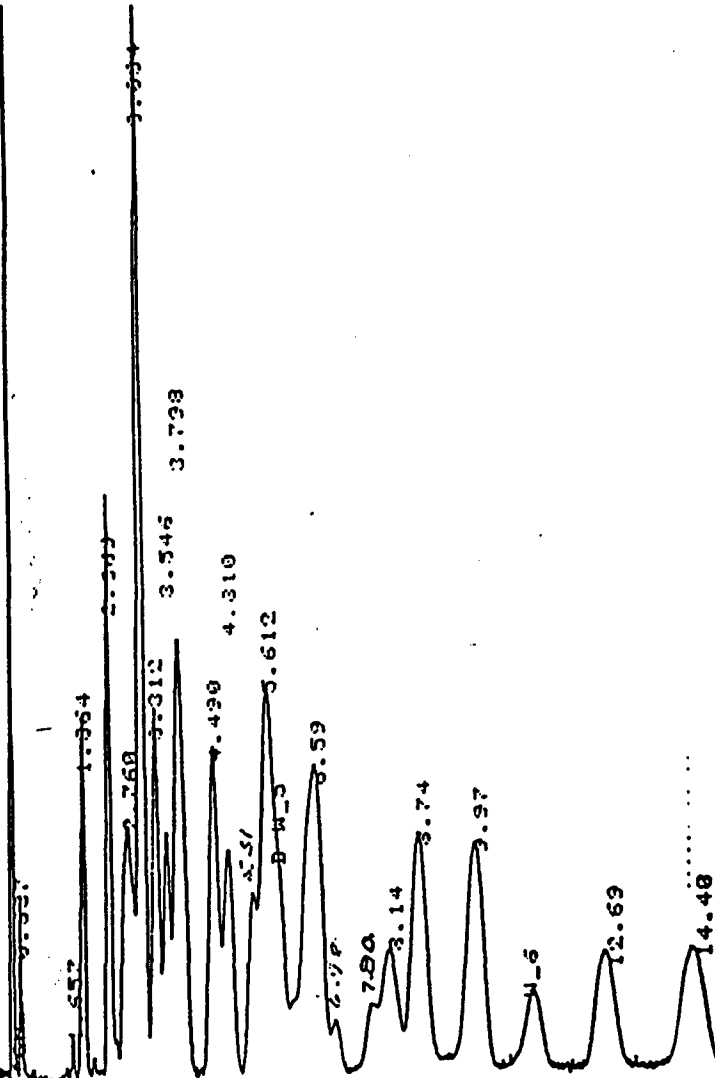


NBH-112-01

HEIGHT REJECT CIRCULAR TOTAL HEIGHT

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D 22 03740-D NP LAST EDITED 17:15.3 88/03/24

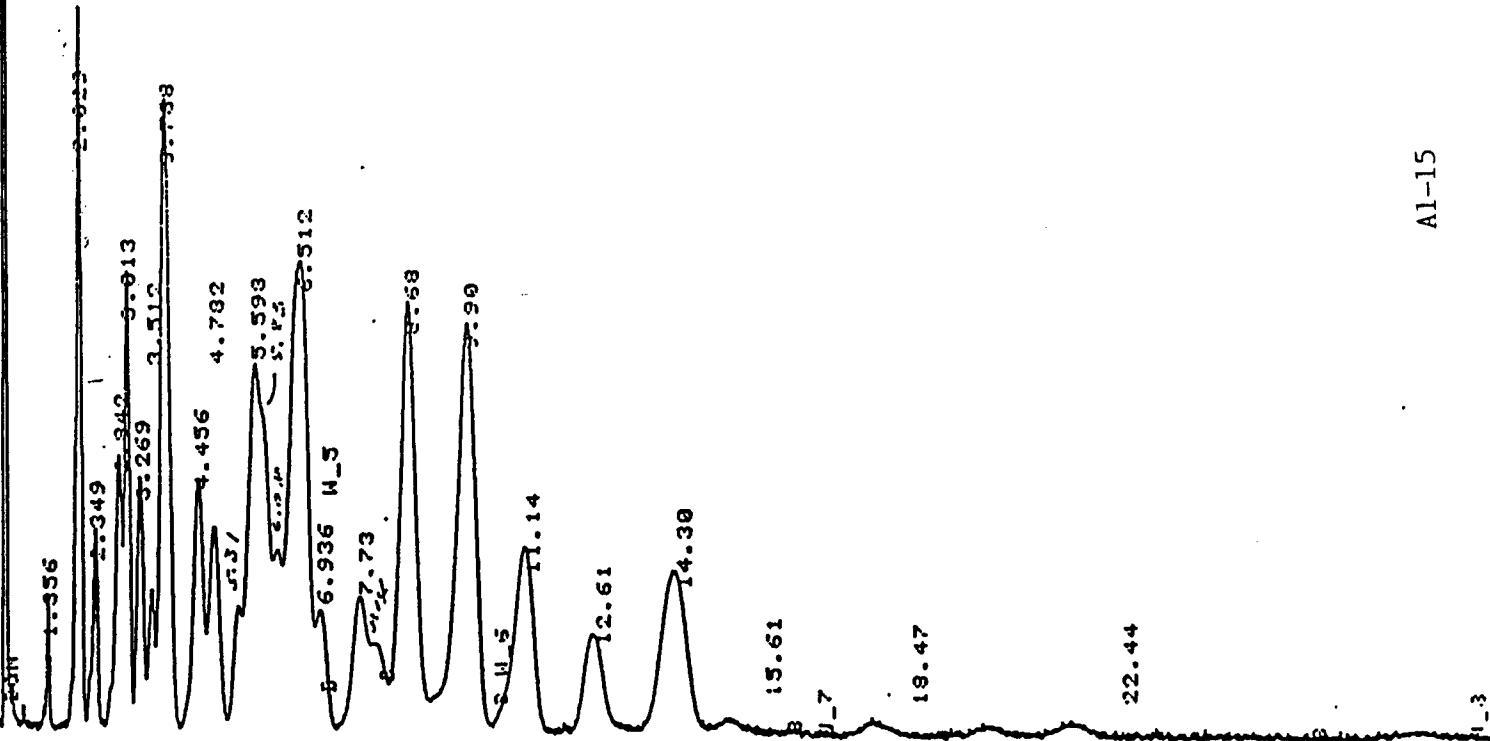
0.0 0.5 NBH-112-50-02 EE 4329 H 7 (F) 250,000



NBH-112-02

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U3740-D MP LAST EDITED 17:15.3 88/03/24

EE 4330 11000 Hz (F) BME 40805 NBH-113-1



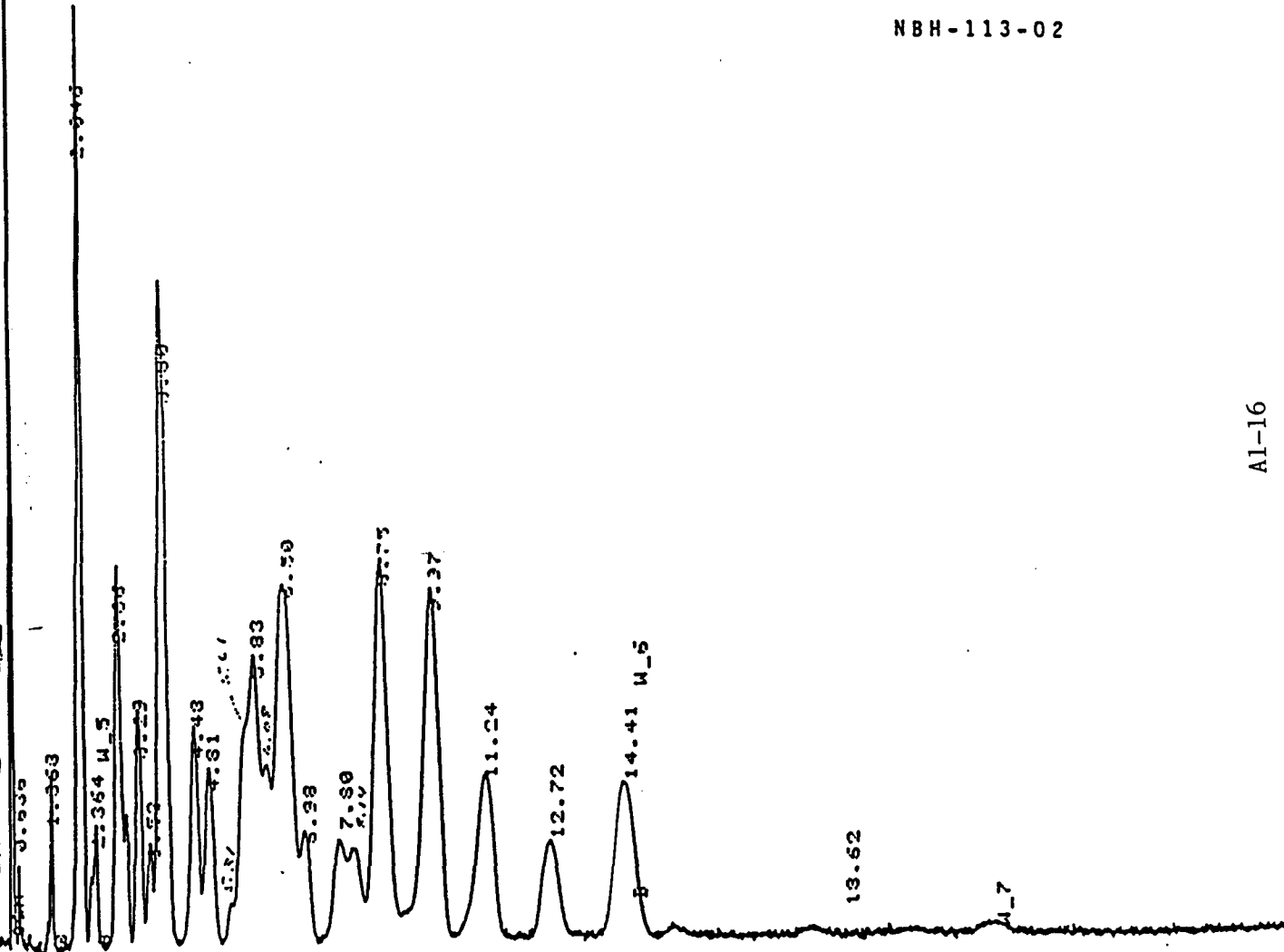
NBH-113-01

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●  
●  
●  
●  
●  
●

03746-D	MF	LMSI ENTRY	191138	00000-1
--10 0-3	NAM-11 3-SB-22	EE 4331	AT	Hq(F)

...:00-5 NBH-113-50-02

EE 4331

$$AT \quad H_9(F)$$


NBH-113-02

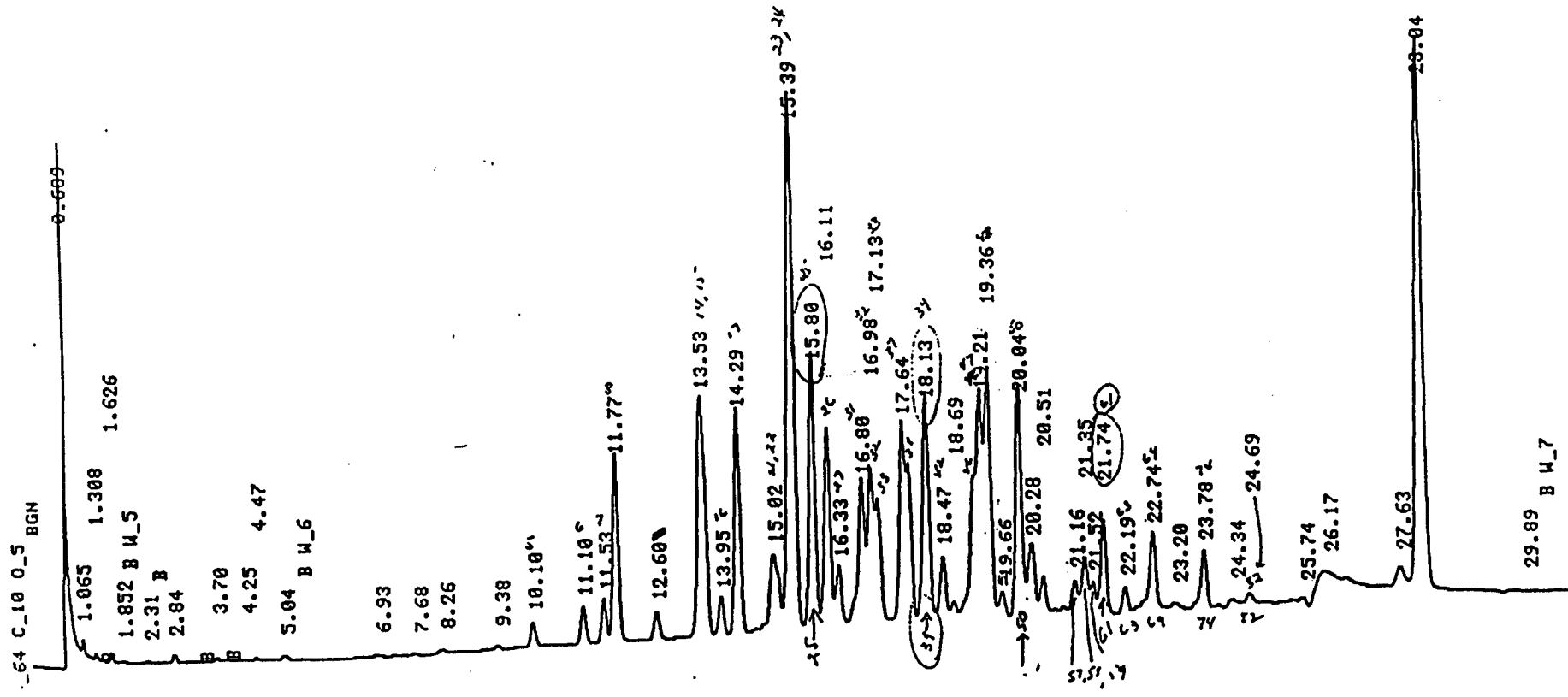
**APPENDIX A-2**

**CAPILLARY COLUMN CHROMATOGRAMS**

2) 2K1  
Anchor  
12V2  
54.

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METHOD 12 CAPILLARY PCB LAST EDITED 04:34.5 80/01/01

AROCLOR 1242



12/5/88

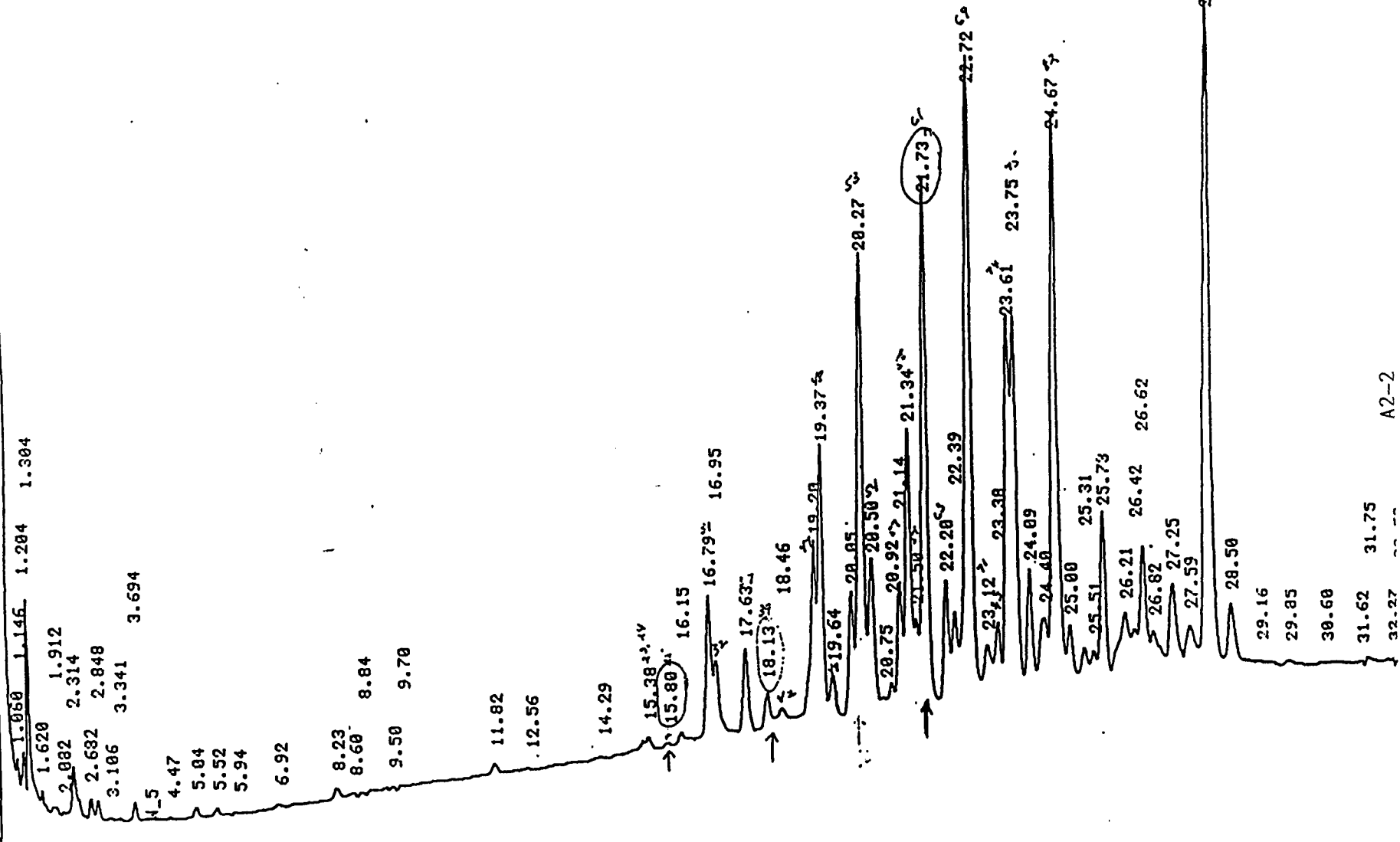
Handwritten  
12/5

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64 C\_10 0\_5 BGN

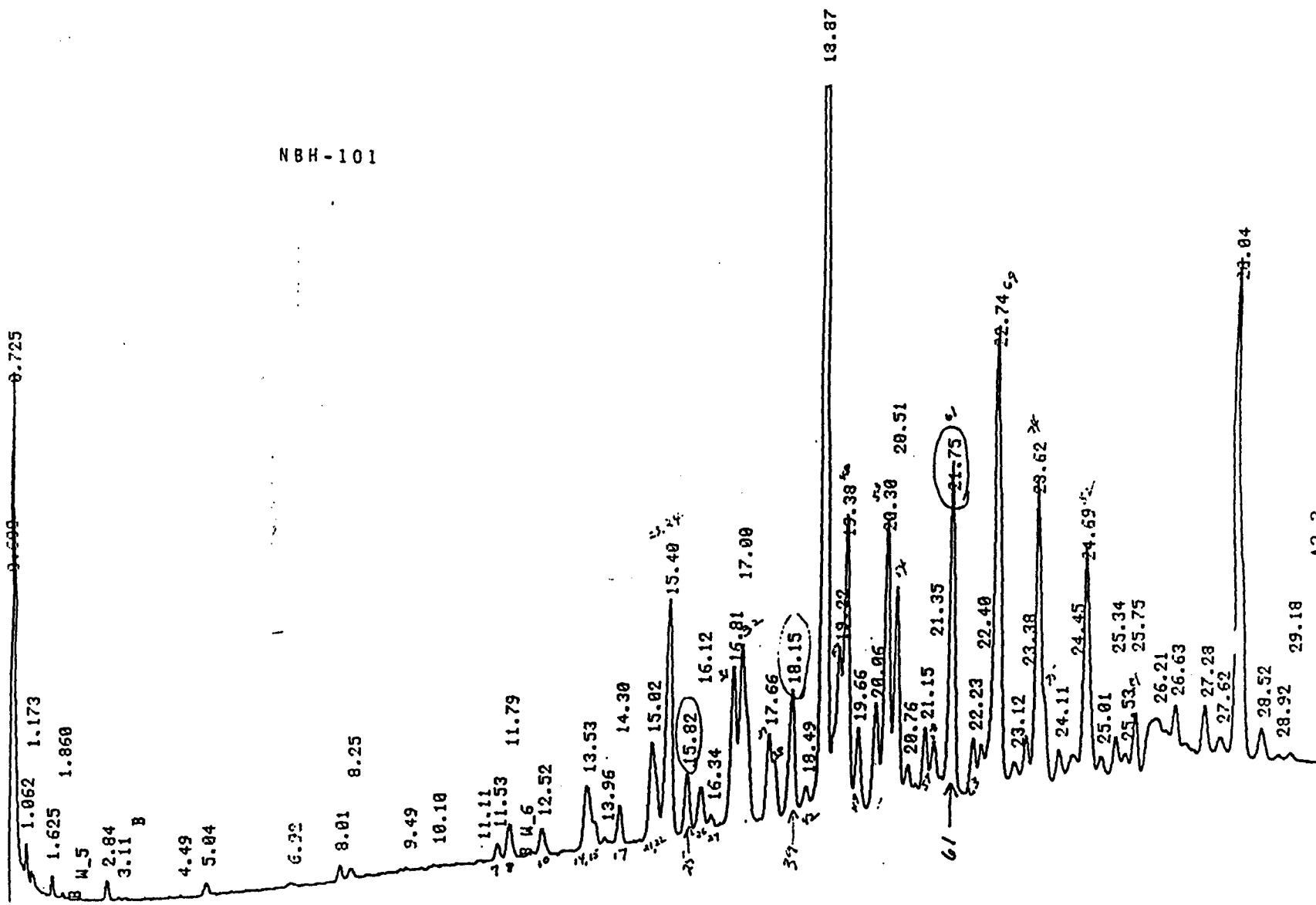
0.686

AROCLOR 1254



RUN 26 STARTED 04:31.3 80/01/02 CAPILLARY PCB  
112 CAPILLARY PCB LAST EDITED 04:34.5 80/01/01

1.10 0.5 BQN



NBH-101

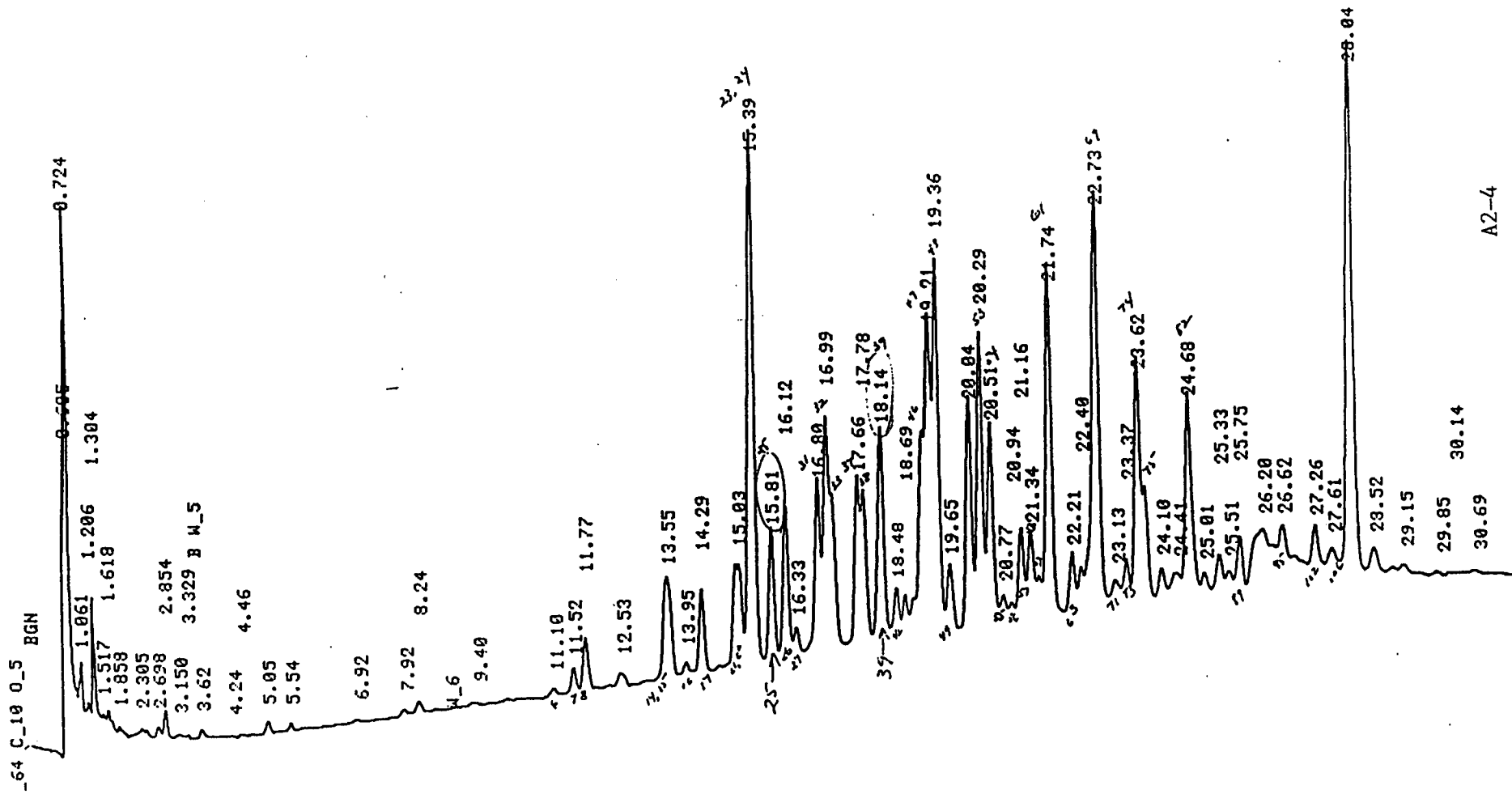


NBH-102

4 10 80-1  
8 C1433

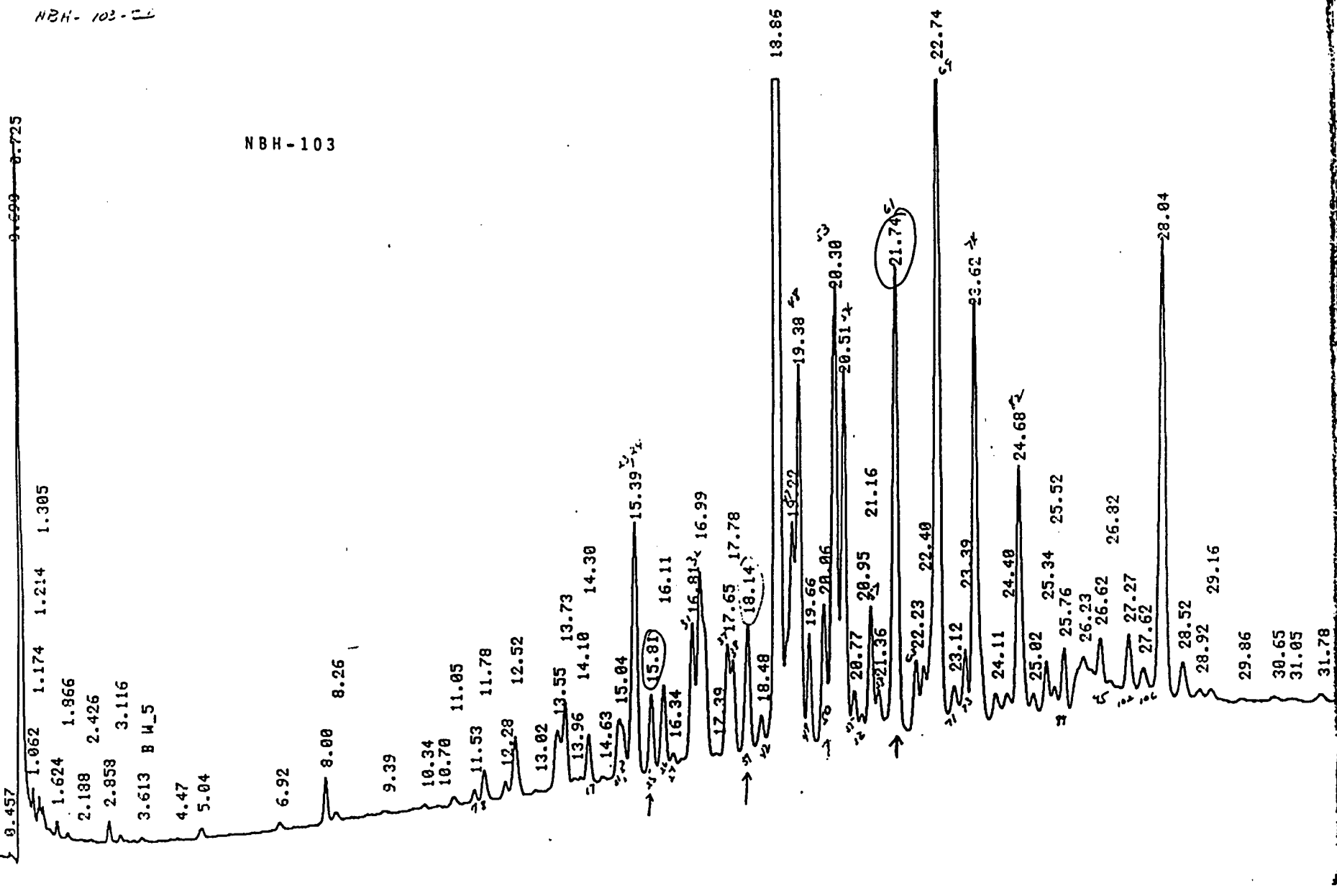
118H-102-5D

E 27 RUN 27 STARTED 05:28.9 80/01/02 CAPILLARY PCB  
ETHOD 12 CAPILLARY PCB LAST EDITED 04:34.5 80/01/01



3 29 RUN 29 STARTED 07:24.1 80/01/82 CAPILLARY PCB  
ETHOD 12 CAPILLARY PCB LAST EDITED 04:34.5 80/01/81

64 C-10 0\_5 BGN



NBH-103

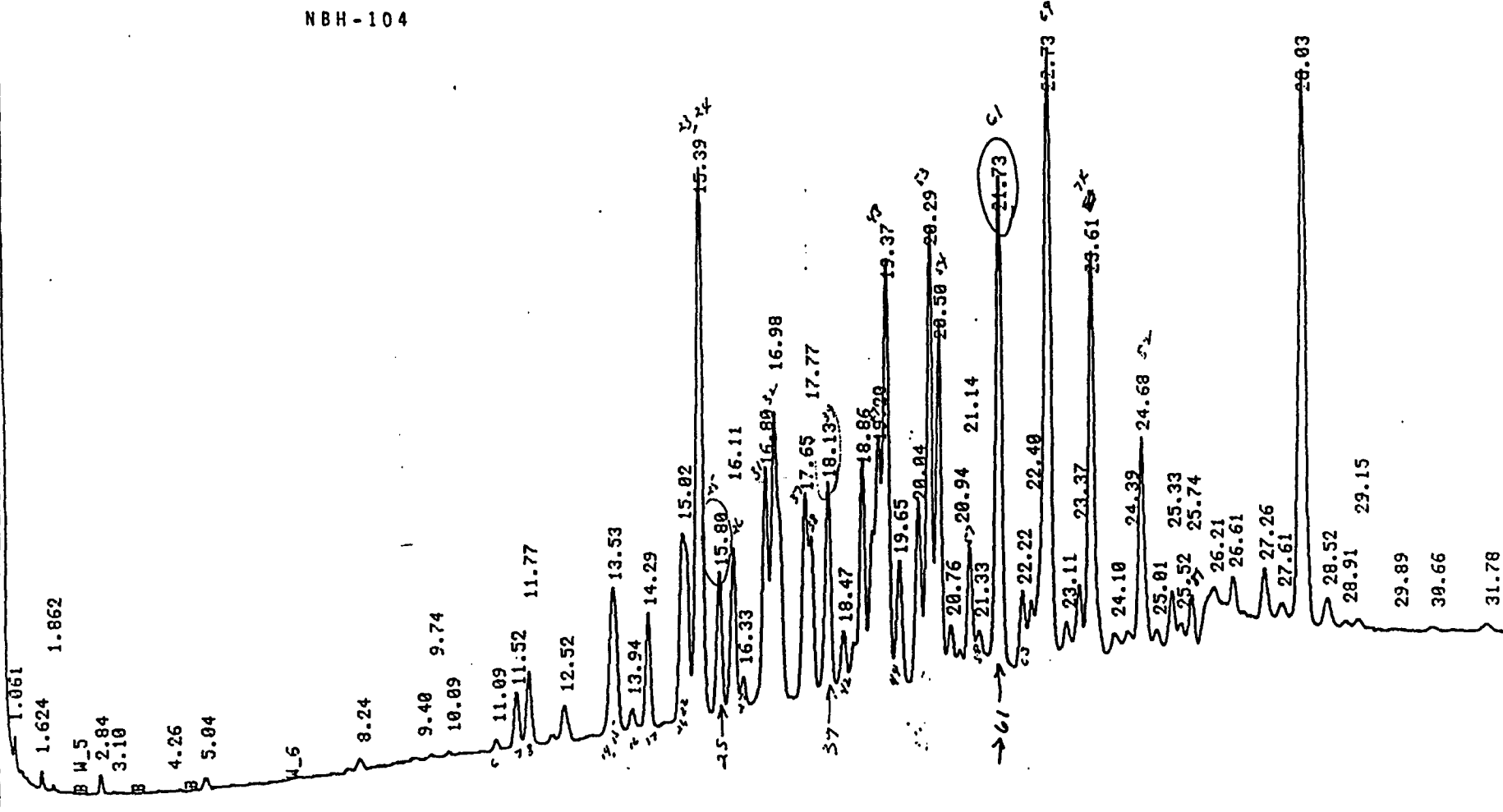
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00 12 CAPILLARY PCB LAST EDITED 04:34.5 80/01/01

