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Determination of Polycyclic Aromatic Hydrocarbons in Some Canadian Commercial Fish, Shellfish, and Meat Products by Liquid Chromatography with Confirmation by Capillary Gas Chromatography–Mass Spectrometry

James F. Lawrence* and Dorcas F. Weber

Eighteen polycyclic aromatic hydrocarbons, 11 of which are known carcinogens (oral, inhalation, dermal, or other) were determined in a variety of selected food commodities available in Canada including smoked and unsmoked seafood products, meat spreads, and fried and char-broiled meats. All samples were carried through a saponification step followed by a liquid–liquid partition, a Florisil column cleanup, and then a second liquid–liquid partition before analysis. Reversed-phase liquid chromatography with fluorescence detection compared well with capillary gas chromatography–mass spectrometry. Total carcinogenic PAH levels ranged from not detectable up to several hundred micrograms per kilogram in some cases (oil from a can of smoked oysters). Most samples contained levels in the low-to-sub micrograms per kilogram range.

Polycyclic aromatic hydrocarbons (PAH) have been the subject of numerous studies related to foods and to their possible effects on human health due to the carcinogenicity of a number of members of this class of compounds. A recent volume of the *Journal of Environmental Pathology and Toxicology* was completely devoted to PAH (Santondonato et al., 1981). Analytical methodology and the occurrence of PAH in foods have been the subject of a comprehensive review (Howard and Fazio, 1980). PAH contamination arises from several sources including processing of food (smoking, direct drying, cooking, natural sources (Suess, 1976), and environmental contamination of air, water, or soil (Tilgner, 1970), the latter being considered as the most important. Grimmer (1968) pointed out that vegetables, not smoked foods nor grilled meat, may be the greatest source of PAH to humans. It has also been estimated that food intake may in fact surpass tobacco smoking as a major contributor to PAH exposure (Santodonato et al., 1981). In Canada publications have appeared concerning the PAH content of smoked and char-boiled foods (Panalaks, 1976) and fish, mollusks, and lobsters (Dunn and Fee, 1979).

A number of approaches have been studied for the extraction of PAH from foodstuffs (Crosby et al., 1981; Lintas et al., 1979; Dunn and Fee, 1979; Kolarovic and Traitler, 1982). The methodology chosen for the present work was based on the extraction procedure developed by Grimmer and Böhnke (1975) with some modification that included the use of a deactivated Florisil column cleanup (Basu and Saxena, 1978) and a dimethylsulfoxide partition for additional purification (Obana et al., 1981; Haenni et al., 1962).

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Table I. PAH Used in This Study

compd no.	IUPAC name	abbreviation
1	fluoranthene	FL
2	pyrene	PY
3	benzo[*b*]fluorene	BbFL
4	3,6-dimethylphenanthrene	DMP
5	benz[*a*]anthracene	BaA
6	perylene	Per
7	benzo[*a*]pyrene	BaP
8	dibenz[*ac*]anthracene	DacA
9	dibenz[*ah*]anthracene	DahA
10	picene	Pi
11	indeno[1,2,3-*cd*]pyrene	IP
12	anthanthrene	An
13	dibenzo[*ae*]pyrene	DaeP
14	9,10-diphenylanthracene	DPA
15	dibenzo[*ai*]pyrene	DaiP
16	dibenzo[*ah*]pyrene	DahP
17	chrysene	Ch
18	dibenzo[*al*]pyrene	DalP

High-pressure liquid chromatography (HPLC) with fluorescence detection has been found to be very suitable for the quantification of PAH in a variety of biological samples (Crosby et al., 1981; Panalaks, 1976; Obana et al., 1981; Joe et al., 1982) with detection limits often in the sub micrograms per kilogram range. The selectivity of the sample purification and detection makes the method very suitable for routine monitoring. However, often it is necessary to confirm high or suspicious results by some other technique to ensure that false positives are eliminated as much as possible. In this regard, gas chroma-

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tography, especially with mass spectrometric detection (GC–MS), serves an invaluable purpose. GC–MS has been used for PAH analyses in biological samples (Lintas et al., 1979; Grimmer and Böhnke, 1975). Both HPLC and GC have been used together either for HPLC fractionation prior to GC analysis (Romanowski et al., 1982) or for comparative purposes (Eadie et al., 1982). In this work we use both techniques for the determination of selected PAH in a variety of fish and meat samples. The GC–MS was used primarily to confirm the HPLC–fluorescence results.

