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ABSTRACT

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The hepatopancreas of five dead lobsters were analyzed by gas chromatography-mass spectrometry. Most samples contained polynuclear aromatic hydrocarbons, benzothiazole, PCB, p,p'-DDE, trans-nonachlor, hexachlorobenzene, and a dichlorobenzene. BHT (2,6-di-tert-butyl-4-methylphenol) was detected in all samples. The metabolite of BHT, 2,6-di-tert-butyl-4-methylene-2,5-cyclohexadienone, was detected in one sample, containing a very high level of BHT. Additional compounds detected in some samples included methyl and ethyl esters of fatty acids, pentyl benzoate, and tentatively identified aliphatic nitriles. Some of the contaminants were determined quantitatively. The origin and significance of the contaminants are discussed.

Key words: BHT, PCB, PAH, GCMS

RÉSUMÉ

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Le pancréas hépatique de cinq homards morts a été analysé par la méthode chromatographie en phase gazeuse-spectrométrie de masse. La plupart des échantillons contenaient des hydrocarbures aromatiques polynucléaires, du benzothiazole, des PCB, du p,p'-DDE, du trans-nonachlore, de l'hexachlorobenzène et du dichlorobenzène. La présence du BHT (di-tert-butyle-2, 6 méthyl-4 phénol) a été détectée dans tous le di-tert échantillons. Le métabolite du BHT, le di-tert-butyle-2,6 méthylène-4 cyclohexadiène-2,5 one, a été découvert dans un échantillon qui contenait un taux élevé de BHT. D'autres composés ont été trouvés dans certains échantillons dont, entre autres, des esters éthylés et méthylés d'acides gras, du benzoate de pentyle, et des nitriles aliphatiques identifiés à titre d'essai. Une analyse quantitative a été faite pour certains contaminants. L'origine des contaminants et leur importance son étudiées.

INTRODUCTION

This report describes the analyses of American lobster (*Homarus americanus*) hepatopancreas (digestive gland) by gas chromatography-mass spectrometry (GCMS). The analyses were performed periodically between 1976 and 1979 on dead lobsters from a "lobster culture" project of the Invertebrates Physiology Program at the Biological Station in St. Andrews, N.B.

The objective was to detect organic contaminants that may be linked to lobster mortality in the culture, and to identify additives to plastics that are leached from the "plumbing" of the lobster culture facility.

METHODS

SAMPLES

Samples of hepatopancreas from the cultured lobsters were obtained by Invertebrates Physiology staff, were wrapped in aluminum foil, and stored frozen (-20°C) until analysis, usually within a few days. In this report the samples are identified by their GCMS file code. Some of the samples were analyzed at several sensitivities to avoid saturation of the MS detector (low sensitivity) or to detect minor components (high sensitivity). Analyses at different sensitivities are identified by a number following the file code.

Sample LSWA is the extract of hepatopancreas from a female lobster from Unit 6 caught in June 1978 and kept until death in the culture system. The sample was analyzed on November 27-29, 1979.

Sample LSWB is the extract of hepatopancreas from lobster #316, reared in the culture system. The sample was analyzed on November 27-29, 1979.

Sample LOBSW originated from the hepatopancreas of a lobster suspected to have died as the result of exposure to creosote during modifications to the seawater intake of the Station. A number of animals died in the culture system. The sample was obtained on July 24, and analyzed on July 25-26, 1979.

Sample CMAILI originated from a lobster found dead in the culture system in August 1977 and was analyzed on August 16, 1977.

Sample LOB-2 originated similarly from a dead, cultured lobster and was analyzed on August 17, 1976.

EXTRACTION AND CLEANUP

Samples of hepatopancreas were ground with anhydrous sodium sulfate (5 g hepatopancreas, 30 g sodium sulfate) and extracted with hexane in Soxhlet extractors for 1 h. Volumes of the extracts were adjusted to 100 mL and concentrations of lipids were determined on aliquots (3 mL). Aliquots corresponding to 1 g lipid, or as much as available, were cleaned up by chromatography on alumina (activated at 800°C for 4 h and deactivated by adding 5% water; 40 g in a 2.5-cm i.d. column per 1 g lipid). The column was eluted with hexane, collecting 400 mL of effluent. The effluent was evaporated on a rotary evaporator to about 1.5 mL and was further cleaned up on a small alumina column (2 g, 0.8 cm i.d.), collecting 20 mL of effluent. The effluent was evaporated just to dryness, re-dissolved in 0.2-0.5 mL hexane, and analyzed by GCMS.

GCMS ANALYSIS

The instrument was a Finnigan Model 1015D quadrupole mass spectrometer, coupled to a Finnigan Model 9000 gas chromatograph. The data were acquired and processed by a Model 6100 Data System. As the analyses were performed occasionally over a number of years, several different GC columns were used. The columns (i.d. 2 mm) contained 3% OV-1 on Chromosorb WHP 60/80 and varied in length from 120-180 cm. Column temperature was programmed, usually from 100-280°C at 8°C/min. The injector and separator temperatures were 220 and 290-305°C, respectively. Electron impact mass spectra were scanned from 50-500 daltons every 3 s. Starting in 1977, the instrument was calibrated by external standards containing C10-C24 normal paraffins, dibutyl- and di-(2-ethylhexyl)phthalate, phenanthrene, fluoranthene, pyrene, 2,6-dimethyl-naphthalene, p,p'DDE, trans-nonachlor, 2,2',4,4',5,5'-hexachlorobiphenyl, and 2,6-di-tert-butyl-4-methylphenol (BHT).

The data were evaluated by a combination of manual and electronic data processing. Listing and documentation of the software are given elsewhere (Zitko 1981).

Peaks and corresponding backgrounds in reconstructed gas chromatograms (RGC) were determined manually. Mass spectra of the peaks were then retrieved and printed out by the program MSPRTC, yielding spectra corrected by background subtraction, or by the program RTRV1. Mass spectra retrieved by this program contain only m/z values maximizing within a specified "window" (usually the RGC maximum, at times including the preceding or the following scan). The printouts were evaluated in conjunction with the NIH/EPA mass spectra data base MSSS. Attempts were made to resolve spectra appearing to result from a mixture of co-eluting compounds by using the program COR7. This program retrieves up to 5 m/z values within a specified narrow scan range, calculates the correlation matrix and, optionally, prints or plots the m/z values for visual inspection. Identified compounds may be quantitated by the program QUANT7. This program retrieves limited mass reconstructed gas chromatograms (LMRGC), detects peaks, establishes the corresponding baselines, integrates the peaks, and, in addition to these parameters, prints background-corrected mass spectra as an identification check.

Unknown or unanticipated m/z values noted during data acquisition or subsequent manual replay were processed further by either RTRVS1 or OUT4. These programs are analogous to RTRV1 and MSPRTC, respectively, except that they keep track of the reasons for retrieving the particular mass spectra by sorting them according to the unknown or unanticipated m/z values. Without this sorting, the situation may become very confusing. Confirmation of identification was performed by the program RGEVA4. This program keeps track of the m/z values leading to the retrieval of the spectra, retrieves up to five background-corrected spectra for one such m/z value and plots m/z values from up to three specified m/z ranges for visual confirmation of identification.

The interpretation of some mass spectra was assisted by program ELANAL (Kavanagh 1980). This program selects empirical formulae best fitting the observed m/z intensities due to the presence of isotopes. The program was modified to run on the Tektronix Plot 50 system since it requires a considerable time and would have hindered other processing on the Data System 6100. A modified version of the program (ISOTOPE) was used to calculate isotopic abundancies for given summary formulae and to compare observed and theoretical abundancies.

Compound identification was aided further by compilations of retention indices of polynuclear aromatic hydrocarbons (PAH) and related compounds (Borwitzky and Schomburg 1979; Eiceman et al. 1979; Lee et al. 1979; Snook et al. 1979) and of various other compounds (Ramsey et al. 1980).

The nomenclature file CHEMNAME (DIALOG, File 31) was searched occasionally to find the range of commonly encountered compounds of a given summary formula.

Throughout the report, compounds or mass spectra are referred to by their scan numbers and by scan numbers relative to that of fluoranthene. The latter facilitate comparisons between samples.

RESULTS AND DISCUSSION

QUALITATIVE ANALYSIS

Sample LSWA

The three major peaks in the reconstructed gas chromatogram (RGC) of this sample (Fig. 1) are pristane (2,6,10,14-tetramethylpentadecane, scan 145,0.76 relative to fluoranthene), fluoranthene (scan 191), and pyrene (scan 199,1.04).

BHT (2,6-di-tert-butyl-4-methylphenol) is present in scan 107,0.56. The small peak in scan 122,0.64 is a C_4-naphthalene (184(18%),169(100%)). The following small peak (scan 127,0.67) contains another C_4 naphthalene and, in addition, a compound yielding a strong ion at m/z 135, that may indicate an alkylphenol. A small peak of phenanthrene or anthracene (molecular ion at m/z 178) is barely visible just after the peak of pristane. Anthracene does not appear to be as stable in environmental samples as phenanthrene and it is likely that the compound is phenanthrene. The small broad peak centered in scan 161,0.85 contains octadecane and 1-phenylnaphthalene (m/z 204).

Mass spectrum of the scan 170,0.89 (Fig. 2) contains a cluster of ions m/z 189-192, corresponding to a mixture of 4H-cyclopenta(def)-phenanthrene (molecular ion m/z 190) and a methylphenanthrene (or methylanthracene, m/z 192). The former occurs in relatively high concentrations in all samples and has not been noticed previously among PAH found in lobster hepatopancreas (Dunn and Fee 1979). The following small peak (scan 178,0.93) is again a PAH with a base (100%) ion at m/z 204. By using MSSS data as a reference (Table 1), this compound was identified as 2-phenylnaphthalene.

The peak in scan 182,0.95 (Fig. 3) contains ions at m/z 55, 69, 83, 97, 111, and 125, 88, and 101 and is apparently a fatty acid ethyl ester. According to its retention time, it may be an ethyl hexadecenoate. Fatty acid esters were much more abundant in sample series LSWB where they are discussed in more detail. For this compound see also Fig. 15.

Table 1. Ion intensities of compound in scan 178,0.93, and of reference compounds.

m/z	200	201	202	203	204	205
Scan 178	5	6	38	30	100	19
1-phenylnaphthalene	8	9	50	70	100	16
2-phenylnaphthalene	<5	5	30	18	100	18
4,5-dihydropyrene	20	18	100	89	92	17

The peak in scan 187,0.98 (Fig. 4) has base ion at m/z 206 and is likely a dimethylphenanthrene (or dimethylanthracene). The mass spectrum also indicates the presence of a fatty acid ethyl ester (m/z 55, 57, 69, 71, 88, 101).