C\_10 0.5 BGN

178H-104 SD

0.686

NBH-104



3H-105-52

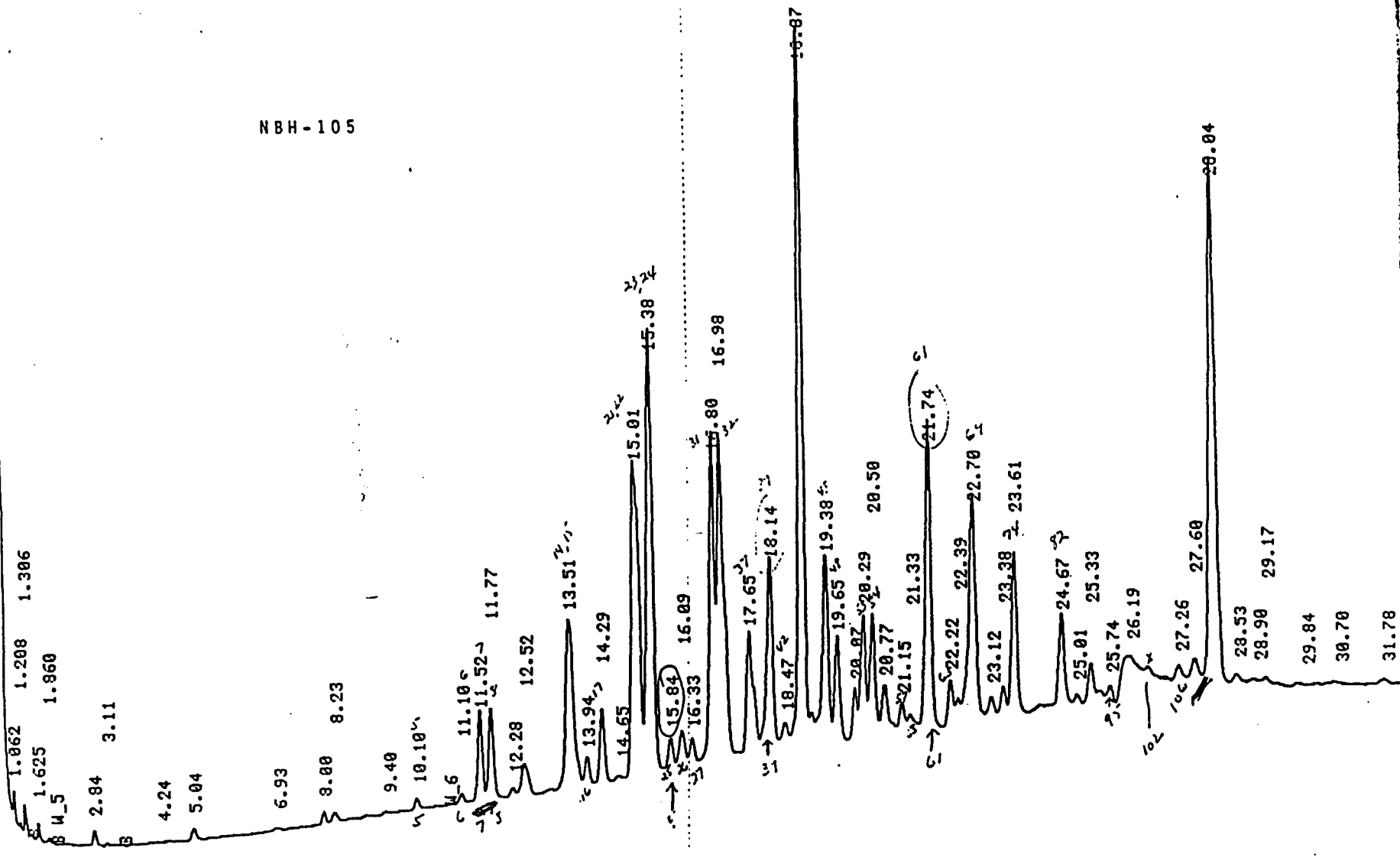
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1001/1000

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C\_10 0.5 BGN

0.588

NBH-105



DS-901-H21

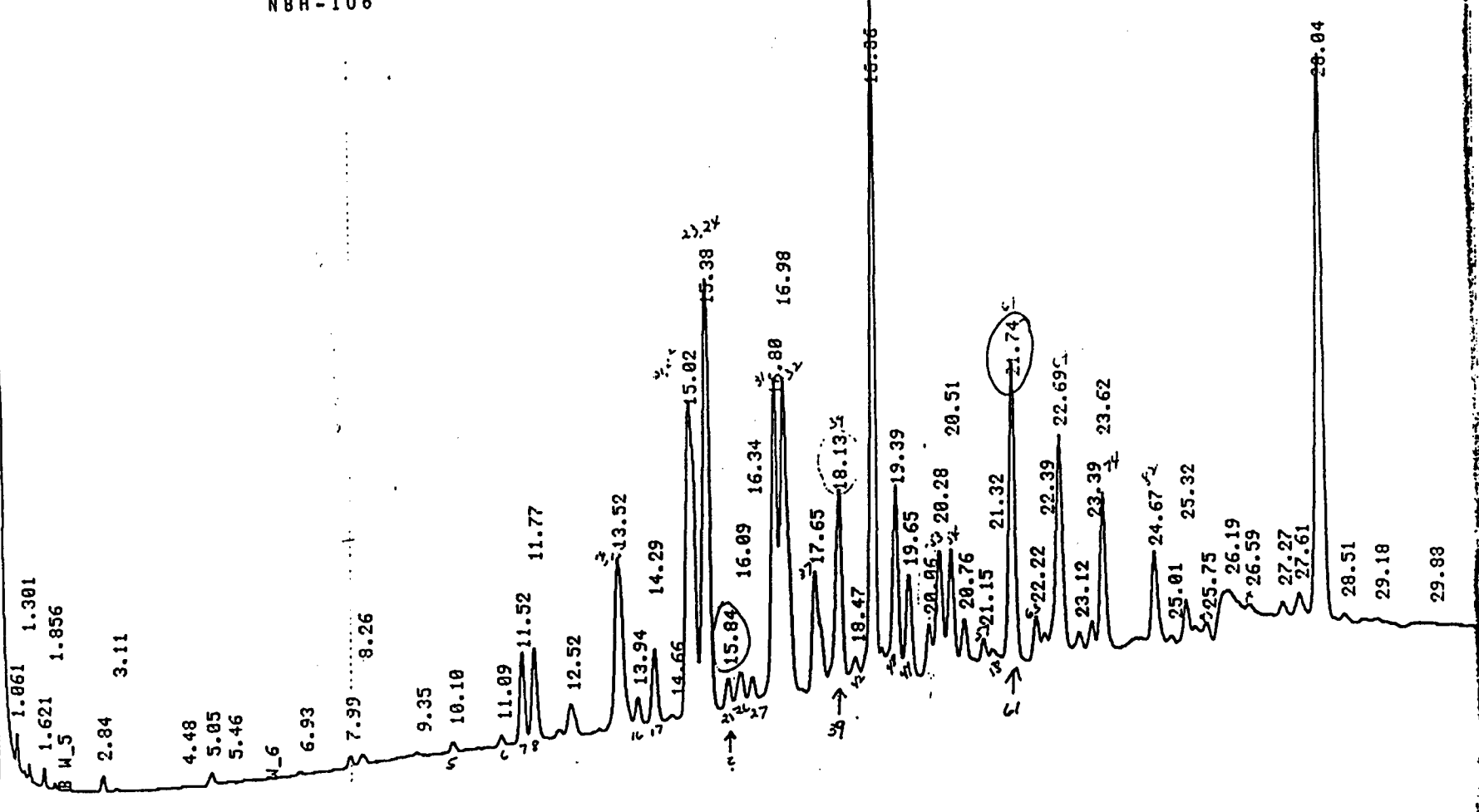
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THOD 12 CAPILLARY PCB LAST EDITED 04:34.5 80/01/01

54 C\_10 0.5 BGN

0.685

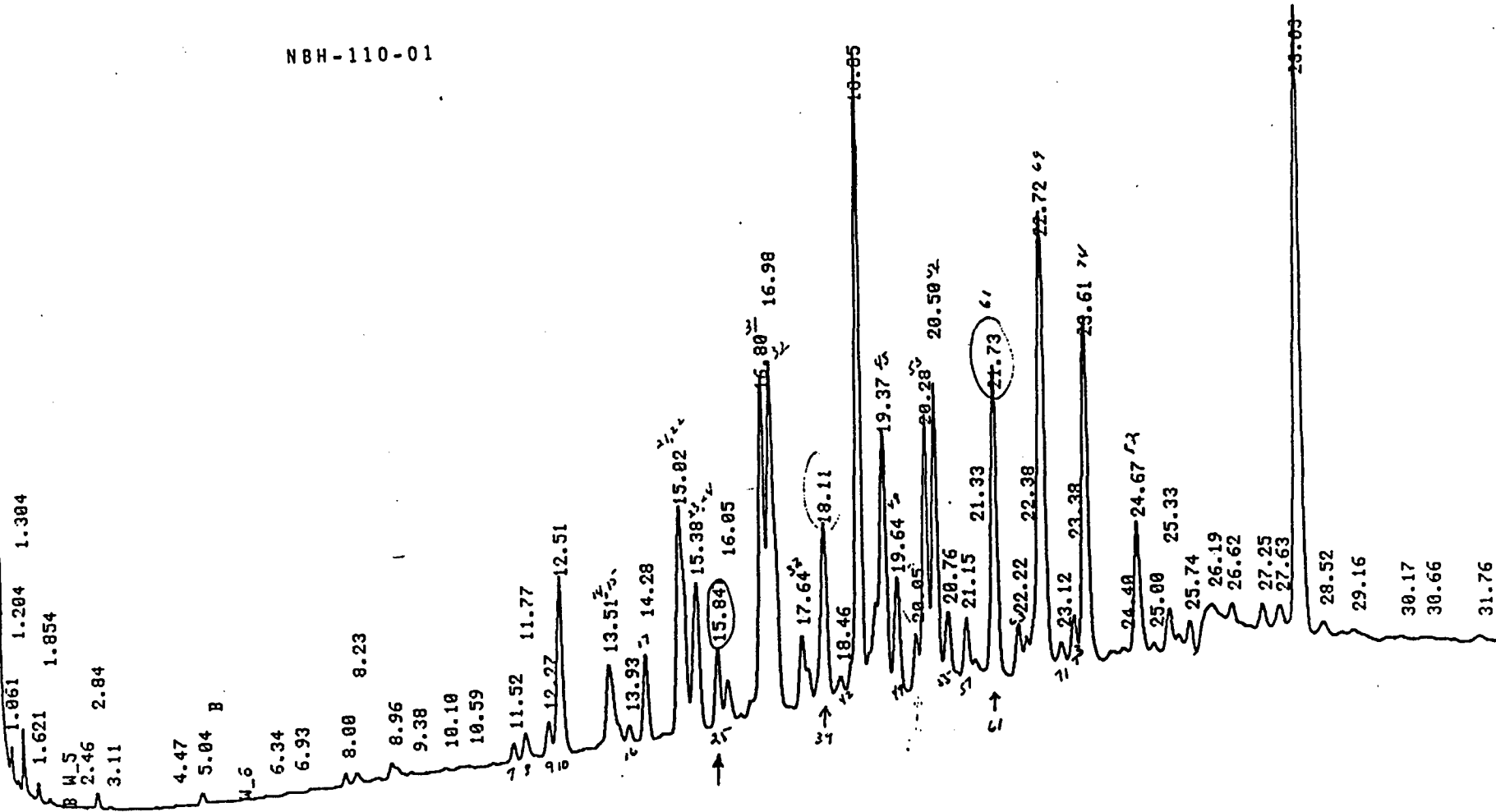
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64 C\_10 0.5 BGN

0.696 0.720



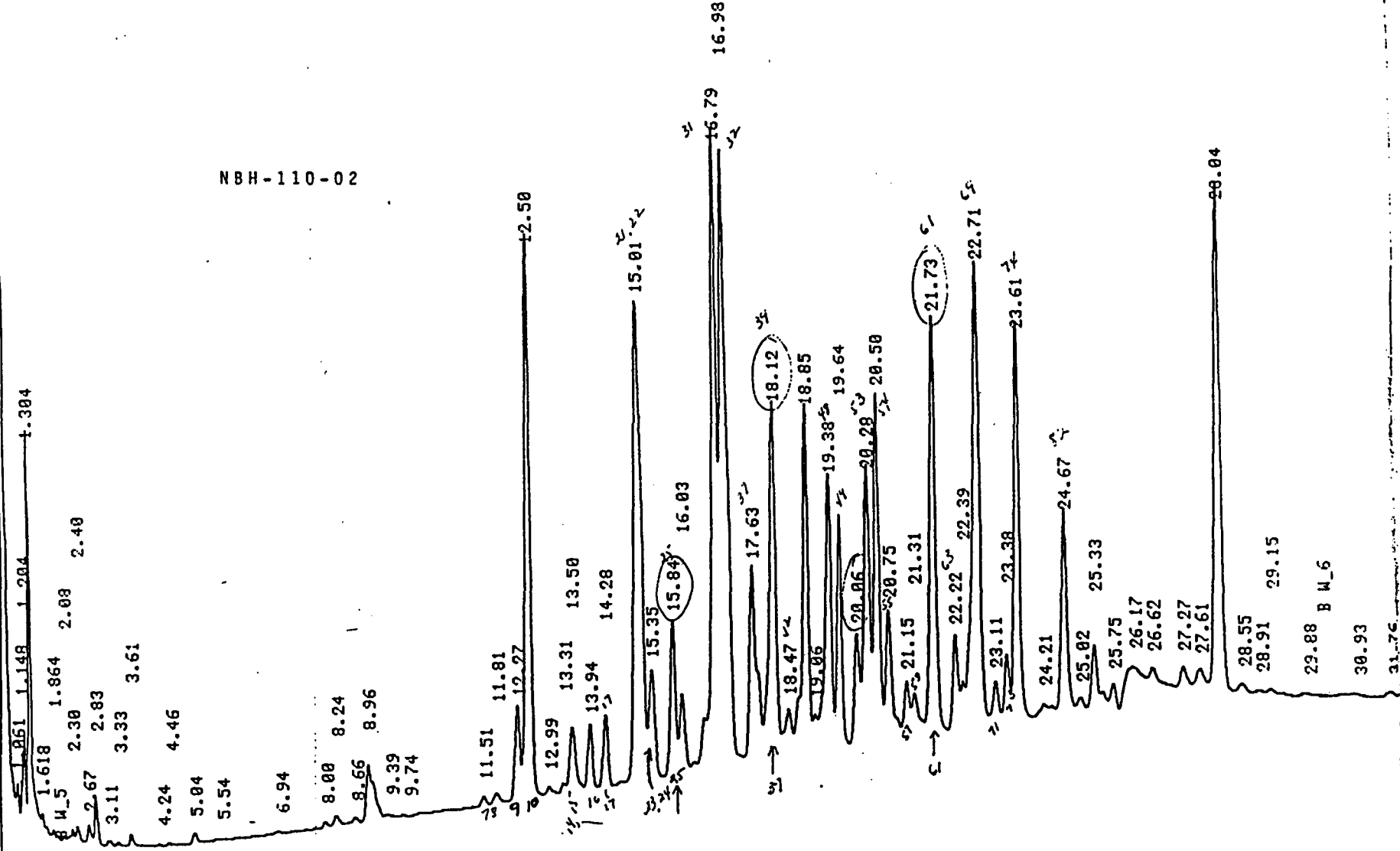
NBH-110-01

36 RUN 36 STARTED 14:07.3 80/01/02 CAPILLARY PCB  
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64 C\_10 0.5 BGN

0.689

NBH-110-02



10-05-111-50-01

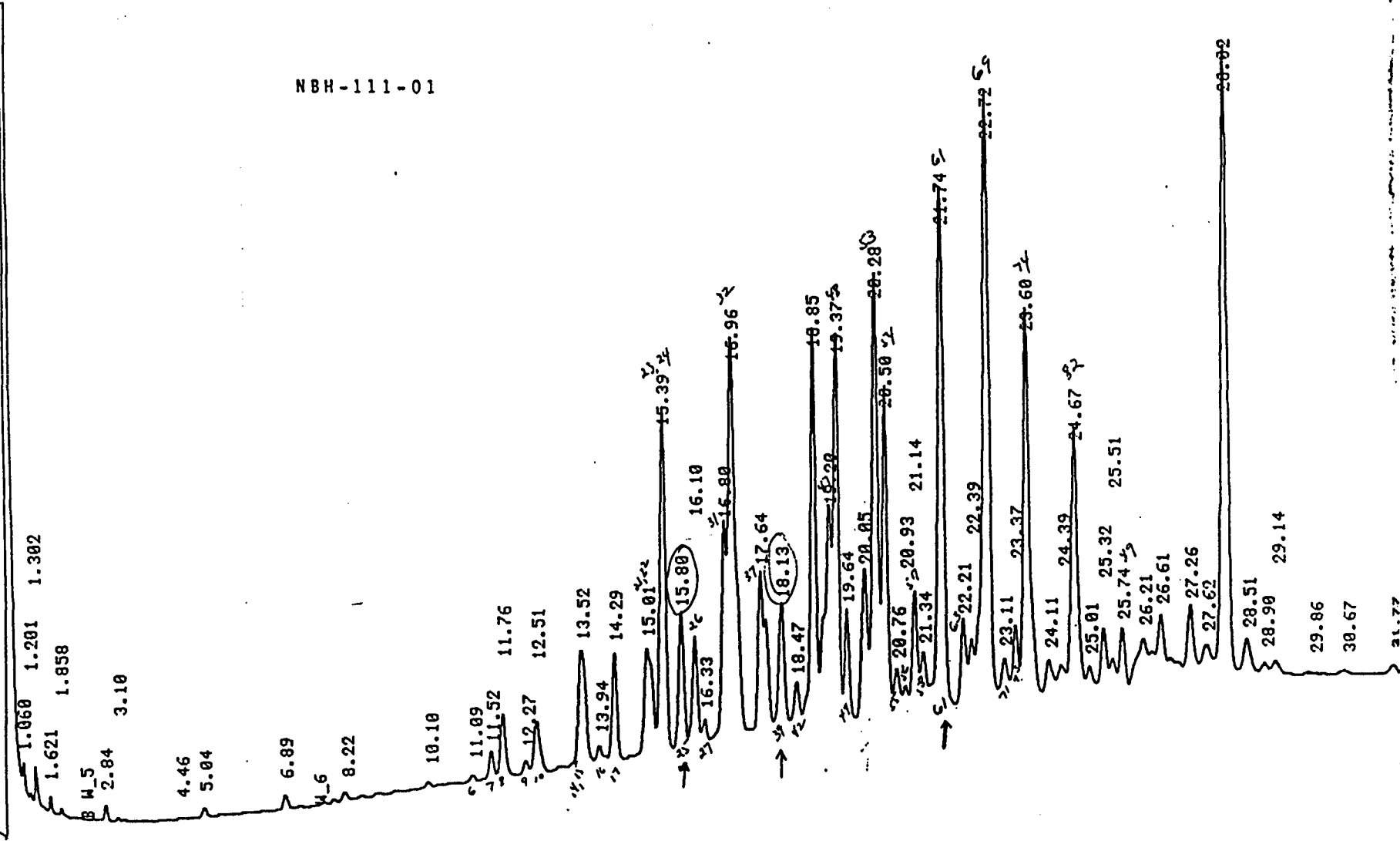
724376

E 62 RUN 62 STARTED 15:03.8 80/01/03 CAPILLARY PCB  
ETHOD 12 CAPILLARY PCB LAST EDITED 04:34.5 80/01/01

\_64 C\_10 0\_5 BGN

0.638

NBH-111-01





N2H-111-50-01

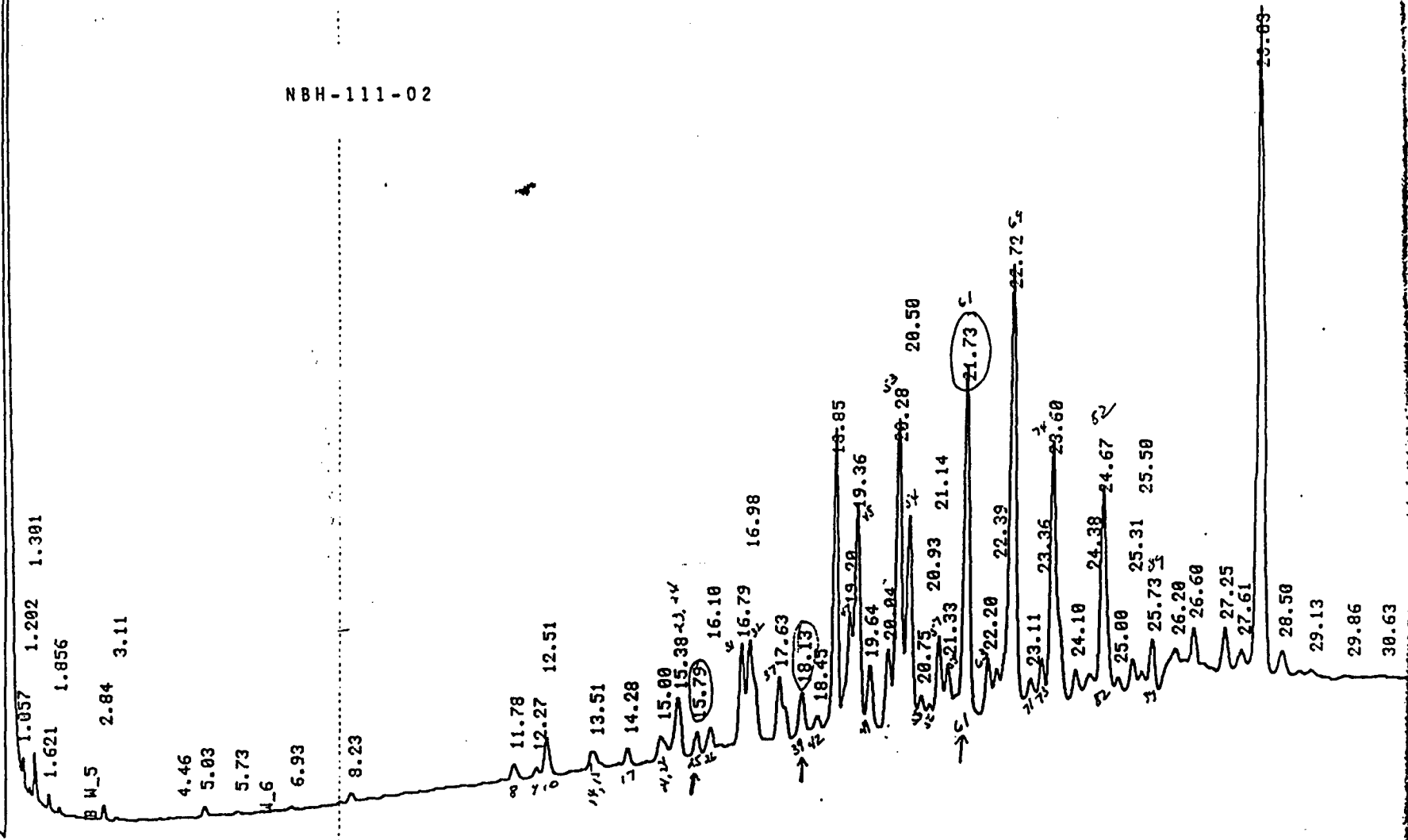
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1/1/80

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METHOD 12 CAPILLARY PCB LAST EDITED 04:34.5 80/01/01

A\_64 C\_10 0.5 BGN

0.6

NBH-111-02

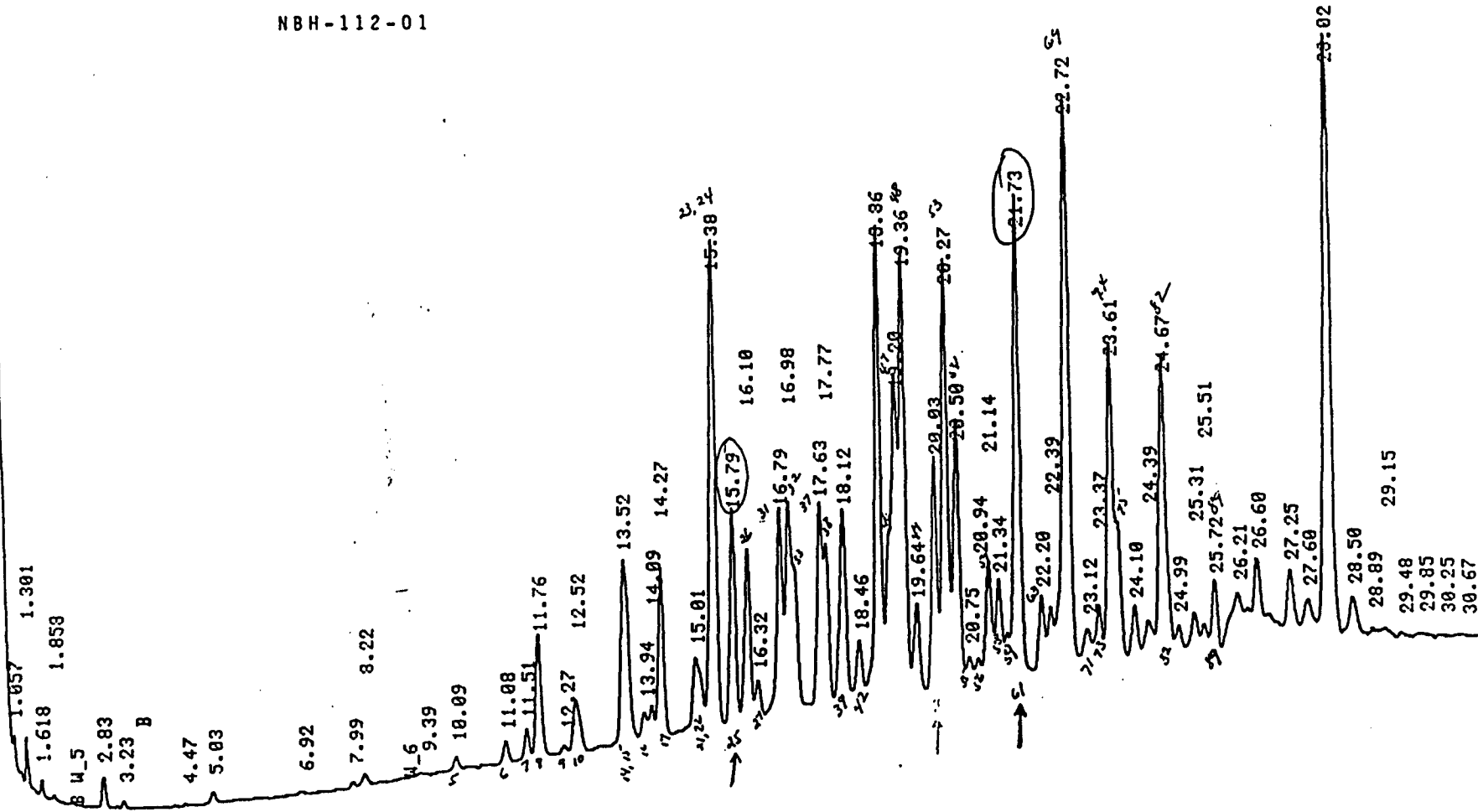


LE 41 RUN 41 STARTED 16:55.3 80/01/02 CAPILLARY PCB  
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3.64 C\_10 0.5 BGN