EXPERIMENTAL SECTION

Reagents. All solvents used were distilled in glass or HPLC grade. Table I lists the PAH studied. Caution should be exercised when handling concentrated solutions of these compounds. Several are proven oral and/or skin-contact carcinogens.

Samples. All commercial samples were purchased from local food retail outlets.

Extraction Procedure. Thirty grams of sample was saponified with 11.2 g of KOH in 100 mL of H_2O/methanol (1/9 v/v) for 3.5–4 h under reflux. The mixture was cooled, diluted with 100 mL of H_2O/methanol (2/8 v/v), and extracted twice with 100 mL of cyclohexane. The aqueous/methanol layer was then discarded. The cyclohexane extracts were combined, washed with 100 mL of H_2O/methanol (1/1, v/v) and 2 × 100 mL of H_2O, filtered through anhydrous sodium sulfate, and concentrated to approximately 1 mL on a rotary evaporator at 30 °C.

Column Cleanup. The concentrated extract was applied to the top of a 5-g, 5% H_2O (by weight) deactivated toluene-washed Florisil column (60–100 mesh) and eluted with 80 mL of toluene. The eluate was collected and rotary evaporated at 35–40 °C to near dryness.

Me_2SO/Hexane Partitioning. The residue from above was dissolved in hexane, transferred quantitatively to a separatory funnel (total 10 mL of solvent), and partitioned with 10 mL of dimethyl sulfoxide (Me_2SO). The Me_2SO layer was collected and the hexane was extracted with another 10-mL portion of Me_2SO. The Me_2SO fractions were then combined, diluted with 40 mL of H_2O, and extracted twice with 20-mL portions of hexane. The hexane extracts were combined, washed with 2 × 40 mL of H_2O, filtered through anhydrous sodium sulfate, and concentrated to near dryness on a rotary evaporator at 30 °C. The residue was dissolved in 2 mL of acetonitrile for analysis.

Liquid Chromatography. HPLC was performed isocratically on an RP-18 Spheri-5 reverse-phase column (5 μm, 25 cm × 4.6 mm id, Brownlee Laboratories) at ambient temperature by using a 30% water/acetonitrile (v/v) mobile phase with a flow rate of 3.0 mL/min. Instrumentation included an Altex Model 110A pump and a Rheodyne syringe-loop injector. The effluent from the column was directed to a Schoeffel FS970 fluorescence detector, which was connected in series to a Waters Model 440 UV (254 nm) detector and a dual-channel strip chart recorder (Linear). The excitation monochromator was set to 250 nm and a >370 nm band-pass filter was used for emission.

Gas Chromatography-Flame Ionization Detection (GC-FID). A Varian Model 1700 GC equipped with a flame ionization detector, modified for capillary work, was employed. A splitless injector was installed and the detector modified to accommodate a capillary column. A DB-5 30-m fused silica column was used with helium as the carrier gas. Injection was made with the column at room temperature followed by rapid heating to 180 °C.

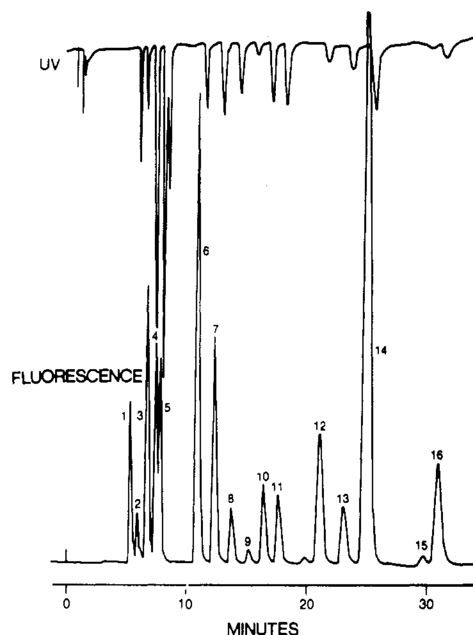

Figure 1. HPLC separation with ultraviolet and fluorescence detection of a standard mixture of PAH. Operating conditions as described in the text. Peak numbers refer to the compounds listed in Table I.

