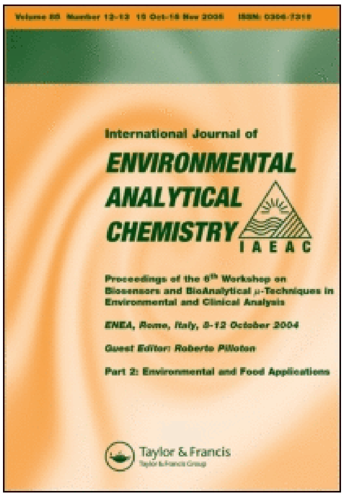

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

The Analysis of Environmental Samples by Mass Spectrometry

R. C. Lao[a]; R. S. Thomas[a]; J. L. Monkman[a]
[a] Air Pollution Control Division Department of the Environment Tunney's, Pasture, Ottawa, Canada

To cite this Article Lao, R. C. , Thomas, R. S. and Monkman, J. L.(1972) 'The Analysis of Environmental Samples by Mass Spectrometry', International Journal of Environmental Analytical Chemistry, 1: 3, 187 — 203

To link to this Article: DOI: 10.1080/03067317208076371

URL: http://dx.doi.org/10.1080/03067317208076371

Intern. J. Environ. Anal. Chem., 1972, Vol. 1, pp. 187–203

Printed in Great Britain

The Analysis of Environmental Samples by Mass Spectrometry†

R. C. LAO, R. S. THOMAS, and J. L. MONKMAN

Air Pollution Control Division
Department of the Environment
Tunney's Pasture, Ottawa, Canada

(*Received October 4, 1971*)

Mass spectral analysis was carried out on shellfish samples taken in the vicinity of the Arrow oil spill at Chedabucto Bay, Nova Scotia. Oil samples were also analyzed, samples being obtained from the tanker and also from the beach.

After extraction of the oil and shellfish samples, group separations were made into aliphatic, aromatic and oxygenated fractions, which were analyzed separately by mass spectrometry. The validity of the group separations was established, since, in the analysis of the so-called aliphatic fraction, no evidence of aromatics could be seen by mass spectrometry.

On the other hand, polycyclic hydrocarbons were found in some of the aromatic fractions. Identification was based upon standard mass spectrometric analysis already performed on known examples of the polycyclics.

It was concluded that the possibility of oil contamination can be confirmed by the mass spectrometric analysis of appropriate samples. It was also concluded that the so-called control samples should have been taken at a greater distance from the oil spill.

INTRODUCTION

During the weeks subsequent to the Arrow oil spill in Chedabucto Bay, Nova Scotia, on February 4, 1970, a programme was established to assess the extent of contamination of the clam beds. Continued observations of soft-

---

† Presented at the Symposium on Recent Advances in the Analytical Chemistry of Organic Pollutants, 54th Canadian Chemical Conference, Halifax, May 31–June 2, 1971.

shell clams (mya arenaria) into the late spring revealed oil extending down most clam burrows. A number of clam beds were closed, pending a study of the quantity and toxicity of oil residues in the clams. Zitko[1] has analyzed clams and demonstrated oil in both the digestive tract and muscle tissue. The ability of clams and other marine life to accumulate a variety of toxic substances has been well documented.[1-3]

Clam samples from contaminated and non-contaminated areas were analyzed for aromatic hydrocarbon content. Clam samples from Janvrin Island and Harbour and Glasgow Head were selected as being representative of areas contaminated by Bunker C oil from the Arrow. Samples of oil from the Arrow's hold and samples scraped off the beaches of Durell Island were taken as contaminant standards. Control samples were provided from the clam beds of Fuller Bridge at Forchu, located some 50 miles north-east along the seaward coast of Cape Breton Island.

PROCEDURE

The clam samples were macerated in a blender and extracted using cyclohexane in a soxhlet extraction apparatus. The extracts in cyclohexane were transferred to borosilicate bottles and stored in the dark under refrigeration prior to separation chromatography. All extracts displayed intense blue fluorescence under long- and short-wave u.v. light. Berkhoff[4] had suggested the major portion of the PAH portion of Arrow oil should consist of mainly naphthalene derivatives with low concentrations of larger condensed molecules.

First attempts to analyze clam extracts or crude oil met failure. The untreated samples were far too complex to be analyzed by mass spectrometry or other conventional spectroscopic techniques. It was necessary to adapt the group separation used during the analysis of PAH in airborne particulates to isolate the aromatic fraction and to permit meaningful interpretation of the analytical data.[4-7]

To effectively separate the samples into aliphatic, aromatic, and heterocyclic components, chromatographic columns 2.5 in. i.d. by 10 in. deep were prepared by slurrying 200-mesh Davidson Silica Gel in iso-octane. The silica gel had previously been activated by heating in an oven at 140°C for two days. The clam extracts were gently reduced to dryness at room temperature by evaporating with a stream of nitrogen; then they were redissolved in hot iso-octane and placed on the columns. The oil samples were placed directly on the column head and each column was capped with glass beads. Development was effected by elution, using 2.5 litres of iso-octane, 1.3 litres of benzene and 1.0 litre of ethanol. All elution solvents were spectro-grade purity or better. Figure 1 shows the flow chart of the clean-up procedure and the resulting fractionation of the sample by the Rosen separation.[8]

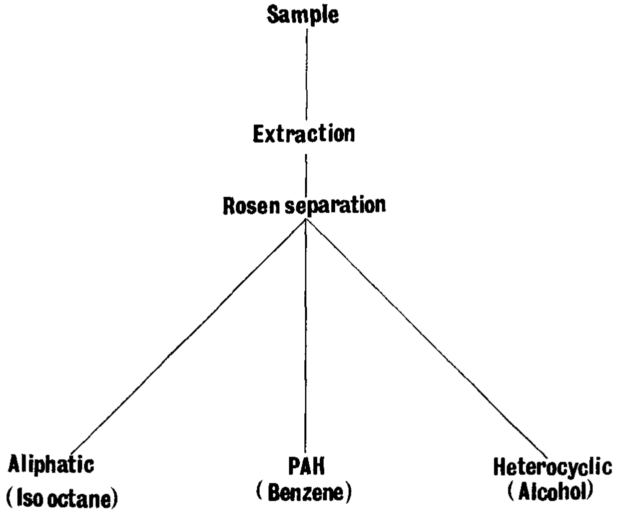

FIGURE 1 Flow chart of Rosen separation.