The broad envelope between scan 206,1.08 and 220,1.15 contains a number of compounds including two methyl-fluoranthenes (or -pyrenes), m/z 216 in scans 211,1.10 and 214,1.12. PAH with m/z 232 are present in scans 213,1.11 (minor) and 218,1.14 (major). A great number of isomeric PAH (methyl-cyclopentenophenanthrenes (-anthracenes), dimethyl-phenylnaphthalenes, etc.) have this molecular ion in their mass spectra. The latter scan also contains a PAH with molecular ion at m/z 218 (dihydrobenzo-fluorenes, cyclopentenophenanthrenes (anthracenes), etc.) and a pentachlorobiphenyl.

The peak in scan 235,1.23 has a base ion m/z 226 corresponding to compounds such as cyclopenta(cd)pyrene and benzo(ghi)fluoranthene. The peak in scan 243,1.27 has a base ion at m/z 228 and is probably benz(a)anthracene, although other isomers such as chrysene, triphenylene, etc. may be present as well. Results of our previous studies indicate that this peak causes a strong response on a DC electron-capture detector, typical of benz(a)-anthracene.

The peak in scan 290,1.52 appears to be squalene (2,6,10,14,18,22-tetracosahexaene, 2,6,-10,15,19,23-hexamethyl) or a related hydrocarbon, with mass spectrum practically identical to that in Fig. 47. The following peak is an artifact caused by column bleed.

Additional minor components, not visible in the RGC, are listed in Table 2.

The compounds with m/z 196/195 (scans 140,0.73 and 147,0.77) could not be identified. Their mass spectra are relatively featureless (Fig. 9, 10) and indicate a hydrocarbon $C_{15}H_{16}$. The strong M-1 ion (195) probably means the presence of a CH_2 or CH_3 group. MSSS contains mass spectra of only four $C_{15}H_{16}$ isomers, none of them corresponding to the observed spectra. An additional 40 compounds are contained in the file CHEMNAME. Most of these can be eliminated because of their anticipated fragmentation patterns. Methyl tetrahydrophenanthrenes (CASRN 70550-38-8 and 22319-44-2) and trimethyl-acenaphthene (CASRN 60826-69-9) could have mass spectra similar to those in scans 140 and 147. The observed ions m/z 182 and 167 appear to belong to another hydrocarbon, $C_{14}H_{14}$, almost co-eluting with $C_{15}H_{16}$. MSSS contains 14 $C_{14}H_{14}$. Most of them are dimethylbiphenyls or tolylphenylmethanes with very similar mass spectra. Hexachlorobenzene (Cl_6 cluster starting at m/z 282) is also present in scan 140,0.73 and can be used as a retention time marker in further attempts to identify this compound.

Further examination of the data is likely to detect additional compounds and, in future studies, some prefractionation of the extract and GC on a capillary column should be used for better resolution. For example, an additional two PAH can be found in close vicinity to fluoranthene and pyrene by detailed examination of the data (Table 3), a PAH with molecular ion at m/z 208, a trimethylfluorene or an isomer, and a PAH with molecular ion at m/z 218, a cyclopentenophenanthrene or isomers.

Sample LSWB

The reconstructed gas chromatogram of LSWB (Fig. 13) differs considerably from that of LSWA (Fig. 1). Pristane (scan 146,0.76) is again a major component, but fluoranthene (scan 193,1.00) and pyrene (scan 198,1.03) are present in relatively lower concentration. In addition, the two major components of LSWB (scans 211,1.09 and 231,1.20) were not, at least as major peaks, present in LSWA.

Mass spectrum of the component in scan 211,1.09 (Fig. 14) has a molecular ion at m/z 310 or 312 and contains a prominent series of monoolefinic fragments (m/z 55, 69, 83). The ions at m/z 88 and 101 indicate an ethyl ester or 2-methyl methyl ester ($CH_2COOC_2H_5 \cdot H$ or $CH(CH_3)COOCH_3 \cdot H$). Since the former is more common, it is assumed that the compound is ethyl oleate, possibly containing some ethyl stearate.

Mass spectra of compounds in scans 157,0.87, 172,0.89, 184,0.95, 187,0.97, 224,1.17, and 236,1.22 also contain ions at m/z 88 and 101 and more or less resemble the spectrum of ethyl oleate. In addition, the scan numbers fall on a straight line when plotted against constant increments on the X-axis (carbon number). This indicates a polymer-homologous series of fatty acids, ranging from C_{14} (scan 157,0.87) to C_{20} (scan 236,1.22). At higher sensitivity, a peak corresponding to C_{12} (scan 123,0.64), is also visible. Of the two acids corresponding to C_{16} (scans 184,0.95 and 187,0.97), mass spectrum of the former is practically identical to spectra of acids in this series (Fig. 15). On the other hand, the ion m/z 88 is the base ion in the spectrum of scan 187, followed in intensity by m/z 101 (Fig. 16). This compound appears to be tetradecanoic acid ethyl ester.

The peaks in scans 231,1.20 and 252,1.31 (Fig. 17, 18) have similar mass spectra, with base ions at m/z 79 and additional intense ions at m/z 67 and 91. Molecular ions are not readily discernible in either case. The intense ions indicate an unsaturated carbon chain with three or more double bonds. The retention times indicate a carbon chain length of 20 and 21 atoms, respectively. Both compounds appear to be fatty acid ethyl esters (relatively weak ions at m/z 88 and 101, no ion at m/z 74). Mass spectrum of ethyl arachidonate (5,8,11,14-eicosatetraenoic acid, all Z), available from MSSS, is similar to the spectra of 231 and 252.

Of the remaining peaks in the RGC, the peak in scan 162,0.84 contains mainly a paraffin (probably phytane, 2,6,10,14-tetramethylhexadecane), traces of PAH (m/z 198 and 204) and traces of a compound yielding ions at m/z 181 and 165 (Fig. 19). The peak in scan 172,0.89 is 4H-cyclopenta(def)phenan-threne, and the peak in scan 236,1.22 contains, in addition to the fatty acid ester, a benzofluoran-thene (m/z 226).

Minor compounds, not obvious from the RGC, resemble closely those in LSWA (Table 1). For example, a dichlorobenzene is present in scan 21,0.11 (Fig. 20) and benzothiazole was found in scan 57,0.30 (Fig. 21). The unidentified PAH m/z 196, coeluting with hexachlorobenzene, is again present in scan 140,0.72 (Fig. 22).

Table 2. Some compounds detected in the extract of LSWA but not visible as separate peaks in the RGC (Fig. 1).

Scan number Max.	Background	Retention time relative to fluoranthene	Main ions in mass spectrum, identification and remarks
19	17	0.09	146(100); a dichlorobenzene
23	22	0.12	68(100); tentatively $C_{10}H_{16}$ such as limonene or bornene; Fig. 5
34	32	0.18	135(100); alkylphenol?
54	52	0.28	135(100) 108(40); benzothiazole
84	82	0.44	170(100) 141(70); diphenyl ether?; Fig. 6
89	range	0.46	156(100) 141(variable); several C_2-naphthalenes
99	97	0.52	154(100); acenaphthene
109	range	0.57	170(100) 155(92); several C_3-naphthalenes
119	116	0.62	149(100); phthalate, alkylphenol?; Fig. 7
124	122	0.65	182(100) 181(80); xanthene; Fig. 8
136	134	0.71	169(100) 184(89); C_4-naphthalene
140	138	0.73	167(100) 182(80) 196(80) 195(79); a mixture of compounds; C_6Cl_6; Fig. 9
147	146	0.77	181(45) 196(35) 195(35); Fig. 10
163	160	0.85	210(100) 195(60); $C_{16}H_{18}$ such as C_4-biphenyl or $C_{15}H_{14}O$; a trichlorobiphenyl also present; Fig. 11
166	163	0.87	192(100); methylphenanthrene
168	166	0.88	192(100); methylphenanthrene
197	195	1.03	208(100); trimethylflourene?
201	199	1.05	218(100); a cyclopentenophenanthrene or another isomeric PAH
203	201	1.06	405 cluster; trans-nonachlor
207	204	1.08	316 cluster; p,p'-DDE
210	range	1.09	216(100) 215(64); several benzofluorenes
216	214	1.12	218(100) 203(53); a PAH
220	217	1.14	405 cluster; cis-nonachlor
229	227	1.20	358 cluster; hexachlorobiphenyl and a polyunsaturated fatty acid ester; Fig. 12
233	230	1.22	226(100); benzofluoranthene
235	232	1.23	226(100); benzofluoranthene
236	234	1.23	358 cluster; hexachlorobiphenyl
242	239	1.26	228(100); chrysene or isomer
249	246	1.30	242(100); methylchrysene or isomer
255	252	1.33	242(100); methylchrysene or isomer
279	274	1.45	252(100); benzopyrenes or isomers
289	284	1.51	252(100); benzopyrenes or isomers

Table 3. Intensities of selected ions in scans 190-205, file LSWA3, indicating the presence of fluoranthene (scan 192,1.00), another PAH with m/z 208 (scan 197,1.03), pyrene (scan 200,1.04), and another PAH with m/z 218 (scan 201,1.05).

Scan	Intensity at m/z				
	202	216	218	204	208
190	320	12	19	121	25
191	4563	12	19	211	25
192	15136	12	25	326	25
193	13280	12	25	243	25
194	6816	12	19	115	25
195	3257	12	38	70	57
196	2016	12	57	44	166
197	1414	19	70	38	224
198	3270	19	64	70	172
199	6739	12	96	243	96
200	6380	12	531	454	76
201	3731	12	1139	403	64
202	2054	19	1024	211	44
203	1190	19	665	115	38
204	870	19	505	70	32
205	614	12	544	57	32

Sample LOBSW

The largest peak in the RGC (Fig. 23) is pristane (scan 142,0.76) and all other major peaks are PAH (phenanthrene in scan 146,0.78, 4H-cyclopenta-(def)phenanthrene in scan 167,0.89, fluoranthene in scan 188,1.00, and pyrene in scan 195,1.04).

The three fairly prominent peaks in scans 173,0.92, 217,1.16, and 240,1.28, as well as the small peaks in scans 223,1.18 and 247,1.31, appear to be fatty acid methyl esters. The mass spectrum of scan 173,0.92 (Fig. 24) indicates a saturated fatty acid (m/z 87, 101, 115, 129, ...) methyl ester (m/z 74 is the base ion). From published retention times this compound appears to be stearic acid methyl ester. The other major fatty acids (Fig. 25, 26) are polyunsaturated methyl esters (m/z 67, 79, 91, 105, 119, 133, ...). Judging from retention times these compounds are C_{20} and C_{22} methyl esters, respectively. The two minor peaks in scans 223 and 247 are the respective saturated fatty acid methyl esters.