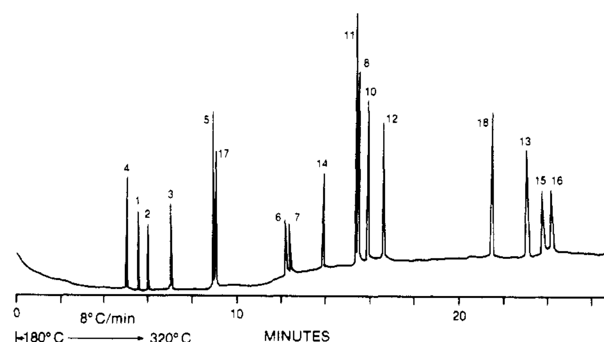

Figure 2. Capillary GC-FID separation of a mixture of 17 PAH. Operating conditions as described in the text. Peak numbers refer to the compounds listed in Table I.

The oven was then programmed from 180 to 320 °C at 8 °C/min and held isothermal until all components were eluted (total analysis time for each sample was approximately 30 min).

Gas Chromatography–Mass Spectrometry (GC–MS). A VG 12000 quadrupole mass spectrometer interfaced with a Dani GC was used. Data were collected and analyzed by a VG 2000 data system. The GC column and temperature programming was the same as described above for GC-FID analysis. An on-column injection technique was employed. The mass spectrometer parameters used were as follows: electron impact energy, 70 eV; emission source, 100 μA; multiplier voltage, 2.5 kV; source temperature, 250 °C.

In the multiple ion detection mode, the ions monitored were m/e 202, 206, 216, 228, 252, 276, 278, and 302, which correspond to the masses of the molecular ions of most of the PAHs screened in this work.

RESULTS AND DISCUSSION

Chromatography. A chromatogram of the separation of the PAH spiking mixture by HPLC–UV–FLR is shown in Figure 1. The HPLC detection limit (2 × noise) was estimated to range from 2 to 27 pg/injection of each PAH component. Figure 2 illustrates the separation by GC-FID of a similar PAH mixture containing 17 components. The

Table II. Percent Recoveries of PAH from Spiked Haddock Fillet[a]

compound	level, (μg/kg) 1.0	2.0	4.0
1, FL	119	111	99
2, PY	106	142	120
3, BbFL	76	77	83
4, DMP	97	96	88
5, BaA	103	98	95
6, Per	28	36	44
7, BaP	38	48	50
8, DacA	88	79	71
9, DahA	61	57	60
10, Pi	93	96	91
11, IP	92	86	86
12, An	24	34	45
13, DacP	78	74	77
14, DPA	89	82	86
15, DaiP	71	82	90
16, DahP	70	77	71

[a] Each value is the average of triplicate analyses.

GC-FID detection limits of most PAHs were in the order of 10 pg/injection, with higher levels (50–100 pg/injection) for the later eluting components such as the dibenzopyrene isomers. However, untreated fish extracts exhibited a large number of interfering peaks, thus raising the detection limit to greater than 10 μg/kg in most samples. Detection limits by GC–MS were in the sub micrograms per kilogram range, which is comparable to that of HPLC with fluorescence detection. Three PAHs had very similar retention times by HPLC on the C_{18} column. Compounds 4 and 5 (3,6-dimethylphenanthrene and benz[a]anthracene) did not exhibit base-line resolution. Also compound 17 (chrysene) coeluted with benz[a]anthracene. All three of these compounds were completely resolved by GC.

Sample Analysis. The efficiency of the extraction and cleanup method was tested by recovery studies. Samples of fresh fish (unprocessed haddock) were spiked with amounts of PAHs sufficient to produce levels equivalent to 1.0, 2.0, and 4.0 μg/kg each. The extracts were analyzed by HPLC and the results are shown in Table II. For all levels an average percent standard deviation of 7.8 was obtained and recoveries of most PAHs were greater than 70%. Previous recovery experiments performed for each step of the extraction and cleanup procedure indicated that the loss in most PAHs occurred during the Florisil column cleanup. The losses can be accounted for by irreversible adsorption (anthanthrene) or photoreaction (benzo[a]pyrene). These phenomena were observed earlier by others (Insco, 1964; Sawicki et al., 1965). In spite of this, detection of all compounds could still be made at levels of 0.1 ppb for most samples analyzed.