0.634

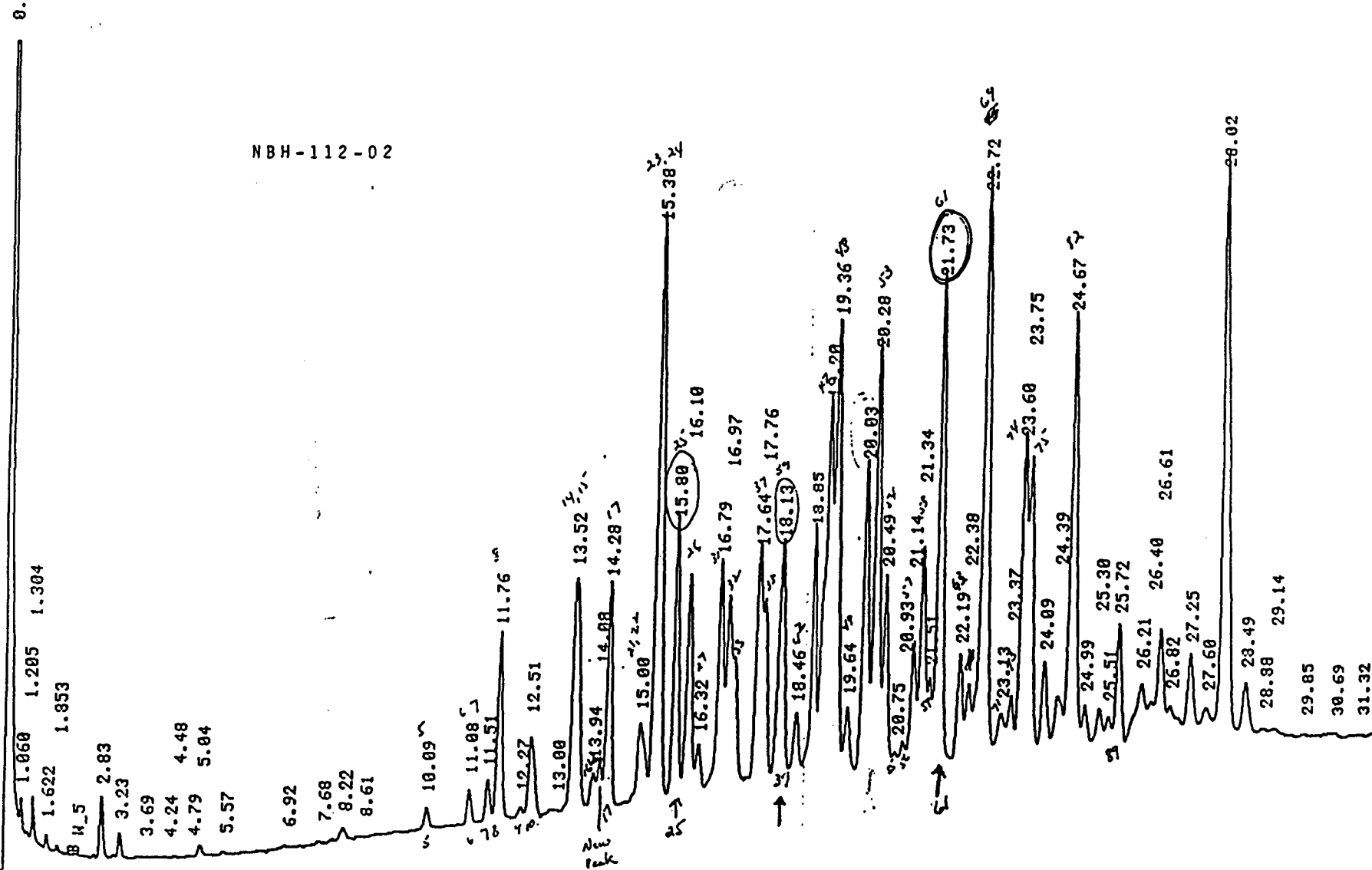
NBH-112-01



125132  
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NBH-112-50-02

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NBH-112-02



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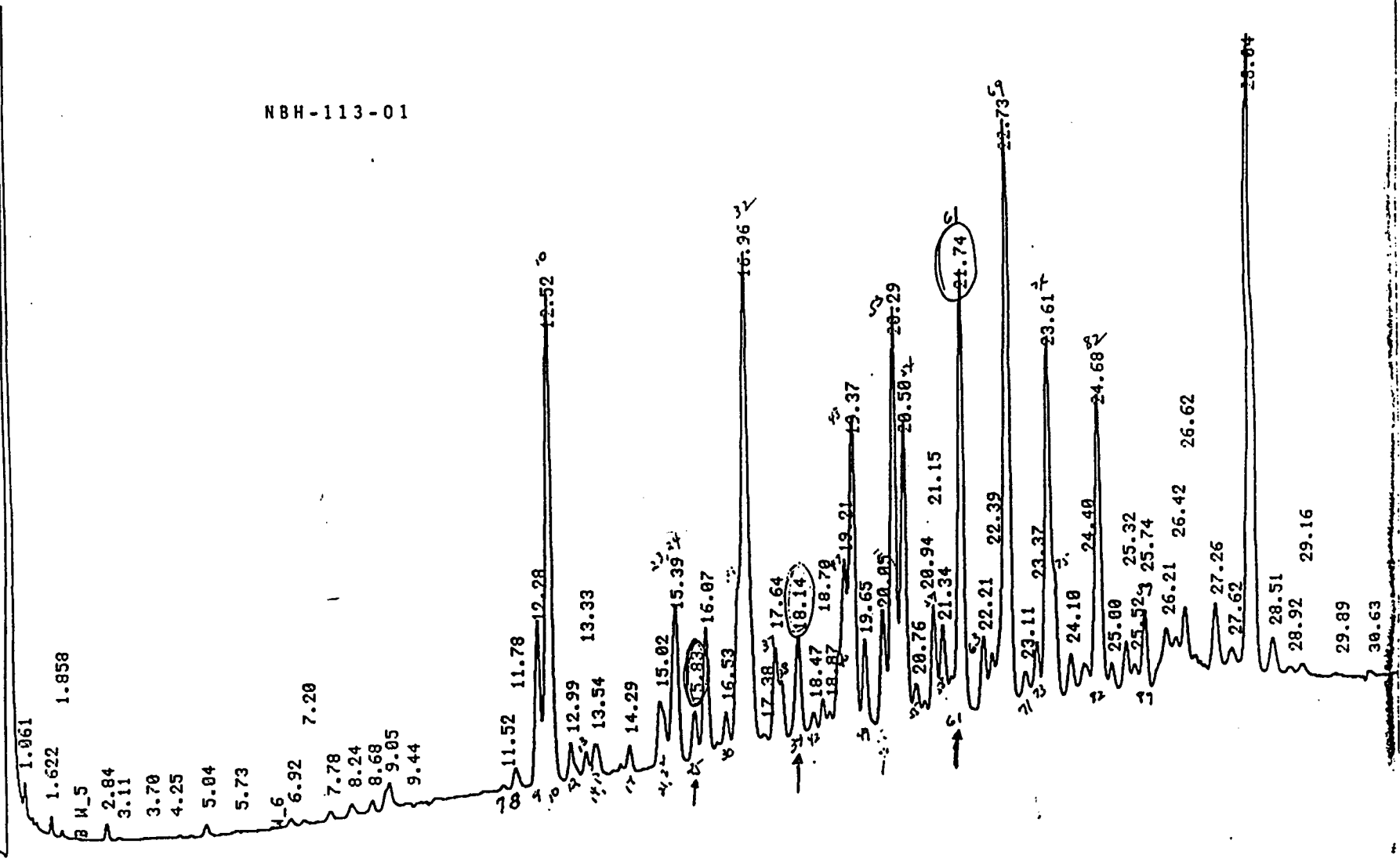
9/21/83

0 RUN 50 STARTED 03:33.8 80/01/03 CAPILLARY PCB  
00 12 CAPILLARY PCB LAST EDITED 04:34.5 80/01/01

C\_10 0.5 BGN

0.686

NBH-113-01



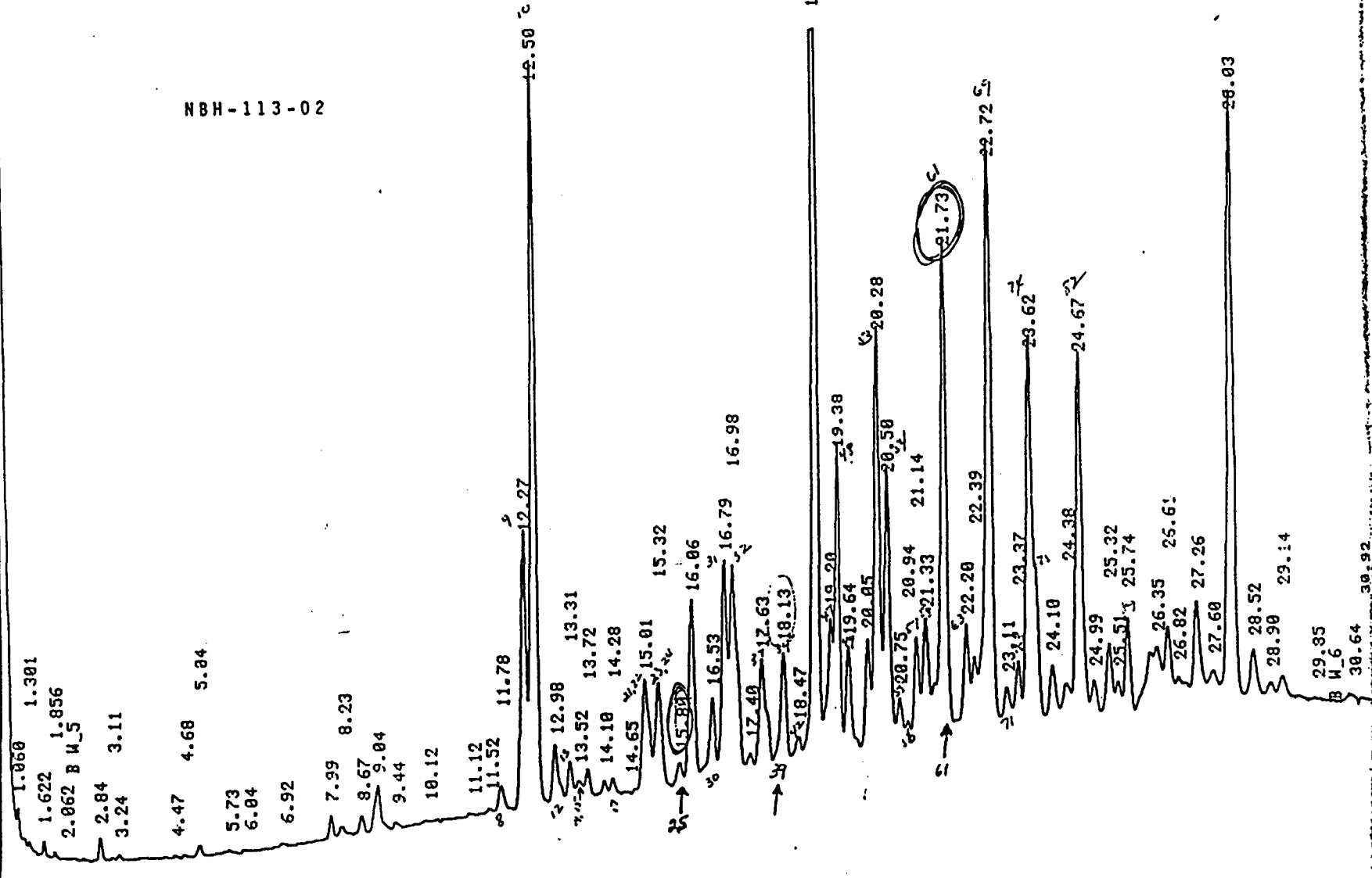
65433

113-53-62

FILE 52 RUN 52 STARTED 05:27.7 80/01/03 CAPILLARY PCB  
% METHOD 12 CAPILLARY PCB LAST EDITED 04:34.5 80/01/01

+ A\_64 C\_10 0.5 BGN

9.0



**APPENDIX B**  
**ITAS CERTIFICATES OF ANALYSIS**



INTERNATIONAL  
TECHNOLOGY  
CORPORATION

## ANALYTICAL SERVICES

5815 Middlebrook Pike • Knoxville, Tennessee 37921 • 615-588-6401



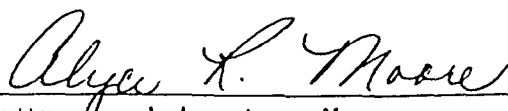
### CERTIFICATE OF ANALYSIS

TO: Balsam Environmental Consultants  
ATTN: Len Sarapas  
59 Stiles Road  
Salem, NH 03079

DATE REPORTED: April 29, 1988  
PROJECT CODE: BME 40786  
ORDER NUMBER:  
PAGE 1 OF 2

Sample Description: Four (4) sediment samples received February 25, 1988

	<u>pH</u> <u>(standard units)</u>	<u>Oil &amp;</u> <u>Grease</u> <u>(mg/kg)</u>	<u>Moisture</u> <u>(% by weight)</u>	<u>Moisture After</u> <u>Air Drying</u> <u>(% by weight)</u>
1-SD, 2/24/88	7.80	760	17.8	0.55
NBH-102-SD, 2/24/88	7.79	11,000	67.8	3.00
NBH-103-SD, 2/24/88	6.68	1,100	51.4	0.50
NBH-104-SD, 2/24/88	7.19	1,600	57.0	1.04

  
Approved by Laboratory Manager

Title



Accredited by the American Association for Laboratory Accreditation in the chemical  
field of testing as listed in the current AALA Directory of Accredited Laboratories

93-9 A

**CERTIFICATE OF ANALYSIS**

TO: Balsam Environmental Consultants  
ATTN: Len Sarapas  
59 Stiles Road  
Salem, NH 03079

DATE REPORTED: July 25, 1989  
PROJECT CODE: BME 40786-Corrected Certificate  
ORDER NUMBER:  
PAGE 2 OF 2

Sample Description: Four (4) sediment samples received February 25, 1988

Concentration units are  $\mu\text{g}/\text{gram}$  (ppm)

	Aroclor 1016, 1232 1242† and/or 1248	Aroclor 1254	Total Aroclors
NBH-101-SD, 2/24/88	4.0 *	5.6 *	9.6
NBH-102-SD, 2/24/88	520 *	300 *	820
NBH-103-SD 2/24/88	19 *	28 *	47
NBH-104-SD 2/24/88	200 *	160 *	360

†Sample Aroclor pattern identified and/or calculated as Aroclor 1242.

\*Sample exhibits alteration of standard Aroclor pattern.

*Alyce R. Moore*  
Approved by \_\_\_\_\_  
Laboratory Manager

Title \_\_\_\_\_





INTERNATIONAL  
TECHNOLOGY  
CORPORATION

## ANALYTICAL SERVICES

5815 Middlebrook Pike • Knoxville, Tennessee 37921 • 615-588-6401



### CERTIFICATE OF ANALYSIS

TO: Balsam Environmental Consultants  
ATTN: Len Sarapas  
59 Stiles Road  
Salem, NH 03079

DATE REPORTED: April 29, 1988  
PROJECT CODE: BME 40805  
ORDER NUMBER:  
PAGE 1 OF 2

Sample Description: Ten (10) sediment samples received March 1, 1988

	<u>pH</u> (standard units)	<u>Oil &amp; Grease</u> (mg/kg)	<u>Moisture</u> (% by weight)	<u>Moisture After Air Drying</u> (% by weight)
NBH-105-SD, 2/25/88	7.39	3,000	57.7	1.24
NBH-106-SD, 2/25/88	7.46	4,500	57.0	1.65
NBH-110-SD-01, 2/25/88	7.19	15,000	53.9	2.82
NBH-110-SD-02, 2/25/88	6.70	17,000	71.4	3.70
NBH-111-SD-01, 2/25/88	6.62	15,000	64.7	3.22
NBH-111-SD-02, 2/25/88	6.44	19,000	74.0	3.52
NBH-112-SD-01, 2/25/88	6.63	22,000	59.5	3.98
NBH-112-SD-02, 2/25/88	6.65	41,000	65.7	5.49
NBH-113-SD-01, 2/25/88	6.97	8,900	70.9	2.71
NBH-113-SD-02, 2/25/88	7.03	11,000	72.9	2.74

*Alyce R. Moore*  
Approved by Laboratory Manager

Title



Accredited by the American Association for Laboratory Accreditation in the chemical  
field of testing as listed in the current AALA Directory of Accredited Laboratories

93-9-85

**CERTIFICATE OF ANALYSIS**

TO: Balsam Environmental Consultants  
ATTN: Len Sarapas  
59 Stiles Road  
Salem, NH 03079

DATE REPORTED: July 25, 1989  
PROJECT CODE: BME 40805-Corrected Certificate  
ORDER NUMBER:  
PAGE 2 OF 2

Sample Description: Ten (10) sediment samples received March 1, 1988


Concentration units are  $\mu\text{g}/\text{gram}$  (ppm)

	Aroclor 1016, 1232 1242† and/or 1248	Aroclor 1254	Total Aroclors
NBH-105-SD, 2/25/88	760 *	360 *	1,100
NBH-106-SD, 2/25/88	660 *	300 *	960
NBH-110-SD-01, 2/25/88	3,200 *	4,400 *	7,600
NBH-110-SD-02, 2/25/88	<5,000 **	11,000 *	11,000
NBH-111-SD-01, 2/25/88	13,000 *	15,000 *	28,000
NBH-111-SD-02, 2/25/88	6,800 *	32,000 *	39,000
NBH-112-SD-01, 2/25/88	19,000	11,000 *	30,000
NBH-112-SD-02, 2/25/88	80,000 *	48,000	130,000
NBH-113-SD-01, 2/25/88	160 *	340 *	500
NBH-113-SD-02, 2/25/88	<48 **	180 *	180

†Sample Aroclor pattern identified and/or calculated as Aroclor 1242.

\*Sample exhibits alteration of standard Aroclor pattern.

\*\*Higher detection limit due to interference.

  
Approved by \_\_\_\_\_  
Laboratory Manager

Title \_\_\_\_\_



APPENDIX V

TASK 8

*Yoakum & Associates, Inc.*

ENVIRONMENTAL CONSULTANTS

TWIN COVE DRIVE  
ROUTE 4, BOX 418  
LENOIR CITY, TENNESSEE 37771  
TELEPHONE: (615) 986-8116

PEGGY L. STEWART  
ANNA M. YOAKUM, Ph.D.

**EVALUATION OF PCB ANALYTICAL DATA FOR SAMPLES ANALYZED  
LAUCKS TESTING LABORATORIES - EPA CASE #5131**

**Prepared for:**

**Nutter, McClennen & Fish  
One International Place  
Boston, Massachusetts 02110-2699**

**Prepared by:**

**YOAKUM & ASSOCIATES, INC.  
Lenoir City, Tennessee 37771**

**September 8, 1989**

**Y & A Project NMF-3003 Task 8**

**DRAFT**

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EVALUATION OF PCB ANALYTICAL DATA FOR SAMPLES  
ANALYZED BY LAUCKS TESTING LABORATORIES -  
EPA CASE #5131

Y & A PROJECT NMF-3003 TASK 8

1.0 TASK 8 BACKGROUND

Environmental Protection Agency (EPA) Case #5131 is composed of 35 samples from the U. S. Army Corps of Engineers (USACE) FIT Sampling Program. Twenty (20) of these samples were analyzed by Rocky Mountain Analytical Laboratories (RMAL) for HSL Organic Compounds. Laucks Testing Laboratories (LTL) analyzed 15 samples for HSL Organic Compounds (except for the volatile fraction). Since the raw data packages from RMAL were not available at the beginning of the EPA Case #5131 evaluation, Task 8 is limited to a review of the PCB data generated by LTL.

The samples analyzed by LTL were sediments collected from five (5) sampling sites in the upper estuary. Site locations are shown on Exhibit 8-1.

2.0 DATA REVIEW AND EVALUATION

2.1 Data Review

The material transmitted by Balsam Environmental Consultants, Inc. (BEC) to Yoakum & Associates, Inc. (YAI) for the Task 8 evaluation included the complete EPA contract laboratory program (CLP) data packages for 15

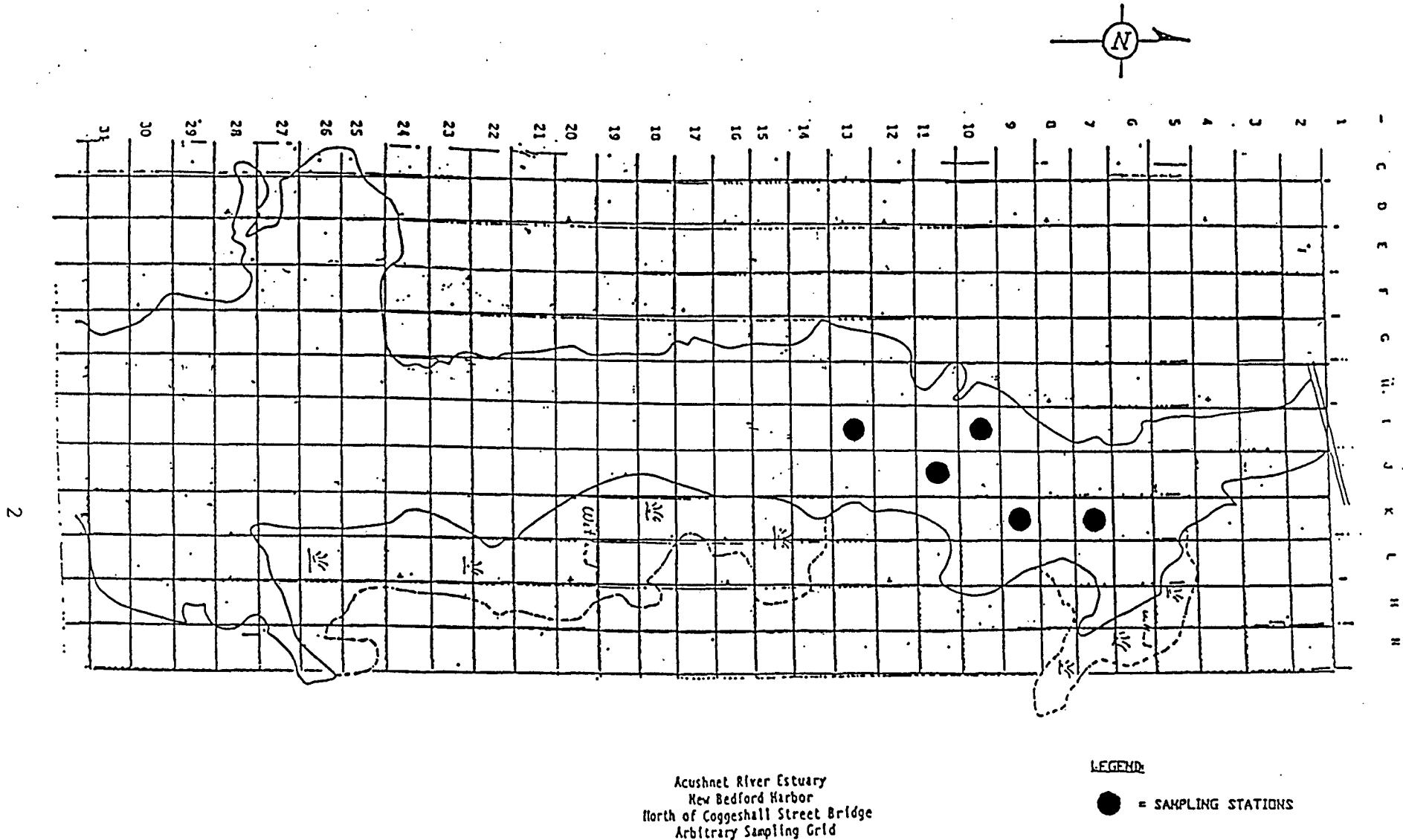


Exhibit 8-1. Location of Samples Analyzed by LTL - EPA Case #5131



samples analyzed by LTL and the data validation letters prepared by NUS Corporation (NUS) for EPA Case No. 5131.

Serious problems were found during the YAI review of the raw analytical data relating to the determination of PCBs in the sediment samples. Problem areas identified include the following:

1. Spurious peaks are present in the chromatograms of the Aroclor standards. This indicates contamination problems in the laboratory. Although the same contamination peaks appear in some of the samples, nothing was done to correct the situation.
2. There is evidence of inadequate sample extract cleanup which resulted in serious matrix effects.
3. The presence of contamination interferences has resulted in unacceptable chromatography for a number of samples.
4. The quality and resolution of the chromatograms are extremely poor; there is a total lack of definition and detail for those generated by packed column and capillary column analysis. In addition, numerous peaks are "off-scale."
5. The Aroclor 1242 quantitation mode is inappropriate for the samples.
6. The presence of Aroclor 1254 in the samples is clearly evident from the packed column chromatograms, the capillary column chromatograms, and the GC/MS confirmation data. However, it is reported as "Not Detected" in all the samples.
7. The quality of the overall work product is poor, and careless mistakes and transcription errors were found.

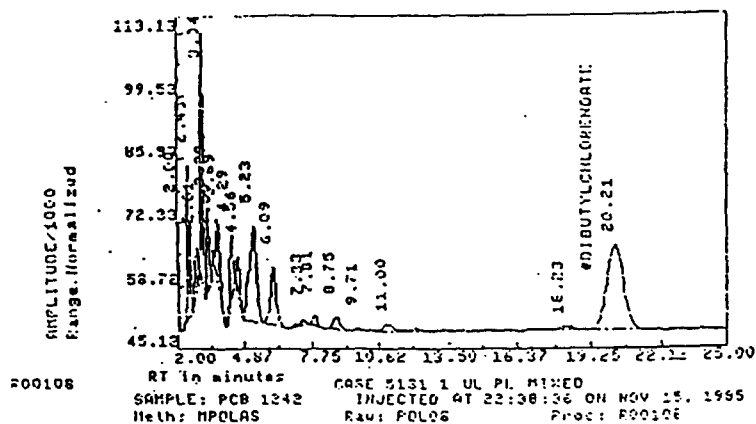
The impact of these data deficiencies on the analytical results is discussed in the next section of this report.

## 2.2 Data Evaluation

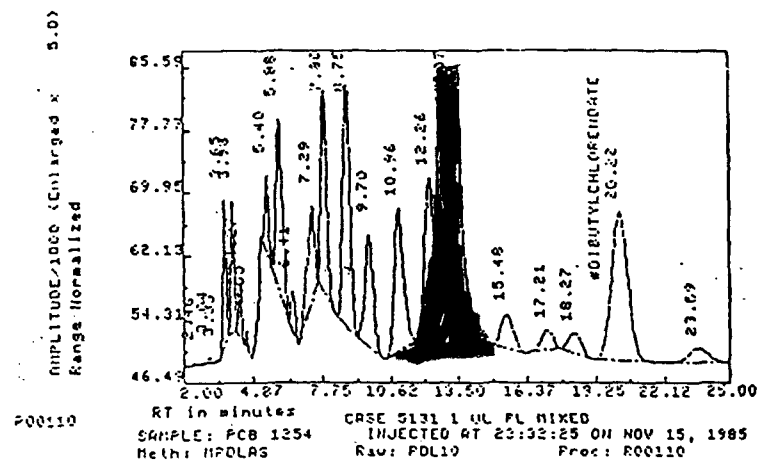
2.2.1 Analytical Methodology. The analytical methods prescribed by the EPA CLP Protocol for the determination of PCBs were not followed in sufficient detail by LTL to produce valid analytical data. As can be seen in the exhibit chromatograms, problems due to interferences from non-PCB contamination were evident in both the Aroclor standards (Exhibit 8-2) and the samples (Exhibit 8-3). In Exhibit 8-2, the Aroclor 1254 standard (b) run 11/15/85 has a huge interference at retention time (RT) 13.07 minutes, but the Aroclor 1242 standard (a) run on the same day shows no contamination. The situation is reversed for the standards run on 11/25/85. The Aroclor 1254 standard (d) is clean and the Aroclor 1242 (c) has an interference at RT 13.12 minutes. It is never accepted practice to proceed with the analysis of samples when there is evidence of laboratory contamination present in the chromatograms of standards.

Three different problems are demonstrated in Exhibit 8-3. Sample AD827 (a) shows severe interference between RTs 5.22 and 6.41 due to the presence of molecular sulfur in the sample. In addition to the characteristic alteration of the

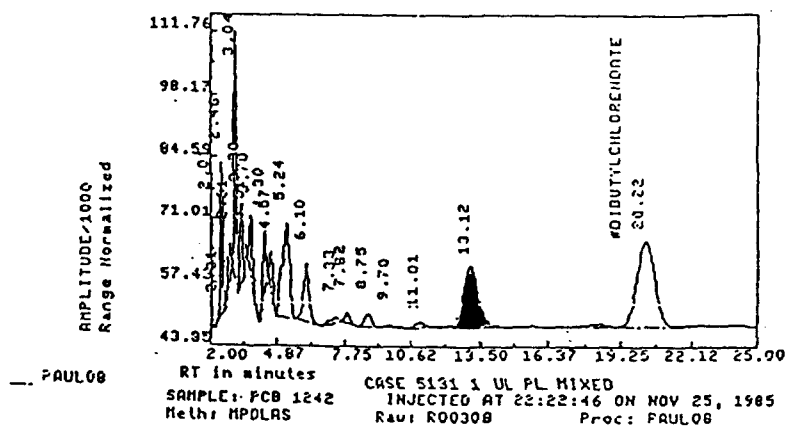
a)



b)



c)



d)

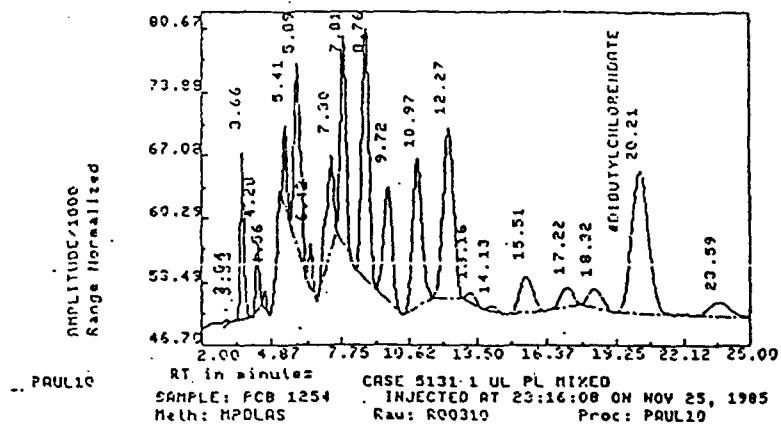
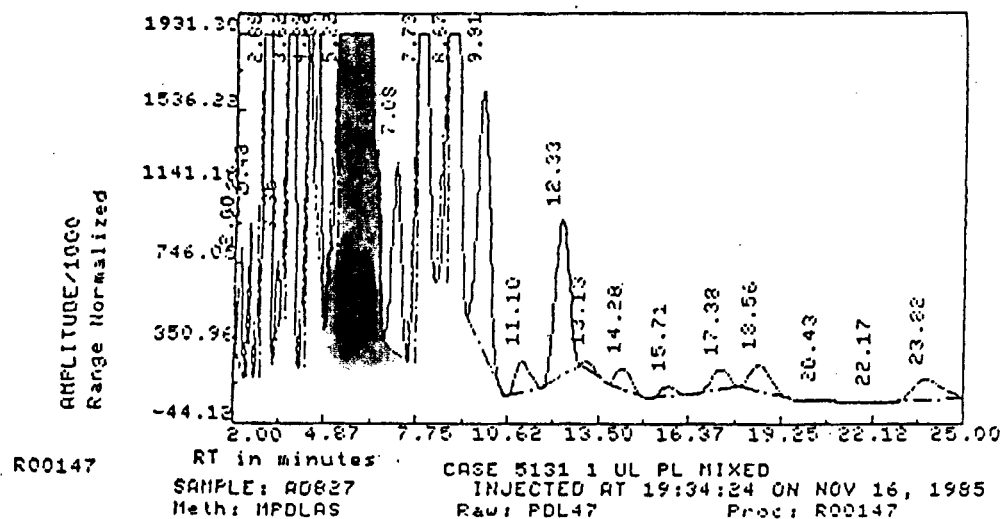
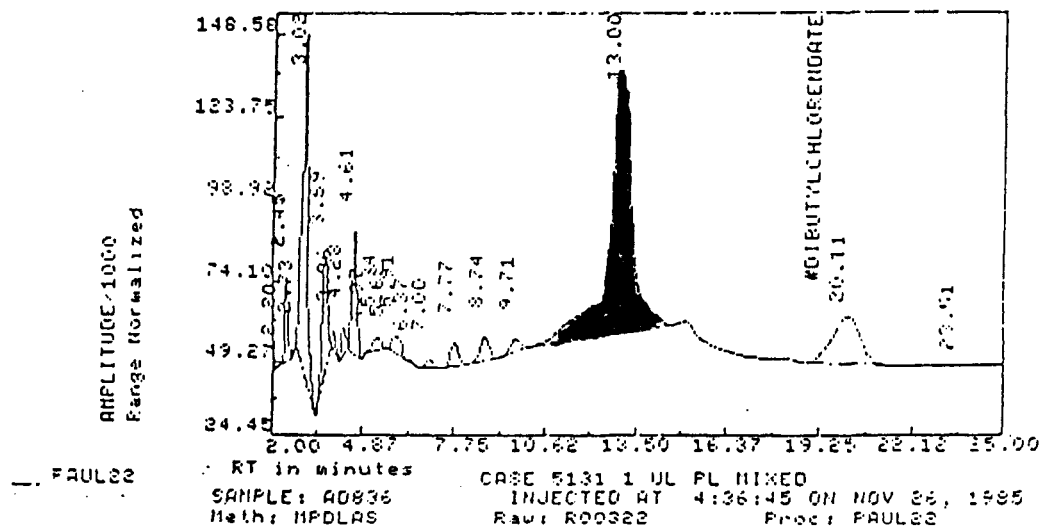


Exhibit 8-2. Illustration of Contamination in Aroclor Standards

a)



b)



c)

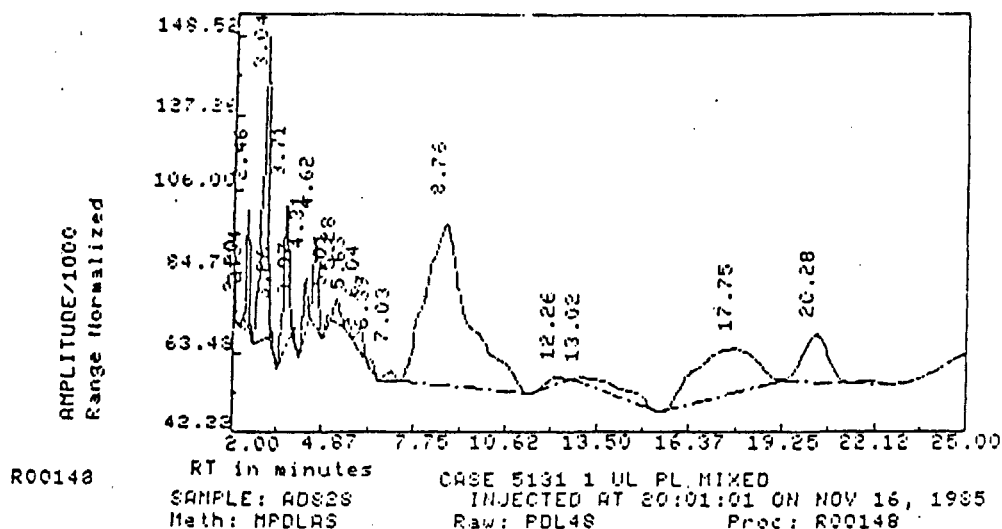


Exhibit 8-3. Illustration of Three Different Non-PCB Interferences in EPA Case #5131 Samples

Aroclor pattern, clearly visible in this sample, sulfur, the presence of sulfur in a number of the samples was confirmed by the GC/MS data (see item #15, Exhibit 8-4). The analysis protocol calls for the use of clean-up procedures for sulfur removal prior to sample analysis; this obviously was not done. Sample AD836 (b) has the same contamination peak at RT 13.00 which was seen in the Aroclor standards in Exhibit 8-2. An example of unacceptable chromatography due to the presence of non-PCB interference is shown in chromatogram (c) for Sample AD828. A number of QA/QC non-compliances occurred because of the matrix effects resulting from the presence of these non-PCB interferences. A rigorous clean-up of the sample extracts would have reduced or eliminated all three of the problems demonstrated in Exhibit 8-3.