Mass spectral analyses were carried out on all the chromatographic fractions. In all spectra the prominent peaks are similar. A limit of m/e = 100 was set for examination since, below this mass, the interferences from the solvents used in preparing the samples would make meaningful interpretation of the spectra extremely difficult. Above this mass limit the most prominent peak is at m/e = 135 and this was selected as a base peak for the calculation of the relative abundance of the spectra.

Figures 2, 3 and 4 are representative of the separated fractions of clam extracts. In the iso-octane fraction (Figure 2) there is no evidence of aromatic hydrocarbons of two condensed rings or larger. The high relative abundance of low mass values less than m/e = 100 confirms the presence of aliphatics and paraffins expected in this fraction. Standard reference spectra of polycyclics are shown in Figures 5, 6 and 7 (Tables I, II and III).

The presence of polycyclic hydrocarbons is demonstrated in Figure 8, for the benzene fraction of the extract. The relative abundance of m/e = 252 to 253, 126 to 125 and 113 to 112 and the doubly charged ions at m/e = 126.5, 125.5, 113.5 and 112.5 offer confirmation of the presence of polycyclic hydrocarbons. These characteristics are clearly established by standard reference spectra mentioned above. Figure 4 is representative of the ethanol fraction from the separation. This spectrum confirms the elution of the aromatic fraction from the column with benzene. The structure below m/e = 100 may be attributed to the solvents used.

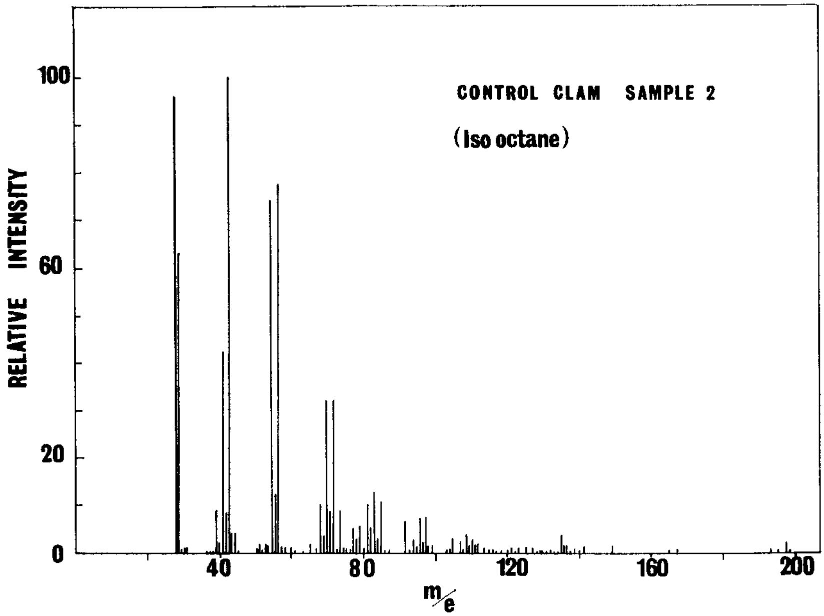

FIGURE 2 Mass spectrum, m/e versus abundance for control sample 2 (iso-octane fraction).

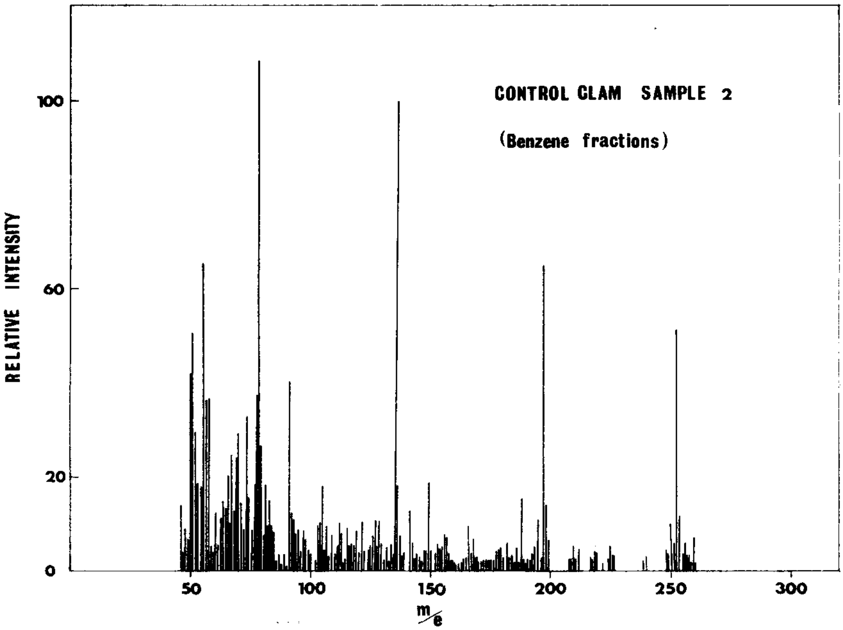

FIGURE 3 Mass spectrum, m/e versus abundance for control sample 2 (benzene fraction).