Table III compares HPLC–fluorescence results with those obtained by GC–MS on samples of commercially purchased cooked hamburgers. Samples A and B were char-broiled while C and D were fried. By HPLC chrysene was measured as benz[a]anthracene since these compounds eluted together. In general, it can be readily observed that commercial char-broiling contributes signficantly to the total carcinogenic PAH content of hamburgers compared to frying where the PAH content is minimal. The effect

Table III. PAH in Hamburgers from Four Sources (μg/kg)

	A (char-broiled)		B (char-broiled)		C (fried)		D (fried)	
	GC–MS[a]	HPLC–FL[b]	GC–MS[a]	HPLC–FL[b]	GC–MS[a]	HPLC–FL[b]	GC–MS[a]	HPLC–FL[b]
FL	>7	6.2	9.6	5.9[c]	0.3	0.1	0.3	0.4
PY	>9	14	14	19	0.4	0.4	0.4	0.5
BbFL	2	0.5	2.9	1.7	–	–	–	–
DMP	0.4	–[d]	0.2	0.6	–	–	–	0.1
BaA	1.1	2.1	1.3	2.8	–	0.1	–	0.2
Per	1.0	0.9	–	1.1	–	–	–	–
BaP	4.0	1.5	2.9	2.9	–	–	–	0.1
DacA	0.2	1.0	–	0.6	–	–	–	–
DahA	–	2.1	–	1.3	–	–	–	–
Pi	–	1.0	0.6	1.6	–	–	–	–
IP	2.0	3.6	–	5.8	–	–	–	–
An	3.0	1.1	2.0	0.8	–	–	–	–
DaeP	0.5	0.4	–	0.7	–	–	–	–
DPA	–	–	–	–	–	–	–	–
DaiP	–	–	–	–	–	–	–	–
DahP	–	0.3	–	0.4	–	–	–	–
Ch	2.0	N[e]	1.9	N	–	N	–	N
DalP	0.3	N	0.3	N	–	N	–	N

[a] One determination only, uncorrected for recovery. [b] HPLC–FL results are averages of triplicate samples for A and B and duplicates for C and D. Uncorrected for recovery. [c] Single value only; replicates were obscured by a large proximate peak. [d] Dashes indicate <0.1 μg/kg. [e] N indicates not analyzed.

Table IV. PAH in Fresh Smoked Fish (μg/kg)

compound	smoked haddock[a]	smoked cod[a]	smoked Digby chix[a]	smoked herring[a]	smoked arctic char[b]	smoked Nova sal[b]
FL	0.3	1.2	9.3	0.6	1.2	d
PY	9.3	12	404	24	8.1	6.6
BbFL	0.4	0.8	13	2.2	–	0.2
DMP	–[c]	–	5.9	0.1	–	8.8
BaA	0.3	0.3	15	0.8	0.2	0.6
Per	–	–	–	–	0.1	0.1
BaP	t[e]	t	t	t	t	t
DahA	1.1	–	40	2.1	–	–
Pi	0.1	–	8.2	1.7	–	–

[a] Average of triplicates. [b] Averages of duplicates [c] Dashes indicate <0.1 μg/kg. [d] Peak obscured by a proximate peak. [e] t = trace observed but not quantifiable.

Table V. PAH in Canned Smoked Fish and Smoked Meat Spreads (μg/kg)[a]

	sardine (1)		sardine (2),	saithe		kippers		cod liver		meat	
compound	fish	oil	fish	fish	oil	fish	oil	liver	oil	beef	pork
FL	1.8	9.6	1.3	–[b]	1.1	0.7	5.8	1.0	2.5	2.1	0.5
PY	3.2	15	8.2	–	6.9	24	152	–	3.0	6.3	1.4
BbFL	0.2	1.2	0.4	–	–	0.6	4.6	–	–	0.2	–
DMP	1.3	6.1	0.4	–	–	–	–	–	0.2	1.2	0.2
BaA	–	–	0.9	–	1.7	0.7	4.8	1.1	0.3	0.8	0.2
Per	0.2	1.5	0.1	–	0.5	–	–	–	–	0.2	–
BaP	0.5	3.1	0.4	–	–	–	–	–	–	0.1	–
DacA	–	–	0.6	–	–	–	–	–	–	–	–

[a] Averages of triplicates. [b] Dashes indicate <0.1 μg/kg.