Peaks in scans 86,0.46 and 89,0.47 are dimethylnaphthalenes (m/z 156 and 141) and the peak in scan 96,0.51 is acenaphthene (m/z 154, 153, 152). The peak in scan 102,0.54 is either a hydrocarbon $C_{13}H_{12}$ or dibenzofuran (Fig. 27). The mass spectrum of the latter agrees well with that of peak 102, except for the presence of an ion m/z 153 which is absent from the published spectrum of dibenzofuran.

BHT is present in low concentration and contributes to the shoulder following the peak of dibenzofuran. Interestingly, there are two peaks with mass spectra of "BHT" as indicated by the limited mass reconstructed gas chromatogram (LMRGC) of ion m/z 205 (Fig. 28) and the corresponding mass spectra of the two peaks (Fig. 29, 30). The compounds must be isomeric butylated toluenes.

The peak in scan 114,0.61 is fluorene (m/z 166, 165). Mass spectrum of the peak in scan 117,0.62 (Fig. 31) indicates a $C_{13}H_{12}$ hydrocarbon, losing readily a CH_3 group. Mass spectra of six $C_{13}H_{12}$ isomers are available in MSSS. None is identical with the observed spectrum. In addition, the peak contains a compound yielding ions at m/z 180 and 165.

Mass spectra of peaks in scans 121,0.68 and 123,0.65 contain ions at m/z 181 and 182 at >90% intensity. The compounds appear to be methyldibenzofurans, but the latter may be xanthene.

Mass spectrum of the small peak in scan 130,0.69 has m/z 179 as the base ion and has additional abundant ions at m/z 180 and 178. The peak probably contains a mixture of methylfluorenes.

Mass spectrum of the peak in scan 134,0.71 has m/z 165 as the base ion and m/z 180 as the molecular ion, indicating a compound similar to the postulated $C_{14}H_{12}$ in scan 117,0.62 (Fig. 31).

The peak in scan 136,0.72 (Fig. 32) contains at least three compounds: the previously encountered and unidentified m/z 196/195, hexachlorobenzene (cluster at m/z 282), and a hydrocarbon $C_{14}H_{14}$ (m/z 182 and 167). This mixture is similar to that found in the sample LSWA (Fig. 9), but the postulated $C_{14}H_{14}$ is not so obvious in the sample LSWB (Fig. 22), which contains, in addition, an unsaturated fatty acid ethyl ester.

Mass spectrum of the small peak in scan 158,0.84 (Fig. 33) also indicates a mixture of compounds, 1-phenylnaphthalene (m/z 204, 203, 202) and methyldibenzothiophene (m/z 198, 197).

The small peak in scan 207,1.10 contains methyl-fluoranthene (or -pyrene), m/z 216, and p,p'-DDE. Two additional methylfluoranthenes or methylpyrenes are present in scans 208,1.11 and 211,1.12. The peak in scan 230,1.23 contains a PAH with molecular ion at m/z 226, such as benzo(mno)fluoranthene or cyclopenta(cd)pyrene. The shoulder (scan 237,1.26) contains a PAH with molecular ion at m/z 228, probably benz(a)anthracene. Additional PAH are

present in scans 257,1.37 (m/z 240) and 282,1.50 (m/z 252). The former may be 4H-cyclopenta(def)-chrysene, 4H-benzo(fg)pyrene, cholanthrene, etc., the latter a benzopyrene, perylene, etc.

Most of the minor components, not visible in the RGC, given in Table 2 for sample LSWA, are present as well.

Sample CMAILI

This sample was analyzed only at high sensitivity, distorting intensities of abundant ions in mass spectra of major peaks in the reconstructed gas chromatogram (Fig. 34). The first major peak (scan 118,0.72) is pristane.

Mass spectrum of the next major peak (scan 131,0.80) contains strong ions at m/z 69, 71, 82, 96, and 110 (Fig. 35, spectrum of a somewhat less intense scan is shown to eliminate some of the distortion). Weaker ions are detectable at m/z 124, 137, 138, 152, 166, 179, 180, 196, and 252. An additional ion, m/z 223, is visible in mass spectrum of scan 131 (Fig. 36, spectrum normalized to m/z 124). The even-mass ions are very likely containing nitrogen and may correspond to a series $C_nH_{2n-2}N$ ($C_8H_{14}N$ - $C_{12}H_{22}N$), and the ion at m/z 223 is possibly the molecular ion $C_{15}H_{29}N$. Ions m/z 196 and 252 do not fit this scheme. The former is probably due to a PAH, the latter to background noise.

MSSS contains three $C_{15}H_{29}N$ compounds. Mass spectrum of one, pentadecanenitrile (CASRN 18300-91-9), is similar but not identical to the spectrum of scan 131. CHEMNAME contains 15 compounds, none of which is an obvious candidate for a contaminant.

The next two large peaks (scan 157,0.96 and 161,0.98) could not be identified. The former (Fig. 37) contains m/z 54 as the base ion. This might indicate a nitrile, but all other major ions have odd masses in contrast to the mass spectrum in Fig. 35. These ions appear to fall into two series (81/83, 95/97, 109/111, and 121, 135, 149), offering a number of interpretation possibilities, but not unambiguous identification.

Mass spectrum of scan 161,0.98 (Fig. 38) contains m/z 96 as the base ion. This again may indicate a nitrile and the indication is supported by the presence of m/z 54. The ion at m/z 202 is due to fluoranthene (peaking in scan 163,1.00). A tetrachlorobiphenyl is also present (Cl cluster at m/z 290).

The last major peak (scan 223,1.37) is di-(2-ethylhexyl)phthalate (DEHP).

In the intermediate, partly resolved group of peaks, the mass spectrum of scan 140,0.87 (Fig. 39) contains m/z 70 as the base ion and resembles mass spectra of 2-unsaturated aldehydes, such as 2-undecenal. The ion at m/z 192 is probably methylphenanthrene.

Ion m/z 71 forms the base of the mass spectrum of scan 146,0.90 (Fig. 40). Since this peak is not well resolved from the preceding one, the baseline correction is quite arbitrary and the compound is not identified.

The number of unusual mass spectra in this sample may be suggesting substandard calibration of the mass spectrometer in this run. As demonstrated on the next three mass spectra, this was not the case.

The isotopic abundancies of ions $C_6H_4Cl_2$ (m/z 146) and C_6H_4Cl (m/z 111) in the spectrum of dichlorobenzene (Fig. 41) have sums of squared deviations from the expected distribution (SUSQ, see program ISOTOPE in Zitko (1981)) of 11 and 254, respectively. Considering that dichlorobenzene is a minor component of the sample, this is a good fit. SUSQ for these ions in mass spectra of dichlorobenzenes in MSSS are 2-3. The spectrum in Fig. 42 also contains intense ions at m/z 105 and 70, probably due to a co-eluting pentyl benzoate.

The isotopic abundancies of the molecular ion of p,p'-DDE, $C_{14}H_8Cl_4$, m/z 316 (scan 178,1.09, Fig. 42) have SUSQ of 25. The comparative value for this ion from the MSSS spectrum is 16. The isotopic abundancies of the ion $C_{10}H_5Cl_8$ (m/z 405) in the spectrum of trans-nonachlor (scan 174,1.07, Fig. 43) have SUSQ of 216 compared to 452 in MSSS.

These examples confirm good performance of the mass spectrometer in this sample. Consequently, spectra of the unidentified compounds are real in terms of m/z values and for the less intense peaks in terms of intensities as well.

Of the minor peaks, the peak in scan 36,0.22 is benzothiazole. The peak in scan 83,0.81 contains m/z 55 as the base ion and additional strong ions are at m/z 71 and 85. The peak is quite broad and very likely contains a mixture of compounds. No identification is possible from the data.

Mass spectrum of the peak in scan 97,0.59 (Fig. 44) has a very intense ion at m/z 71. From the isotopic distribution the ion is most probably C_5H_{11}. C_4H_7O is somewhat less likely. A number of compounds in MSSS yield similar spectra, not specific enough for identification.

Mass spectrum of the adjacent peak (scan 99,0.61) contains m/z 55 as the base ion. Additional intense ions are at m/z 56(40%), 68(37%), 70(25%), 81(54%), 82(51%), 96(33%), and 97(34%). The compound has not been identified.

Mass spectrum of the peak in scan 104,0.64 (Fig. 45) resembles spectra of polyunsaturated fatty acid methyl esters, but the retention time is too short for the common compounds of this type.

Many of the compounds listed in Table 2 are identifiable as minor components of this sample as well. Some of the retention time "benchmarks" are BHT (scan 80,0.49), phenanthrene (scan 123,0.75), fluoranthene (scan 163,1.00), and pyrene (scan 169,1.04).

Sample LOB-2

The reconstructed gas chromatogram (Fig. 46) contains four major peaks and is otherwise quite featureless in comparison with RGC's of the other samples. The largest peak (scan 55,0.42) is BHT. The next large peak (scan 91,0.69) is pristane. The peak in scan 194,1.47 is DEHP, and the peak in scan 234,1.77 appears to be squalene (2,6,10,14,18,22-tetracosahexaene,2,6,10,15,19,23-hexamethyl) or a related hydrocarbon. The mass spectrum is reproduced in Fig. 47.

Many of the small peaks (scans 73,0.55, 81,0.61, 104,0.79, 119,0.90, 133,1.01, 171,1.30, and 183,1.39) are paraffins. In addition to a paraffin, the peak in scan 133,1.01, and those in scans 146,1.11, 157,1.19, and 178,1.34 contain intense ions at m/z 58, suggesting amines, particularly in combination with another strong ion at m/z 72 (scans 133 and 146).

The small peak in scan 50,0.38 (Fig. 48) is 2,6-di-tert-butyl-4-methylene-2,5-cyclohexadienone, identified previously as a hepatic metabolite of BHT in rats (Takahashi and Hiraga 1979).

PAH are present in relatively low concentrations. For example, fluoranthene and pyrene are in scans 132,1.00 and 138,1.05, respectively. Of chlorinated hydrocarbons, dichlorobenzene and hexachlorobenzene are not detectable. p,p'-DDE is present in scan 148,1.12.

QUANTITATIVE ANALYSIS

With the exception of the 1977 sample (LOB-2), the response of the mass spectrometer was calibrated on a set of external standards and the concentrations of a number of compounds were determined (Table 4).