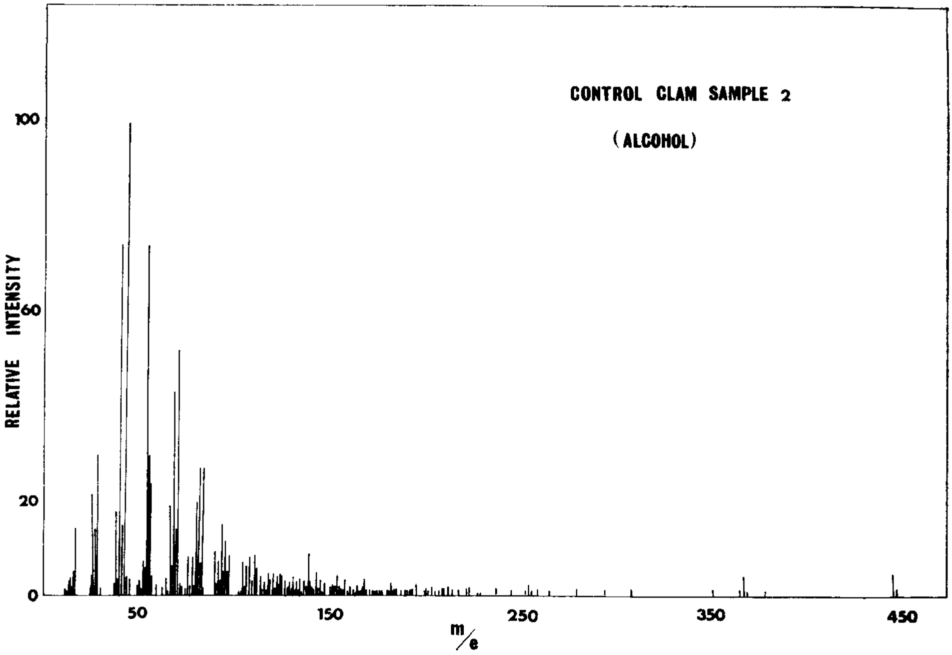

FIGURE 4 Mass spectrum, m/e versus abundance for control sample 2 (alcohol fraction).

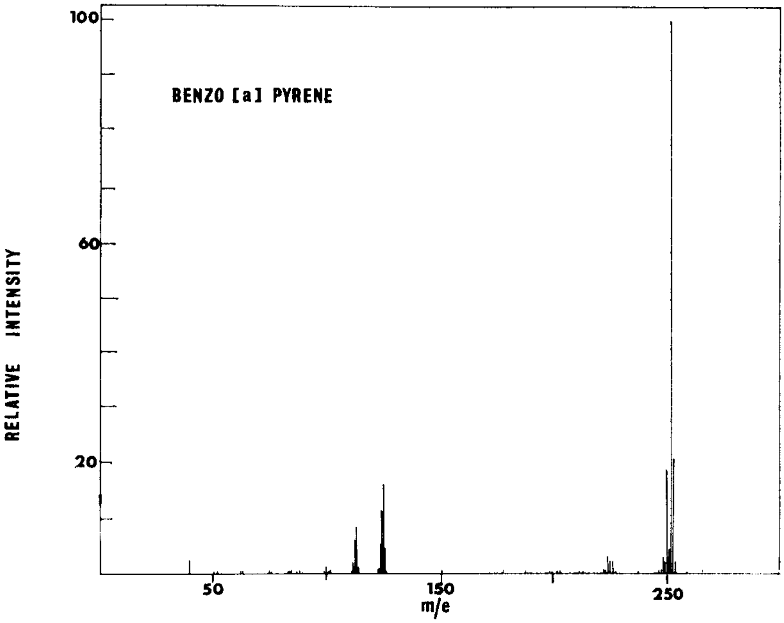

FIGURE 5 Mass spectrum, m/e versus abundance for BaP.

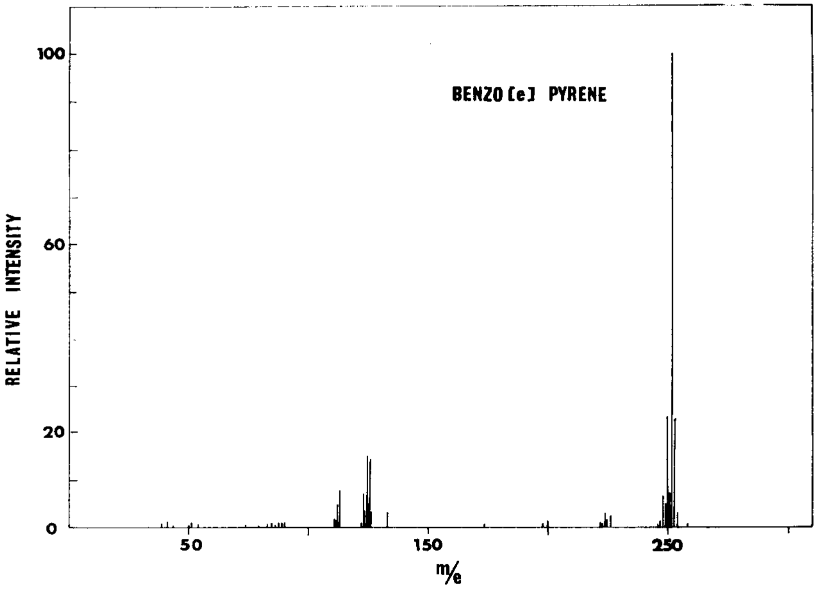

FIGURE 6 Mass spectrum, m/e versus abundance for BeP.

