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Mass Fragmentographic Determination of Polymethylbiphenyl in Foods Contaminated with Petroleum Products

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Biphenyl has been used for a long time as a fungistat to prevent decay of fresh citrus fruits. In Japan its use was permitted in 1971 for grapefruits, lemons, and oranges with a maximum allowable residue level of 70 ppm and only for the purpose of strage and transfer of citrus through the use of biphenyl-impregnated pads. The FAO/WHO has proposed that its acceptable daily intake for man be 0.125 mg per kg body weight.

Since petroleum oils contain polymethylbiphenyl (PMBP), foods contaminated with petroleum products from various sources will also contain it. Several reviews about the occurrence and analytical methods for the determination of higher polycyclic aromatic hydrocarbons such as benzpyrene in foods have appeared (HOWARD & FAZIO 1980). However, relatively little attention has been given to the investigation and the determination of lower aromatic hydrocarbons in food due to their noncarcinogenic nature.

We have previously reported a analytical method for polymethylnaphthalene (PMN) and polymethylphenanthrene (PMP) which could be quite useful as a fingerprinting identification to indicate petroleum contamination of marine organisms (ADACHI 1980).

The objectives of this study were to determine PMN and PMP to confirm the petroleum contamination of foods and also to describe a procedure for determining PMBP in several foods by means of mass fragmentography (MF). Residue data for PMN, PMP, and PMBP are also reported.

EXPERIMENTAL

Reagents and Samples. Reagents used were identical to those in our previous report (ADACHI 1980). All samples (unpolished rice, dried soybean, peanut, coffee, green tea, beef, pork, chicken, egg, milk) were purchased from retail markets.

Extraction and Cleanup. 20-50 g Each of powdered unpolished rice, dried soybean, and green tea and 100 g each of homogenized beef, pork, and chicken were extracted for 12 h with ethanol in a Soxhlet extraction apparatus (a fritted glass thimble was used instead of a paper filter cup thimble). Each extract was saponified with 5 g KOH for 3 h.

The extracted crude fat from 200 g each of egg and milk was saponified as described above.

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The extraction and a Florisil column cleanup procedure were performed according to our previous peport.

Activated Charcoal Column Chromatography. The concentrated extract was poured onto an 0.5 g activated charcoal column and eluted succesively with 50 mL hexane, 100 mL ethyl acetate, 200 mL dichloromethane, and 250 mL benzene. The dichloromethane fraction for PMN and PMBP and benzene fraction for PMP were separately collected for analysis.

Mass Fragmentography. GC-MS instrumental and operating conditions were the same as described previously with the exception of oven temperature programming from 140 to 210°C at 3°C/min for MF of PMBP.

RESULTS and DISCUSSION

Polymethylnaphthalene (PMN) and Polymethylphenanthrene(PMP) in Foods. In a previous paper, we reported on the usefulness of the MF procedure for PMN and PMP which could be very useful indicators of petroleum contamination.

The MF peak profiles of beef, unpolished rice, green tea, and dried soybean were very similar to those of grade A crude oil or kerosene as shown in Fig. 1 and Fig. 2.

The information presented herein contains enough evidence to strongly support the hypothesis that a wide variety of foods must be contaminated with petroleum oil.

Determination of Polymethylbiphenyl (PMBP) in Foods. Benzene (purity min. 99.5%) used in an activated charcoal chromatography is a petroleum product and contains trace amount of alkylbenzenes and diaromatics such as PMN and PMBP. Because PMBP could not be removed thoroughly from the benzene by redistillation, the dichloromethane fraction obtained using 0.5 g of activated charcoal was used for analysis of PMN and PMBP. In practice, each of their MF was in general not subjected to interference from each other and other components in this fraction.

Furthermore, a thick paper filter cup thimble used in a Soxhlet extraction is liable to cause erroneous results because of extractable interference peaks from the paper cup.