In most samples, the concentrations of fluoranthene and pyrene are extremely high. The source of these hydrocarbons is very likely creosote leaching into seawater from the wharf. On the other hand, dimetnylnaphthalenes may originate both from creosote and from fuel oils spilled in the vicinity of the wharf.

Relative concentrations of major PAH in lobster hepatopancreas sample LSWA3 and in a sample of creosote (not necessarily identical to creosote used on the wharf) are given in Table 5.

As can be seen from Table 5, the lower molecular weight PAH are much less abundant in lobster hepatopancreas in comparison with creosote. This may be caused in part by their higher solubility in water (lower octanol/water partition coefficient) and, consequently lower bioaccumulation, and, in part, metabolism and excretion of metabolites. Norway lobsters are able to metabolize phenanthrene (Palmork and Solbakken 1979). Metabolism may be responsible also for the relative depletion of pyrene. From structural considerations, one would expect that pyrene is metabolized easier than fluoranthene. The relative concentration of benz(a)anthracene is lower in lobster hepatopancreas than in creosote. This may be caused by diminishing

Table 4. Concentration of selected compounds in lobster hepatopancreas.

Compound	Concentration (µg/g lipid) in sample			
	LSWA	LSWB	LOBSW	CMAILI
Dimethylnaphthalenes	0.35	0.18	4.24	2.30
BHT	7.22	0.70	2.80	1.02
Phenanthrene	1.66	0.67	28.1	3.06
Fluoranthene	60.7	24.4	54.8	4.83
Pyrene	32.1	15.4	63.6	7.15
p,p'-DDE	2.95	0.95	1.92	0.53
Hexachlorobiphenyls	0.91	0.55	1.15	0.18
trans-nonachlor	0.078	0.070	0.12	0.12
Dichlorobenzene	32.5[a]	29.8[a]	25.4[a]	63.9[a]
Hexachlorobenzene	5.24[a]	2.78[a]	5.20[a]	1.01[a]
Lipid concentration, %	19.5	25.6	31.8	not available

[a] In counts/g lipid; mass spectrometer not calibrated in terms of concentration.

Table 5. Relative concentrations (% fluoranthene) of major PAH in lobster hepatopancreas (LSWA3) and in a creosote sample.

PAH	m/z	Retention time relative to fluoranthene	Relative concentration (% fluoranthene)	
			LSWA3	Cresote
Fluorene	166	0.61	ND	130
Phenanthrene	178	0.79	2.8	550
Me- "	192	0.89	7.1	51
Fluoranthene	202	1.00	100	100
Pyrene	202	1.04	37	66
Me-fluoranthene	216	1.11	5.7	53
Benzofluoranthenes	226	1.23	2.0	2.8
Benz(a)anthracene	228	1.27	7.7	29

availability of higher molecular weight PAH because of their extremely low solubility in water.

Phenylnaphthalenes could not be detected conclusively in the creosote sample. It may be that these compounds originate from another source or that they are accumulated selectively by the lobsters. 4H-cyclopenta(def)phenanthrene (m/z 190) appears to be enriched in the lobsters in comparison with methylphenanthrene.

BHT (2,6-di-tert-butyl-4-methylphenol) almost certainly originates from plastics used in the lobster culture facility. Its concentration in the sample LOB-2 was much higher than in any of the samples analyzed subsequently. Unfortunately, BHT was not identified when this sample was analyzed and, consequently, was not quantitated. The range of BHT concentrations (Table 4) is about one order of magnitude, similar to the range of PAH concentrations.

The concentrations of p,p'-DDE and trans-nonachlor are similar to those found in local aquatic fauna. Hexachlorobenzene is also a common contaminant of aquatic fauna in this area. Diet is probably the main source of these compounds in the cultured lobsters. It is not known which isomer(s) of dichlorobenzene are present. General occurrence of dichlorobenzenes in aquatic fauna in this area is not known. Dichlorobenzenes would not be detected under "normal" (isothermal) gas chromatography used for routine determinations of organochlorine compounds in aquatic fauna. From properties of dichlorobenzenes (relatively high solubility in water, volatility, and biodegradability), one would not expect them to be widely spread contaminants. The source of the dichlorobenzene is probably associated with the lobster culture facility.

Hexachlorobiphenyls are the most abundant PCB components in the samples. The reported concentrations (Table 4) are not directly comparable to the usually given concentrations in terms of Aroclor 1254. The familiar "PCB pattern" obtained by electron-capture detectors was simulated by plots of sum of the major tetra- to hexachlorobiphenyl ions (m/z 290, 292, 326, 328, 360, 362) for Aroclor 1254 (Fig. 49) and for sample LSWA2 (Fig. 50). PCB pattern of the other samples was similar.

ORIGIN OF THE CONTAMINANTS

The origin of the quantitated contaminants was discussed in the preceding section. Of the non-quantitated compounds, pristane, phytane and squalene, the last two detected only occasionally, must be natural constituents of the hepatopancreas, although their concentration may be influenced by factors such as diet. On the other hand, there is little doubt that the other chemicals are contaminants.

Benzothiazole, found universally, and pentyl benzoate, found in one sample, certainly originate from materials used in the facility. Somewhat surprisingly, phthalates were not encountered as generally as one would have expected. Only one sample contained a relatively high level of DEHP, and dibutyl phthalate has not been detected.

The origin of the C_nH_{2n-14} hydrocarbons (from $C_{13}H_{12}$ to $C_{15}H_{16}$), detected in most samples, is not clear. These hydrocarbons may be derivatives of biphenyl, hexahydrofluorene, acenaphthene, or tetrahydrophenanthrene. In addition, the isotopic abundance accuracy of the mass spectral data is not sufficient to eliminate the possibility that this series of compounds contains oxygen.

The nitriles, tentatively identified in one sample, may not necessarily be present in the hepatopancreas as nitriles. It is possible that they are formed from other nitrogen-containing compounds such as amines or imidazolines during gas chromatography.

The presence of esters of fatty acids, particularly ethyl esters, is surprising. Methyl and isopropyl, but apparently not ethyl esters, are used occasionally in surface-active formulations. Such formulations are almost always based on saturated or monounsaturated fatty acids and yet, polyunsaturated fatty acid esters were detected in several samples. Esterification of extracted fatty acids could not have occurred during extraction and cleanup. Since the presence of fatty acid esters was not anticipated and confirmed by standards, there is a slight possibility of misidentification. A likely source of the esters would be diet fortification by fatty acid preparations, but apparently no such additives have been used.

TOXICOLOGICAL SIGNIFICANCE

Only dead lobsters were analyzed and concentration of contaminants in healthy lobsters is not known. Even if this information were available, the toxicological significance could not be assessed without toxicity tests, linking exposure conditions, effects, and concentration of contaminants in tissues. Since this background is not available, the toxicological significance can be discussed only tentatively, based on general toxicological properties of the contaminants and on judgment.

The concentrations of organochlorine compounds are within the range of contamination of marine fauna in this area. It seems from general experience that these levels are not significant toxicologically, but dichlorobenzene is of some concern. Relative to the other organochlorine contaminants regularly found in aquatic fauna, dichlorobenzenes may be metabolized readily via potentially hazardous arene oxides to dichlorophenols, more toxic than the parent compounds.

The toxicity of creosote to lobsters has been studied (McLeese and Metcalfe 1979). The 96-h LC50 for adult lobsters is about 2 mg/L. The concentration of creosote in the hepatopancreas, associated with mortality, is 20-50 mg/g lipid. Unfortunately, this concentration of "total creosote" is determined by fluorescence and is not comparable to the concentrations of individual PAH given in this report. The concentration of creosote in water of the lobster culture facility is likely to be in or below the low µg/L range, three to four orders of magnitude below the 96-h LC50. However, the possibility that long-term exposure to such concentration may eventually lead to mortality cannot be excluded. The concentrations of fluoranthene and pyrene in most of the dead lobsters are high enough to cause concern. These two hydrocarbons may be just indicators of exposure to creosote. Lower molecular weight aromatic hydrocarbons such as derivatives of naphthalene and phenanthrene are probably toxicologically more significant because of metabolism to reactive intermediates and more toxic phenols. It

appears that some of the lobsters might have died as a result of exposure to aromatic hydrocarbons, whether from creosote or other sources.

According to limited toxicity tests (McLeese 1977, unpubl.), BHT does not appear exceedingly toxic to lobsters during acute, short-term exposure and no relationship between toxicity and tissue concentration of BHT is available. An extremely high concentration of BHT was found in one sample and the possibility that this lobster died as a result of exposure to BHT cannot be ruled out. The BHT oxidation product, 2,6-di-tert-butyl-4-methylene-2,5-cylohexadienone, is probably quite a reactive compound able to bind to a variety of biochemicals, thus causing unknown, long-term, toxicological consequences.

The aliphatic nitriles, whether as such or as indicators of the presence of other aliphatic nitrogen compounds, are a cause for concern. Quaternary ammonium compounds, imidazolines, and long chain aliphatic amines are usually highly toxic to aquatic fauna. It is unfortunate that the data do not allow a more definitive identification of these compounds.

Fatty acid esters do not appear highly toxic, although some toxicity, based on their surface activity, is likely when these esters are administered in water.

CONCLUSIONS

The report shows that cultured lobsters contain contaminants. Some contaminants are the same as found in local biota. Of these, PAH are present at much higher levels because of their elevated levels in water used by the facility. Other contaminants originate from materials used in the facility, such as plastic pipes, paint, sealants, etc. Toxicological information on these compounds is scanty and the situation is aggravated by the long-term nature of the exposure. At least some of the analyzed lobsters might have died as a result of exposure to contaminants.

The results underline the fact that cultured animals are not free of contaminants. Actually, they may be more contaminated than their counterparts in the wild. To limit the extent of contamination, construction materials used in the facilities should be screened beforehand for leaching of chemicals. The "complete" composition of cleaning and disinfecting formulations, and of all other materials used within the facilities, even if not in direct contact with the animals, should be known. Toxicity and bioaccumulation potential can be estimated or, when in doubt, determined, and the most acceptable materials may be selected. Aromatic hydrocarbons including PAH will cause contamination and, possibly, sublethal effects and mortality, as long as water intakes remain in the vicinity of creosoted structures and in areas of high boat activity. If water intakes cannot be relocated, a treatment system may have to be considered.

Particular attention should be given to broodstock holding facilities. Broodstock animals are likely to remain in the facilities for a considerable time and chronic effects are usually first observable as reproduction impairment.

The presence of contaminants in the diet must be considered as well. "Trash" fish, fish offal, commercial fish food, etc., may contain elevated concentrations of contaminants.