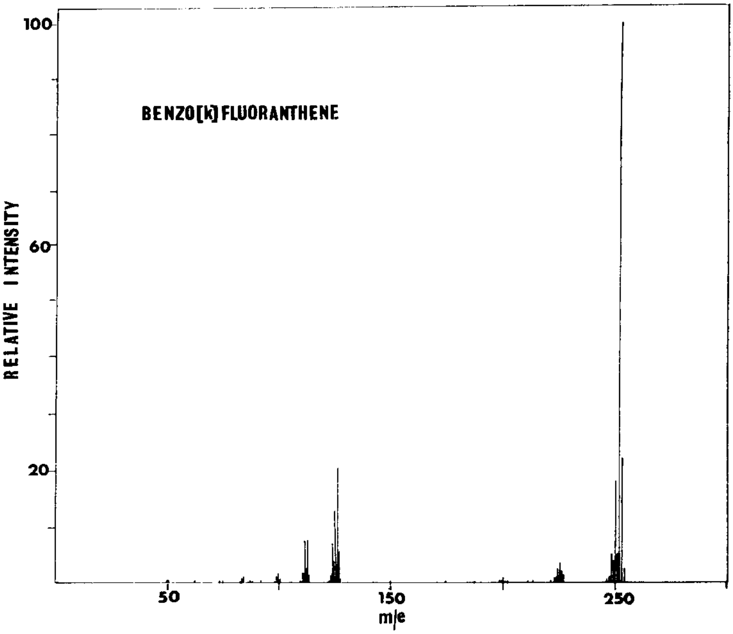

FIGURE 7 Mass spectrum, m/e versus abundance for BkF.

TABLE I

Mass spectral data of benzo(a)pyrene

Mass-Charge Ratio, m/e	Relative Intensity	Mass-Charge Ratio, m/e	Relative Intensity	Mass-Charge Ratio, m/e	Relative Intensity
39.0	2.76	82.7	0.23	108.0	0.01
40.0	0.04	83.0	0.64	109.0	0.08
41.0	0.02	83.3	0.84	110.0	0.38
42.0	0.01	83.7	0.26	110.5	0.17
43.0	0.02	84.0	1.10	111.0	1.65
44.0	0.04	84.3	0.17	111.5	1.42
49.0	0.01	84.7	0.01	112.0	5.15
50.0	0.70	85.0	0.16	112.5	1.79
51.0	0.56	85.5	0.08	113.0	8.26
52.0	0.08	86.0	0.69	113.5	16.10
53.0	0.01	86.5	0.07	114.0	0.20
55.0	0.02	87.0	1.02	114.5	0.01
56.0	0.01	87.5	0.08	115.0	0.01
57.0	0.01	88.0	0.34	116.0	0.02
61.0	0.13	88.5	0.03	117.0	0.03
62.0	0.54	89.0	0.07	117.5	0.11
63.0	0.81	90.0	0.01	118.0	0.07
64.0	0.07	91.0	0.46	118.5	0.14
65.0	0.03	92.0	0.27	119.0	0.03
67.0	0.03	92.5	0.01	119.5	0.04
68.0	0.01	93.0	0.37	120.0	0.02
69.0	0.01	93.5	0.14	121.0	0.03
73.0	0.07	94.0	0.04	122.0	0.39
73.5	0.07	94.5	0.04	122.5	0.08
74.0	0.95	95.0	0.46	123.0	0.92
74.3	0.02	97.0	0.05	123.5	0.85
74.5	0.02	97.5	0.03	124.0	5.31
74.7	0.06	98.0	0.82	124.5	2.69
75.0	0.68	98.5	0.11	125.0	11.46
75.3	0.11	99.0	1.30	125.5	2.67
75.7	0.02	99.5	0.53	126.0	16.39
76.0	0.18	100.0	1.54	126.5	3.56
77.0	0.14	100.5	0.35	127.0	0.64
78.0	0.08	101.0	0.76	127.5	0.03
79.0	0.36	101.5	0.13	128.0	0.02
79.5	0.02	102.0	0.03	129.0	0.05
80.0	0.02	105.0	0.05	129.5	0.01
80.5	0.01	105.0	0.19	130.0	0.01
81.0	0.46	106.0	0.09	130.5	0.02
81.5	0.03	106.5	0.15	131.0	0.01
82.0	0.40	107.0	0.03	131.5	0.04
82.3	0.08	107.5	0.01	132.0	0.03