Recoveries of standard compounds (biphenyl, 3-methylbiphenyl, 4-methylbiphenyl, 3,3'-dimethylbiphenyl, and 4,4'-dimethylbiphenyl) from an 0.5 g activated charcoal column were greater than 80% in the working range 0.1 to 10 μg. The reproducibility of the method used, as judged from the results of the triplicate analyses, clearly appears satisfactory within 10%.

The ions used for MF of PMBP were the molecular ion peaks at m/e 154 (BP), 168 (MBP), 182 (DMBP), and 196 (TMBP).

The percentage relative intensity of molecular ion peak, calculated from the ten most intense peaks in reference data, are given in Table 1. The molecular ion intensity of PMBP is nearly identical with the exception of biphenyl methylated at the

2-position and ethyl or isopropyl-substituted biphenyl which are present in relatively small amounts in crude petroleum and the parent biphenyl.

TABLE 1. Alkylbiphenyl contents in crude petroleum (MAIR & MAYER 1964, YEW & MAIR 1966) and the percentage relative intensity of molecular ion (STENHAGEN et al. 1974).

Compound	Content (%) in crude petroleum	Molecular ion peak (%)
Bipenyl	0.008	47.5
2-Methylbiphenyl	0.002	30.0
3-Methylbiphenyl	0.009	39.6
4-Methylbiphenyl	0.005	35.8
2,2'-Dimethylbiphenyl		22.4
2,3'-Dimethylbiphenyl		22.4
2,4'-Dimethylbiphenyl		25.3
2,5'-Dimethylbiphenyl	0.001	
2-Ethylbiphenyl		22.4
3-Ethylbiphenyl	0.001	
3,3'-Dimethylbiphenyl	0.003	37.4
3,4-Dimethylbiphenyl	0.0036	
3,4'-Dimethylbiphenyl	0.0063	38.5
4,4'-Dimethylbiphenyl	0.0045	38.0
3,3',5-Trimethylbiphenyl	0.0055	
3,4',5-Trimethylbiphenyl	0.0029	
Isopropylbiphenyl	0.0004	

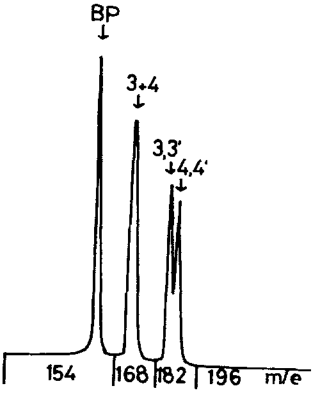


Fig. 1 Mass fragmentogram of 200 pg each of standard PMBP.