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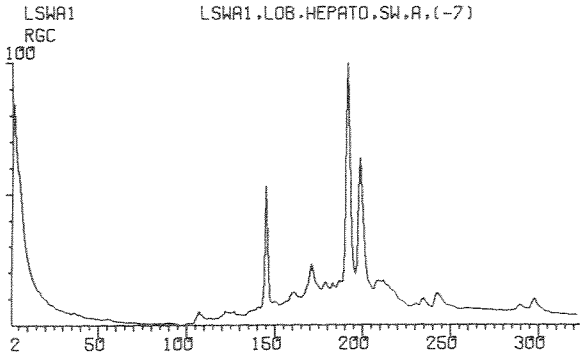

Fig. 1. Reconstructed gas chromatogram (RGC) of sample LSWA1. Major peaks: pristane (scan 145,0.76 relative to fluoranthene), fluoranthene (scan 191), pyrene (scan 199,1.04).

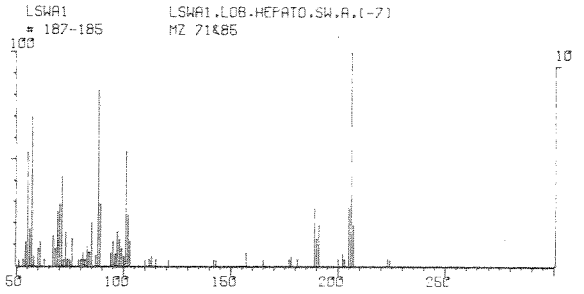

Fig. 4. Mass spectrum of scan 187,0.98 corrected for background in scan 185. Dimethylphenanthrene (or anthracene, m/z 206), and a fatty acid ethyl ester (m/z 55, 57, 69, 71, 88, 101).

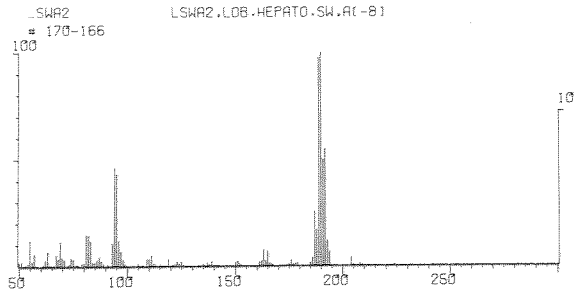

Fig. 2. Mass spectrum of scan 170,0.89 corrected for background in scan 166. m/z 190 is molecular ion of 4H-cyclopenta(def)phenanthrene, m/z 192 is molecular ion of methylphenanthrene (or methylanthracene).

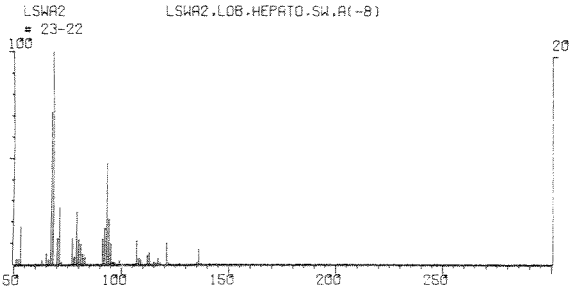

Fig. 5. Mass spectrum of scan 23,0.12 corrected for background in scan 22 (see Table 2).

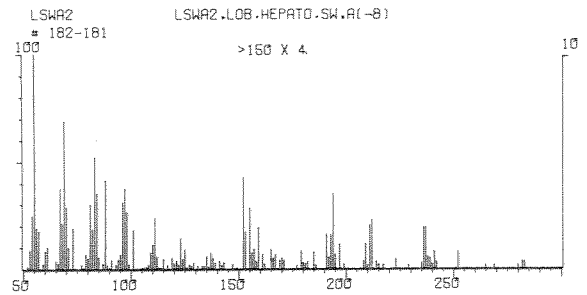

Fig. 3. Mass spectrum of scan 182,0.95 corrected for background in scan 181. Intense ions belong to the monoolefinic series C_nH_{2n-1} (55, 69, 83). Ions at m/z 88 and 101 indicate an ethyl ester or 1-methyl methyl ester.

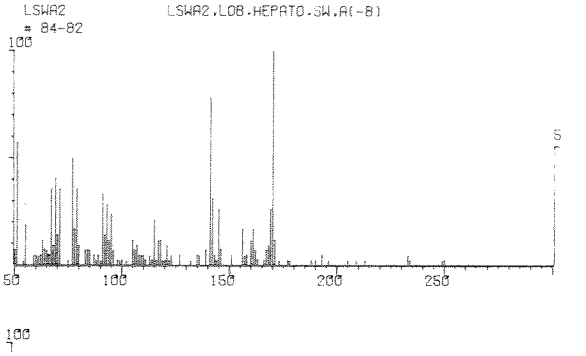

Fig. 6. Mass spectrum of scan 84,0.44 corrected for background in scan 82. Diphenyl ether (m/z 170, 141) (see Table 2).

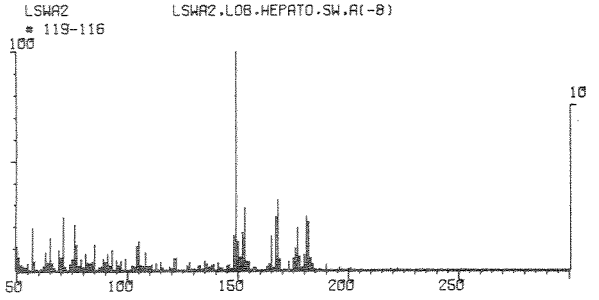

Fig. 7. Mass spectrum of scan 119,0.62 corrected for background in scan 116. An unusual phthalate eluting before dibutylphthalate or alkylphenol (m/z 149).

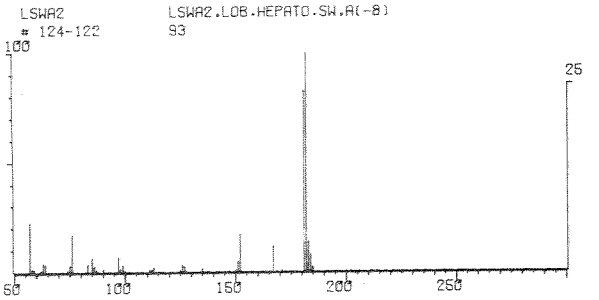

Fig. 8. Mass spectrum of scan 124,0.65 corrected for background in scan 122. Xanthene (m/z 182).

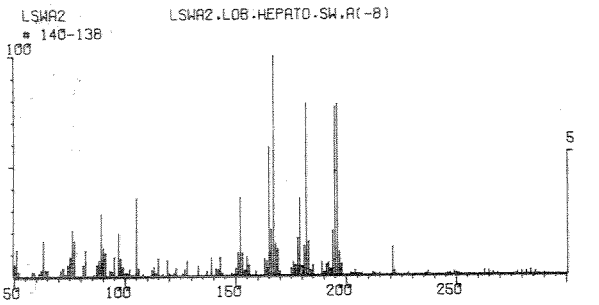

Fig. 9. Mass spectrum of scan 140,0.73 corrected for background in scan 138. A mixture of compounds, a hydrocarbon $C_{14}H_{14}$ (m/z 182 and 167), a hydrocarbon $C_{15}H_{16}$ (m/z 196 and 195), and a trace of hexachlorobenzene (cluster at m/z 282) (see Table 2 and text).

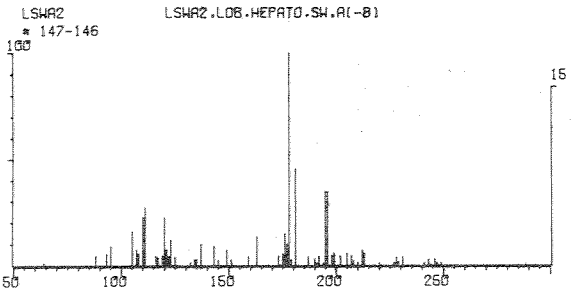

Fig. 10. Mass spectrum of scan 147,0.77 corrected for background in scan 146. Another $C_{15}H_{16}$ hydrocarbon? (see Fig. 9, Table 2, and text).

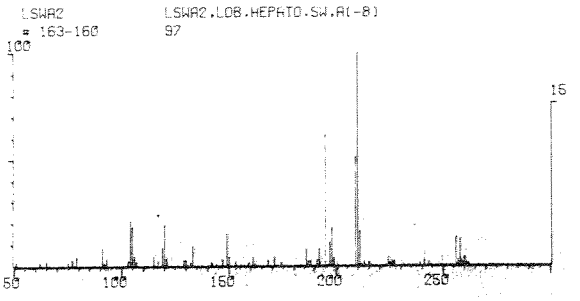

Fig. 11. Mass spectrum of scan 163,0.85 corrected for background in scan 160. $C_{16}H_{18}$ or $C_{15}H_{14}O$ (m/z 210) fragmenting by CH_3 loss (m/z 195). A trichlorobiphenyl (cluster at m/z 256) (see Table 2).

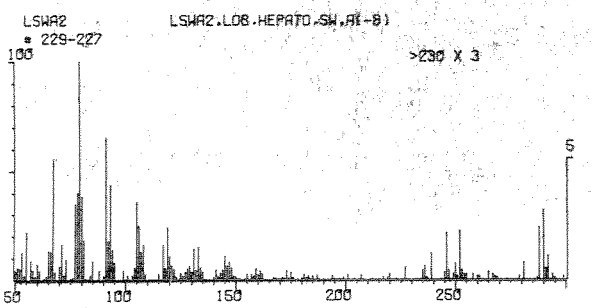

Fig. 12. Mass spectrum of scan 229,1.20 corrected for background in scan 227. Hexachlorobiphenyl (cluster at m/z 358) and a polyunsaturated fatty acid ester (m/z 67, 79, 91, ...).

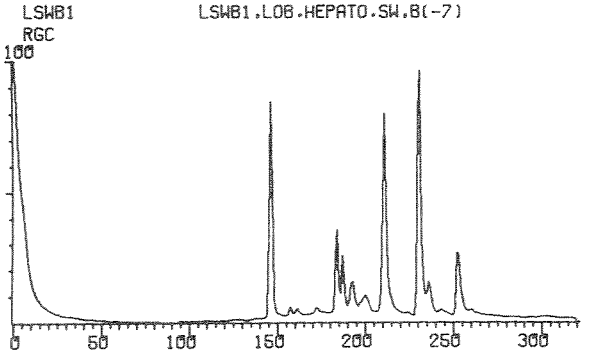

Fig. 13. Reconstructed gas chromatogram (RGC) of sample LSWB1. Major peaks: pristane (scan 146,0.76), fatty acid esters in scans 211,1.09 and 231,1.20.