Continued overleaf

Table I—*continued*

Mass-Charge Ratio, m/e	Relative Intensity	Mass-Charge Ratio, m/e	Relative Intensity	Mass-Charge Ratio, m/e	Relative Intensity
132.5	0.03	183.0	0.01	227.0	0.30
133.0	0.09	184.0	0.01	228.0	0.19
133.5	0.01	185.0	0.09	229.0	0.03
134.0	0.18	186.0	0.09	230.0	0.01
135.0	0.16	187.0	0.24	231.0	0.01
136.0	0.04	188.0	0.06	233.0	0.01
137.0	0.08	189.0	0.10	234.0	0.01
138.0	0.03	190.0	0.01	235.0	0.07
139.0	0.03	194.0	0.01	236.0	0.04
145.0	0.01	195.0	0.01	237.0	0.21
146.0	0.17	196.0	0.01	238.0	0.04
147.0	0.10	197.0	0.09	239.0	0.03
148.0	0.05	198.0	0.67	240.0	0.01
149.0	0.11	199.0	0.38	245.0	0.03
150.0	0.30	200.0	0.93	246.0	0.50
151.0	0.11	201.0	0.33	247.0	0.62
152.0	0.03	202.0	0.64	248.0	4.19
158.0	0.06	203.0	0.11	249.0	2.76
159.0	0.06	204.0	0.01	250.0	19.34
160.0	0.01	208.0	0.01	251.0	5.87
161.0	0.10	209.0	0.06	252.0	*100.00*
162.0	0.06	210.0	0.06	253.0	21.49
163.0	0.13	211.0	0.31	254.0	2.24
164.0	0.03	212.0	0.11	255.0	0.15
165.0	0.01	213.0	0.30	256.0	0.02
170.0	0.05	214.0	0.06	257.0	0.01
171.0	0.03	215.0	0.05	258.0	0.21
172.0	0.02	216.0	0.08	259.0	0.04
173.0	0.07	217.0	0.02	260.0	0.01
174.0	0.36	220.0	0.02	261.0	0.01
175.0	0.14	221.0	0.27	263.0	0.05
176.0	0.08	222.0	0.96	264.0	0.02
177.0	0.01	223.0	0.84	265.0	0.11
180.0	0.01	224.0	3.06	266.0	0.42
181.0	0.01	225.0	2.27	267.0	0.08
182.0	0.01	226.0	2.33		

TABLE II

Mass spectral data of benzo(e)pyrene

Mass-Charge Ratio, m/e	Relative Intensity	Mass-Charge Ratio, m/e	Relative Intensity	Mass-Charge Ratio, m/e	Relative Intensity
39.0	0.51	82.0	0.02	116.0	0.09
40.0	0.11	82.3	0.09	116.5	0.07
41.0	0.70	82.7	0.22	117.0	0.14
42.0	0.16	83.0	0.46	117.5	0.16
43.0	0.25	83.3	0.75	118.0	0.16
44.0	0.07	83.7	0.28	118.5	0.17
45.0	0.17	84.0	0.68	119.0	0.07
46.0	0.05	84.3	0.13	119.5	0.07
48.0	0.04	84.7	0.01	120.0	0.05
49.0	0.05	85.0	0.07	122.0	0.26
50.0	0.30	85.5	0.04	122.5	0.29
51.0	0.46	86.0	0.33	123.0	1.18
52.0	0.28	86.5	0.09	123.5	0.95
53.0	0.14	87.0	0.72	124.0	6.95
54.0	0.42	88.0	0.34	124.5	3.58
55.0	0.28	91.0	0.95	125.0	15.53
56.0	0.21	98.0	0.39	125.5	4.72
57.0	0.34	98.5	0.14	126.0	14.47
61.0	0.04	99.0	1.33	126.5	3.16
62.0	0.25	99.5	0.46	127.0	0.57
63.0	0.57	100.0	1.34	127.5	0.07
64.0	0.09	100.5	0.33	128.0	0.21
65.0	0.12	101.0	0.37	128.5	0.07
66.0	0.05	102.0	0.16	129.0	0.34
67.0	0.05	103.0	0.11	129.5	0.07
68.0	0.02	104.0	0.04	130.0	0.07
69.0	0.05	105.0	0.33	130.5	0.09
70.0	0.04	105.5	0.24	131.0	0.11
71.0	0.04	106.0	0.60	131.5	0.13
73.0	0.05	106.5	0.14	132.0	0.13
73.5	0.05	107.0	0.11	132.5	0.11
74.0	0.46	108.0	0.04	133.0	6.14
75.0	0.38	109.0	0.07	133.5	0.07
75.3	0.11	110.0	0.33	134.0	0.13
75.7	0.04	110.5	0.37	135.0	0.18
76.0	0.18	111.0	1.75	136.0	0.04
77.0	0.28	111.5	1.44	137.0	0.05
78.0	0.40	112.0	4.72	146.0	0.13
79.0	0.12	112.5	1.63	147.0	0.11
80.0	0.03	113.0	7.76	148.0	0.07
80.5	0.01	114.0	0.15	149.0	0.13
81.0	0.08	115.5	0.08	150.0	0.24

Continued overleaf

Table II—*continued*

Mass-Charge Ratio, m/e	Relative Intensity	Mass-Charge Ratio, m/e	Relative Intensity	Mass-Charge Ratio, m/e	Relative Intensity
151.0	0.07	201.0	0.29	236.0	0.11
152.0	0.04	202.0	0.29	237.0	0.21
158.0	0.05	203.0	0.10	238.0	0.08
159.0	0.07	204.0	0.09	239.0	0.07
160.0	0.05	205.0	0.09	240.0	0.05
161.0	0.08	206.0	0.09	245.0	0.21
162.0	0.07	209.0	0.08	246.0	1.34
163.0	0.08	210.0	0.12	247.0	1.14
170.0	0.07	211.0	0.46	248.0	5.16
171.0	0.07	212.0	0.13	249.0	3.68
172.0	0.07	213.0	0.31	250.0	23.95
173.0	0.11	214.0	0.07	251.0	7.15
174.0	0.41	219.0	0.07	252.0	*100.00*
175.0	0.16	220.0	0.13	253.0	21.14
176.0	0.09	221.0	0.30	254.0	2.14
185.0	0.12	222.0	1.18	255.0	0.16
186.0	0.13	223.0	1.22	256.0	0.20
187.0	0.28	224.0	2.94	257.0	0.11
188.0	0.13	225.0	1.65	258.0	1.34
189.0	0.07	226.0	2.17	259.0	0.30
191.0	0.16	227.0	0.51	260.0	0.10
194.0	0.05	228.0	0.09	261.0	0.07
195.0	0.07	230.0	0.05	263.0	0.13
196.0	0.07	231.0	0.07	264.0	0.11
197.0	0.16	232.0	0.07	265.0	0.18
198.0	0.71	233.0	0.08	266.0	0.62
199.0	0.47	234.0	0.08	267.0	0.17
200.0	0.87	235.0	0.13		