#### 2.2.2 Identification and Quantitation of Aroclors.

Aroclor 1016 and/or 1242, as well as Aroclor 1254, are present in the samples. Because of the extremely poor quality of the chromatograms, it is impossible to distinguish between Aroclor 1016 and Aroclor 1242 in the samples since Aroclor 1254 is also present. Therefore, it is appropriate to use the notation "Aroclor 1016/1242" in this document.

LAUCKS TESTING LABORATORIES, INC.  
940 S. Harney, Seattle, WA 98108  
(206) 767-5060

SAMPLE NUMBER  
( AD826 )

Organics Analysis Data Sheet  
(Page 4)  
Tentatively Identified Compounds

	CAS Number	Compound Name	Frac	Scan	Conc (ug/kg)
1.		Unknown	ABN	202	8760J
2.	33146451	Biphenyl, dichloro-	ABN	1055	5060J
3.	33146451	" "	ABN	1064	5320J
4.	38444869	Biphenyl, trichloro-	ABN	1148	3990J
5.	25323686	" "	ABN	1172	6730J
6.		Unknown	ABN	1176	5030J
7.	38444869	Biphenyl, trichloro-	ABN	1184	9750J
8.	25323686	" "	ABN	1186	10200J
9.	52663588	Biphenyl, tetrachloro-	ABN	1230	7940J
10.	41464408	" "	ABN	1235	7550J
11.		Unknown	ABN	1239	4740J
12.	52663588	Biphenyl, tetrachloro-	ABN	1256	5230J
13.	25323686	Biphenyl, trichloro-	ABN	1261	3400J
14.	32598111	Biphenyl, tetrachloro-	ABN	1272	4730J
15.	<del>41464497</del>	<del>Sulfur, mol.</del>	ABN	1297	3970J
16.	41464497	Biphenyl, tetrachloro-	ABN	1310	8730J
17.	31508006	Biphenyl, pentachloro-	ABN	1337	5800J
18.	25429292	" "	ABN	1344	5060J
19.	25429292	" "	ABN	1382	6300J
20.	25429292	" "	ABN	1413	4320J
21.		Unknown	ABN	1867	5020J

174

Form I, Part B

en/11-85

Exhibit 8-4. GC/MS Confirmation of Sulfur  
Contamination in EPA Case #5131 Sample

The presence of Aroclor 1254 is clearly demonstrated in the packed column chromatogram (Exhibit 8-5) for Sample AD830. Aroclor 1254 is also evident in the capillary column chromatogram (a) and the GC/MS confirmation data (b) for this sample (Exhibit 8-6). Despite this overwhelming evidence indicating the presence of Aroclor 1254 in the sample, it was reported as "Not Detected" by LTL.

The quantitation of total PCBs in the samples is erroneous because of the failure to include the contribution due to the presence of Aroclor 1254. In addition, the reported Aroclor 1242 quantitations are biased low. Only one retention time window (2.99-3.09 minutes) was used for the Aroclor 1242 quantitation (see Exhibit 8-7). As a result, peak enhancements of other Aroclor 1242 peaks due to biotransformation in the samples were ignored, and the presence of new PCB congeners formed during PCB degradation was not included in the quantitation.

#### 2.2.3 Pattern Alterations in LTL Samples.

Frequently, PCB alteration processes produce chromatographic pattern changes which are subtle and difficult to detect unless the chromatogram is of high quality. Also, it is extremely important that

Pesticide/PCBs

a)

CONCENTRATION: MEDIUM

DATE EXTRACTED/PREPARED: NOVEMBER 7, 1985

DATE ANALYZED: NOVEMBER 17, 1985

CONC/DIL FACTOR: 1.0

CAS Number		ug/Kg	
319-84-6	Alpha-BHC	204 U	
319-85-7	Beta-BHC	204 U	
319-85-8	Delta-BHC	204 U	
58-89-9	Gamma-BHC (Lindane)	204 U	
76-44-8	Heptachlor	204 U	
309-00-2	Aldrin	204 U	
1024-57-3	Heptachlor Epoxide	204 U	
959-98-8	Endosulfan I	204 U	
60-57-1	Dieldrin	569 U	
72-55-9	4-4' DDE	569 U	U -- INDICATES COMPOUND WAS ANALYZED FOR BUT NOT DETECTED
72-20-8	Endrin	569 U	
33213-65-9	Endosulfan II	569 U	J -- INDICATES COMPOUND WAS IDENTIFIED BUT RESULT WAS BELOW SPECIFIED DETECTION LIMITS
72-54-8	4-4' DDD	569 U	
1031-07-8	Endosulfan Sulfate	569 U	
50-29-3	4-4' DDT	569 U	C -- INDICATES COMPOUND HAS BEEN CONFIRMED BY GC/MS
72-43-5	Methoxychlor	2044 U	
53494-70-5	Endrin Ketone	569 U	D -- INDICATES ANALYTE WAS FOUND IN BLANK AS WELL AS SAMPLE
57-74-9	Chlordane	2044 U	
8001-35-2	Toxaphene	5600 U	
12674-11-2	Aroclor-1016	2044 U	
11104-28-2	Aroclor-1221	2044 U	
11141-16-5	Aroclor-1232	2044 U	
53469-21-9	Aroclor-1242	2090000 C	
12672-29-6	Aroclor-1248	2044 U	
11097-69-1	Aroclor-1254	5600 U	
11096-82-5	Aroclor-1260	5600 U	

Vi = Volume of extract injected (ul)  
Ws = Weight of sample extracted (g)  
Vt = Volume of total extract (ul)

Ws = 0.42 Vt = 1000 Vi = 1.0

b)

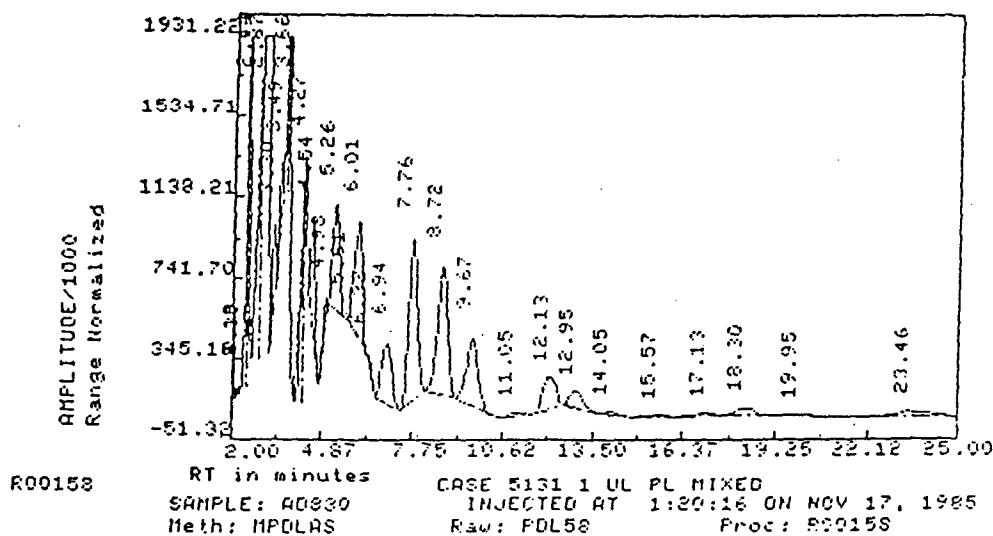
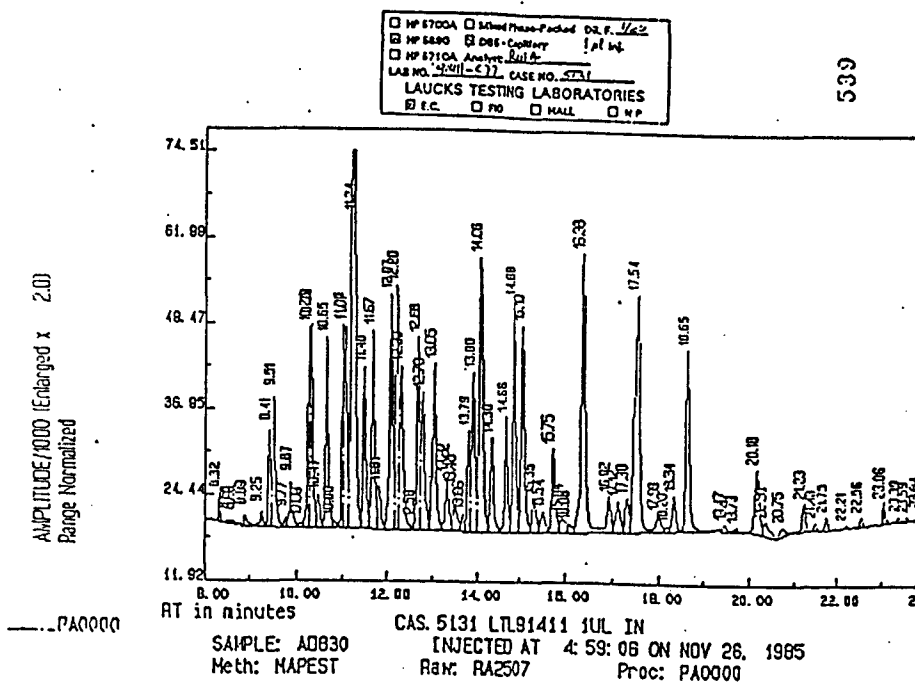


Exhibit 8-5. Analysis Report (a) and Packed Column Chromatogram (b) for Sample AD830



a)



b)

LAUCKS TESTING LABORATORIES, INC.  
410 S. Marney, Seattle, WA 98108  
(206) 767-5040

SAMPLE NUMBER  
AD830

File data: HC20711M  
411-C77 SAMPLE1A0830

CASE15121 1 GM TO 1 ML + IS/DFTTP

Organics Analysis Data Sheet  
(Page 4)  
Tentatively Identified Compounds

CAS Number	Compound Name	Fract	Scan	Conc
35144451	dichlorobiphenyl	48M	1437	1070000
35144451	dichlorobiphenyl	48M	1445	1040000
25223488	trichlorobiphenyl	48M	1125	1010000
35144451	dichlorobiphenyl	48M	1128	1310000
25223488	trichlorobiphenyl	48M	1150	1270000
35144451	dichlorobiphenyl	48M	1174	1180000
38444869	.	48M	1177	715000
38444869	.	48M	1184	2190000
38444869	.	48M	1188	2150000
38444869	.	48M	1209	788000
352442588	tetrachlorobiphenyl	48M	1222	1540000
352442588	tetrachlorobiphenyl	48M	1237	1470000
41444419	.	48M	1258	1190000
0	unknown	48M	1262	693000
0	unknown (tetrachlorobiphenyl?)	48M	1275	624000
0	unknown (pentachlorobiphenyl?)	48M	1312	1430000
27486732	pentachlorobiphenyl	48M	1320	517000
0	unknown	48M	1329	204000
0	unknown (pentachlorobiphenyl?)	48M	1332	502000
38200017	pentachlorobiphenyl	48M	1347	1070000
25429292	.	48M	1416	884000
32712046	hexachlorobiphenyl	48M	1442	141000

Form 1, Part B

AN/11-85

Exhibit 8-6. Capillary Column Chromatogram (a) and GC/MS Confirmation Report (b) for Sample AD830

CASE NUMBER: 5131  
CONTRACT NUMBER: 69-01-6964

CASE NUMBER: 5131  
CONTRACT NUMBER: 69-01-6964

1106

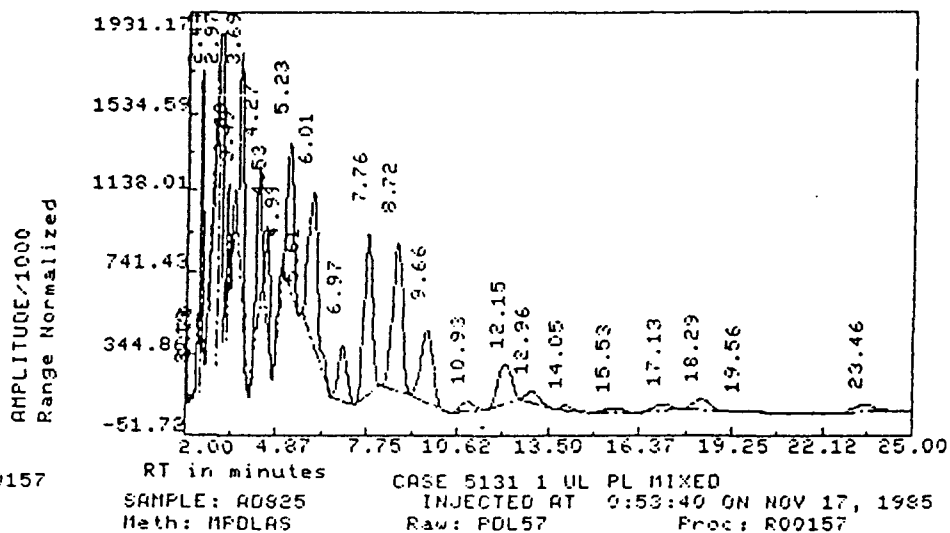
Exhibit 8-7. Report of RT Window for Aroclor 1242  
Quantitation of Packed Column Data

the full pattern be displayed and that all peaks remain "on scale," with the most intense peaks giving between 90 and 95% full-scale deflection. The failure of the LTL chromatograms to meet these criteria made the pattern alteration assessments a difficult task. However, by using both the packed column and capillary column chromatograms, it was possible to identify three alteration sources in the LTL chromatograms. They are

1. the presence of more than one Aroclor in the samples,
2. the presence of sulfur and other non-PCB interferences, and
3. degradation of Aroclor 1254 in the sediments, characterized by significant reductions of the higher chlorinated congeners (mainly penta- and hexachlorobiphenyls).

In cases where the LTL packed-column chromatograms were clear of interferences, the patterns resembled those of other New Bedford Harbor (NBH) studies (See Exhibit 8-8 for a comparison of LTL sample AD825 and Task 7 sample NBH-111-01.). Although peak resolution was somewhat improved in the LTL capillary chromatograms (see Exhibit 8-9), evidence of environmental aging losses of lower chlorinated congeners and the presence of new congeners in the Aroclor 1016/1242 region were difficult to assess.

a)



b)

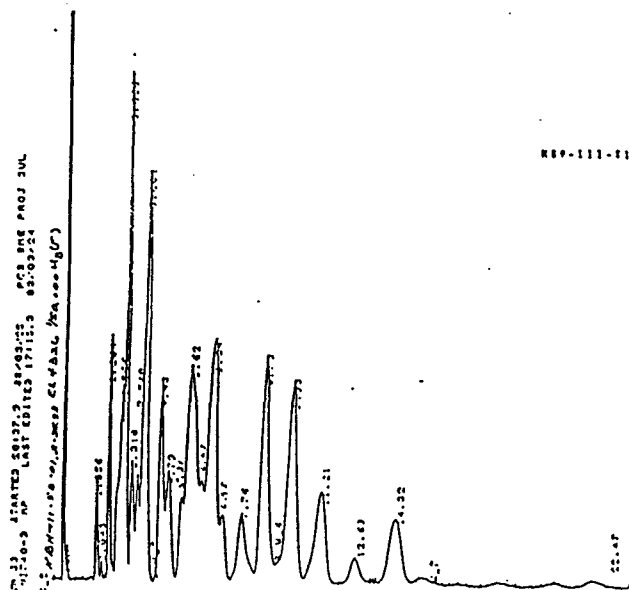
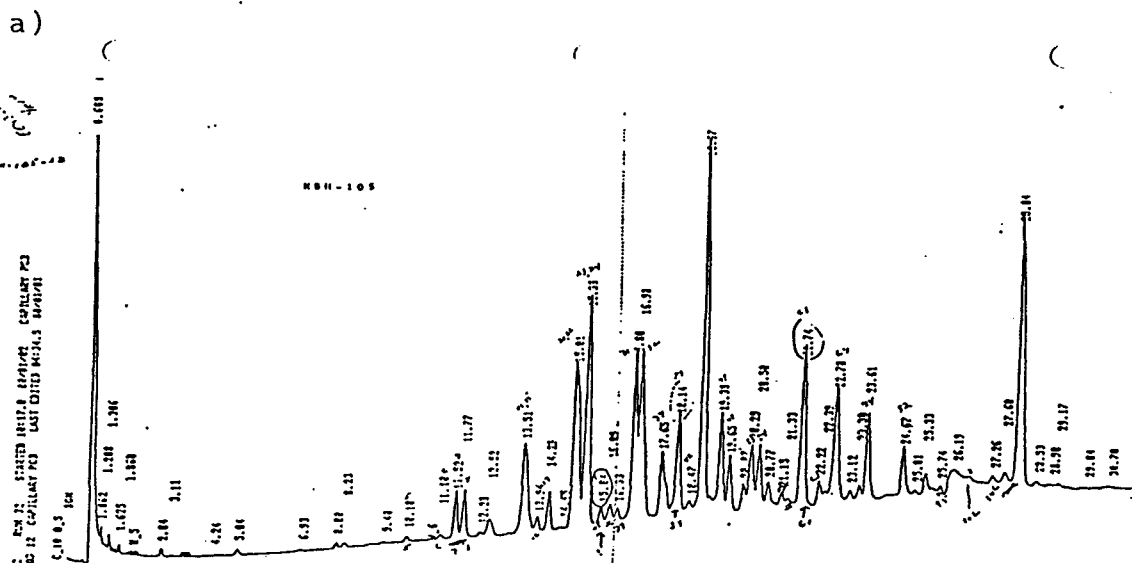


Exhibit 8-8. Comparison of Chromatograms for Task 8 Sample AD825 (a) and Task 7 Sample NBH-111-01 (b)



### 3.0 OVERALL ASSESSMENT

The quality of the data generated by LTL under this task is so poor that, in the opinion of YAI, the PCB results are useless. The only useful information that can be derived from the study is that the samples confirm, qualitatively, the Task 2 and Task 7 assessments. They do not represent a unique situation in the upper estuary where Aroclor 1242 is the only Aroclor present in the samples.

The gross deficiencies present in these data packages should have been found during the NUS data validation audit. However, the only restriction placed on the data was that "All positive results and minimum detection limits should be considered estimates in light of holding time non-compliance."

### 4.0 RECOMMENDATION

Because of the misleading nature of the data generated by this project (EPA Case #5131), it is the recommendation of the author that all data for the 15 samples analyzed by LTL be rejected and excluded from the NBH database.

**APPENDIX A**

**TERMS AND ABBREVIATIONS**

Table A-1. TERMS

"Additive Effect": To heighten or increase the intensity of a peak in a chromatogram (enhancement).

Anaerobe: A microorganism that flourishes without free oxygen.

Anaerobic microbial (bio)degradation: The reduction of a chemical component from a higher to a lower type by the action of anaerobic microbes.

Anaerobic biotransformations: Changes brought about as the result of the action of anaerobic bacteria.

Anaerobic dechlorination: A specific PCB microbial degradation process whereby chlorine is selectively removed from a congener as the result of anaerobic microbial actions.

Aroclor: Trade name (Monsanto) for a series of commercial PCB and polychlorinated terphenyl mixtures marketed in the United States.

Aroclor degradation: A reductive modification with respect to the proportions of the individual PCB congeners present in the specific Aroclor.

Aroclor transformation: Any change (either reduction or enhancement) in the unique characteristic of the composition of a specific Aroclor.

Chromatogram: A tracing of the detector output from a chromatograph which consists of a series of peaks observed over time.

Chromatographic pattern alteration: Any change or modification which occurs in the chromatogram produced by a known reference material (e.g., a specific Aroclor).

Congener: One of the 209 PCBs or other group of compounds, not necessarily the same homolog.

Degrade: To reduce from a higher to a lower type.

Enhance: To heighten or increase in intensity.



Table A-1. TERMS (Cont'd)

Environmental aging (weathering): The process whereby the Aroclor(s) present in an environmental sample undergoes modification with respect to the proportions of individual PCB congeners present as the result of partial vaporization, adsorption onto surfaces, and/or extraction into water. True molecular solution in water is shown (on chromatograms) as the non-selective loss of the more volatile and more water-soluble congeners from the Aroclors in the sediments.

"High-end drop-off": The pattern alteration observed when higher chlorinated PCB congeners (usually penta- and hexa-) undergo anaerobic dechlorination.

High resolution gas-liquid chromatography: Gas chromatography with a capillary column.

Homolog: One of the 10 degrees of chlorination of PCBs ( $C_{12}H_9Cl$  through  $C_{12}Cl_{10}$ ) or other group of compounds varying by systematic addition of a substituent.

Isomer: Any PCB or other compound which has the same molecular formula, but different positional substitutions. 2,2'-Dichlorobiphenyl and 2,3-dichlorobiphenyl are isomeric; 4-chlorobiphenyl and 2,3,4-trichlorobiphenyl are not.

"Low-end drop-off": The pattern alteration observed when lower chlorinated PCB congeners are removed from samples by weathering.

Part per million (ppm): One part in 10<sup>6</sup>.

Pattern alterations: Changes in a characteristic chromatographic pattern. The effect of the changes will be reflected by peak enhancements, reductions, or both. (See chromatographic pattern alterations.)

Polychlorinated biphenyl (PCB): One of 209 individual compounds having the molecular formula  $C_{12}H_nCl_{10-n}$ , where  $n = 0-9$ . This definition includes monochlorobiphenyls, but not biphenyl.

PCB degradation: A conversion whereby a PCB congener of a higher chlorine content is reduced (converted) to one of a lower chlorine content.

PCB transformation: Any change whereby a PCB congener is converted into another compound.

Table A-1. TERMS (Cont'd)

Qualitative: Having to do with establishing the presence or identity of a compound.

Quantitative: Having to do with measuring the amount or concentration of a compound in a sample.

Retention time: Time between injection and detection of a compound on a chromatographic system under specified conditions, expressed in seconds or minutes.

Transformation: Any change which gives a different appearance.

Weathering: A process which gives a compositional change in an Aroclor residue (see environmental aging).

APPENDIX VI

TASK 10

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**CLASSIFICATION OF AROCLOR TRANSFORMATIONS IN  
UPPER ESTUARY SEDIMENT SAMPLES  
(USACE FIT SAMPLING PROGRAM)**

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**Y & A Project NMF-3003 Task 10**

**DRAFT**

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**CLASSIFICATION OF AROCLOR TRANSFORMATIONS IN  
UPPER ESTUARY SEDIMENT SAMPLES  
(USACE FIT SAMPLING PROGRAM)**

**Y & A PROJECT NMF-3003 TASK 10**

**1.0 INTRODUCTION**

Significant and frequently extensive Aroclor pattern alterations have been observed in the chromatograms of sediment samples taken from the Acushnet River upper estuary (Y & A Project NMF-3003 Tasks 2 and 7). In 1988, a special research project was undertaken to evaluate PCB transformations in upper estuary samples. The results for the first phase of this study are contained in the Task 7 final report (Yoakum, 1989).

As the result of this special investigation, a qualitative system was developed for classifying Aroclor transformations based on pattern alterations observed in packed column GC/EC chromatograms. Task 10 involves the application of this classification system to sample chromatograms from the USACE FIT sampling program. The transformations observed in chromatograms from Tasks 2, 3, and 8 have been classified.

**2.0 CLASSIFICATION CRITERIA FOR PACKED COLUMN GC/EC  
CHROMATOGRAMS**

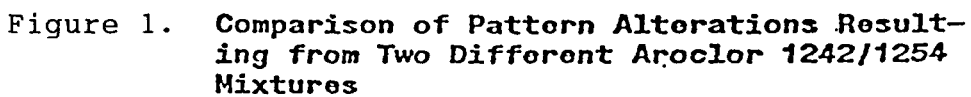
A detailed evaluation of the Task 7 chromatograms revealed that three basic alteration sources were

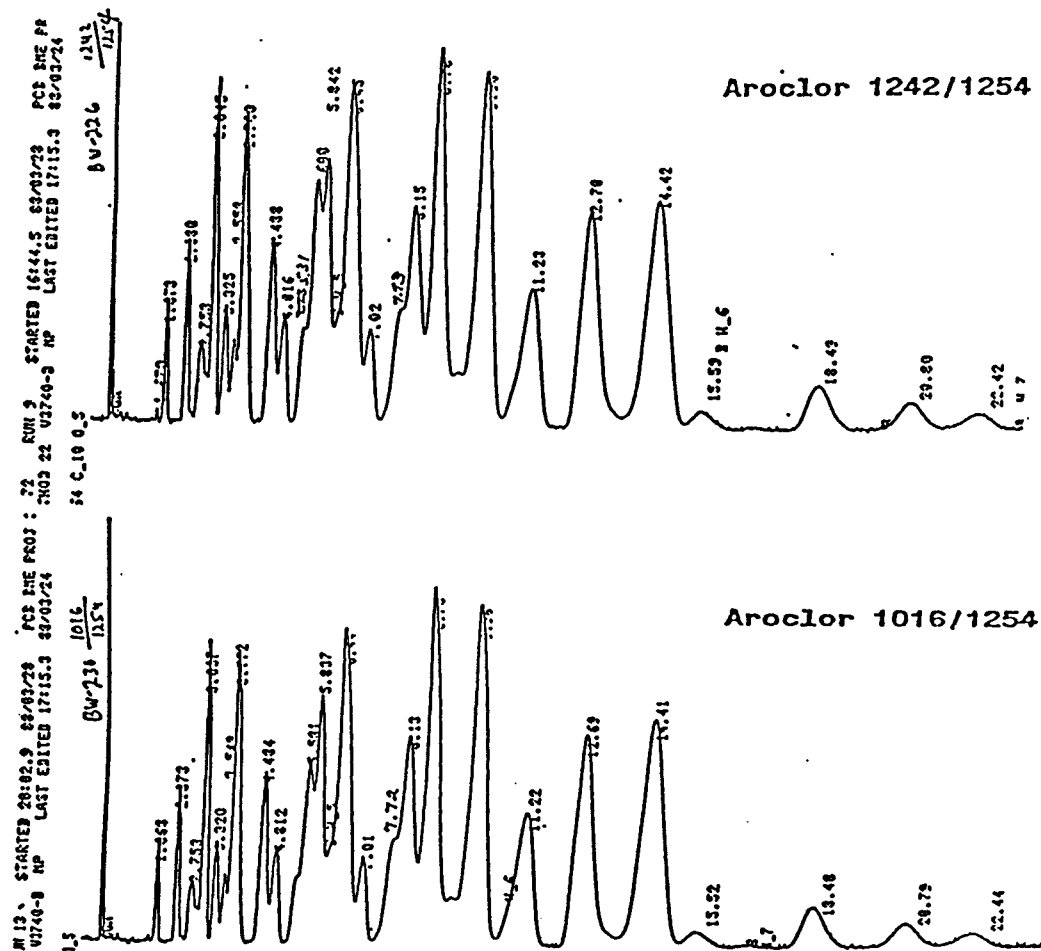
responsible for the wide variety of patterns observed:  
namely,

- o variable ratios of Aroclor 1016/1242 to Aroclor 1254,
- o environmental "weathering," and
- o compositional distribution alterations of the PCB congeners present due to anaerobic dechlorination transformations.

The impacts of these alteration sources are different and operate independently of one another. As a consequence, a single, so-called "standard" pattern was not seen. Nonetheless, an experienced PCB analyst can recognize the patterns and ascertain the impacts associated with each of the different alteration sources.

Pattern alterations due to variable Aroclor ratios (see Figure 1) are additive in nature and were readily apparent in the New Bedford Harbor (NBH) samples. It should be noted, however, that based solely upon packed column data, no distinction can be made between Aroclor 1016 and Aroclor 1242, in the presence of Aroclor 1254. See illustration in Figure 2. For this reason, the notation Aroclor 1016/1242 is used throughout this report. Generally, weathering effects (due to partial vaporization, adsorption onto surfaces, and/or extraction into water) were minimal compared to the anaerobic dechlorination changes observed and were most obvious in the Aroclor 1016/1242 region of the Task 3 chromatograms. A more detailed discussion of Aroclor pattern alteration sources





(complete with demonstrative chromatograms) can be found in the Task 11 Final Report (Yoakum, 1989).

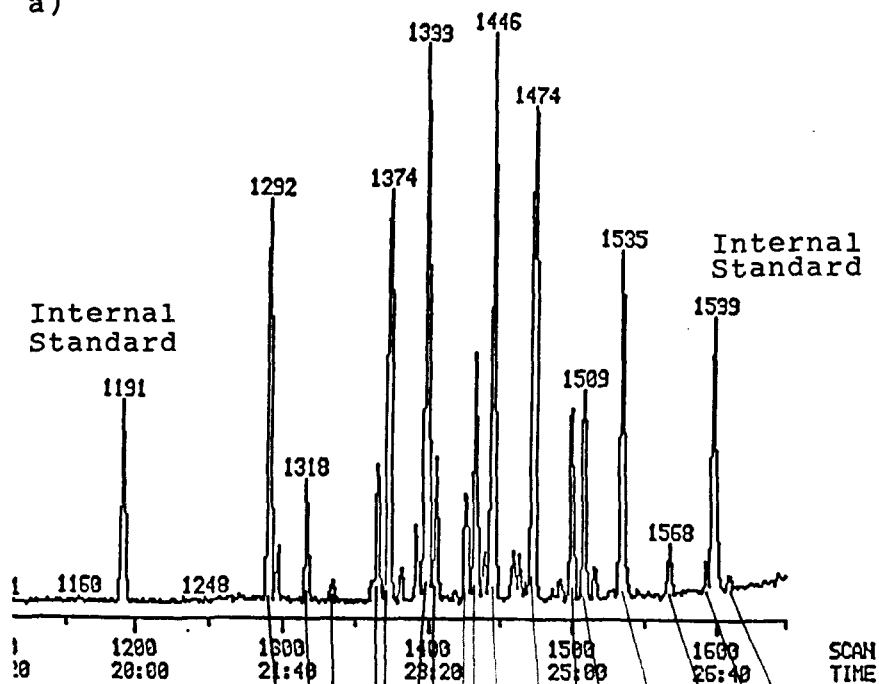
When the compositional ratio changes are discounted, a multiphased sequence of transformation changes, resulting from different stages of development of the anaerobic dechlorination phenomenon, is apparent. Because of the cascading effect of the dechlorination transformations and the uniqueness of the Aroclor patterns exhibited by the various alteration sources, a qualitative classification of the degree of Aroclor transformations occurring in NBH samples is possible.