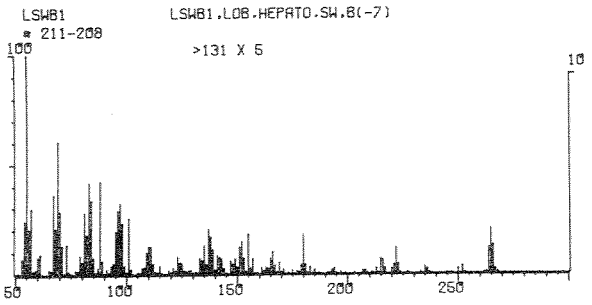

Fig. 14. Mass spectrum of scan 211,1.09 corrected for background in scan 208. Interpreted as ethyl oleate (series of monoolefinic ions at m/z 55, 69, 83. Ions at m/z 88 and 101 indicate ethyl ester.

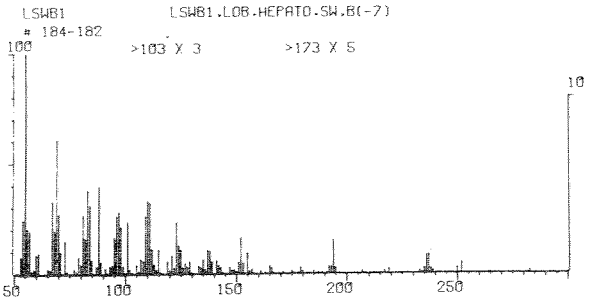

Fig. 15. Mass spectrum of scan 184,0.95 corrected for background in scan 182. Interpreted as tetradecenoic acid ethyl ester.

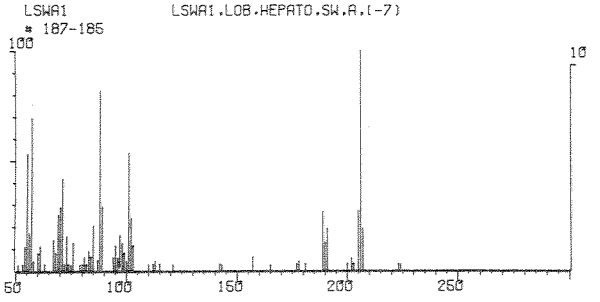

Fig. 16. Mass spectrum of scan 187,0.97 corrected for background in scan 186. Ions indicating ethyl ester (m/z 88 and 101) more prominent than in Fig. 15. Interpreted as tetradecanoic acid ethyl ester.

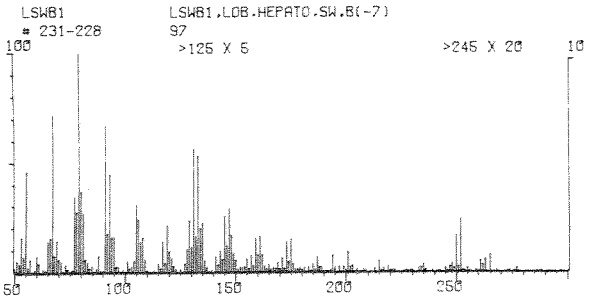

Fig. 17. Mass spectrum of scan 231,1.20 corrected for background in scan 228. Main ions at m/z 79, 67, and 91. Interpreted as polyunsaturated fatty acid ethyl ester (m/z 88 and 101).

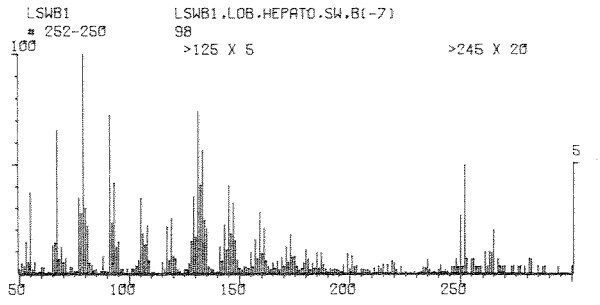

Fig. 18. Mass spectrum of scan 252,1.31 corrected for background in scan 250 (see Fig. 17).

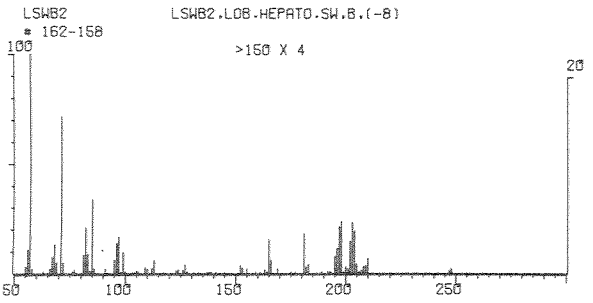

Fig. 19. Mass spectrum of scan 162,0.84 corrected for background in scan 158. A mixture of compounds: a paraffin (m/z 57, 71, 85), probably phytane (2,6,10,14-tetramethylhexadecane), PAH (m/z 198, 204), and a compound yielding ions at m/z 181 and 165.

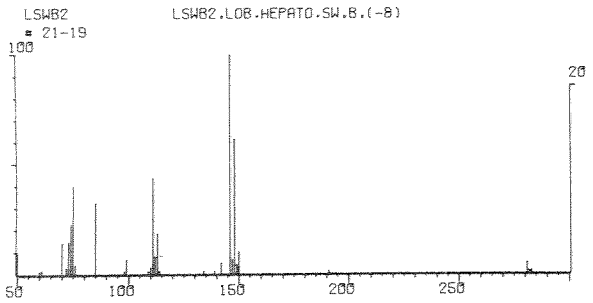

Fig. 20. Mass spectrum of scan 21,0.11 corrected for background in scan 19. Dichlorobenzene (m/z 146-2Cl, 111-1Cl).

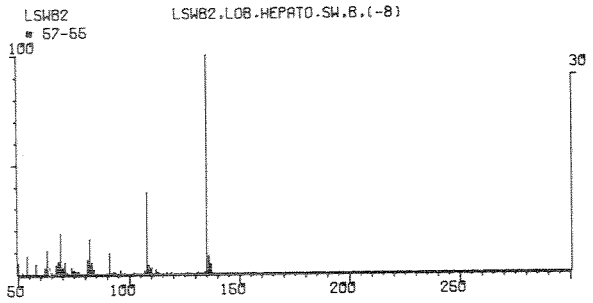

Fig. 21. Mass spectrum of scan 57,0.30 corrected for background in scan 55. Benzothiazole.

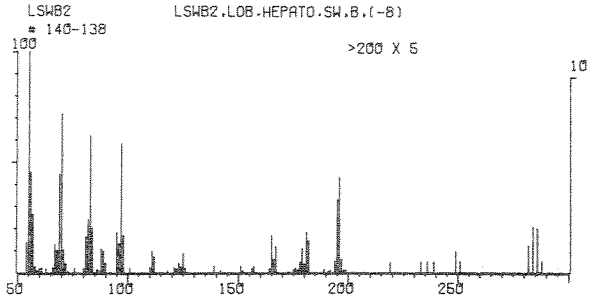

Fig. 22. Mass spectrum of scan 140,0.72 corrected for background in scan 138. A mixture of compounds: an unidentified PAH m/z 196 (see also sample series LSWA), coeluting with hexachlorobenzene (cluster at m/z 282), and an unsaturated fatty acid ethyl ester (m/z 55, 69, 83, 97, 88, 101).

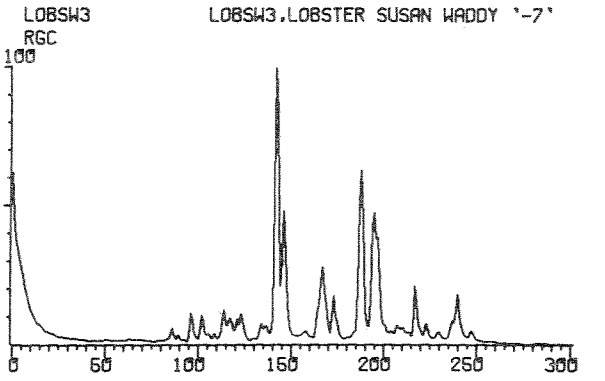

Fig. 23. Reconstructed gas chromatogram (RGC) of sample LOBSW3. Major peaks are: pristane (scan 142,0.76) and polycyclic aromatic hydrocarbons, phenanthrene (scan 146,0.78), 4H-cyclopenta(def)-phenanthrene (scan 167,0.89), fluoranthene (scan 188,1.00), and pyrene (scan 195,1.04).

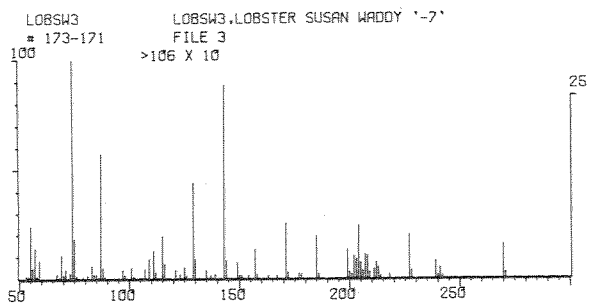

Fig. 24. Mass spectrum of scan 173,0.98 corrected for background in scan 171. Interpreted as stearic acid methyl ester (m/z 87, 101, 115, 119) and m/z 74 indicating methyl ester.

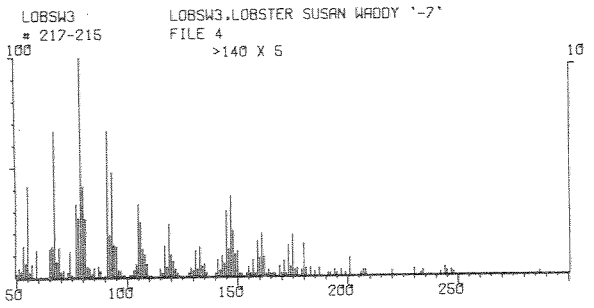

Fig. 25. Mass spectrum of scan 217,1.16 corrected for background in scan 215. Interpreted as a polyunsaturated fatty acid (C_{20}) methyl ester (m/z 67, 79, 91, 105, 119).