Table VI. PAH in Lake Ontario Fish Samples (μg/kg)[a]

compound	white perch	crappies	smelt	smelt	eel	catfish
2,3,7,8-TCDD[b]	0.006	ND[d]	0.023	0.026	0.030	0.016
FL	1.1	0.6	1.0	0.6	1.4	0.8
PY	2.3	1.1	1.0	1.4	1.9	1.8
BbFL	0.1	–[c]	–	–	0.2	0.2
DMP	0.5	0.1	0.1	0.2	0.3	0.3
BaA	0.4	0.2	0.2	0.1	0.2	0.3
Per	–	–	–	–	–	0.1
BaP	–	0.1	0.1	–	–	–
DacA	–	–	0.1	0.2	0.8	–
DahA	–	–	1.6	2.2	2.9	–
Pi	–	–	–	–	0.1	–
IP	0.1	–	–	–	0.1	–
total PAH	4.5	2.1	4.1	4.7	7.9	3.5

[a] Averages of duplicates. [b] From Ryan (1983). [c] Dashes indicate <0.1 μg/kg. [d] ND = not detected.

Table VII. PAH in Canned Mussels and Oysters (μg/kg)

	smoked Mussel			smoked oyster						
	A,[a]	B[b]		A[b]		B[b]		C,[a]	D,[a]	
compound	mussel	mussel	oil	oyster	oil	oyster	oil	oyster	oyster	oyster[b]
FL	35	7.1	70	44	41	21	223	42	14	36
PY	116	44	359	119	1122	66	678	100	31	21
BbFL	8.5	2.9	37	4.1	70	2.0	37	4.9	–	2.5
DMP	–[c]	3.7	32	–	–	–	–	1.2	4.5	2.5
BaA	11	0.8	5.0	12	103	12	86	18	11	29
Per	29	0.7	5.3	3.8	35	1.9	17	4.4	1.8	3.7
BaP	3.9	1.0	8.8	7.7	75	1.6	15	3.9	0.4	0.8
Pi	–	–	–	3.2	21	1.3	12	1.8	–	–
IP	–	2.2	15	6.8	57	2.7	33	5.4	–	6.0
DaeP	–	–	–	1.7	18	–	–	–	–	–
DPA	–	–	–	0.3	2.3	–	–	–	–	–
DacA	–	–	–	–	–	–	–	3.1	2.9	5.9
DahA	–	–	–	–	–	–	–	7.2	–	7.9
total carcinogenic[d]	14.9	4.0	28.8	28.2	253	16	134	38.6	14.3	49.6

[a] Average of duplicates. [b] Average of triplicates. [c] Dashes indicate <0.1 μg/kg. [d] BaA + BaP + IP + DaeP + DacA + DahA.

of char-broiling on PAH formation in meats is well documented (Panalaks, 1976; Lijinsky and Shubik, 1964; Lijinsky and Ross, 1967).

A series of smoked fish were analyzed and the results are presented in Table IV. The PAH content was found to be related to the degree of smoking with lightly smoked products such as smoked haddock, cod, and arctic char having low levels of PAH while the more heavily smoked fish (smoked herring, Digby chix) had higher levels. The benzo[*a*]pyrene content of all smoked fish samples was at the detection limit (~0.05 μg/kg) and not quantifiable. The PAH levels in general are similar to those found earlier (Panalaks, 1976). Table V shows results for canned smoked fish as well as two canned smoked meat spreads. In general, the PAH levels are low, and in the case of kippers (smoked herring) there is essentially no difference between the fresh (Table IV) and canned product. Figure 3 compares chromatograms of a fresh haddock sample compared with one that was smoked that had a relatively low PAH content (see Table IV). The fresh unsmoked fish contained little or no detectable PAH. A small survey of fresh fish caught in Lake Ontario where PAH levels might be expected to be higher than the Atlantic ocean showed no significant PAH concentrations. Table VI shows the results obtained. These same fish samples were analyzed previously for 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD)(Ryan, 1983), and the results, with the exception of white perch, correlated directly with PAH content, with eel having the highest dioxin level and crappies the least, the others being intermediate. The total PAH levels found in these samples were relatively low and are somewhat expected since it has been shown that vertebrate fish rapidly metabolize PAH, which would thus lead to low steady-state levels in the tissues (Payne, 1977; Lee et al., 1972).