TABLE III

Mass spectral data of benzo(k)fluoranthene

Mass-Charge Ratio, m/e	Relative Intensity	Mass-Charge Ratio, m/e	Relative Intensity	Mass-Charge Ratio, m/e	Relative Intensity
36.0	0.15	82.3	0.16	113.5	1.38
38.0	0.13	82.7	0.18	114.0	0.43
39.0	0.36	83.0	0.89	115.0	0.51
40.0	0.07	83.3	0.61	117.0	0.17
41.0	0.09	83.7	0.21	118.0	0.10
42.0	0.07	84.0	1.01	118.5	0.18
43.0	0.07	84.3	0.26	119.0	0.07
44.0	0.07	84.7	0.05	119.5	0.07
45.0	0.07	85.0	0.08	120.0	0.07
50.0	0.30	85.5	0.05	121.0	0.05
51.0	0.33	86.0	0.63	122.0	0.28
52.0	0.13	86.5	0.08	122.5	0.24
53.0	0.05	87.0	1.15	123.0	0.90
55.0	0.07	87.5	0.15	123.5	0.92
56.0	0.07	88.0	0.50	124.0	5.74
57.0	0.06	88.5	0.17	124.5	2.93
61.0	0.07	89.0	0.45	125.0	12.65
62.0	0.25	90.0	0.05	125.5	3.27
63.0	0.50	91.0	0.50	126.0	20.56
64.0	0.07	92.0	0.31	126.5	4.95
65.0	0.07	93.0	0.31	127.0	0.96
66.0	0.07	93.5	0.10	127.5	0.17
67.0	0.05	94.0	0.07	128.0	0.27
68.0	0.04	98.0	0.88	132.0	0.08
69.0	0.05	98.5	0.15	133.0	0.10
70.0	0.06	99.0	1.68	134.0	0.13
71.0	0.05	99.5	0.60	135.0	0.13
73.0	0.08	100.0	2.22	136.0	0.05
73.5	0.08	100.5	0.51	137.0	0.07
74.0	0.53	101.0	1.26	138.0	0.05
74.3	0.03	105.0	0.13	139.0	0.07
74.7	0.10	105.5	0.18	146.0	0.12
75.0	0.56	106.0	0.15	147.0	0.08
75.3	0.16	106.5	0.13	148.0	0.07
75.7	0.12	109.0	0.10	149.0	0.15
76.0	0.23	110.0	0.43	150.0	0.40
77.0	0.18	110.5	0.52	151.0	0.13
78.0	0.17	111.0	2.16	152.0	0.07
79.0	0.05	111.5	1.79	153.0	0.05
80.0	0.05	112.0	6.62	158.0	0.08
81.0	0.08	112.5	2.11	159.0	0.07
82.0	0.45	113.0	7.76	160.0	0.05

Continued overleaf

Table III—*continued*

Mass-Charge Ratio, m/e	Relative Intensity	Mass-Charge Ratio, m/e	Relative Intensity	Mass-Charge Ratio, m/e	Relative Intensity
161.0	0.12	201.0	0.36	235.0	0.17
162.0	0.10	202.0	0.81	236.0	0.08
163.0	0.25	203.0	0.10	237.0	0.25
164.0	0.07	209.0	0.27	245.0	0.17
170.0	0.07	210.0	0.70	246.0	0.70
171.0	0.07	211.0	0.39	247.0	0.91
172.0	0.07	212.0	0.15	248.0	4.46
173.0	0.10	213.0	0.36	249.0	2.93
174.0	0.41	214.0	0.07	250.0	18.69
175.0	0.18	220.0	0.07	251.0	5.17
176.0	0.18	221.0	0.25	252.0	*100.00*
185.0	0.12	222.0	1.04	253.0	21.54
186.0	0.12	223.0	1.18	254.0	2.31
187.0	0.31	224.0	3.21	255.0	0.19
188.0	0.08	225.0	1.99	263.0	0.06
189.0	0.08	226.0	1.90	264.0	0.06
197.0	0.13	227.0	0.35	265.0	0.08
198.0	0.68	228.0	0.07	266.0	0.16
199.0	0.51	233.0	0.04	267.0	0.08
200.0	0.81	234.0	0.07		

All samples were run under the same conditions on a Hitachi Perkin-Elmer RMU-6D mass spectrometer. The ionizing voltage of 70 eV was used as standard with an acceleration voltage of 2500 volts. The chamber temperature was maintained at 100°C which was more than adequate to acquire sufficient sample pressure. The background throughout the experiments was held to 3×10^{-7} Torr and sample spectra were taken at pressures of 7 to 8×10^{-7} Torr. Under these conditions, useful spectra for the compounds of the benzopyrene family may be attained with sample weights of 1 to 10 ng.