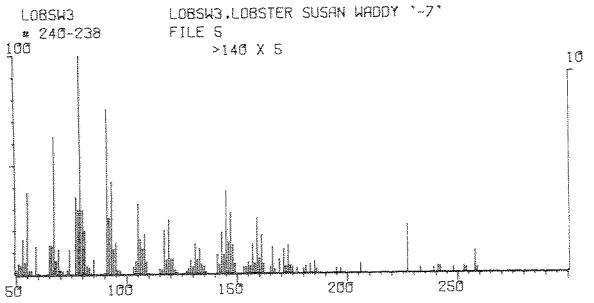

Fig. 26. Mass spectrum of scan 240,1.28 corrected for background in scan 238. Interpreted as a polyunsaturated fatty acid (C_{22}) methyl ester (see also Fig. 25).

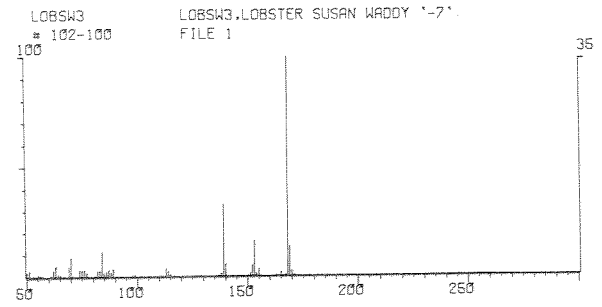

Fig. 27. Mass spectrum of scan 102,0.54 corrected for background in scan 100. A hydrocarbon $C_{13}H_{12}$ or dibenzofuran.

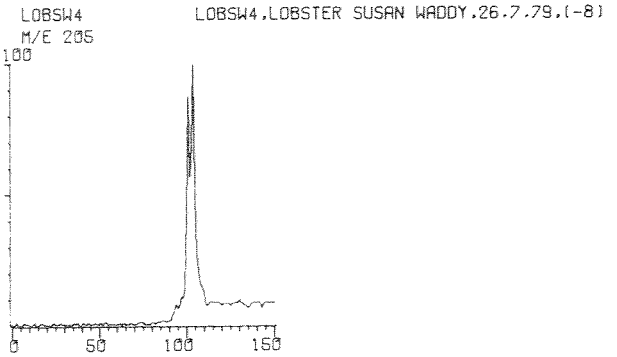

Fig. 28. Limited mass reconstructed gas chromatogram (LMRGC) for m/z 205 (base ion of BHT).

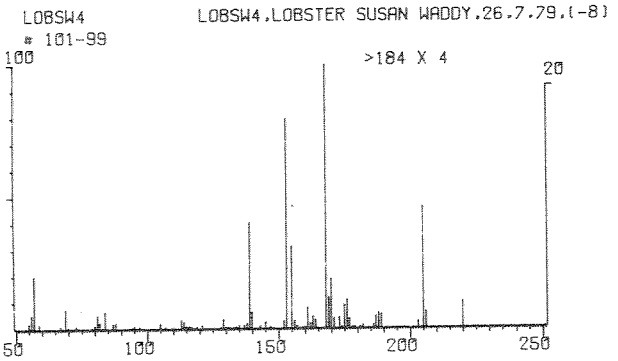

Fig. 29. Mass spectrum of scan 101,0.54 corrected for background in scan 99. Interpreted as butylated hydroxytoluene.

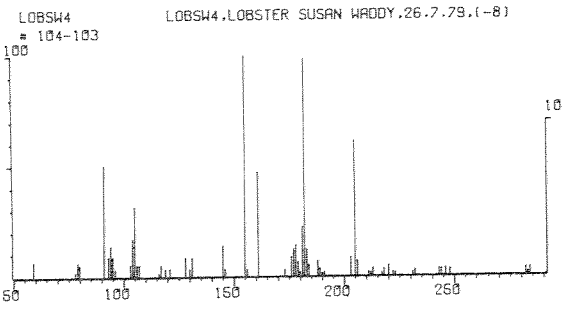

Fig. 30. Mass spectrum of scan 104,0.55 corrected for background in scan 103. Interpreted as butylated hydroxytoluene. Compare with Fig. 29. Mass spectra in Fig. 29 and 30 correspond to the m/z 205 maxima in Fig. 28.

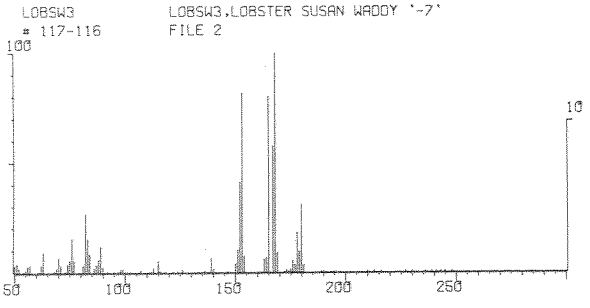

Fig. 31. Mass spectrum of scan 117,0.62 corrected for background in scan 116. Interpreted as a mixture of hydrocarbons, $C_{13}H_{12}$ (m/z 168 and 153) and $C_{14}H_{12}$ (m/z 180 and 165).

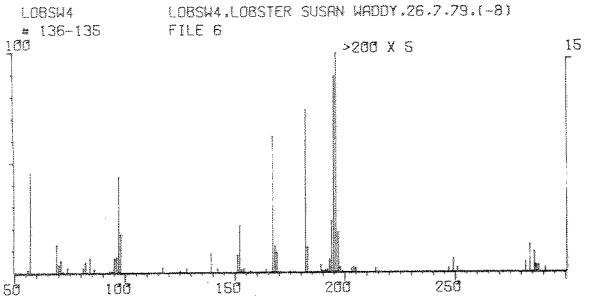

Fig. 32. Mass spectrum of scan 136,0.72 corrected for background in scan 135. A mixture of compounds: unidentified compound m/z 196 (compare to Fig. 9 and Fig. 22), hexachlorobenzene (cluster at m/z 282) and a compound yielding ions at m/z 182 and 165.

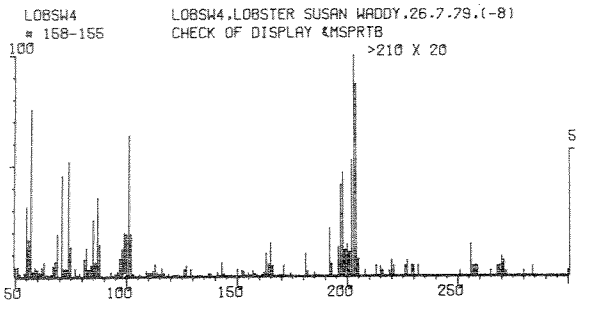

Fig. 33. Mass spectrum of scan 158,0.84 corrected for background in scan 155. A mixture of compounds interpreted as 1-phenylnaphthalene (m/z 204, 203, 202) and methyl dibenzothiophene (m/z 198, 197).

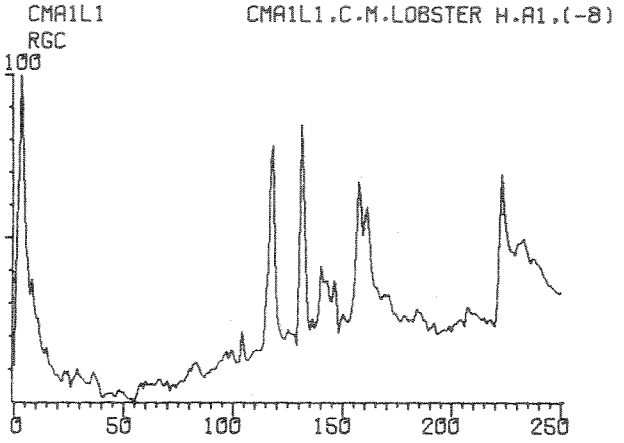

Fig. 34. Reconstructed gas chromatogram (RGC) of sample CMA1L1. Major peaks are: pristane (scan 118,0.72), a nitrogen compound, probably nitrile (scan 131,0.80), and DEHP (scan 223,1.37). The two partly resolved peaks in scans 157,0.96 and 161,0.98 have not been identified.

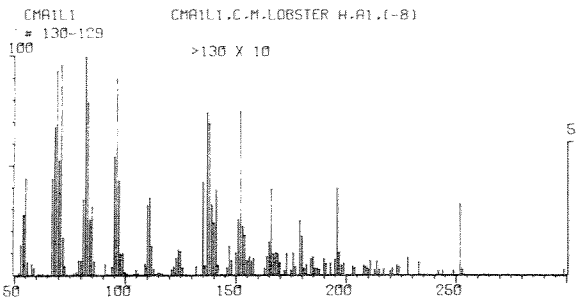

Fig. 35. Mass spectrum of scan 130,0.80 corrected for background in scan 129. Major ions are at m/z 69, 71, 82, 96, and 110 (see also Fig. 36).

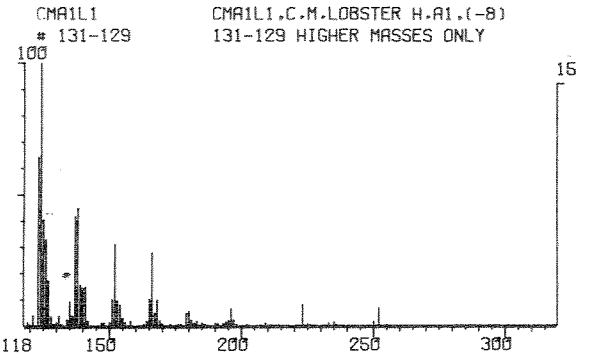

Fig. 36. Mass spectrum of scan 131,0.80 corrected for background in scan 129. Only ions above m/z 118 are displayed (see also Fig. 35). Note that all major ions have even masses (124, 138, 152, 166), indicating the presence of nitrogen. Tentatively interpreted as an aliphatic nitrile.

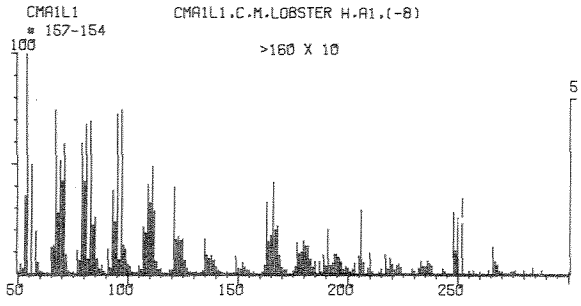

Fig. 37. Mass spectrum of scan 157,0.96 corrected for background in scan 154. Base ion is m/z 54, which is quite uncommon, may indicate a nitrile. Other major ions appear to form two series (81/83, 95/97, 109/111 and 121, 135, 149). Unidentified.