In contrast to the fish samples analyzed, canned mollusks showed much higher PAH levels. Table VII shows results for smoked mussels and smoked and unsmoked oysters. All samples were imported. Total carcinogenic PAH ranged from 4.0 to 49.6 μg/kg in the samples ana-

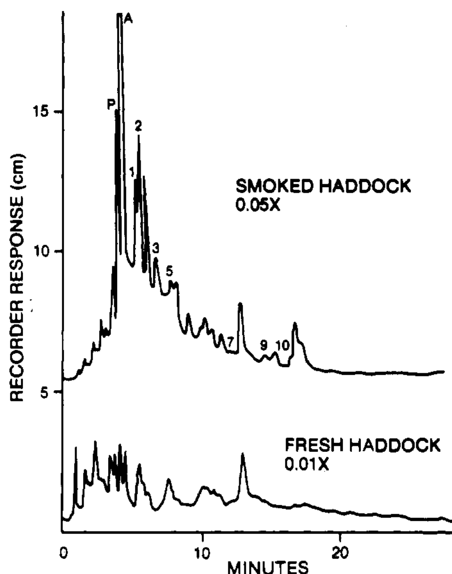

Figure 3. Comparison of HPLC chromatograms (florescence detection) for fresh and smoked haddock. Lower chromatogram was obtained at a 5× more sensitive detector setting. Other conditions as described in the text. P = phenanthrene; A = anthracene. Peak numbers refer to the compounds listed in Table I.

Table VIII. PAH in Canned Lobster (μg/kg)

compound	lobster spread[a]	lobster spread[b]	lobster spread[b]	lobster meat[a]	lobster meat[b]
FL	103	8.1	50	5.3	2.3
PY	67	8.5	27	6.3	2.0
BbFL	2.1	0.7	8.3	–	0.3
BaA	29	2.0	9.1	1.7	0.6
Per	14	1.2	6.8	0.4	0.5
BaP	25	0.7	3.6	–	0.4
DacA	2.9	–[c]	–	–	–
DahA	72	–	–	–	–
Pi	15	1.8	2.3	–	0.5
IP	25	2.8	8.0	–	1.0
DaeP	6.0	–	–	–	0.2
An	5.8	–	–	–	–
total carcinogenic[d]	165.7	5.5	20.7	1.7	2.2

[a] Averages of triplicates. [b] Averages of duplicates. [c] Dashes indicate <0.1 μg/kg. [d] BaA + BaP + DacA + DahA + IP + DaeP + An.

lyzed. The oil associated with these products was approximately 7–8 times more concentrated in PAH than the food itself. It is possible that these high levels are due mainly to environmental contamination since it has been demonstrated previously that mollusks tend to accumulate PAH due to their inability to metabolize and excrete them (Dunn and Fee, 1979; Payne, 1977). The high levels in the oil might result from leaching the lipophilic PAH from the tissues, although some vegetable oils have been shown to contain elevated levels of PAH due to environmental contamination of the initial vegetables (Kolarovic and Traitler, 1982; Grimmer and Hildebrandt, 1967). In Table V, the oil associated with the canned vertebrate fish tissues had much lower PAH levels than in the canned mollusks. By comparing the smoked and unsmoked oyster results in Table VII, it can be seen that the smoking process does not contribute significantly to the overall PAH levels.

Table VIII lists results obtained for canned lobster products including lobster spread (containing mainly the hepatopancreas) and lobster meat. In one case (sample 1) the total carcinogenic PAH was very high at 165.7 μg/kg. Two other samples of spread (samples 2 and 3) were analyzed later and found to contain considerably less PAH. The canned lobster meat contained very low levels. Figure 4 shows a chromatographic result for sample 1. The relatively high level of PAH in lobster hepatopancreas has been observed before and is attributable in part to creosote contamination during impoundment (Dunn and Fee, 1979) or from marine contamination from other sources (Sirota and Uthe, 1982). This digestive organ has been found to selectively accumulate PAH by about 10-fold compared to tail meat (Dunn and Fee, 1979). This may explain why the lobster meat sample was lower than the other canned lobster samples in Table VIII.

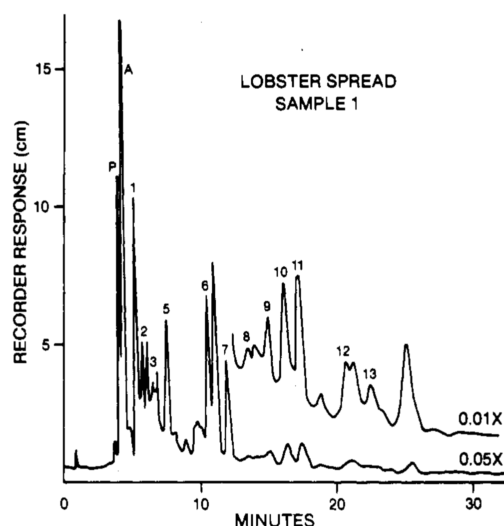

Figure 4. HPLC chromatogram of an extract of lobster spread (sample 1, Table VIII). Fluorescence detection. Conditions as described in the text. P = phenanthrene; A = anthracene. Peak numbers refer to the compounds listed in Table I.