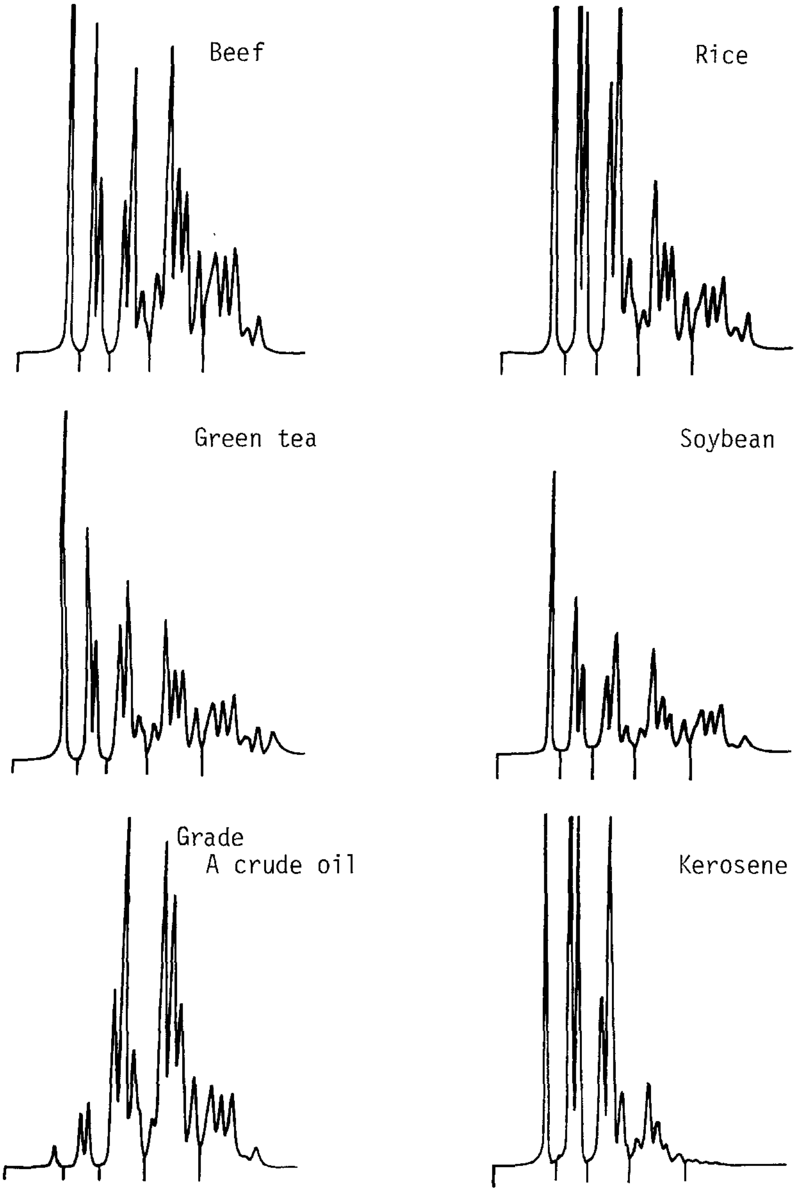
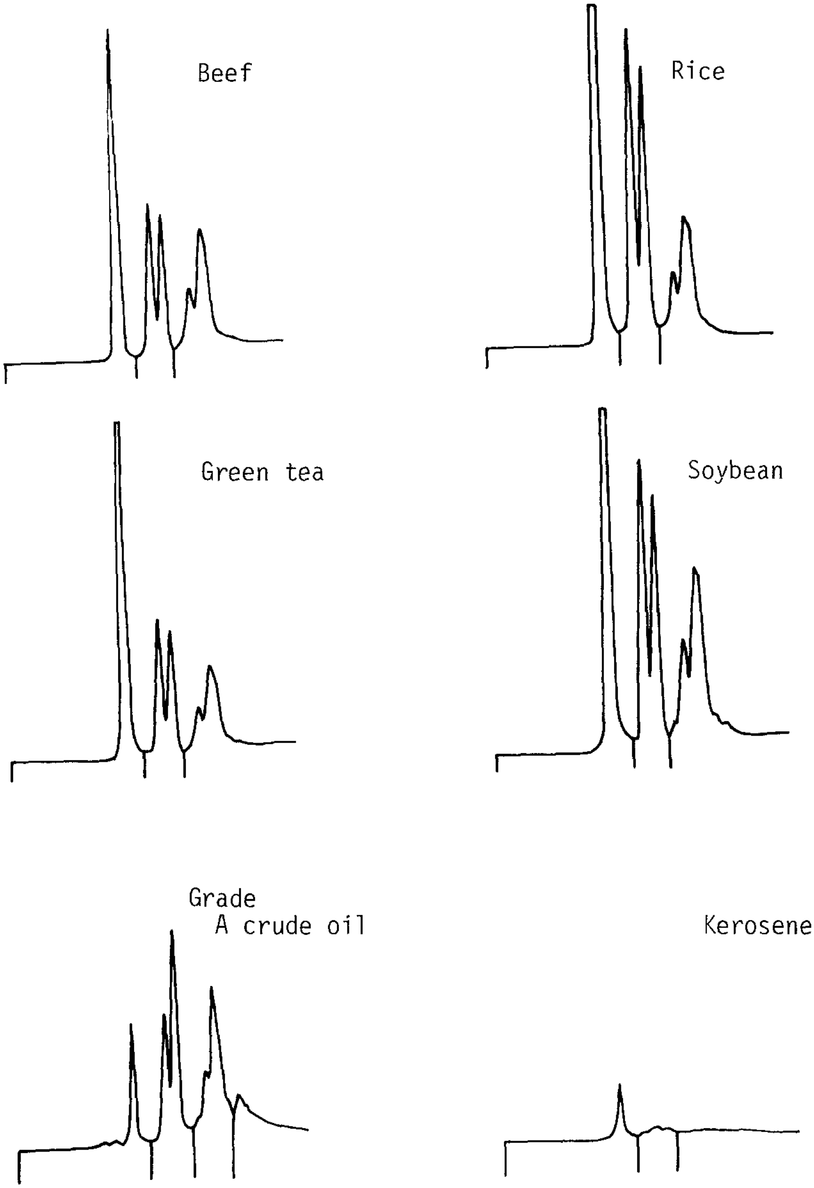