All of the packed column chromatograms evaluated for this project were produced using the primary analysis column prescribed by EPA for PCB determinations (1.5% SP-2250/1.95% SP-2401 mixed phase on Supelcoport). This coating affords the best resolution available from a packed column for the major Aroclor components. As can be seen from Figure 3, the PCB congener elution sequence for this column (b) closely parallels that of the DB-5 capillary column (a) used in the Task 7 investigations. In fact, the separation of the hexa congener (2,2',4,4',5,5') at RT 11.20 from the peak at RT 12.67 composed of the hexa (2,2',3,3',4,6') and penta (2,3,3',4,4') congeners is better than that of the DB-5 capillary column. As a consequence, any transformations associated with the reductive dechlorination of the major PCB components present in the original Aroclor(s) can be tracked easily using packed

130M/IUM 40-325010C/M 1UL INJ  
QUAN: A 0, 1.0 J 0 BASE: U 20, 3

5168.

a)



b)

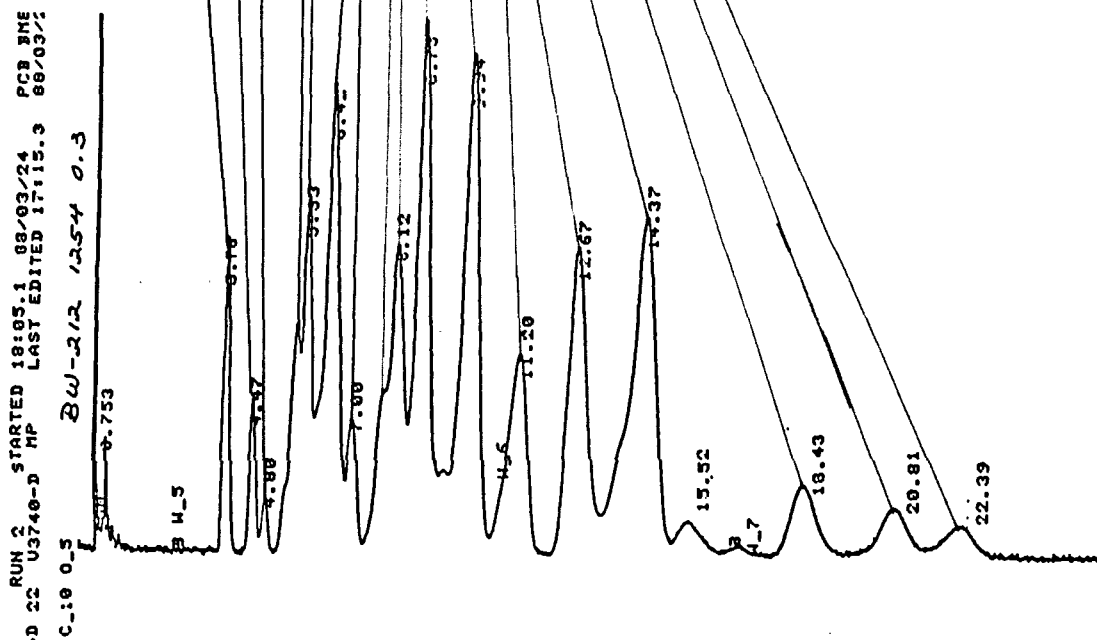


Figure 3. Comparison of GC/MS Capillary Column RIC (a) and GC/EC Mixed Phase Packed Column Chromatogram (b) for Aroclor 1254

column chromatograms. Subtleties cannot be seen, but the big picture of what is occurring is most clear.

The following definitions apply to the classification evaluations for Aroclor transformations shown on mixed phase (1.5% SP-2250/1.95% SP-2401) packed column chromatograms:

1. Slight alteration of Aroclor 1016/1242, sample shows "low-end" congener reduction for first two indicator peaks at RTs 1.86 and 2.37.
2. Moderate alteration of Aroclor 1016/1242, sample shows "low-end" congener reduction for all three indicator peaks (RTs 1.86, 2.37, and 3.03), some reduction of peaks at RTs 3.30 and 3.56.
3. Advanced alteration of Aroclor 1016/1242, sample exhibits significant reductions or the complete absence in the three normal pattern indicator peaks and the peaks at RTs 3.30 and 3.56.
4. Slight alteration of Aroclor 1254, sample shows "high-end" congener reduction of peaks at RTs 8.15 and 12.70.
5. Moderate alteration of Aroclor 1254, pattern demonstrates "high-end" congener reduction and enhancement of peaks in the transition region.
6. Advanced alteration of Aroclor 1254, sample shows complete absence of peaks at RTs 8.15 and 12.70, significant reduction of "high-end" congeners as well as transition region peaks, and a new peak at RT 2.87 is present.

Examples of the application of pattern alteration classifications to the Task 7 samples are shown in Figures 4-6. The pattern alterations illustrated are as follows:

Figure 4. Sample NBH-112-02: No apparent alteration of either Aroclor 1016/1242 or Aroclor 1254.

Figure 5. Sample NBH-101: Moderate alteration for both Aroclor 1016/1242 and Aroclor 1254.



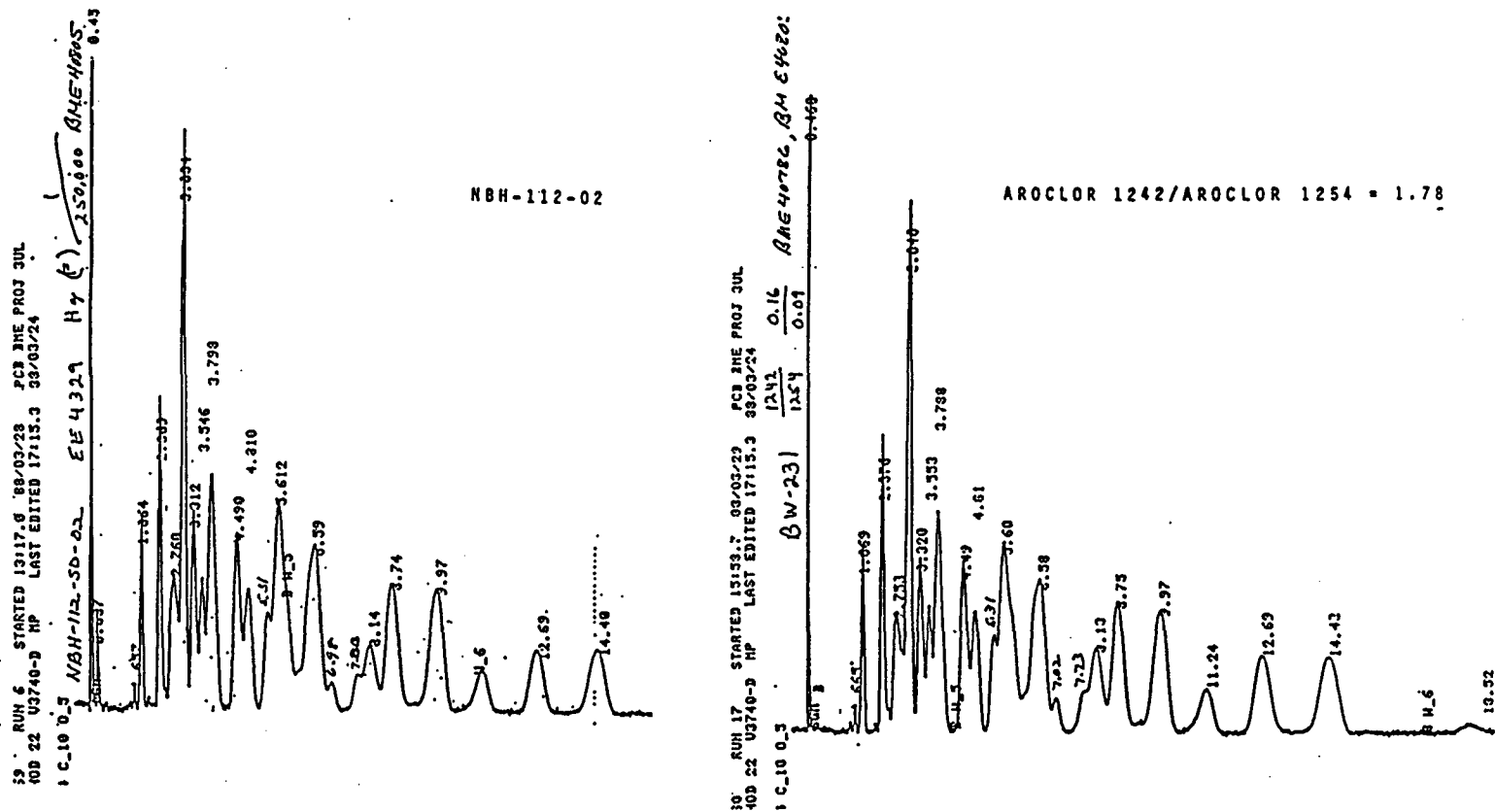


Figure 4. Comparison of Mixed Aroclor Standard and Sample NBH-112-01 Which Shows No Apparent Pattern Alterations

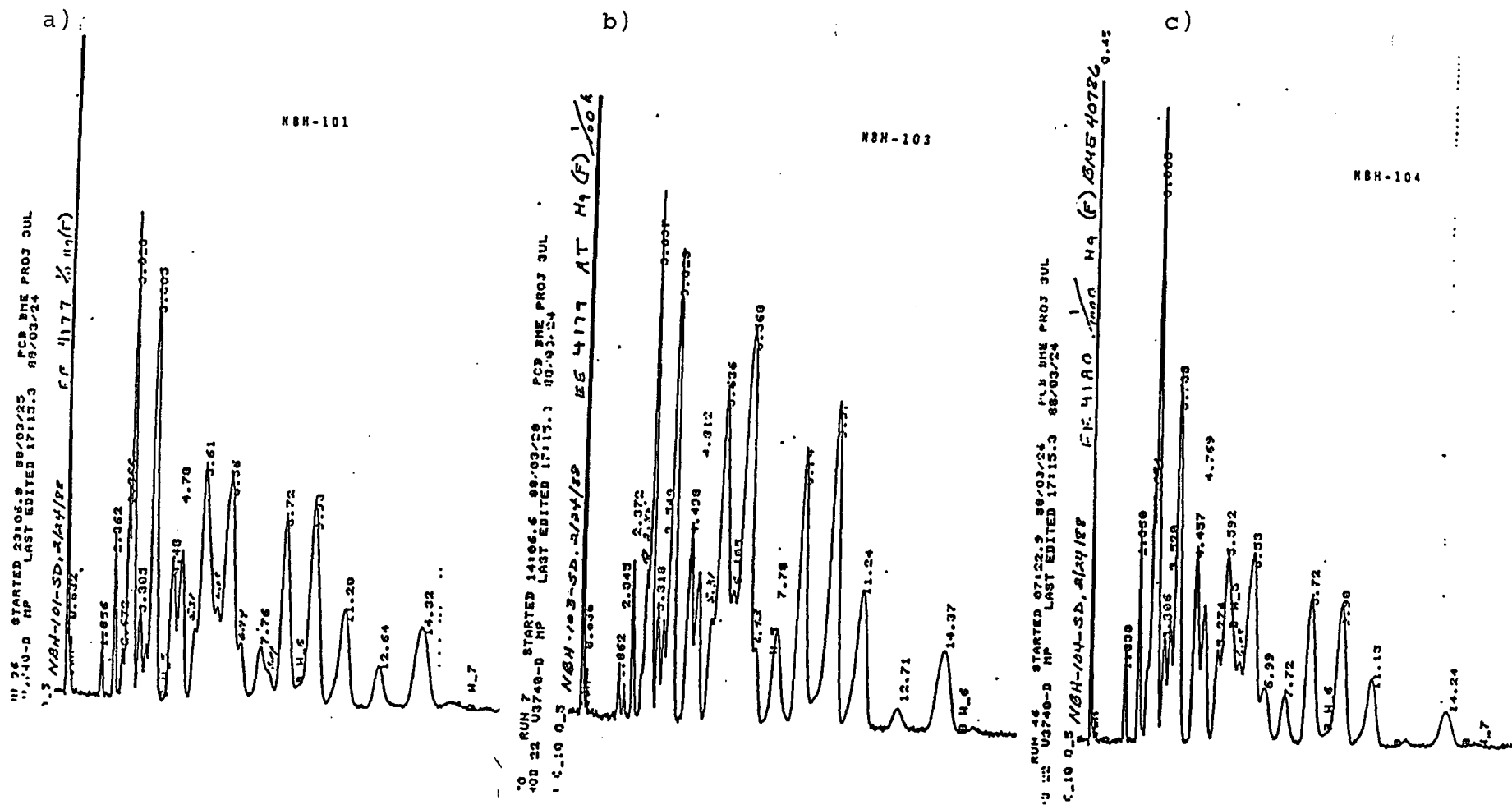
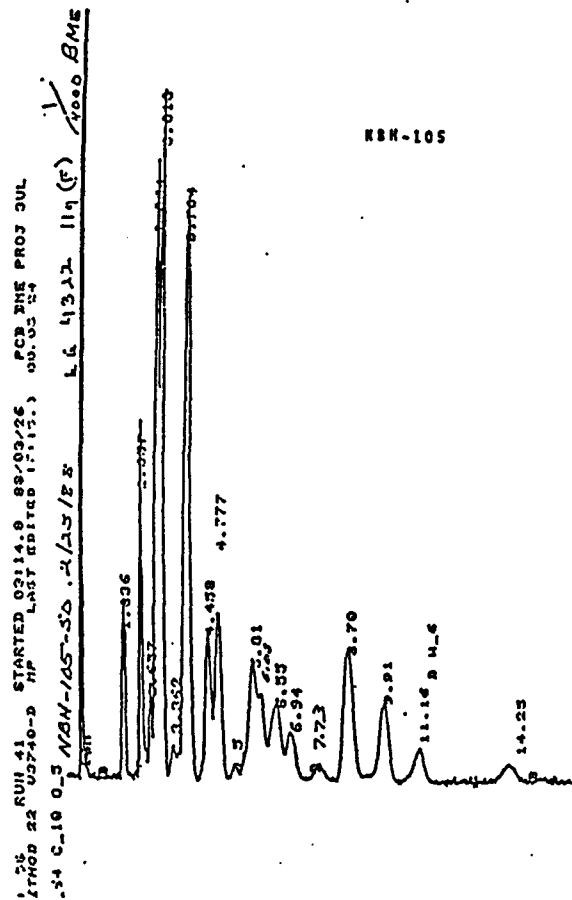
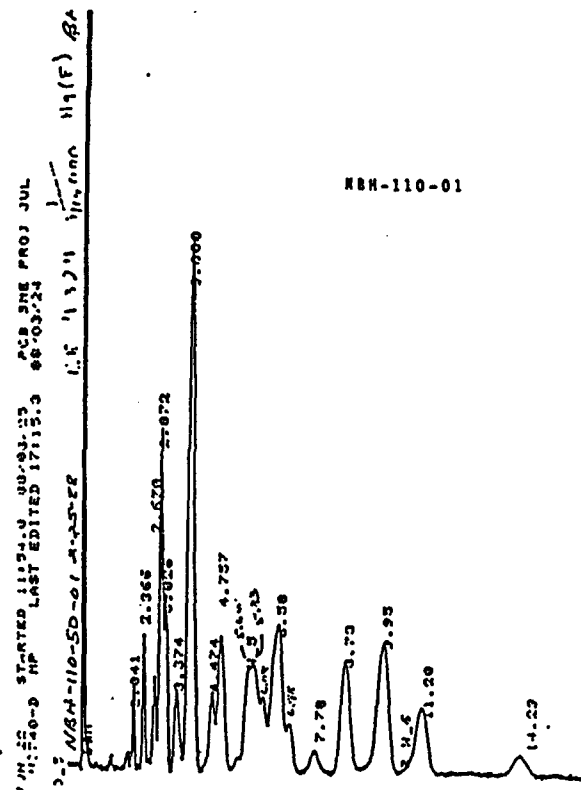


Figure 5. Illustration of Progressive Aroclor 1254 Alteration ( $a < b < c$ ) and Two Stages of Aroclor 1016/1242 Alteration ( $c < a = b$ )

a)



b)



c)

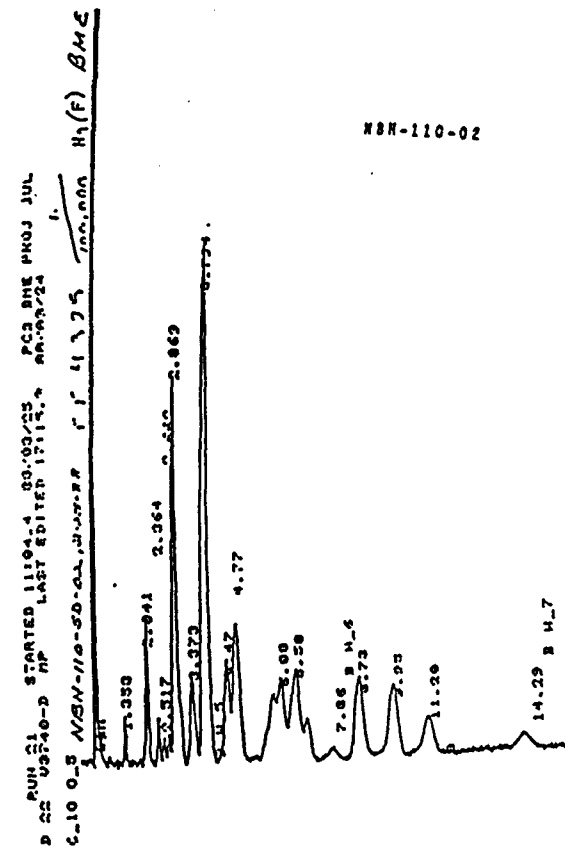


Figure 6. Illustration of Subtle Changes Observed in Advanced Stages of Aroclor 1254 Transformation and Moderate to Advanced Transformation of Aroclor 1016/1242 (a**=c**)

Sample NBH-103: Moderate alteration for Aroclor 1016/1242 and moderate to advanced alteration of Aroclor 1254.

Sample NBH-104: Slight alteration of Aroclor 1016/1242 and moderate to advanced alteration of Aroclor 1254.

Figure 6. Sample NBH-105: Moderate alteration for Aroclor 1016/1242 and advanced alteration for Aroclor 1254.

Samples NBH-110-01 and NBH-110-02: Advanced alteration for both Aroclor 1016/1242 and Aroclor 1254.

The most significant Aroclor pattern alterations exhibited by many of the NBH samples are those due to anaerobic dechlorination. New peaks are present in the patterns and significant reductions of the higher-chlorinated (penta- and hexa-) congeners are evident. Peak enhancements, reductions and disappearances have also occurred in all regions of the chromatograms. Samples exhibiting advanced Aroclor 1254 transformations show wide distribution variations among the tri- and tetrachlorobiphenyl congeners. The peaks at RTs 2.87 and 3.80 are known to be the major transformation products formed during the anaerobic dechlorination of Aroclor 1254. Samples undergoing Aroclor 1016/1242 transformations show alterations in the lower chlorinated (di- and tri-) peak distributions and, in some samples, the complete disappearance of a number of peaks. Many samples show Aroclor 1016/1242 weathering; however, the pattern alterations seen in the Aroclor 1016/1242 region of the chromatograms are far too extensive to be explained solely by reference to weathering.

There is preliminary evidence to indicate that transformation of both Aroclor 1016/1242 and Aroclor 1254 are proceeding simultaneously by a step-wise dechlorination process which is exhibited by the cascading effect seen in the chromatograms. Based on data evaluations performed to date, it appears that only one transformation process is occurring in New Bedford Harbor and the pattern differences demonstrated by the samples are related to the differing rates at which the dechlorination of the various PCB congeners is occurring.

### 3.0 CLASSIFICATION OF AROCLOR TRANSFORMATIONS IN SEDIMENTS FROM THE UPPER ESTUARY OF THE ACUSHNET RIVER

All of the Task 2 and 3 chromatograms were classified according to the criteria given in Section 2.0. For Task 8, both the packed column and capillary column chromatograms were used for the classifications.

#### 3.1 Samples Analyzed by USACE New England Division of Water Quality Laboratory (Task 2)

The results for the Task 2 chromatograms are presented in Table 1. The Aroclor transformation classifications for these samples are in close agreement with those derived from the Task 7 samples.

#### 3.2 Samples Analyzed by Cambridge Analytical Associates - EPA Case #5058 (Task 3)

Pattern alteration classifications for the Task 3 chromatograms are found in Table 2. The only Aroclor transformation observed was that due to the environmental

TABLE 1. CLASSIFICATION OF AROCLOR TRANSFORMATIONS  
FOR TASK 2 SAMPLES (USACE)

Field Grid No.	Stratum (Inches)	Lab ID No.	Total PCBs (ppm)	Sulfur	Transformation ^	
					1016/1242	1254
E-25-1	0-12	9910A	90.7	*	M	M
	12-24	9910B	2.08	-	(1)	(1)
	24-30	9910C	0.21	*	A	A
E-27-1	0-24	9912A	26.7	*	M	M
	24-33	9912B	1.10	*	A	A
G-13-1	0-10	9914A	79.8	*	M	M to A
	24-36	9914C	0.08	*	(1)	(1)
G-17-2	0-24	9918A	1147 (2)	-	M	M to A
	24-38	9918B	577	*	M to A	A
	45-49	9919D	3.31	***	(2)	None
Chromatogram Missing	-65	9919E	5.79			
G-18	0-12	0030A	312 (2)	*	M	M
	12-24	0030B	1440	*	M	M to A
	24-36	0030C	375	**	A	A
G-20-2	0-12	9921A	12.6	*	M	M to A
	24-36	9921C	0.29	**	(1)	(1)
G-29-1	0-15	9922A	22.6	-	M	M
	15-27	9922B	0.55	*	(1)	(1)
H-12	0-12	0042A	8370	-	M	M
	12-24	0042B	3740	*	(2)	A
H-17	0-6	9877A	499	*	M	A
	6-18	9877B	4.05	-	(2)	(2)
	18-36	9877C	1.15	-	(1)	(1)
H-21	0-12	9869A	448	*	M	M to A
	12-24	9869B	2.04 (2)	*	(1)	(1)
	24-37	9869C	0.19	*	(1)	(1)
H-25	0-12	9907A	160	**	S to M	M
	24-33	9907C	0.16 (2)	**	(1)	(1)
H-33	0-12	9859A	2.42	-	S	S
	24-36	9858C	0.04	*	(1)	(1)
I-3-1	0-18	9925A	938	*	M	A
	18-28	9925B	0.22	***	(2)	(2)

(1) Chromatogram intensity insufficient to classify.

(2) Interference present.

\*, \*\*, \*\*\* = Intensity of sulfur interference.

- = Not detected in sample.

Transformation Key

S = Slight

M = Moderate

A = Advanced

TABLE 1. CLASSIFICATION OF AROCLOR TRANSFORMATIONS  
FOR TASK 2 SAMPLES (USACE) - Cont'd.

Field Grid No.	Stratum (Inches)	Lab ID No.	Total PCBs (ppm)	Sulfur	Transformation ^	
					1016/1242	1254
I-9-1	0-22	9927A	146	*	M to A	M to A
	22-29	9928B	0.10 (2)	***	(1)	(1)
I-11-1	0-13	9930A	36000	-	M	M to A
	13-24	9930B	68.4 (2)	*	M	A
	24-36	9930C	1.06	*	(1)	(1)
I-11-2	0-12	9932A	22500	-	S	M
	12-24	9932B	11200	*	S	M
I-12	0-12	0047A	1370	-	M	A
	12-24	0047B	73	-	A	A
I-15	0-6	9902A	882	**	M	A
	6-24	9902B	16.1	*	M	A
	24-36	9902C	0.63	**	(1)	(1)
I-19	0-13	9786A	911	*	M	A
	24-37	9786C	<0.01	***	-	-
I-23	0-24	9840A	441	*	M	M to A
	24-36	9840B	0.34	***	(1)	(1)
I-28	0-12	9848A	177	**	M	M
	24-38	9848C	0.02	***	-	-
I-31	0-8	9778A	22.4	-	M	M
	8-24	9778B	0.27	-	(1)	(1)
J-5-1	0-24	9934A	282	*	M	A
	24-36	9934B	0.20	***	(1)	(2)
J-7	0-1	0052A	21800	-	None	None
	5.5-6.5	0052C	76100 (2)	-	None	None
	12-13	0052D	54000	-	None	None
	30-40	0052G	92.3	-	None	None
J-8-2	0-24	9938A	2540	*	M	A
	24-32	9938B	1.22	*	(2)	(2)
J-10	0-12	0055A	8560	*	M	M
	12-24	0055B	0.74	**	-	-
J-12	0-5	0058A	173 (2)	*	M	A

(1) Chromatogram intensity insufficient to classify.

(2) Interference present.

\*, \*\*, \*\*\* = Intensity of sulfur interference.

- = Not detected in sample.

^Transformation Key

S = Slight

M = Moderate

A = Advanced

TABLE 1. CLASSIFICATION OF AROCLOR TRANSFORMATIONS  
FOR TASK 2 SAMPLES (USACE) - Cont'd:

Field Grid No.	Stratum (Inches)	Lab ID No.	Total PCBs (ppm)	Sulfur	Transformation <sup>^</sup>	
					1016/1242	1254
J-13-2	0-8	9941A	139 (2)	*	M to A	A
	8-20	9941B	0.14	**	(1)	(2)
J-15-1	0-16	9942A	58.2	-	M	A
J-17-2	0-12	9945A	139	*	M	A
	12-24	9945B	0.04	-	(1)	(1)
J-20-2	0-16	9947A	3.54	*	S	S
K-5-2	0-12	9949A	440	*	M	A
	12-24	9949B	2.34	**	M to A	A
	24-33	9949C	0.05 (2)	-	(1)	(1)
K-26-1	0-12	9950A	42.4	*	M to A	A
	12-22	9950B	0.04	***	(1)	(1)
K-28-1	0-8	9953A	16.5	*	M	A
	8-20	9953B	0.06	-	(1)	(1)
K-32-1	0-12	9954A	2.56	-	(2)	(2)
	12-23	9954B	0.02	-	-	-
L-10-1	0-11	9956A	318	*	M	A
	24-36	9956C	0.08	*	-	-
L-29-2	0-12	9962A	29.1 (2)	**	M	M
	24-36	9962C	0.06	**	(1)	(1)
M-6-2	0-24	9965A	607	-	M	A
	24-31	9965B	0.35	-	-	-
M-27-1	0-16	9967A	51.8	**	S	S
	16-26	9967B	0.02 (2)	**	(2)	(2)

(1) Chromatogram intensity insufficient to classify.

(2) Interference present.

\*, \*\*, \*\*\* = Intensity of sulfur interference.

- = Not detected in sample.

<sup>^</sup>Transformation Key

S = Slight

M = Moderate

A = Advanced



TABLE 2. CLASSIFICATION OF AROCLOR TRANSFORMATIONS FOR TASK 3  
SAMPLES (EPA CASE #5058)

Field Grid	Sample Number	Depth (Inches)	Total PCBs (ppm)	Aroclor 1016/1242 Transformation^	Aroclor 1254 Transformation
K-20	AD586	0-12	60.	S to M	None
L-19	AD587	12-24	ND	-	-
L-19	AD588	0-12	ND	-	-
K-19	AD589	0-12	0.69	-	None
K-17	AD590	0-12	0.15	-	None
K-15	AD591	0-12	ND	-	-
K-14	AD592	0-12	161.	M	None
N-7	AD593	0-12	2.6	M	None
N-6	AD594	0-12	6.8	M	None
L-5	AD595	0-12	550.	VS	None
M-26	AD596	0-12	0.24	-	None
M-22	AD597	12-24	ND	-	-
L-25	AD598	0-12	1.5	-	None
L-20	AD599	0-12	49.	M	None
K-16	AD600	0-12	1.5	M	None

^Transformation Key

VS = Very Slight

S = Slight

M = Moderate

- = Aroclor Not Detected in Sample

aging of the Aroclor 1016/1242 in the samples. No evidence of biotransformation was seen.

### 3.3 Samples Analyzed by Laucks Testing Laboratory - EPA Case #5131 (Task 8)

The quality of the Task 8 packed column chromatograms was so poor that classifications of Aroclor transformations for many samples could not be performed based on these data alone. Classification of Aroclor transformations was accomplished, however, by using the capillary column chromatograms as supplements. Transformation classifications for the Task 8 samples are contained in Table 3. Total PCB values, as reported to EPA, are included in this table. It should be noted, however, that these results are in error and the concentrations are grossly under-reported. No contribution was calculated for Aroclor 1254 and none of the dechlorination enhancements occurring in the Aroclor 1016/1242 region due to transformation products were included in the Aroclor 1242 data.

### 3.4 Aroclor Transformations Observed in Task 7 Research Investigation

The samples for the Task 7 investigation were collected from the same general area in which the USACE FIT sampling program was performed (see Figure 7). The transformations observed in these samples are presented in Table 4 for comparison purposes.