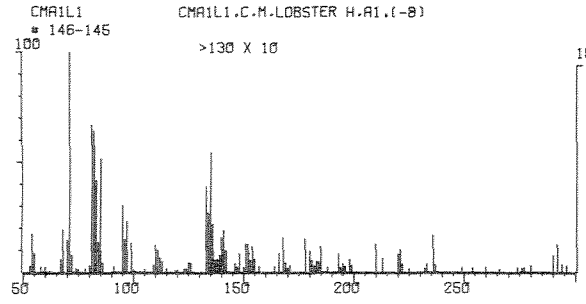

Fig. 40. Mass spectrum of scan 146,0.90 corrected for background in scan 145. Base ion is at m/z 71. Unidentified.

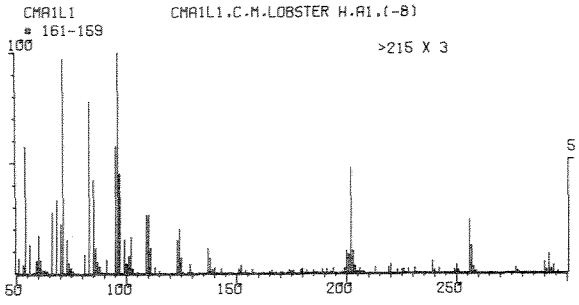

Fig. 38. Mass spectrum of scan 161,0.98 corrected for background in scan 159. A mixture of compounds. The strong ions at m/z 96 and 54 may indicate a nitrile. The ion at m/z 202 is due to fluoranthene (peaking in scan 163). A tetrachlorobiphenyl is also present (cluster at m/z 290).

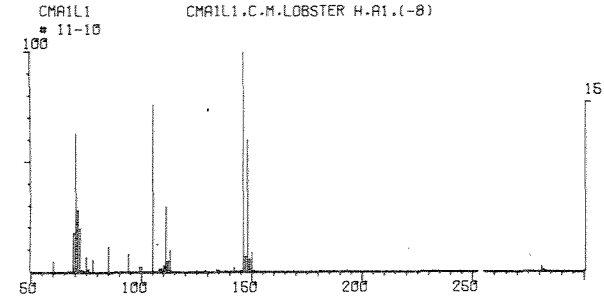

Fig. 41. Mass spectrum of scan 11,0.07 corrected for background in scan 10, presented to illustrate the performance of the mass spectrometer on this sample. A dichlorobenzene (m/z 146 and 111). Also contains a compound yielding ions at m/z 105 and 70, probably a pentyl benzoate. Compare with Fig. 20.

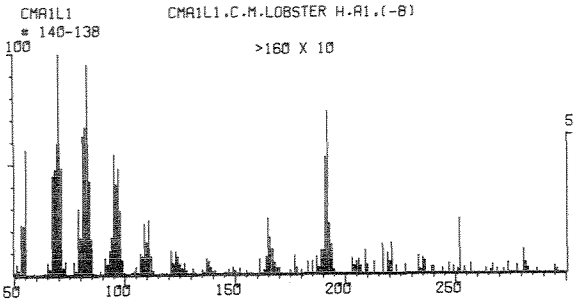

Fig. 39. Mass spectrum of scan 140,0.87 corrected for background in scan 138. Major ions are at m/z 55, 70, 83. Possibly a 2-unsaturated aldehyde. The ion at m/z 192 is probably due to a methyl-phenanthrene.

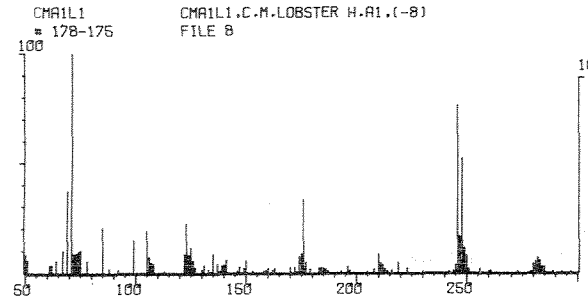

Fig. 42. Mass spectrum of scan 178,1.09 corrected for background in scan 175, presented to illustrate the performance of the mass spectrometer on this sample. p,p'-DDE (clusters at 316 and 246).

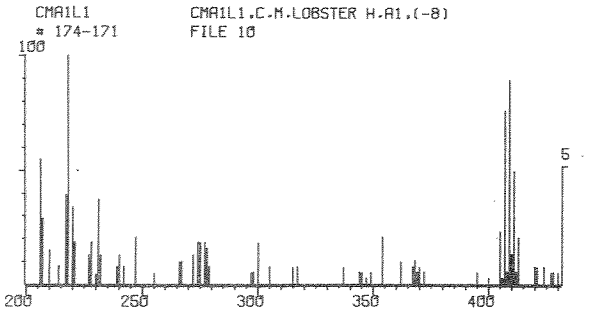

Fig. 43. Mass spectrum of scan 174,1.07 corrected for background in scan 171, presented to illustrate the performance of the mass spectrometer on this sample. trans-nonachlor (cluster at m/z 405).

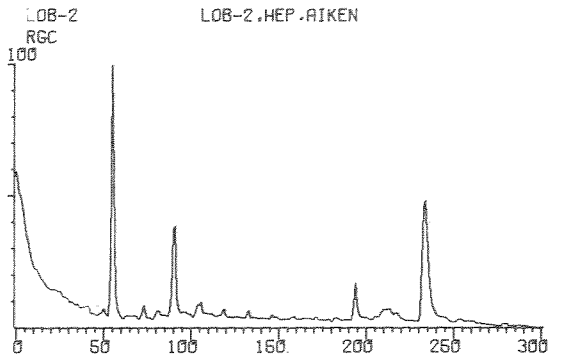

Fig. 46. Reconstructed gas chromatogram of sample LOB-2. Major peaks are: BHT (scan 55,0.42), pristane (scan 91,0.69), DEHP (scan 194,1.47), and a hydrocarbon, possibly squalene (scan 234,1.77).

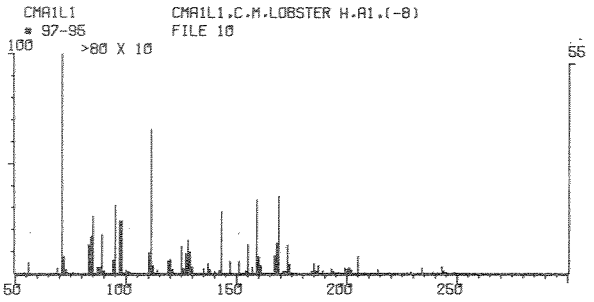

Fig. 44. Mass spectrum of scan 97,0.59 corrected for background in scan 95. Very intense ion at m/z 71. A number of compounds yield a similar spectrum, not specific enough for identification.

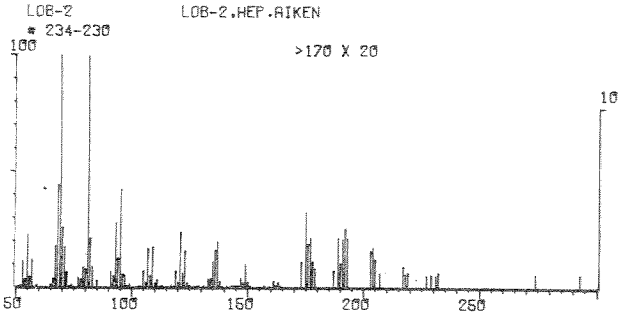

Fig. 47. Mass spectrum of scan 234,1.77 corrected for background in scan 230. Major ions at m/z 69 and 81. Interpreted as squalene (2,6,10,14,18,22-tetracosahexaene,2,6,10,15,19,23-hexamethyl) or a similar hydrocarbon.

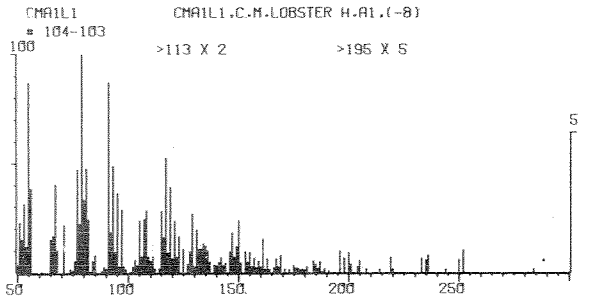

Fig. 45. Mass spectrum of scan 104,0.64 corrected for background in scan 103. Resembles a polyunsaturated fatty acid methyl ester (compare with Fig. 25, 26), but has a very short retention time.

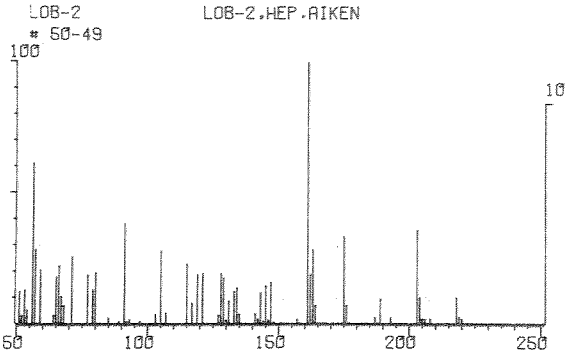

Fig. 48. Mass spectrum of scan 50,0.38 corrected for background in scan 49. Base ion at m/z 161, molecular ion m/z 218. 2,6-di-tert-butyl-4-methylene-2,5-cyclohexadienone, a metabolite of BHT.

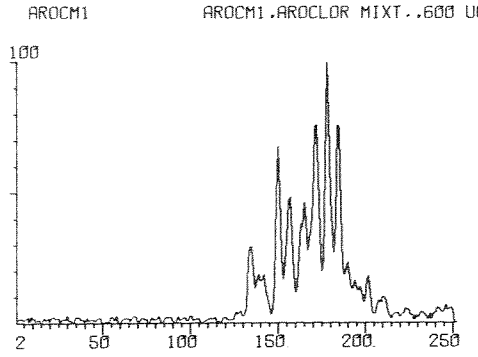

Fig. 49. Simulated gas chromatographic profile of Aroclor 1254. Compare to Fig. 50.

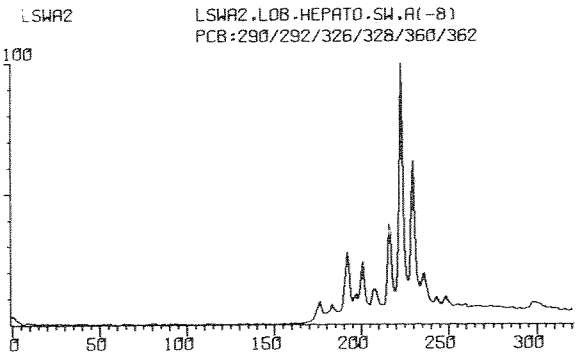

Fig. 50. Simulated gas chromatographic profile of PCB in sample LSWA2.