Fig. 2 Mass fragmentograms of PMN in foods.



Beef

Rice

Green tea

Soybean

Grade
A crude oil

Kerosene

Fig. 3 Mass fragmentograms of PMP in Foods.

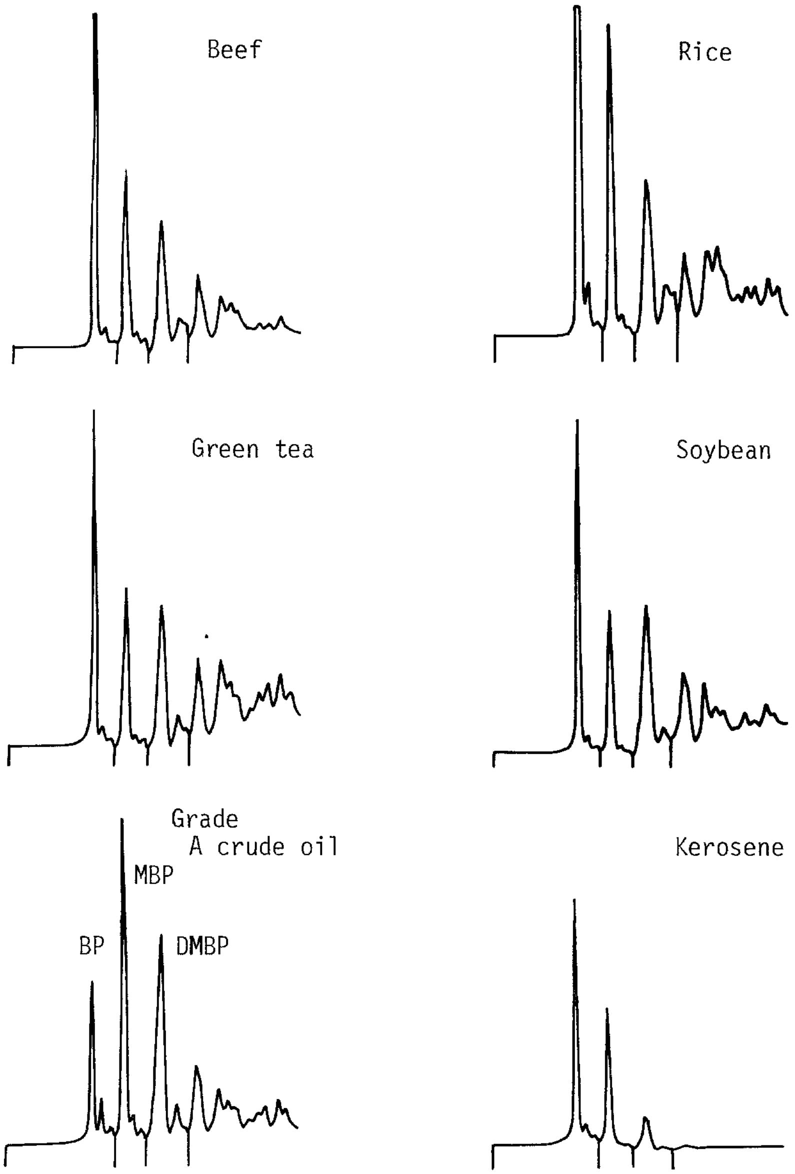


Fig. 4 Mass fragmentograms of PMBP in foods.

TABLE 2. Concentrations of PMN, PMBP, and PMP in foods (ppm).

Commodity	N	MN	DMN	TMN	TeMN	BP	MBP	DMBP	P	MP	DMP
Unpolished rice	0.077	0.13	0.16	0.099	0.039	0.052	0.025	0.018	0.069	0.033	0.019
Soybean	0.006	0.009	0.014	0.016	0.008	0.002	0.002	0.004	0.027	0.015	0.011
Peanut	0.030	0.030	0.080	0.12	0.056	0.050	0.004	0.005	0.040	0.073	0.056
Coffee	0.009	0.008	0.018	0.029	0.012	0.003	0.005	0.006	0.030	0.031	0.035
Green tea	0.003	0.031	0.15	0.19	0.052	0.004	0.005	0.007	0.086	0.052	0.037
Pork	0.005	0.004	0.005	0.009	0.003	0.001	0.001	0.001	0.003	0.002	0.001
Beef	0.005	0.005	0.006	0.011	0.004	0.001	0.001	0.001	0.004	0.004	0.003
Chicken	0.007	0.005	0.003	0.002	0.001	0.001	0.001	ND	0.002	0.002	0.001
Egg	0.001	0.001	0.001	0.001	0.001	ND	ND	ND	0.001	0.001	0.001
Milk	ND	ND	ND	0.001	ND	ND	ND	ND	ND	ND	ND
A Crude oil (%)	0.00	0.10	0.38	0.37	0.14	0.02	0.12	0.12	0.03	0.06	0.06
Kerosene (%)	0.07	0.30	0.29	0.17	0.08	0.03	0.05	0.01	0.00	0.00	0.00

N = Naphthalene, BP = Biphenyl, P = Phenanthrene ; M = Methyl, DM = Dimethyl, TM =Trimethyl, TeM = Tetramethyl.

Mass fragmentogram of five different PMBP is shown in Fig. 1. Several foods were analysed by the method described above. The MF peaks profiles of the PMBP in the foods were very similar to that of a grade A crude oil or kerosene as shown in Fig. 4.

Consideration. This study has focused on the determination of PMBP in foods contaminated with petroleum oil. Food products (for example, citrus) known to have been treated with biphenyl as a fungistat have been excluded.

With the exception of egg and milk, trace quantities of PMBP were found. Residue levels found are shown in Table 2 along with the residue levels found for PMN and PMP. The results of this limited survey suggest that we must give careful consideration to the intake of PMBP (as well as PMN and PMP) in the total diet resulting from contamination of a variety of foodstuffs.

To obtain a detailed knowledge of the identities and the residue concentrations of oil pollutant and of oil pollution sources is of great importance due to their potential genetic hazard to man.

We are particularly interested in the relatively high concentrations of PMN, PMBP, and PMP found in rice since it is consumed in large quantities in many countries, such as Japan.

Major routes of oil contamination suspected at the present time are general environmental pollution from atomospheric fallout, industrial wastes, and exhaust gas from automobiles and contaminations by oil spills from oil engines, direct drying with fuel oil, and wide use of petroleum emulsions as pesticide formulations in agriculture.

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