TABLE 3. CLASSIFICATION OF AROCLOR TRANSFORMATIONS FOR TASK 8  
SAMPLES (EPA CASE #5131)

Field Grid	Sample Number	Depth (Inches)	Total PCBs (ppm)	Aroclor 1016/1242 Transformation^	Aroclor 1254 Transformation^
K-7	AD826	0-6	370.	M	A
	AD827	6-12	121.	M to A	A
	AD828	12-24	1.5	M	A
	AD829	24-D	1.1	M	A
K-9	AD830	8-20	2090.	M	A
	AD831	20-30	74.	M	A
I-10	AD832	6-12	2660.	M	A
	AD834	24-D	41.	M	A
J-11	AD835	0-6	1140.	M	A
	AD836	6-12	8.5	M	A
	AD837	12-24	14.	M	A
	AD838	12-24	6.1	M	A
	AD839	24-D	ND	-	-
I-13	AD825	0-6	2250.	M	A

^Transformation Key

M = Moderate

A = Advanced

- = Aroclor Not Detected in Sample

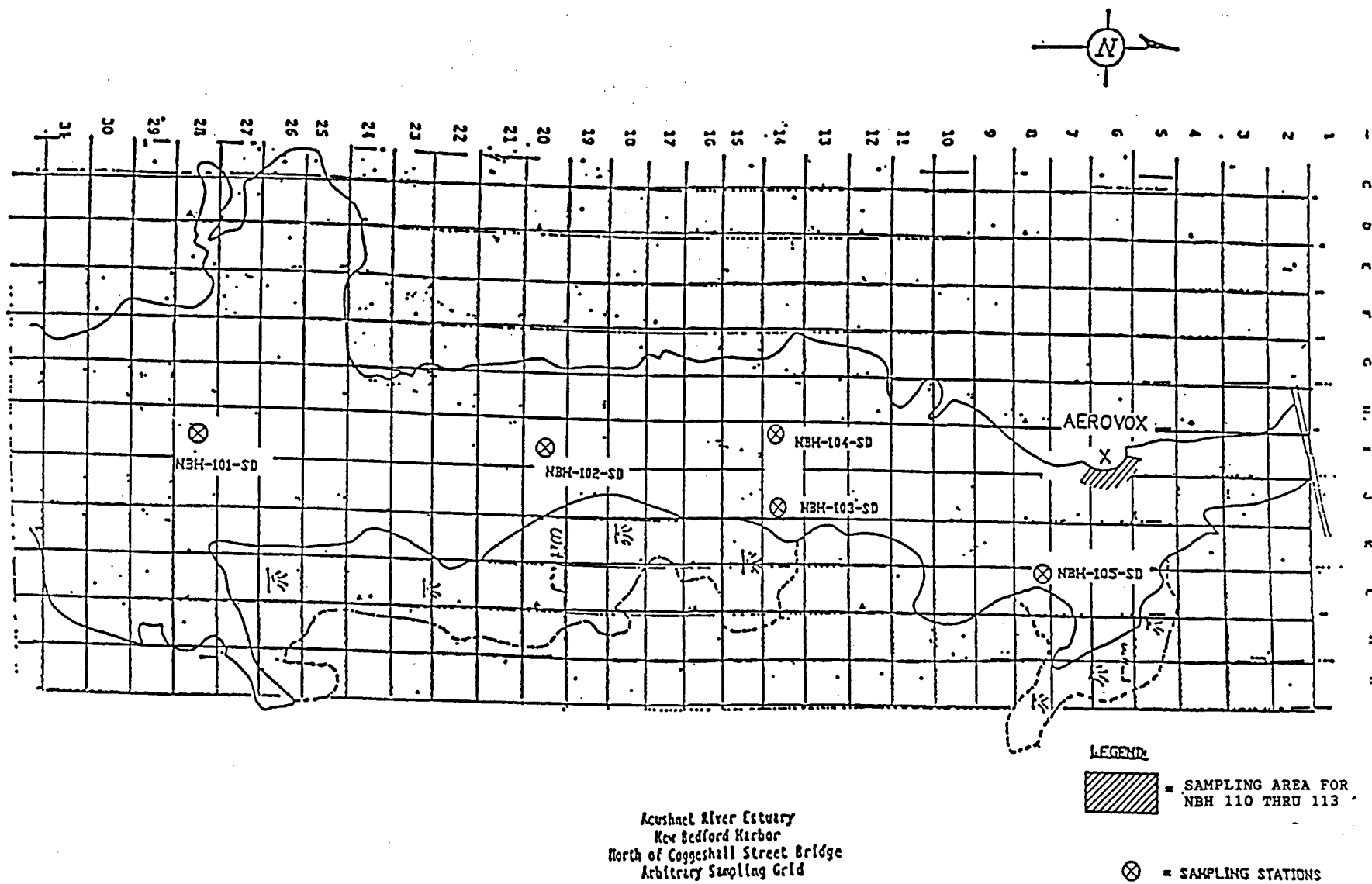


Figure 7. Task 7 Sample Locations

TABLE 4. AROCLOR TRANSFORMATIONS DEMONSTRATED BY TASK 7 SAMPLES

Sample	Depth (Inches)	Total PCBs (ppm)	Aroclor 1016/1242 Transformation^	Aroclor 1254 Transformation^
NBH-101	0-19	9.6	M	M
NBH-102	0-19	820.	S	S
NBH-103	0-19	47.	M	M to A
NBH-104	0-18	360.	S	M to A
NBH-105	0-18	1,100.	M	A
NBH-106	0-18	960.	M	A
NBH-110-01	0-3	7,600.	A	A
NBH-110-02	3-6	11,000.	A	A
NBH-111-01	0-3	28,000.	M	M to A
NBH-111-02	3-6	39,000.	M	M
NBH-112-01	0-3	30,000.	None	S
NBH-112-02	3-6	130,000.	None	None
NBH-113-01	0-3	500.	A	M
NBH-113-02	3-6	180.	A	S

## ^Transformation Key

S = Slight  
 M = Moderate  
 A = Advanced

## 4.0 DISCUSSION OF RESULTS

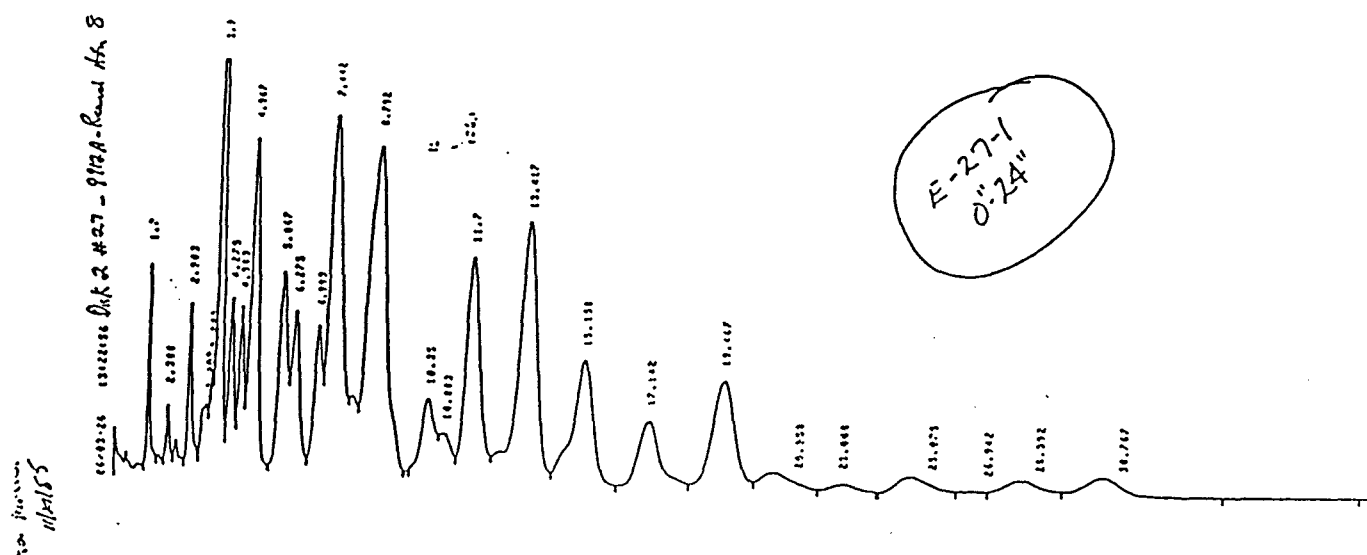
### 4.1 Transformations Observed in USACE FIT Samples

#### 4.1.1 Samples Analyzed by USACE New England Division of Water Quality Laboratory (Task 2).

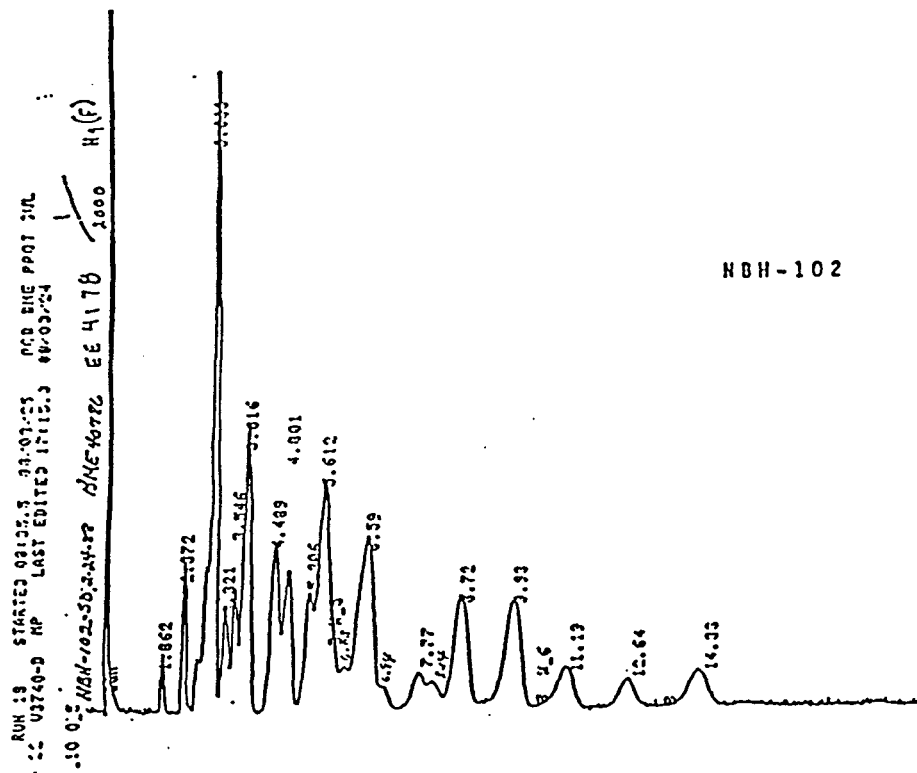
Transformations observed in the Task 2 samples are in excellent agreement with those found in the Task 7 investigation with regard to both extent and location. The close resemblance of pattern alterations is shown for samples from the southern (Figure 8), middle (Figure 9) and northern reaches (Figure 10) of the upper estuary.

The most advanced transformation of Aroclor 1016/1242 (4 sites) occurred at depths greater than 12 inches for the Task 2 samples. Moderate to advanced Aroclor 1016/1242 transformation was observed in Task 2 samples at five sampling sites. Sixty-four percent (64%) of the Task 2 samples showed moderate pattern alterations in the Aroclor 1016/1242 regions of their chromatograms.

Moderate to advanced and advanced Aroclor 1254 transformations were seen in 62% of the Task 2 samples and 50% of the samples from Task 7. The similarity of the advanced Aroclor 1016/1242 and Aroclor 1254 alteration patterns is demonstrated in Figure 11, where chromatogram (a) is from Task 7 and chromatogram (b) is from Task 2.



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NBH-102

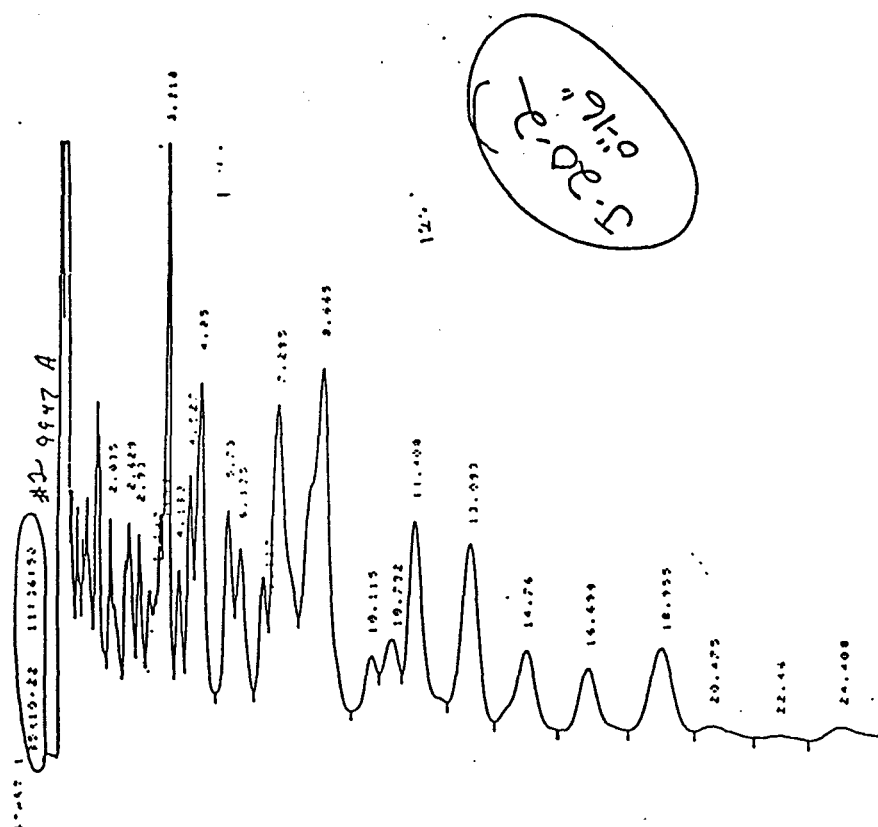


Figure 9. Chromatograms for Task 7 (NBH-102) and Task 2 (J-20-2) - Middle Area of Estuary







A number of USACE samples (Task 2), especially those taken at depths below 12 inches, appear to show a more advanced Aroclor 1254 degradation than was observed in any of the Task 7 samples. The chromatograms for three of these samples are shown in Figure 12. The tri-, tetra-, and pentachlorobiphenyls are reduced significantly in these samples, and the occurrence of the very early eluting peaks suggests the presence of new mono- and dichlorobiphenyls and possibly even biphenyl. This pattern of dechlorination has been observed at other PCB spill sites where extensive dechlorination of Aroclor 1254 and Aroclor 1260 has occurred.

Progressive transformation of both Aroclor 1016/1242 and Aroclor 1254 was observed in the USACE samples. For a more detailed discussion of Aroclor pattern alterations in general and anaerobic biotransformations in New Bedford Harbor (NBH) sediments in particular, the reader is referred to the Yoakum & Associates (YAI) final reports for Task 11 and Task 7, respectively. As was the case for Task 7, one Task 2 sampling site (J-7) showed little if any evidence of PCB transformations (see Figure 13). Both of these sites contained the highest concentration of PCBs found in the respective

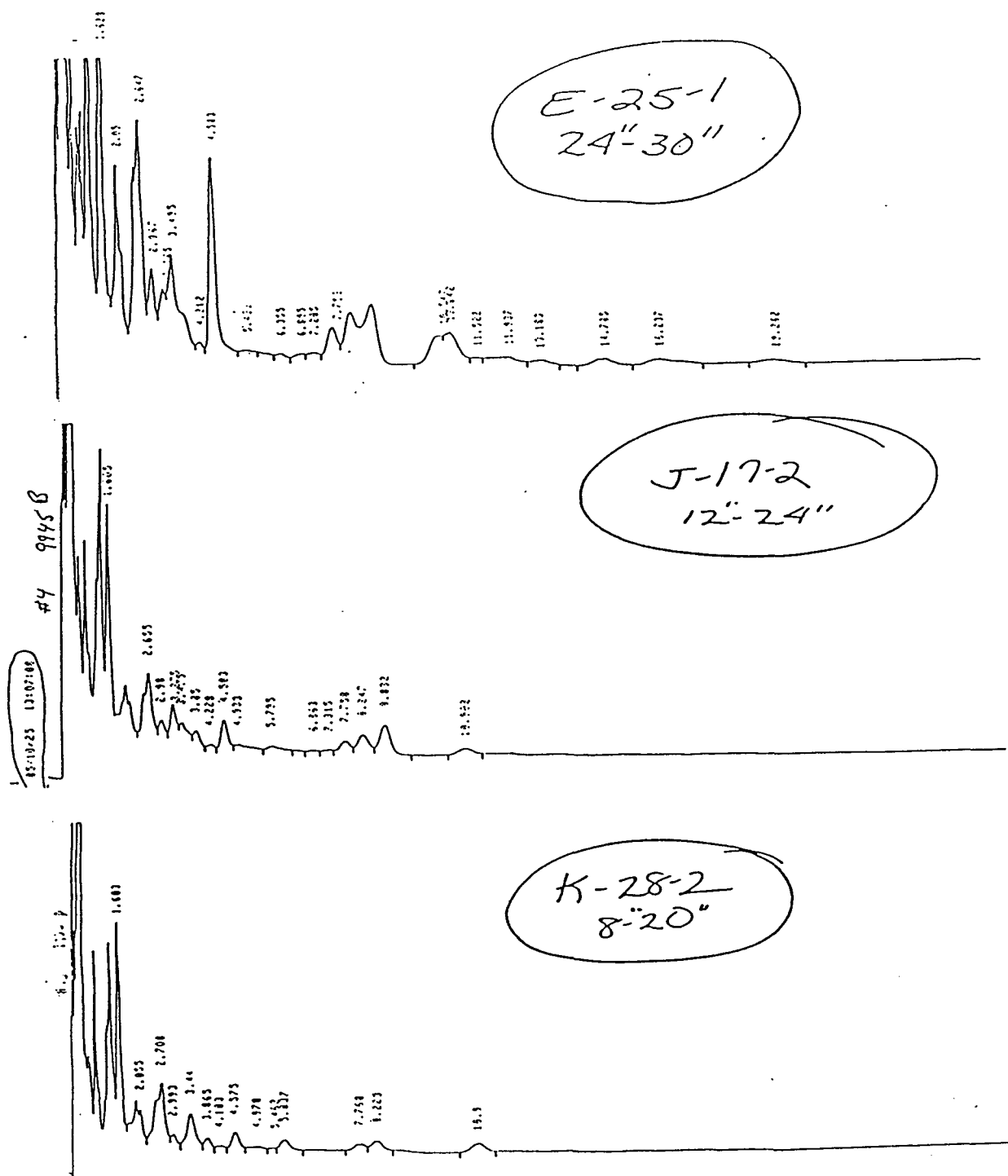
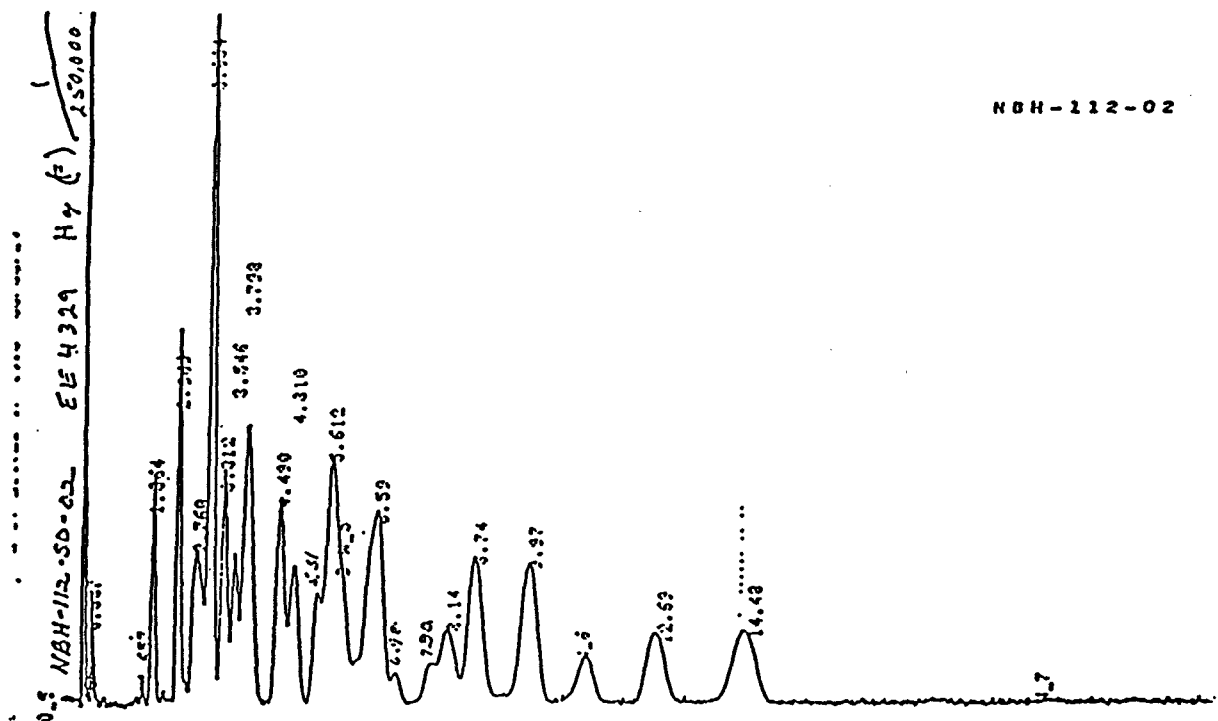


Figure 12. Task 2 Chromatograms Exhibiting More Advanced Aroclor 1254 Degradation



NBH-112-02

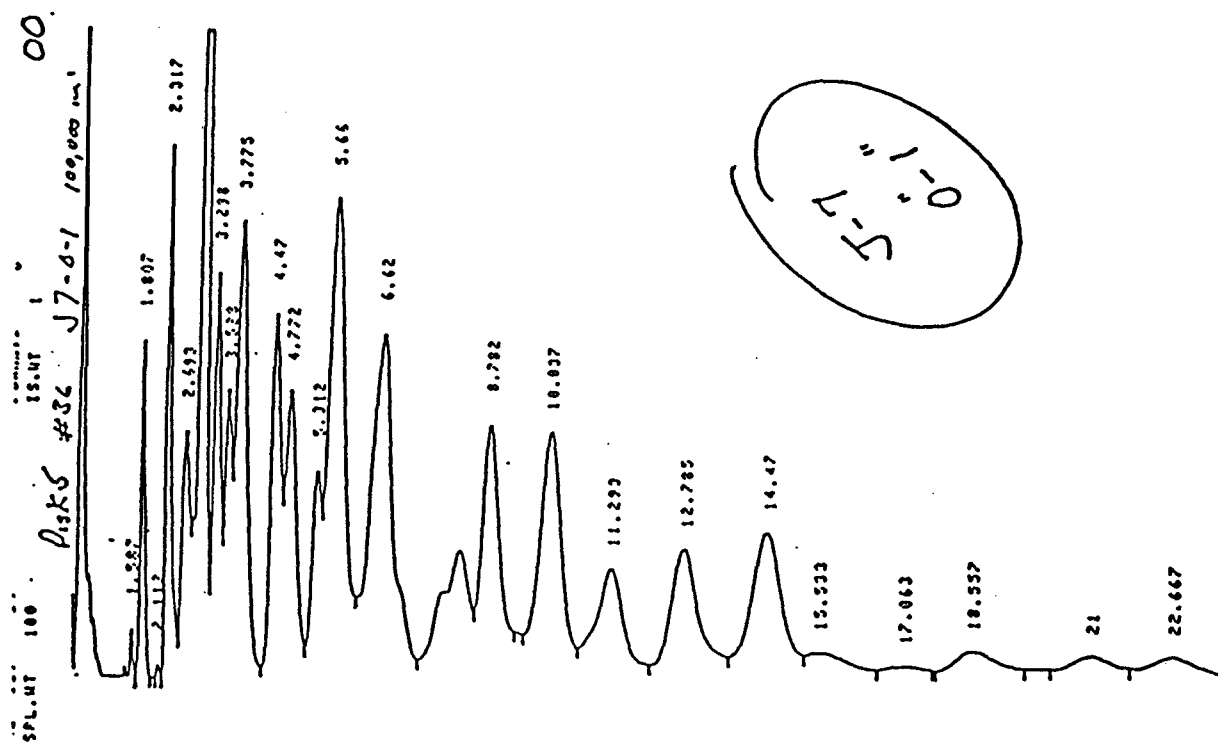


Figure 13. Task 7 (NBH-112-02) and Task 2 (J-7)  
Samples - No PCB Transformations Evident

studies, 76,100 ppm for J-7 (Task 2) and 130,000 ppm for NBH-112-02.

#### 4.1.2 Samples Analyzed by Cambridge Analytical

Associates - EPA Case #5058 (Task 3). The only Aroclor transformation observed in these samples was that due to the environmental aging of the Aroclor 1016/1242. This finding is consistent with that observed for soils at other spill sites. The Task 3 samples are soils collected from a wetlands area; anaerobic dechlorination has been observed only in sediments. Aroclor 1254 pattern alteration was observed in only one sample (AD586). No evidence of biotransformation was seen in any of the samples.

#### 4.1.3 Samples Analyzed by Laucks Testing Laboratory - EPA Case #5131 (Task 8).

Moderate transformations were seen in the Aroclor 1016/1242 region of these chromatograms. Biotransformation in the samples was indicated by the advanced Aroclor 1254 pattern alterations observed at all five of the sampling locations.

#### 4.1.4 Aroclor Transformations Observed in Task 7 Research Investigation.

Per the discussions in Section 4.1.1, transformations in Task 7 samples closely paralleled those observed in the Task 2

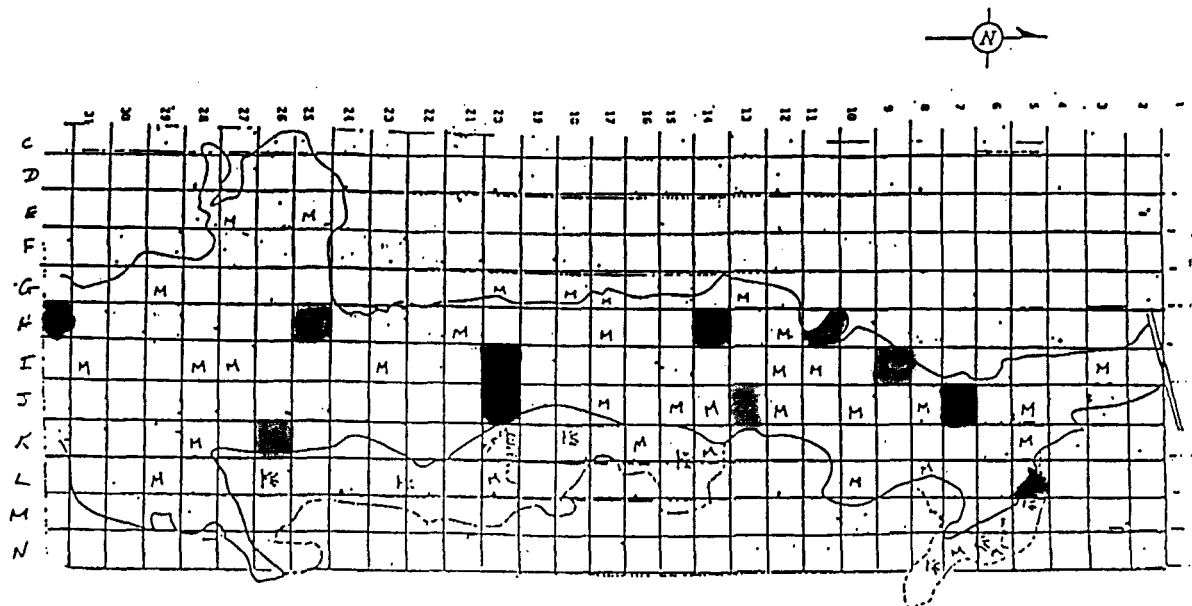
samples. The situation for the eight (8) samples collected in the proximity of the Aerovox plant ran the full spectrum from no apparent transformation for sample NBH-112-02 to advanced transformation for both samples from location NBH-110. Total PCB concentrations for the samples ranged from a low of 180 ppm to a high of 130,000 ppm, with a mean concentration of 30,790 ppm.

#### 4.2 Overview of Transformations in the Upper Estuary of the Acushnet River (north of Coggeshall Street Bridge)

4.2.1 Extent and Distribution of Aroclor Transformations. Plots have been prepared showing the spatial distribution and degree of transformation for both Aroclor 1016/1242 and Aroclor 1254, including all of the data from Tasks 2, 3, 7, and 8. Figure 14 represents samples from the 0-12" depth stratum. A similar plot for sediment depths greater than 12 inches is shown in Figure 15. A color-code has been used to represent the transformation classifications as follows:

- Green = Advanced
- Blue = Moderate to Advanced
- Yellow = Moderate
- Orange = Slight to Moderate
- Pink = Slight
- Red = None

a) Aroclor 1016/1242, Depth 0-12"



b) Aroclor 1254, Depth 0-12"

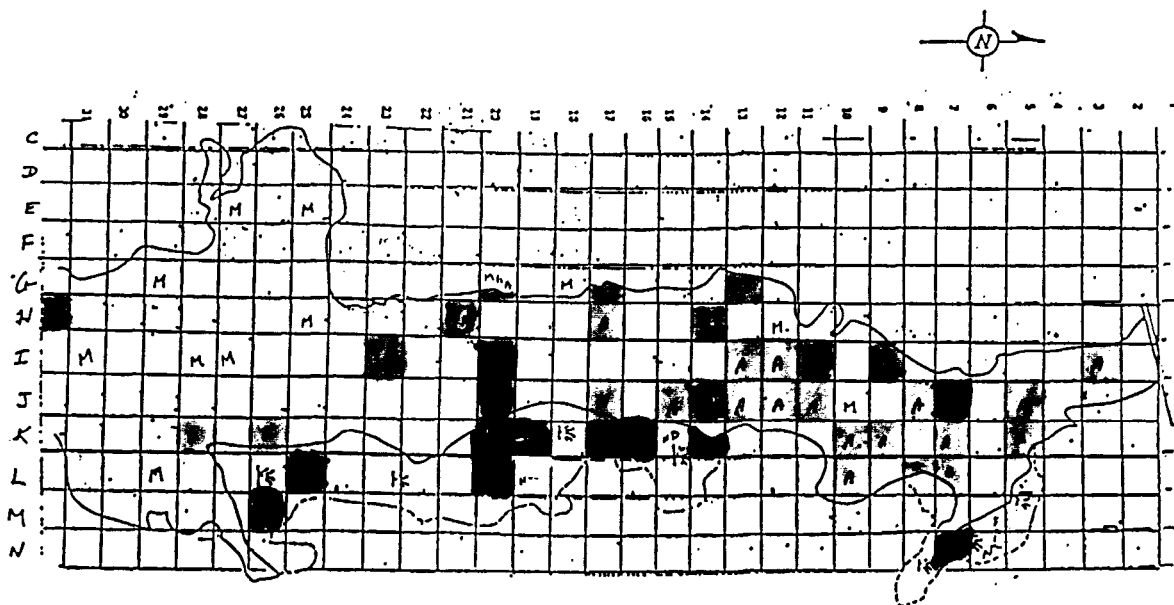
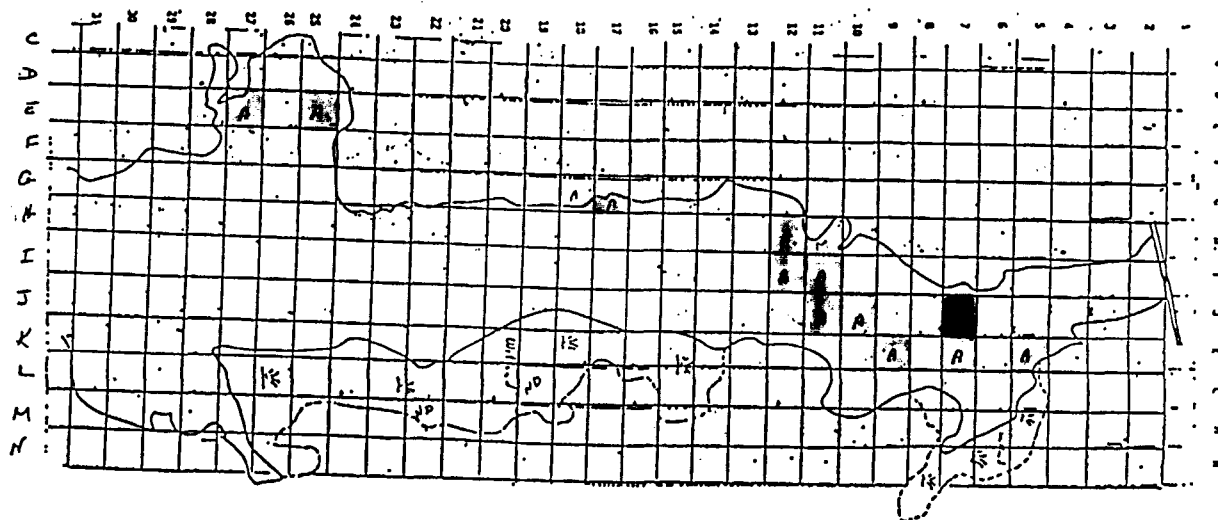
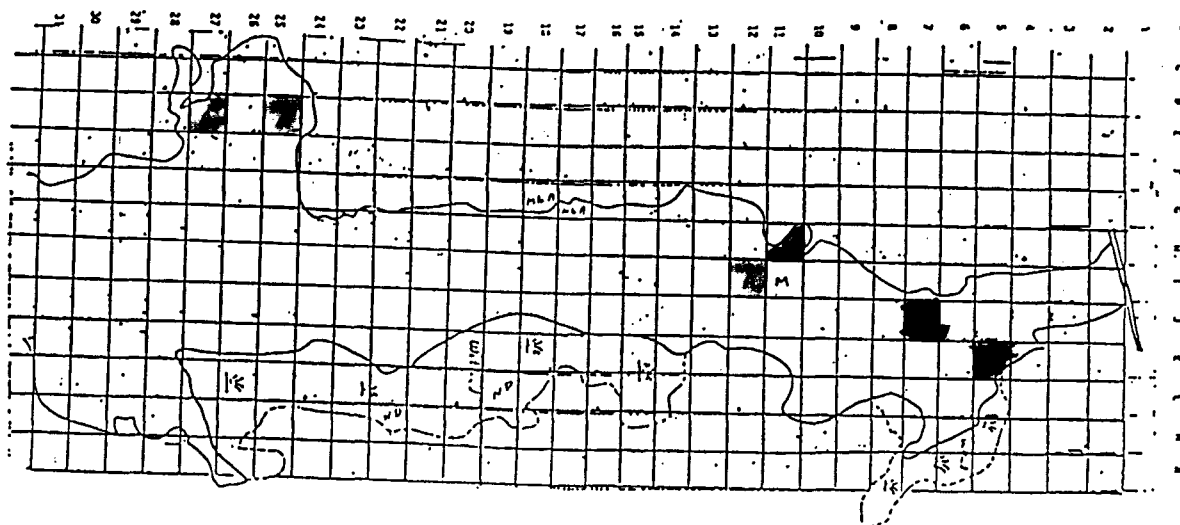


Figure 14. Aroclor Transformations in Upper Estuary Samples (Depth 0-12")





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Based on the data presented in Figure 14, the following observations can be made for the 0-12 inch depth stratum:

1. The moderate transformation classification for Aroclor 1016/1242 predominates, and is observed at 73% of the sites. Its distribution is widespread throughout the entire upper estuary.
2. For Aroclor 1254, 45% of the sediment sites show advanced transformations; all but two of these sites are located in the northern half of the upper estuary. Advanced Aroclor 1254 transformations are seen in two-thirds of the samples from the northern half of the upper estuary.
3. Moderate, moderate to advanced and advanced transformations for Aroclor 1254 are present in all but three of the sites in the southern half of the estuary (14 of 17 locations or 82%).
4. In the wetland soils, "moderate" transformations have occurred for Aroclor 1016/1242. No transformations were observed for Aroclor 1254.