DISCUSSION

All samples of clams and oil showed the presence in the benzene fraction of a compound with m/e = 252. Although present in the unseparated mixtures, the spectra of low concentrations of aromatics were masked by the fragmentation ions of the higher concentrations of the remaining constituents of the gross sample. Certain other constituents prevailed in all samples studied. Peaks at m/e = 197 and m/e = 135 persisted throughout all samples and

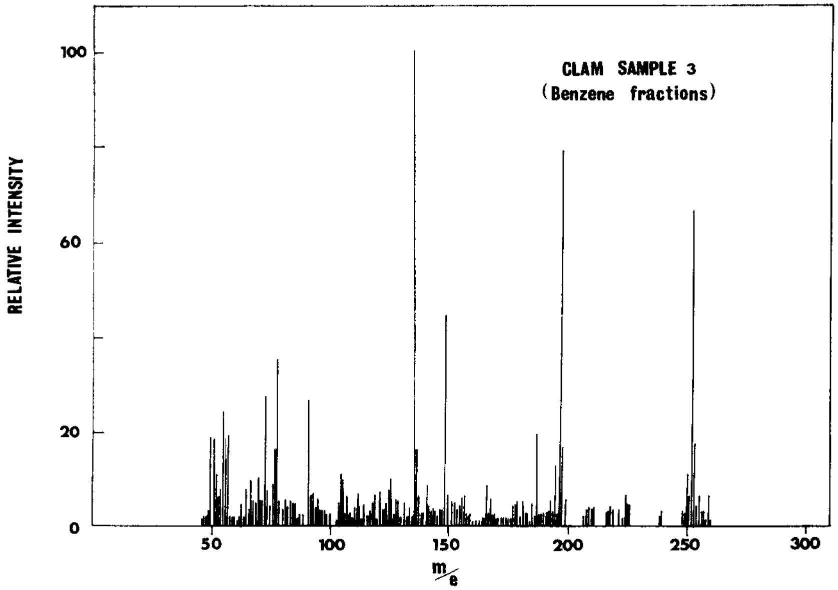

FIGURE 8 Mass spectrum, m/e versus abundance for clam sample 3 (benzene fraction).

separated fractions. In addition, a broad diffuse metastable peak at m/e = 187 to 189 accompanied these persistent bands.

Oil

The oil samples, in addition to the persistent peaks at m/e = 197, 135 and m* = 185 to 187, showed the distinctive peak grouping around m/e = 252, which characterizes the $C_{20}H_{12}$ condensed aromatics of the benzo[a]pyrene family of isomers. The characteristic doubly charged peaks at m/e = 126.5, 126, 125.5, 113.5, and 113 reinforce this interpretation. Above m/e = 252 the grouping of peaks at 264 to 267 with low intensities are impurities (or alkyl derivatives) usually found in the analyses of members of the benzopyrene family of isomers (Figure 9).

Clams

A similar chemical composition for the benzene fractions for oil samples is suggested by the spectra of all clam samples, both contaminated and control. In each sample examined, the characteristic intense peaks and broad diffuse metastable structure were present in the spectra. The m/e = 252 grouping

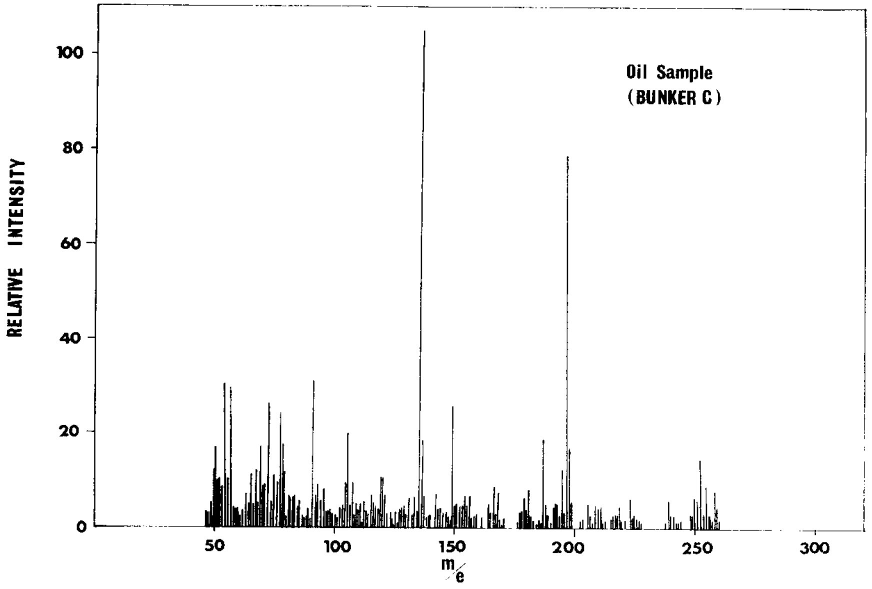

FIGURE 9 Mass spectrum, m/e versus abundance for Bunker C oil sample (benzene fraction).

and associated doubly charged ion peaks (m/e = 126, m/e = 125, m/e = 113 and m/e = 112) were also prominent in the spectra.

On comparison, there appeared to be little difference between the spectra of benzene fractions of oil samples and clam samples. The relative abundance ratio of the distinctive grouping at m/e = 252 common to all spectra compared favourably with standard reference spectra for the prominent members of this isomeric family, namely benzo[a]pyrene, benzo[e]pyrene and benzo[k]-fluoranthene (see Tables I, II and III, Figures 5, 6 and 7). The first two of these isomers have demonstrated carcinogenic activity.