CONCLUSION

The results of this study indicate that the Canadian exposure to PAH from fish and meat products is similar to that in other countries. It appears that elevated levels of carcinogenic PAH results from char-broiling of meats, environmental contamination of mollusks and lobsters, and to a lesser degree smoking of foods. Although these products may not be consumed to a great extent on the average, regional differences in food consumption (e.g., coastal dwellers tend to eat much more seafood) can put some segments of the population at a higher level of exposure to PAH. Due to the lack of standards, the results reported herein do not include other important PAH, such as benzo[*e*]pyrene, benzo[*b*]fluoranthrene, or benzo[*k*]-fluoranthene, all of which have been reported in foods and which might have been present in the samples analyzed herein.

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Determination of Polycyclic Aromatic Hydrocarbons in Canadian Samples of Processed Vegetable and Dairy Products by Liquid Chromatography with Fluorescence Detection

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An HPLC–fluorescence method was developed and used for the determination of 15 polycyclic aromatic hydrocarbons (PAH) in samples of milled wheat, finished cereals, milk powders, malt, spinach, and cooking oils. Results showed that the bran portion of milled wheat as well as finished bran cereal had a considerably higher PAH content than other fractions or finished products. The use of direct heating for drying milk powders and malt was found in some cases to lead to elevated levels of PAH, and these were found to correlate with levels of nitrosamines present. Three samples of spinach had very low levels of PAH while two of three types of cooking oils had levels of carcinogenic PAH in the low micrograms per kilogram range.

It has been amply demonstrated in the literature that plant food can become contaminated with polycyclic aromatic hydrocarbons (PAH) through environmental pollution particularly via the air and through food processing such as direct drying (Howard and Fazio, 1980). Because of the potential for PAH contamination of vegetables, we initiated a limited survey of selected products, available in Canada. The results, reported herein, will help to estimate the total exposure to PAH for Canadians.

EXPERIMENTAL SECTION

Reagents. All solvents were distilled in glass or HPLC grade. The polycyclic aromatic hydrocarbons used in this work are listed in the preceding paper (Lawrence and Weber, 1984). Dimethyl sulfoxide (Me_2SO was either Baker analyzed grade (J. T. Baker) or Aldrich Gold Label Me_2SO (Aldrich Chem. Co.).

Samples. All commercial samples were purchased from local outlets. The wheat milling fractions were obtained from an experimental milling study and the malt samples obtained through commercial producers for the brewing industry.

Apparatus. High-pressure liquid chromatography (HPLC) was carried out by using an Altex Model 110A pump and a 5-μm Spheri-5 RP-18 reversed-phase column (25 cm × 4.6 mm i.d.) (Brownlee Laboratories) at ambient temperature with a mobile phase (isocratic) of water/acetonitrile (30/70 v/v) at a flow rate of 2.0 or 3.0 mL/min. The compounds were detected with a Schoeffel Model FS 970 fluorescence detector connected in series with a Waters Model 440 UV detector set at 254 nm. The fluorescence wavelengths were 250 nm (excitation) and >370 nm (emission).

Sample Analysis. The extraction and cleanup procedure was carried out exactly as described earlier (Lawrence and Weber, 1984). The method was based on the procedure developed by Grimmer and Böhnke (1975) with some modifications such as Florisil cleanup (Basu and Saxena, 1978) and Me_2SO partition (Haenni et al., 1962). The method involves initial saponification with alcoholic KOH, an aqueous/cyclohexane partition, and then Florisil cleanup. A Me_2SO/hexane partition was employed before final HPLC analysis.

RESULTS AND DISCUSSION

The methodology used proved to be adequate for the quantification of the PAH down to 0.1 μg/kg or less in the products examined. Recoveries of PAH carried through the complete method generally were greater than 75% at the 1 μg/kg level, the exceptions being BaP (38%), DahA (61%), Per (28%), and An (24%). These compounds were found to be partially lost during the Florisil cleanup step. Since the recoveries for the other 11 PAH were acceptable, no attempts were made to alter the cleanup procedure to

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