In sediment depths greater than 12 inches the following conditions are notable from review of Figure 15.

1. Moderate to advanced and advanced transformations of Aroclor 1016/1242 are present at 6 of the 9 sites (67%) where PCBs were detected in sufficient amounts to be classified.
2. Advanced transformation of Aroclor 1254 was observed at 12 of the 14 sites (86%) where the presence of PCBs could be confirmed.

In summary, Aroclor transformations were observed at 97% of the sediment sampling sites. Only two sites,

one each from Task 2 and Task 7, showed no apparent Aroclor pattern alterations.

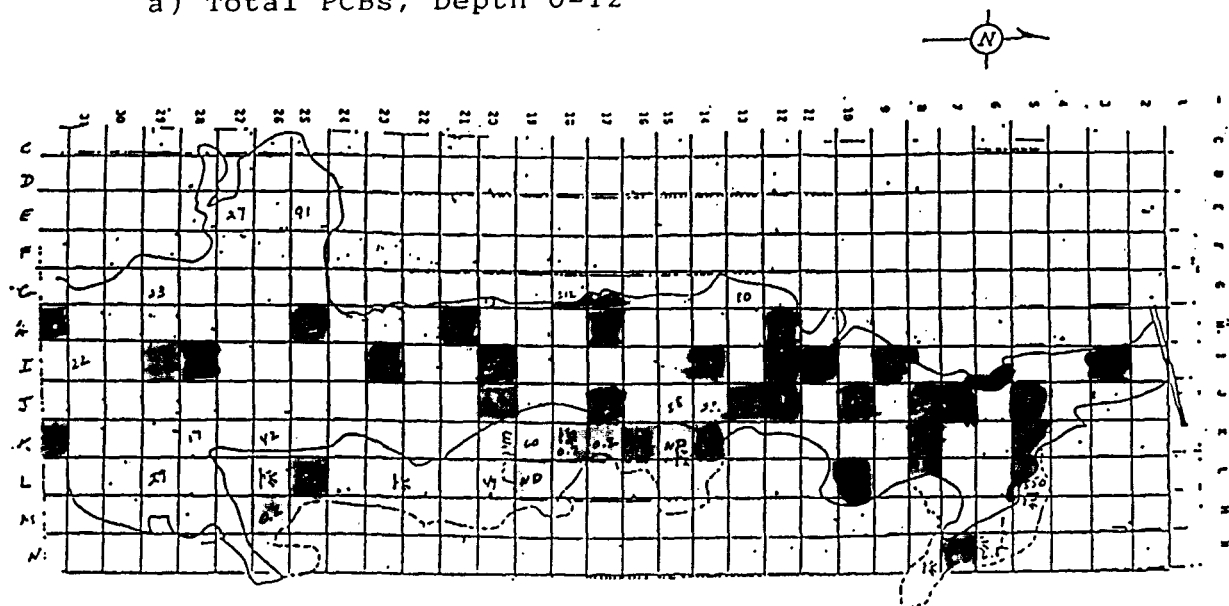
4.2.2 Evaluation of Sediment PCB Concentrations and Aroclor Transformations. Total PCB concentrations (ppm) for the 0-12" and >12" sediment depths have been plotted in Figure 16. Concentration ranges have been color-coded as follows:

<u>PCB Concentration (ppm)</u>	<u>Color</u>
<1	= Green
1-9.9	= Blue
10-99	= Yellow
100-999	= Orange
1000-9999	= Pink
>10,000	= Red

A comparison of Figures 14 and 16 shows that there does not appear to be a correlation between the moderate Aroclor 1016/1242 transformation and total PCB concentrations in the upper estuary. However, in the northern half of the upper estuary, there is a direct correlation between high total PCB concentrations (up to 36,000 ppm) and the advanced transformation of Aroclor 1254.

By comparing Figures 15 and 16, it is seen that for areas of concern relative to total PCB concentrations at depths >12 inches, advanced transformations of both Aroclor 1016/1242 and Aroclor 1254 are occurring.

a) Total PCBs, Depth 0-12"



b) Total PCBs, Depth >12"

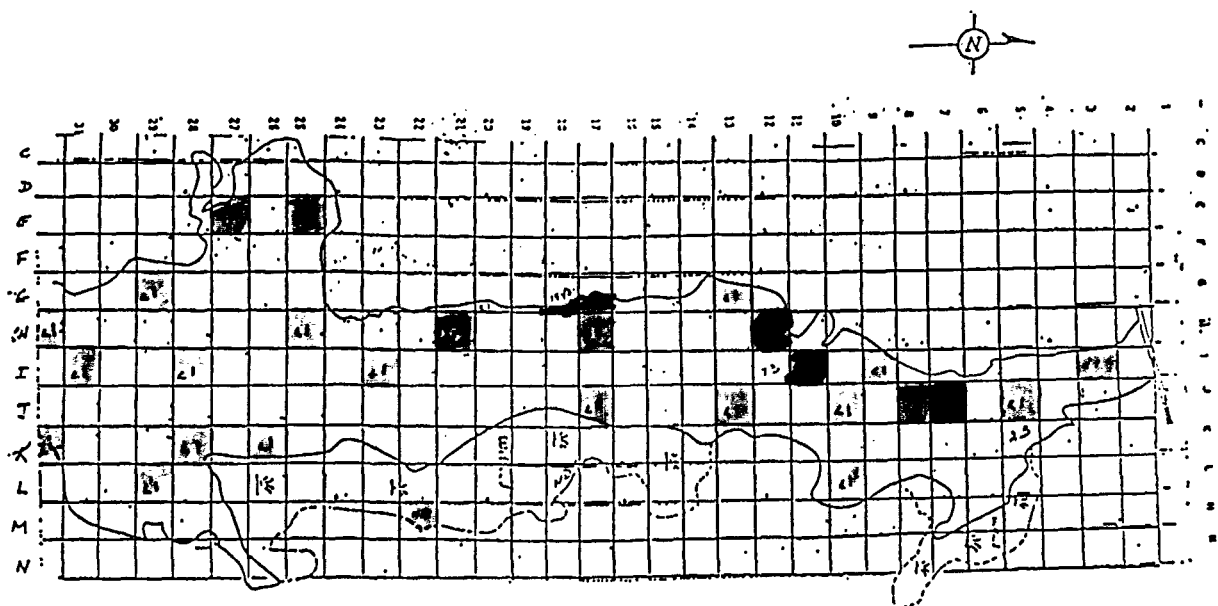


Figure 16. Total PCB Concentration (ppm) Profiles of Upper Estuary

## 5.0 SUMMARY

By using the sample chromatograms from the USACE FIT Sampling Program and the transformation classification system developed by YAI, the extent and distribution of Aroclor transformations in upper estuary samples have been determined. The chromatograms show strong evidence of biotransformations of the type associated primarily with the anaerobic dechlorination of PCBs at approximately 97% of the sampling sites located in the upper estuary of the Acushnet River.

## REFERENCES

1. Method 617, "Organochloride Pesticides and PCBs," EMSL, U. S. Environmental Protection Agency: Cincinnati, OH (1982).
2. Method 8080, "Organochlorine Pesticides and PCBs," Test Methods for Evaluating Solid Waste, SW-846, 2nd Ed., U. S. Environmental Protection Agency, Office of Solid Waste and Emergency Response: Washington, DC (1982).
3. Yoakum, A. M., "Special Research Report - Evaluation of PCB Transformations in New Bedford Harbor Sediments," Task 7 Final Report, Yoakum and Associates, Inc.: Lenoir City, TN (1989).
4. Yoakum, A.M., "PCB Background Information Relevant to the New Bedford Harbor Project," Task 11 Final Report, Yoakum and Associates, Inc.: Lenoir City, TN (1989).

**APPENDIX A**

**TERMS AND ABBREVIATIONS**

Table A-1. TERMS

"Additive Effect": To heighten or increase the intensity of a peak in a chromatogram (enhancement).

Anaerobe: A microorganism that flourishes without free oxygen.

Anaerobic microbial (bio)degradation: The reduction of a chemical component from a higher to a lower type by the action of anaerobic microbes.

Anaerobic biotransformations: Changes brought about as the result of the action of anaerobic bacteria.

Anaerobic dechlorination: A specific PCB microbial degradation process whereby chlorine is selectively removed from a congener as the result of anaerobic microbial actions.

Aroclor: Trade name (Monsanto) for a series of commercial PCB and polychlorinated terphenyl mixtures marketed in the United States.

Aroclor degradation: A reductive modification with respect to the proportions of the individual PCB congeners present in the specific Aroclor.

Aroclor transformation: Any change (either reduction or enhancement) in the unique characteristic of the composition of a specific Aroclor.

Chromatogram: A tracing of the detector output from a chromatograph which consists of a series of peaks observed over time.

Chromatographic pattern alteration: Any change or modification which occurs in the chromatogram produced by a known reference material (e.g., a specific Aroclor).

Congener: One of the 209 PCBs or other group of compounds, not necessarily the same homolog.

Degrade: To reduce from a higher to a lower type.

Enhance: To heighten or increase in intensity.

Table A-1. TERMS (Cont'd)

Environmental aging (weathering): The process whereby the Aroclor(s) present in an environmental sample undergoes modification with respect to the proportions of individual PCB congeners present as the result of partial vaporization, adsorption onto surfaces, and/or extraction into water. True molecular solution in water is shown (on chromatograms) as the non-selective loss of the more volatile and more water-soluble congeners from the Aroclors in the sediments.

"High-end drop-off": The pattern alteration observed when higher chlorinated PCB congeners (usually penta- and hexa-) undergo anaerobic dechlorination.

High resolution gas-liquid chromatography: Gas chromatography with a capillary column.

Homolog: One of the 10 degrees of chlorination of PCBs ( $C_{12}H_9Cl$  through  $C_{12}Cl_{10}$ ) or other group of compounds varying by systematic addition of a substituent.

Isomer: Any PCB or other compound which has the same molecular formula, but different positional substitutions. 2,2'-Dichlorobiphenyl and 2,3-dichlorobiphenyl are isomeric; 4-chlorobiphenyl and 2,3,4-trichlorobiphenyl are not.

"Low-end drop-off": The pattern alteration observed when lower chlorinated PCB congeners are removed from samples by weathering.

Part per million (ppm): One part in 10<sup>6</sup>.

Pattern alterations: Changes in a characteristic chromatographic pattern. The effect of the changes will be reflected by peak enhancements, reductions, or both. (See chromatographic pattern alterations.)

Polychlorinated biphenyl (PCB): One of 209 individual compounds having the molecular formula  $C_{12}H_nCl_{10-n}$ , where  $n = 0-9$ . This definition includes monochlorobiphenyls, but not biphenyl.

PCB degradation: A conversion whereby a PCB congener of a higher chlorine content is reduced (converted) to one of a lower chlorine content.

PCB transformation: Any change whereby a PCB congener is converted into another compound.



Table A-1. TERMS (Cont'd)

Qualitative: Having to do with establishing the presence or identity of a compound.

Quantitative: Having to do with measuring the amount or concentration of a compound in a sample.

Retention time: Time between injection and detection of a compound on a chromatographic system under specified conditions, expressed in seconds or minutes.

Transformation: Any change which gives a different appearance.

Weathering: A process which gives a compositional change in an Aroclor residue (see environmental aging).

**Table A-2. ABBREVIATIONS**

<b>BEC</b>	<b>Balsam Environmental Consultants, Inc.</b>
<b>EPA</b>	<b>(U.S.) Environmental Protection Agency</b>
<b>GC</b>	<b>Gas-liquid chromatography (column type unspecified)</b>
<b>GC/EC</b>	<b>Gas chromatography/electron capture</b>
<b>GC/MS</b>	<b>Gas-liquid chromatography/mass spectrometry (ionization mode unspecified)</b>
<b>NBH</b>	<b>New Bedford Harbor</b>
<b>PCB</b>	<b>Polychlorinated biphenyl</b>
<b>ppm</b>	<b>Parts per million (<math>10^{-6}</math>)</b>
<b>RT</b>	<b>Retention time</b>
<b>USACE</b>	<b>(U.S.) Army Corps of Engineers</b>
<b>YAI</b>	<b>Yoakum &amp; Associates, Inc.</b>

APPENDIX VII

TASK 12

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**REVIEW OF PCB ANALYTICAL DATA AND THE  
CLASSIFICATION OF AROCLOR TRANSFORMATIONS FOR  
SELECTED NUS/GZA DRILLING STATIONS**

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**September 8, 1989**

**Y & A Project NMF-3003 Task 12**

**DRAFT**

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REVIEW OF PCB ANALYTICAL DATA AND THE  
CLASSIFICATION OF AROCLOR TRANSFORMATIONS FOR  
SELECTED NUS/GZA DRILLING STATIONS

Y & A PROJECT NMF-3003 TASK 12

1.0 INTRODUCTION

The Task 12 assignment involved the evaluation of 23 samples from nine sediment sampling stations from the NUS/GZA drilling program. Aroclor 1248 was reported to be present at all of the sites. Three stations were chosen from each of the middle, lower, and outer harbor areas for evaluation purposes. The locations of the selected stations are noted on Figure 1. Four EPA contract laboratories--York Laboratories, Division of YWC; S-Cubed, Division of Maxwell Laboratories, Inc.; ERCO, Division of ENSCO, Inc.; and PEI Associates, Inc.--performed the PCB analyses.

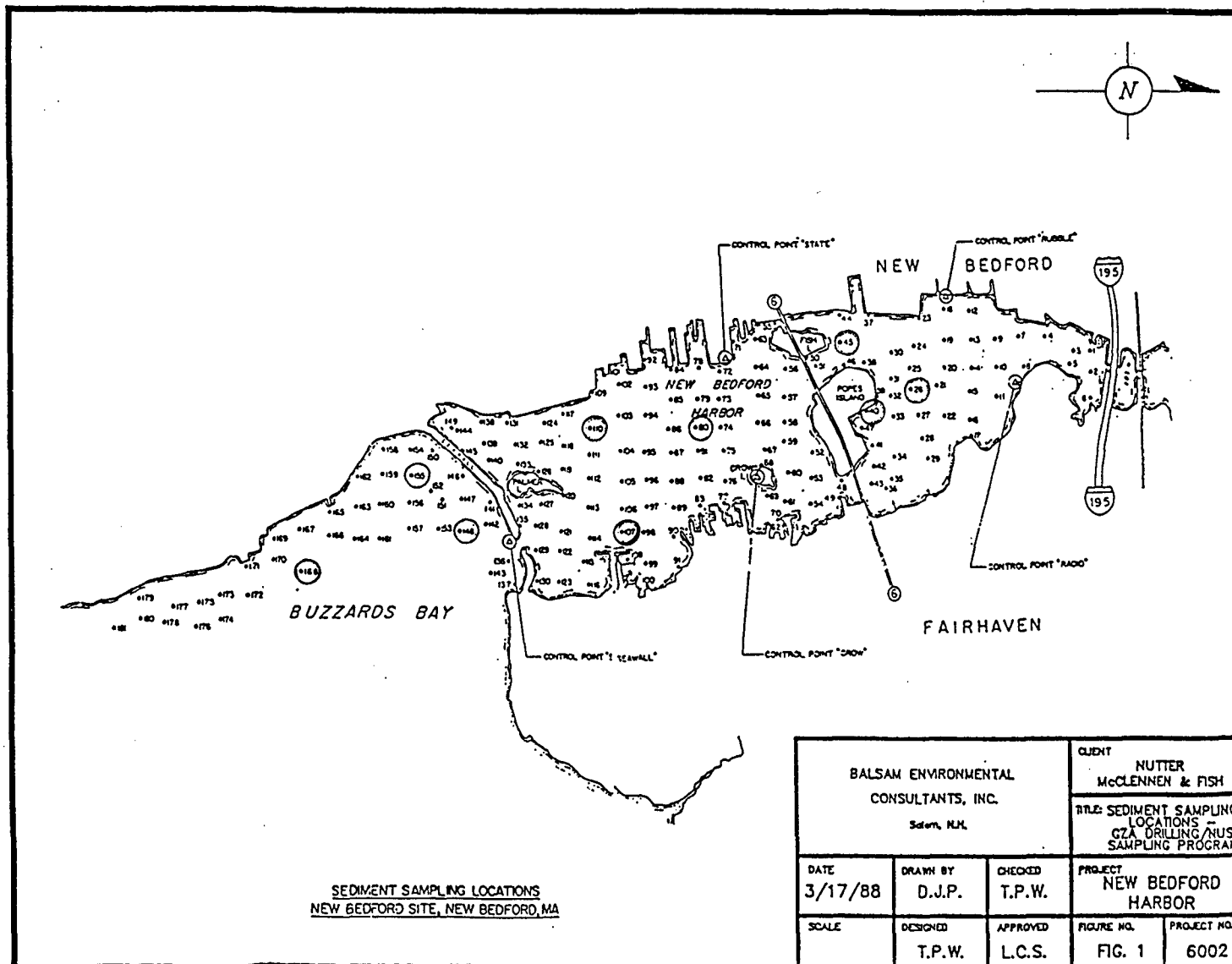
2.0 DATA REVIEW

Two key problems were observed during the review of the Task 12 chromatograms:

1. Sulfur is present in seven of the samples,
2. The quality of the chromatograms for five samples is extremely poor because of background interference.

Both of these problems indicate inadequate clean-up of the sample extracts prior to analysis.

The electron capture detector, used in the determination of PCBs by gas chromatography, is considered a selective,





chlorine sensitive detector. It does, however, respond to numerous non-PCB compounds when they are present in the sample extracts. Non-PCB interferences of the type observed in these samples can be completely removed, or at least significantly reduced, when the appropriate clean-up procedures are employed.

#### 2.1 Sulfur Interference

Sulfur is a common contaminant in sediment samples. Its presence, however, is easily recognized when it is present at high concentrations because of its uniquely characteristic chromatographic pattern. Sulfur interferences observed in five of the Task 12 samples are illustrated in Figure 2; chromatograms (a) through (e) demonstrate progressively decreasing concentrations of sulfur in the sample extracts. Sulfur was observed in samples analyzed by PEI and S-Cubed.

#### 2.2 Background Interference

Pattern alterations due to the presence of non-halogen containing compound interferences can occur either as discrete peaks or as non-descript background disturbances of the type illustrated in Figure 3. This effect frequently results from oil and grease contamination. The presence of this type of interference creates serious matrix effects which have an adverse impact on data quality. Many of the chromatograms generated by York Laboratories had this problem.

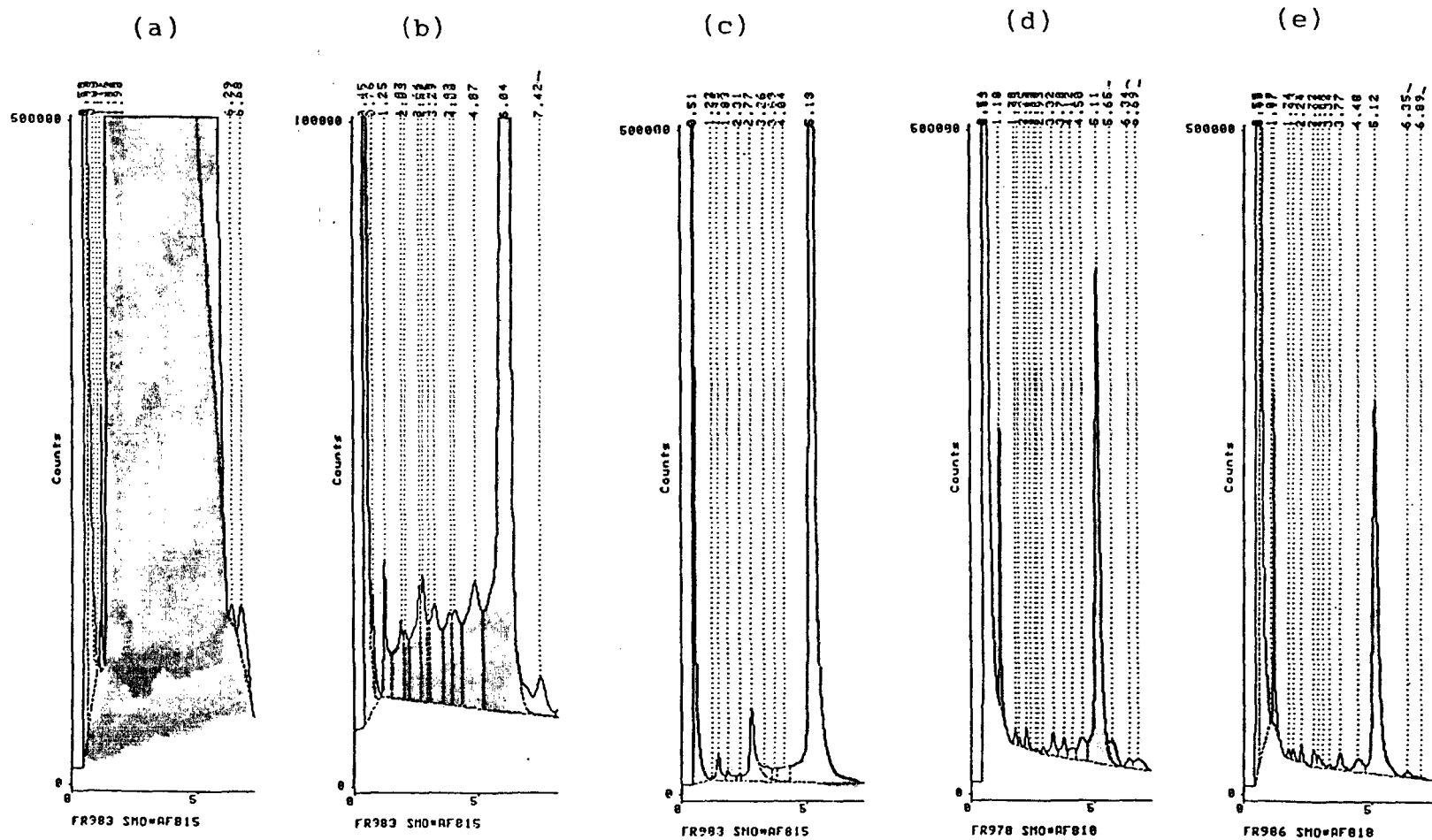


Figure 2. Sulfur Interference in Task 12 Samples

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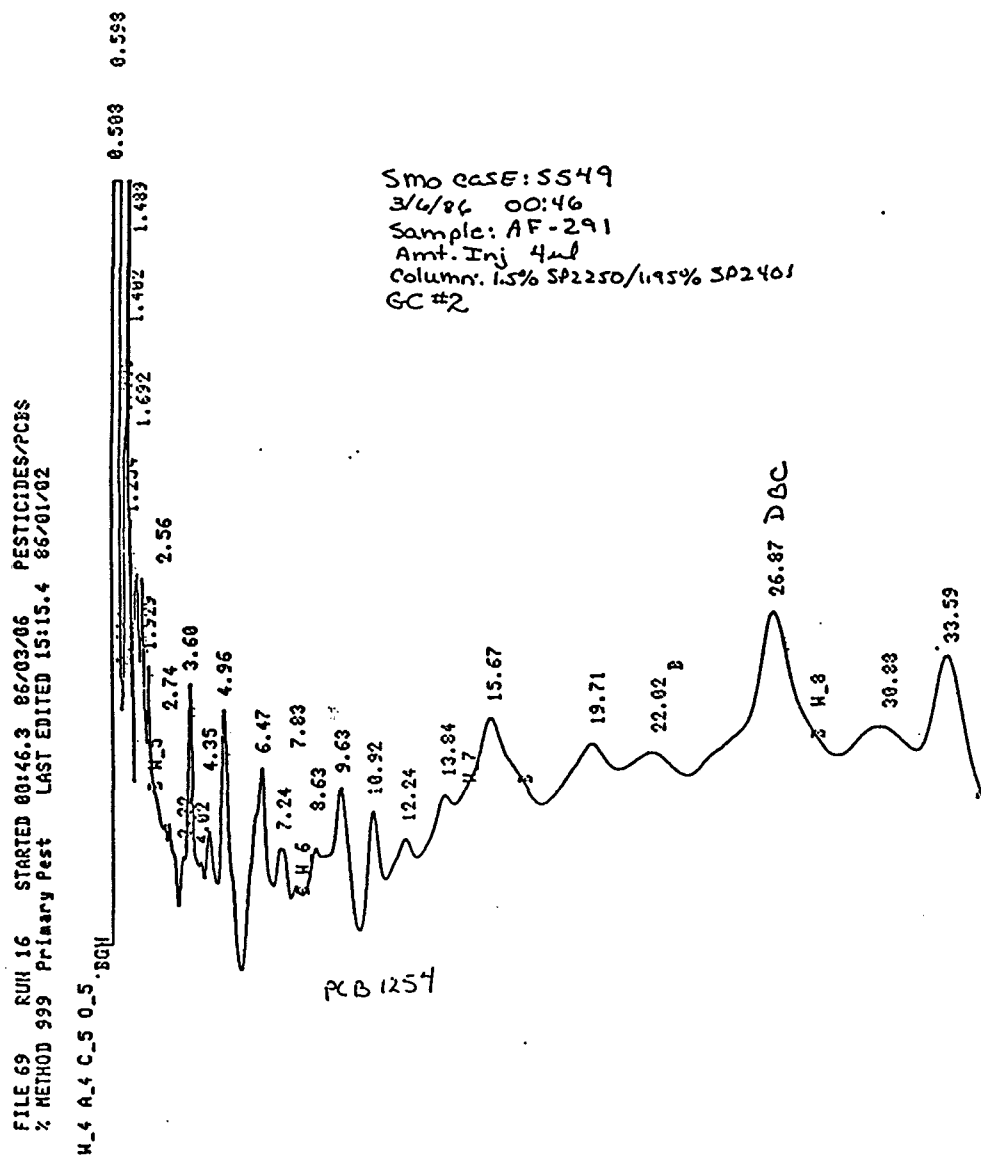


Figure 3. Chromatogram Illustrating Background Interference from Non-halogen Containing Compound

### 3.0 DATA EVALUATION

#### 3.1 Pattern Alterations in Task 12 Samples

Pattern alteration resulting from the environmental aging of Aroclor 1016/1242 was observed in all but one of the samples (AF270) where PCBs were detected.

Environmental aging or "weathering" is defined as the process whereby the Aroclor(s) present in an environmental sample undergoes modification with respect to the proportions of individual PCB congeners present as the result of partial vaporization, adsorption onto surfaces, and/or extraction into water. The Aroclor pattern alterations which occur as the result of weathering are distinctively different from those which result from anaerobic PCB degradation.

During weathering, Aroclors 1016 and 1242 experience a non-selective loss of the more volatile or soluble congeners, yielding a residue which demonstrates low-end drop-off and, usually, a high-end enhancement of peaks. As a result, the pattern of the "weathered" Aroclor 1016/1242 residue resembles the pattern of Aroclor 1248, the next higher chlorinated Aroclor in the percent chlorination sequence. This phenomenon is demonstrated in Figure 4. Chromatogram (a) is a standard of Aroclor 1016. A severely weathered Aroclor 1016 residue is shown in chromatogram (b). This chromatogram (b) has a

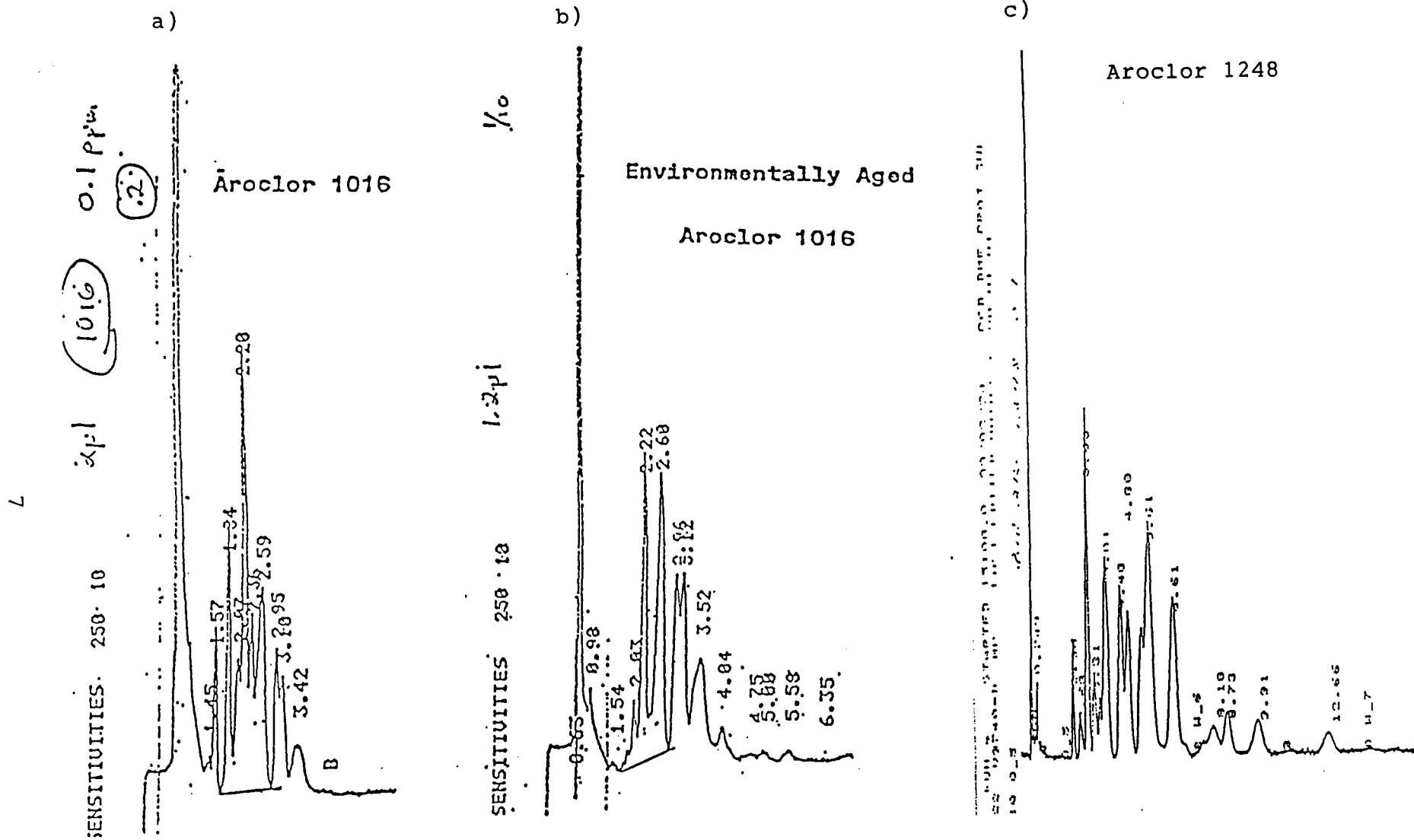


Figure 4. Demonstration of Pattern Alteration Due to Weathering

congener distribution in the tri- and tetrachloribiphenyl region which is very similar to that of chromatogram (c), which is an Aroclor 1248 standard. Less advanced environmental aging of Aroclor 1016/1242 is shown in chromatogram (a) of Figure 5. The environmental aging indicator peaks for Aroclor 1016/1242 in Sample AF811 (a) and a mixed Aroclor 1242/1254 standard (b) are highlighted in yellow.

Evidence of Aroclor 1254 pattern alteration as the result of the biotransformation of PCBs was seen in 60 percent (9 of 15) of the PCB-containing samples. Sediments from six of the nine sampling sites selected for review showed "high-end" drop-off of the Aroclor 1254 pattern. Only one sample, AF214 from site #155, showed pattern alterations which suggested biotransformation in the Aroclor 1016/1242 region of the chromatogram. The chromatogram for this sample is contained in Figure 6. The Aroclor 1254 alterations (color-coded blue) can be seen by comparing the sample chromatogram (b) to the Aroclor 1254 standard (c). In addition, interference peaks in the sample due to sulfur interference are color-coded green, and are comparable to the similarly highlighted peaks in the demonstrated chromatogram (a).