The benzo[a]pyrene family of isomers has received attention in the fields of air pollution monitoring and control since the most common sources of these compounds are emmission products of the combustion of carbonaceous fuels. A number of analytical methods using extraction, chromatography and detection by ultraviolet absorption and/or fluorescence spectroscopy have been proposed.[9-12] Recently, methods utilizing gas chromatography and mass spectrometry have been applied to this analytical problem with encouraging results.[13-15] The literature for levels of aromatic hydrocarbons in the marine environment, though less extensive, is receiving increasing attention.[16,17]

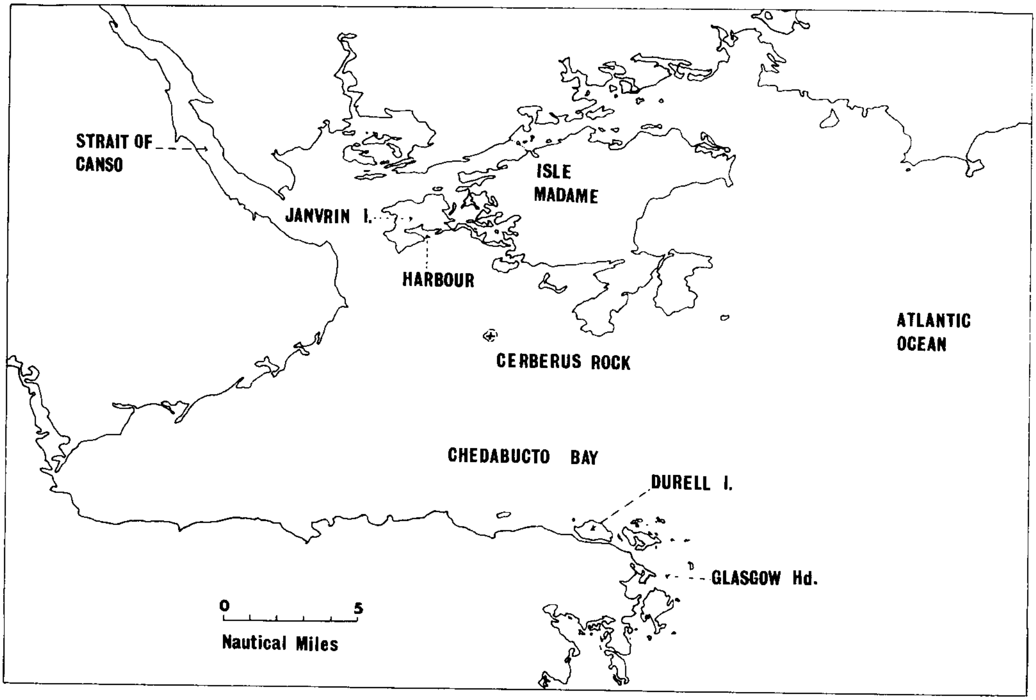

FIGURE 10 Map of area surrounding the Arrow Oil Spill.

A recent development in the latter field was revealed by investigators in France,[18] whose studies of coastal plankton and anaerobic bacteria from isolated regions have shown 3 to 4 μg of benzo[a]pyrene per 100 g of weight sample. Experiments were conducted on cultures of clostridium isolated from plankton and fed on lipid extracts of marine plankton in sea water for a 15-day period, after which time samples were taken for analysis. The samples contained benzo[a]pyrene in amounts from 12 to 800 μg per 100 g wet weight sample.

CONCLUSIONS

Although members of the benzo[a]pyrene family were detected in clams exposed to oil from the Arrow Bunker C spill, similar compounds were isolated in clams taken from areas thought to be oil free. If the control samples were representative of background levels of benzo[a]pyrene-type compounds, the exposed clams showed little or no contamination by aromatic hydrocarbons directly attributable to Bunker C. If, however, the beds at Forchu (Figure 10) had accumulated aromatic hydrocarbons from exhaust emissions from fuel-powered fishing craft in the area or other sources the blank reference for control clam samples is meaningless. The persistent peaks at $m/e = 197, 135$ and $m^* = 185$ to 187 would suggest that the control clam beds had been exposed to oil with characteristics similar to Bunker C.

References

1. V. Zitko and W. V. Carson, Project Oil Chemistry Report to Task Force Operation Oil (1970).
2. G. Löfroth, Ecological Research Committee Bulletin No. 4, Swedish Wat. Sci. Res. Coun. (1970).
3. J. C. Medcoff, A. H. Leim, A. B. Needler, A. W. H. Needler, J. Gibbard, and J. Naubert, *Bull. Fish. Res. Bd. Canada* **75**, 1–32 (1947).
4. A. Berkhoff, Med. Res. Div. of Esso Research and Engineering Co., Report to Task Force Operation Oil, 35 (1970).
5. P. Valori and N. Ann, *Igiene e Microbiol.* 4 (1966).
6. G. E. Moore, R. S. Thomas, and J. L. Monkman, *J. Chromatogr.* **26**, 456 (1967).
7. E. Sawicki, T. R. Hauser, and T. W. Stanley, *Int. J. Air Pollut.* **2**, 253 (1960).
8. A. A. Rosen and F. M. Middleton, *Anal. Chem.* **27**, 790 (1955).
9. P. Wedgewood and R. L. Cooper, *Analyst* **78**, 170 (1953).
10. D. Hoffman and E. L. Wynder, *Cancer* **15**, 103–108 (1962).
11. L. Dubois and J. L. Monkman, *Int. J. Air Poll.* **9**, 131 (1965).
12. B. T. Commins, *Nat. Cancer Inst. Monograph* **3**, 225 (1961).
13. R. Perry, Paper CP37E, 2nd Int. Clean Air Congress, Washington, D.C. (1970).
14. J. Oro and J. Han, *J. Gas Chromatogr.*, 780 (1967).

15. R. C. Lao, paper presented at 19th Annual Conference Am. Soc. Mass Spectrometry, Atlanta, Ga. June 1971.
16. H. J. Cahnmann, *Anal. Chem.* **29**, 1307 (1957).
17. H. J. Cahnmann, *Anal. Chem.* **29**, 1312 (1957).
18. M. Héros, P. Chovin, *et al.*, Press release, La Presse, Montreal, October 17, 1970, and private communications.