### 3.2 Identification and Quantitation of Aroclors

Aroclor 1016 and/or 1242, as well as Aroclor 1254 are present in the samples. Aroclor 1016 and Aroclor

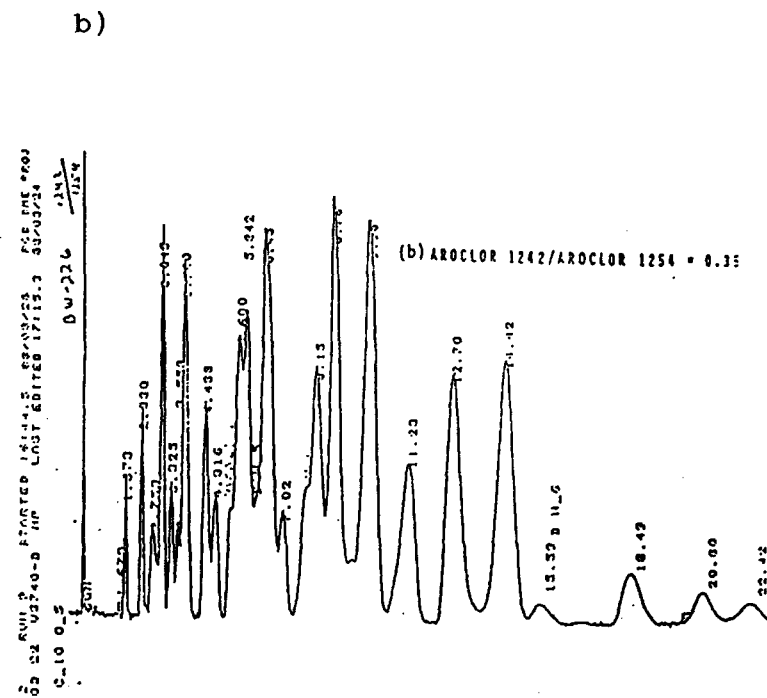


Figure 5. Illustration of Environmental Aging of Aroclor 1016/1242 in Task 12 Sample AF811 (a)

b) Sample AF 214

c) Aroclor 1254

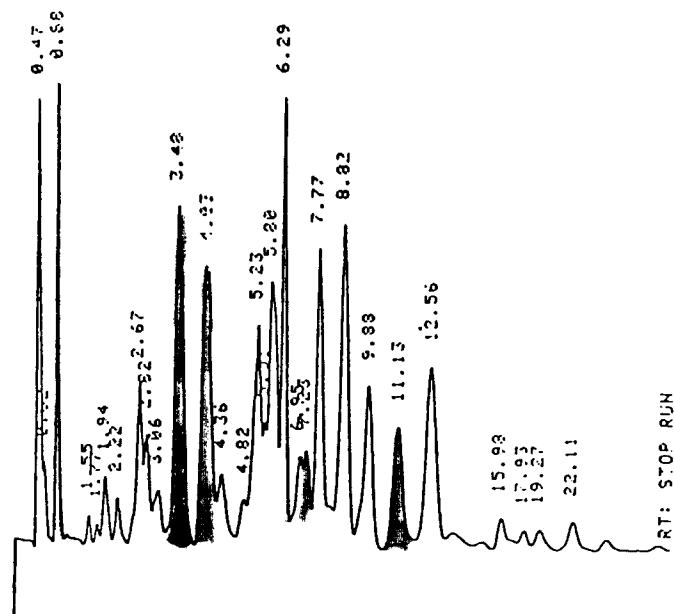


Figure 6. Illustration of Aroclor 1254 Alterations and Sulfur Interference in Sample AF214

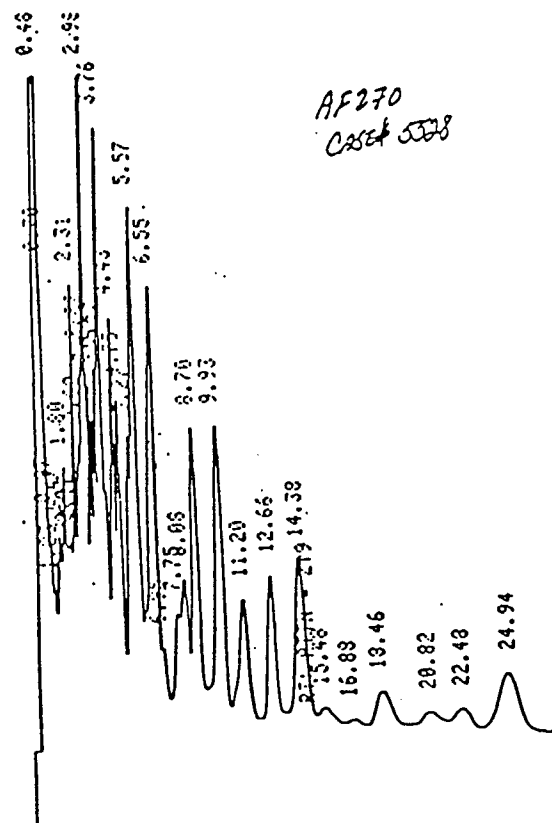


1242 have similar PCB congener distributions in the di-, tri-, and tetrachlorobiphenyl region of the chromatograms. These similarities make it most difficult to distinguish between Aroclor 1016 and Aroclor 1242 in a sample when Aroclor 1254 is also present in that sample. Therefore, the notation Aroclor 1016/1242 is used throughout this document. A more complete discussion of this problem can be found in the Task 11 PCB reference document.

Chromatogram (a) of Figure 7 illustrates little (if any) pattern alteration for Aroclor 1016/1242 and no alteration for Aroclor 1254. A mixed standard containing a 1.78 ratio of Aroclor 1242 to Aroclor 1254 is shown for comparison in chromatogram (b). However, this sample (AF270) was identified by ERCO as containing Aroclor 1248 and Aroclor 1254.

The weathering of Aroclor 1016/1242 is somewhat more advanced in the balance of the samples where PCBs were detected. The degree of weathering of Aroclor 1016/1242 defined as "Very Slight" is illustrated by chromatogram (a) for sample AF811 in Figure 5. The PCBs present in this sample were identified by PEI as being Aroclor 1242 and Aroclor 1254. As can be seen in Figure 8, the weathering of Aroclor 1016/1242, classified as "slight" in samples AF274 and AF400, is not as advanced as that of

a)



b)

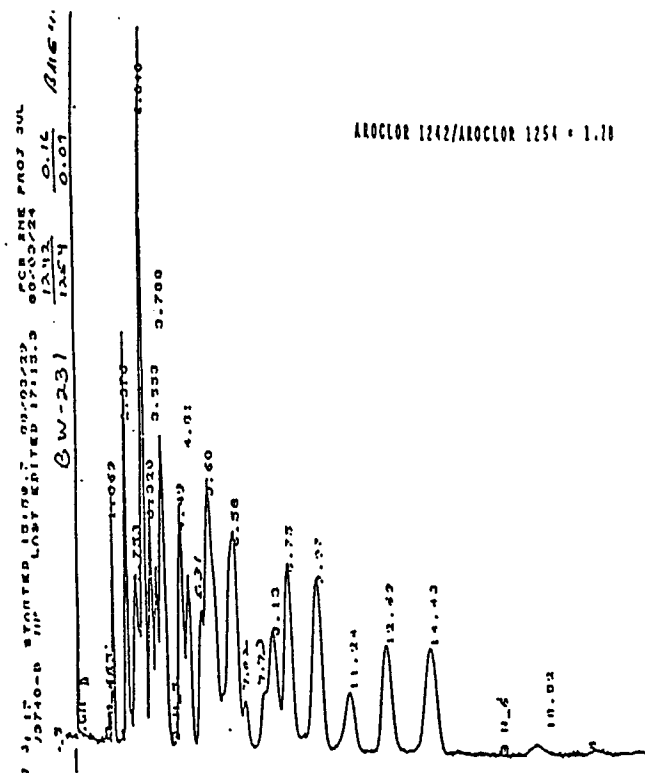


Figure 7. Comparisons of Chromatograms for Task 12 Sample AF270 (a) and Aroclor 1242/Aroclor 1254 Mixed Standard (b)

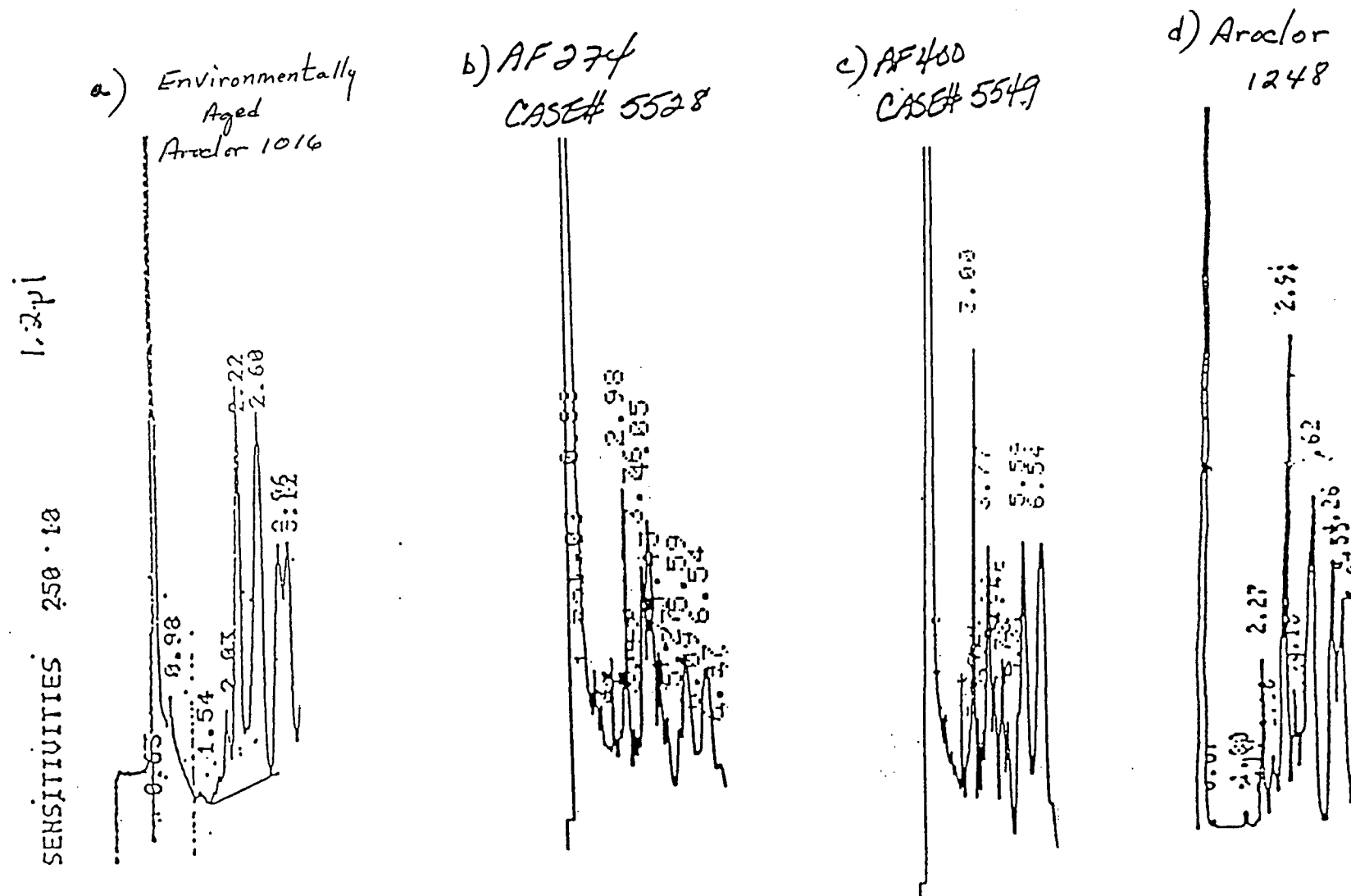


Figure 8. Comparison of Environmentally Aged Aroclor 1016/1242 and Aroclor 1248 Standard

the environmentally aged Aroclor 1016 in chromatogram (a). There is, however, a close resemblance between the two samples (b and c) and the Aroclor 1248 standard. These samples were identified by ERCO as containing Aroclor 1248 as well as Aroclor 1254. In fact, three of the four laboratories involved with the project identified the weathered Aroclor 1016/1242 as Aroclor 1248. Since no new congeners occurred in these samples as the result of weathering (as opposed to the occurrence of new congeners in biotransformed samples), the use of Aroclor 1248 for the quantitation of these samples will yield valid quantitative results because there is no exclusion of PCB peaks from the area quantitations.

#### 4.0 CLASSIFICATION OF PCB TRANSFORMATIONS IN TASK 12 SAMPLES

A system for qualitatively classifying the degree of PCB transformation observed in sediment samples from New Bedford Harbor was developed as a part of Y & A Project NMF-3003 Task 7. By expanding this same system, the following definitions can be applied to the classification of Aroclor transformations observed in the Task 12 samples:

1. Very Slight alteration of Aroclor 1016/1242, sample shows "low-end" reduction of the first two indicator peaks.
2. Slight alteration of Aroclor 1016/1242, reduction of first two indicator peaks much more obvious.
3. Slight alteration of Aroclor 1254, pattern demonstrates "high-end" congener reduction.

4. Moderate alteration of Aroclor 1254, pattern demonstrates "high-end" congener reduction and enhancement of peaks in the transition (tetrachlorobiphenyl) region of chromatogram.

Classification of the pattern alterations observed in the Task 12 samples reviewed by Yoakum & Associates, Inc. (YAI) is summarized in Table 1; an evaluation of chromatogram quality and the degree of sulfur interference present is also included here.

A comparison of representative chromatograms from Task 12 and Task 7 is provided in Figure 9. The chromatograms (a and c) for samples AF-302 and NBH-112-02, respectively, show no evidence of Aroclor 1254 alteration. Slight alteration of both Aroclor 1016/1242 and Aroclor 1254 is shown by sample AF290 (b) from Task 12 and NBH-102 (d) from Task 7.

## 5.0 OVERALL ASSESSMENT

The Task 12 data evaluation has shown the following:

1. The clean-up procedures required by the CLP analysis protocol apparently were not followed by three of the participating laboratories since sulfur and background interferences were present in a number of the samples.
2. The predominant PCBs found in the samples are Aroclor 1016/1242 and Aroclor 1254.
3. The environmentally aged Aroclor 1016/1242 was misidentified by three of the four laboratories as Aroclor 1248. The impact of this misidentification on the quantitative data is minimal, however, since much of the data has been qualified as quantitative estimates by the EPA auditors due to unrelated QA/QC deficiencies.

TABLE 1. CLASSIFICATION OF PCB TRANSFORMATIONS IN TASK 12 SAMPLES  
(GZA/NUS SEDIMENT PROGRAM)

<u>Location Grid #</u>	<u>26</u>	<u>26</u>	<u>26</u>	<u>26</u>
SMO Number	AF290	AF810	AF291	AF292
Sample Depth (inches)	0-6	6-12	12-18	24-30
Analytical Lab	York	PEI	York	York
EPA Case #	5549	6054	5549	5549
Reported Results (ppm)				
Aroclor 1242	-	-	-	-
Aroclor 1248	J23.	-	-	J0.02
Aroclor 1254	J21.	0.59	J0.60	J0.06
YAI EVALUATION				
Chromatogram Quality	G	P	P	P
Sulfur Interference	-	***	-	-
Alteration Classification				
Aroclor 1016/1242	S	-	(2)	(2)
Aroclor 1254	S	(1)	(2)	(2)
Alteration Source				
Aroclor 1016/1242	EA	-	(2)	(2)
Aroclor 1254	T	(1)	(2)	(2)

Notes: (1) Chromatogram intensity insufficient to classify.

(2) Non-PCB interference present.

\*, \*\*, \*\*\* = Intensity of sulfur interference.

- = Not detected in sample.

Chromatogram Quality

G = Good  
A = Acceptable  
P = Poor

Alteration Source

EA = Environmental Aging  
T = Transformation

Alteration Classification

VS = Very Slight  
S = Slight  
M = Moderate  
A = Advanced

TABLE 1. CLASSIFICATION OF PCB TRANSFORMATIONS IN TASK 12 SAMPLES  
(GZA/NUS SEDIMENT PROGRAM) - Cont'd.

<u>Location Grid #</u>	<u>40</u>	<u>40</u>	<u>40</u>	<u>40</u>
SMO Number	AF302	AF811	AF303	AF304
Sample Depth (inches)	0-6	6-12	12-18	24-30
Analytical Lab	York	PEI	York	York
EPA Case #	5549	6054	5549	5549
Reported Results (ppm)				
Aroclor 1242	-	J7.9	-	-
Aroclor 1248	J7.1	-	J3.6	-
Aroclor 1254	J2.6	J8.8	J8.7	J0.67
YAI EVALUATION				
Chromatogram Quality	G	A	P	A
Sulfur Interference	-	-	-	-
Alteration Classification				
Aroclor 1016/1242	VS	VS	VS	-
Aroclor 1254	None	None	None	None
Alteration Source				
Aroclor 1016/1242	EA	EA	EA	-
Aroclor 1254	-	-	-	-

Notes: (1) Chromatogram intensity insufficient to classify.  
 (2) Non-PCB interference present.  
 \*, \*\*, \*\*\* = Intensity of sulfur interference.  
 - = Not detected in sample.

<u>Chromatogram Quality</u>	<u>Alteration Source</u>	<u>Alteration Classification</u>
G = Good A = Acceptable P = Poor	EA = Environmental Aging T = Transformation	VS = Very Slight S = Slight M = Moderate A = Advanced

TABLE 1. CLASSIFICATION OF PCB TRANSFORMATIONS IN TASK 12 SAMPLES  
(GZA/NUS SEDIMENT PROGRAM) - Cont'd.

<u>Location Grid #</u>	<u>45</u>	<u>45</u>	<u>45</u>	<u>45</u>	<u>45</u>
SMO Number	AF399	AF815	AF400	AF851	AF864
Sample Depth (inches)	0-6	6-12	12-18	24-36	24-36
Analytical Lab	ERCO	PEI	ERCO	ERCO	ERCO
EPA Case #	5549	6054	5549	5549	5549
Reported Results (ppm)					
Aroclor 1242	-	-	-	-	-
Aroclor 1248	1.7	-	2.9	0.56	0.91
Aroclor 1254	1.9	7.0	3.3	0.70	1.20
YAI EVALUATION					
Chromatogram Quality	A	P	A	A	A
Sulfur Interference	-	***	-	-	-
Alteration Classification					
Aroclor 1016/1242	S	(2)	S	S	S
Aroclor 1254	S	(2)	S	S	S
Alteration Source					
Aroclor 1016/1242	EA	(2)	EA	EA	EA
Aroclor 1254	T	(2)	T	T	T

Notes: (1) Chromatogram intensity insufficient to classify.  
(2) Non-PCB interference present.  
\*, \*\*, \*\*\* = Intensity of sulfur present.  
- = Not detected in sample.

<u>Chromatogram Quality</u>	<u>Alteration Source</u>	<u>Alteration Classification</u>
G = Good	EA = Environmental Aging	VS = Very Slight
A = Acceptable	T = Transformation	S = Slight
P = Poor		M = Moderate
		A = Advanced



TABLE 1. CLASSIFICATION OF PCB TRANSFORMATIONS IN TASK 12 SAMPLES  
(GZA/NUS SEDIMENT PROGRAM) - Cont'd

<u>Location Grid #</u>	<u>80</u>	<u>107</u>	<u>110</u>	<u>148</u>	<u>155</u>
SMO Number	AE357	AE512	AF270	AF274	AF214
Sample Depth (inches)	0-6	0-6	0-6	0-6	0-6
Analytical Lab	ERCO	YORK	ERCO	ERCO	S <sup>3</sup>
EPA Case #	5549	5450	5528	5528	5503
Reported Results (ppm)					
Aroclor 1242	-	-	-	-	-
Aroclor 1248	1.7	0.84	J9.8	J1.6	J2.4
Aroclor 1254	1.3	0.64	J3.8	J0.98	J7.7
YAI EVALUATION					
Chromatogram Quality	A	A	A	G	A
Sulfur Interference	-	-	-	-	*
Alteration Classification					
Aroclor 1016/1242	S	S	None	S	A
Aroclor 1254	S	None	None	S	M
Alteration Source					
Aroclor 1016/1242	EA	EA	-	EA	EA/T
Aroclor 1254	T	-	-	T	T

Notes: (1) Chromatogram intensity insufficient to classify.

(2) Non-PCB interference present.

\*, \*\*, \*\*\* = Intensity of sulfur present.

- = Not detected in sample.

Chromatogram Quality

G = Good  
A = Acceptable  
P = Poor

Alteration Source

EA = Environmental Aging  
T = Transformation

Alteration Classification

VS = Very Slight  
S = Slight  
M = Moderate  
A = Advanced

TABLE 1. CLASSIFICATION OF PCB TRANSFORMATIONS IN TASK 12 SAMPLES  
(GZA/NUS SEDIMENT PROGRAM) - Cont'd.

<u>Location Grid #</u>	<u>168</u>	<u>168</u>	<u>168</u>	<u>168</u>	<u>168</u>
SMO Number	AF275	AF818	AF276	AF277	AF278
Sample Depth (inches)	0-6	6-12	12-18	24-30	30-36
Analytical Lab	ERCO	PEI	ERCO	ERCO	ERCO
EPA Case #	5528	6054	5528	5528	5528
Reported Results (ppm)					
Aroclor 1242	-	-	-	-	-
Aroclor 1248	J1.1	-	-	-	-
Aroclor 1254	J1.1	-	-	J0.006	J0.001
YAI EVALUATION					
Chromatogram Quality	A	A	A	A	A
Sulfur Interference	-	**	*	*	*
Alteration Classification					
Aroclor 1016/1242	(1)	-	-	-	-
Aroclor 1254	S	-	-	-	-
Alteration Source					
Aroclor 1016/1242	(1)	-	-	-	-
Aroclor 1254	T	-	-	-	-

Notes: (1) Chromatogram intensity insufficient to classify.  
 (2) Non-PCB interference present.  
 \*, \*\*, \*\*\* = Intensity of sulfur interference.  
 - = Not detected in sample.

Chromatogram Quality

G = Good  
 A = Acceptable  
 P = Poor

Alteration Source

EA = Environmental Aging  
 T = Transformation

Alteration Classification

VS = Very Slight  
 S = Slight  
 M = Moderate  
 A = Advanced

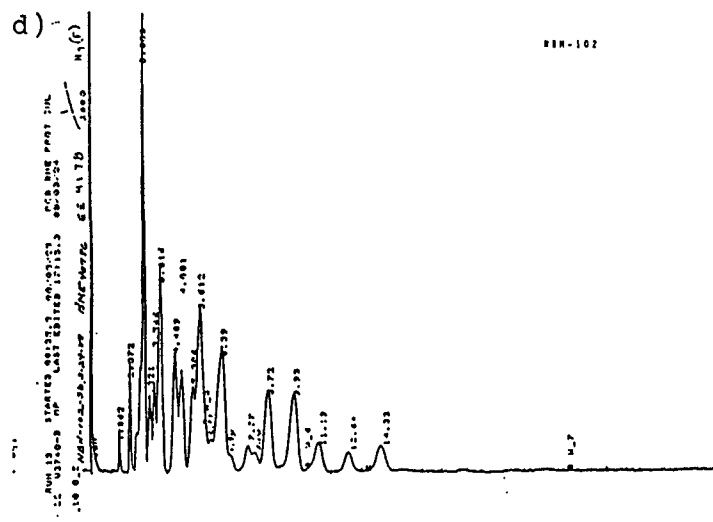
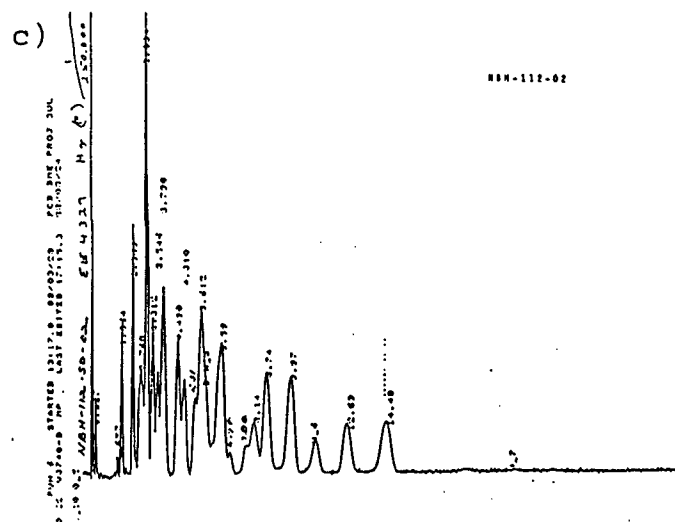
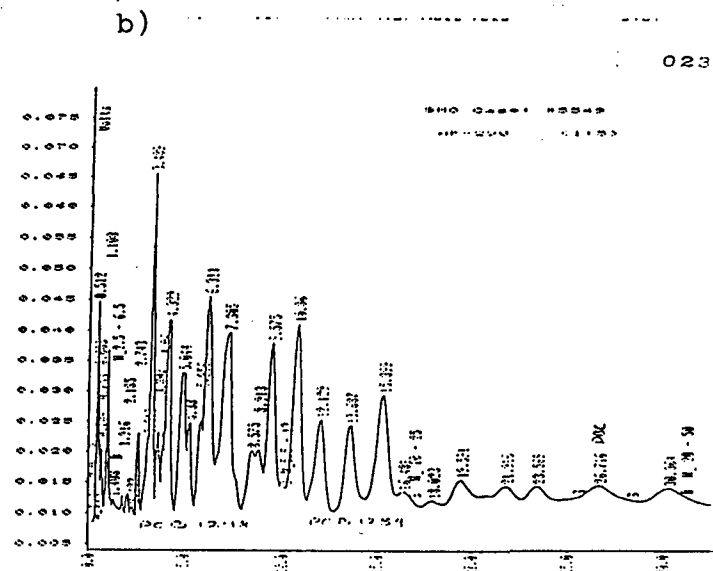
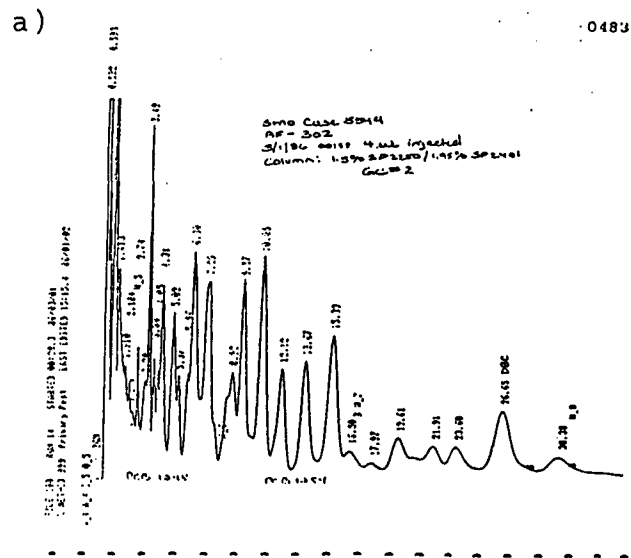


Figure 9. Comparison of Chromatograms for Task 12 Samples (a & b) and Task 7 Samples (c & d)

4. Chromatographic pattern alterations arising from one or more of the following sources were present:

- o the presence of Aroclor mixtures with wide variations in mixture ratios;
- o non-PCB interferences;
- o partial loss of lower chlorinated congeners resulting from environmental aging losses; and
- o changes in congener distributions as the result of anaerobic degradation of PCBs (biotransformations).

5. Anaerobic degradation of Aroclor 1254 was observed in samples from six of the nine sampling sites included in this review. It was seen in two of three middle harbor samples, one of three lower harbor samples, and three of three samples from the outer harbor region.

## 6.0 SUMMARY

The PCB transformations observed in the samples selected for evaluation from the nine NUS/GZA sampling sites are significantly less extensive than those observed in upper estuary samples. Transformations in the Aroclor 1016/1242 region of the chromatograms appear to be the result of environmental aging. In the sixty percent of the review samples where Aroclor 1254 pattern alterations were observed, the source of alterations is probably biodegradation.

Based on the Task 12 findings, an expansion of the effort to include additional NUS/GZA drilling stations would further define the boundaries and extent of biotransformation presently occurring in the lower, middle, and outer harbor areas.

**APPENDIX A**

**TERMS AND ABBREVIATIONS**

Table A-1. TERMS

"Additive Effect": To heighten or increase the intensity of a peak in a chromatogram (enhancement).

Anaerobe: A microorganism that flourishes without free oxygen.

Anaerobic microbial (bio)degradation: The reduction of a chemical component from a higher to a lower type by the action of anaerobic microbes.

Anaerobic biotransformations: Changes brought about as the result of the action of anaerobic bacteria.

Anaerobic dechlorination: A specific PCB microbial degradation process whereby chlorine is selectively removed from a congener as the result of anaerobic microbial actions.

Aroclor: Trade name (Monsanto) for a series of commercial PCB and polychlorinated terphenyl mixtures marketed in the United States.

Aroclor degradation: A reductive modification with respect to the proportions of the individual PCB congeners present in the specific Aroclor.

Aroclor transformation: Any change (either reduction or enhancement) in the unique characteristic of the composition of a specific Aroclor.

Chromatogram: A tracing of the detector output from a chromatograph which consists of a series of peaks observed over time.

Chromatographic pattern alteration: Any change or modification which occurs in the chromatogram produced by a known reference material (e.g., a specific Aroclor).

Congener: One of the 209 PCBs or other group of compounds, not necessarily the same homolog.

Degrade: To reduce from a higher to a lower type.

Enhance: To heighten or increase in intensity.

Table A-1. TERMS (Cont'd)

Environmental aging (weathering): The process whereby the Aroclor(s) present in an environmental sample undergoes modification with respect to the proportions of individual PCB congeners present as the result of partial vaporization, adsorption onto surfaces, and/or extraction into water. True molecular solution in water is shown (on chromatograms) as the non-selective loss of the more volatile and more water-soluble congeners from the Aroclors in the sediments.

"High-end drop-off": The pattern alteration observed when higher chlorinated PCB congeners (usually penta- and hexa-) undergo anaerobic dechlorination.

High resolution gas-liquid chromatography: Gas chromatography with a capillary column.

Homolog: One of the 10 degrees of chlorination of PCBs ( $C_{12}H_9Cl$  through  $C_{12}Cl_{10}$ ) or other group of compounds varying by systematic addition of a substituent.

Isomer: Any PCB or other compound which has the same molecular formula, but different positional substitutions. 2,2'-Dichlorobiphenyl and 2,3-dichlorobiphenyl are isomeric; 4-chlorobiphenyl and 2,3,4-trichlorobiphenyl are not.

"Low-end drop-off": The pattern alteration observed when lower chlorinated PCB congeners are removed from samples by weathering.

Part per million (ppm): One part in  $10^6$ .

Pattern alterations: Changes in a characteristic chromatographic pattern. The effect of the changes will be reflected by peak enhancements, reductions, or both. (See chromatographic pattern alterations.)

Polychlorinated biphenyl (PCB): One of 209 individual compounds having the molecular formula  $C_{12}H_nCl_{10-n}$ , where  $n = 0-9$ . This definition includes monochlorobiphenyls, but not biphenyl.

PCB degradation: A conversion whereby a PCB congener of a higher chlorine content is reduced (converted) to one of a lower chlorine content.

PCB transformation: Any change whereby a PCB congener is converted into another compound.

Table A-1. TERMS (Cont'd)

Qualitative: Having to do with establishing the presence or identity of a compound.

Quantitative: Having to do with measuring the amount or concentration of a compound in a sample.

Retention time: Time between injection and detection of a compound on a chromatographic system under specified conditions, expressed in seconds or minutes.

Transformation: Any change which gives a different appearance.

Weathering: A process which gives a compositional change in an Aroclor residue (see environmental aging).



Table A-2. ABBREVIATIONS

BEC	Balsam Environmental Consultants, Inc.
CLP	(EPA) Contract Laboratory Program
EPA	(U.S.) Environmental Protection Agency
GC	Gas-liquid chromatography (column type unspecified)
GC/EC	Gas chromatography/electron capture
GC/MS	Gas-liquid chromatography/mass spectrometry (ionization mode unspecified)
NBH	New Bedford Harbor
PCB	Polychlorinated biphenyl
ppm	Parts per million ( $10^{-6}$ )
QA/QC	Quality Assurance/Quality Control
RT	Retention time
YAI	Yoakum & Associates, Inc.