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Kinetics of polycyclic aromatic hydrocarbon sorption from liquid smoke flavour into low density polyethylene packaging

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A liquid smoke flavour (LSF) was spiked with a mixture of polycyclic aromatic hydrocarbons (PAHs) at a total concentration of 91·1 μg/kg and filled into low density polyethylene bottles. The changes of PAH concentrations in LSF were followed for 164 h, using a high-performance liquid chromatography method with selective fluorimetric detection. During this time the concentrations of PAHs in LSF dropped to zero. Assuming that the rate-limiting step of the sorption onto the packaging material is the diffusion in the solution, a kinetic equation of the sorption was derived and diffusion coefficients for individual compounds were obtained.

INTRODUCTION

The presence of polycyclic aromatic hydrocarbons (PAHs) in foods or food additives is one of the important problems of food contamination. Because of their high carcinogenic activity they are frequently determined in various foods and food additives (Silvester, 1980; Fritz & Soós, 1981; Stijve & Hischenhuber, 1987; Menichini *et al.*, 1991).

Special attention is given to food products which are flavoured with smoke, grilled, or dried using hot combustion products because the highest amounts of PAHs are found therein (Binnemann, 1979; Fretheim, 1983; Lawrence & Weber, 1984; Speer *et al.*, 1990; Šimko *et al.*, 1991).

The use of liquid smoke flavours (LSFs) in the smoking process has resulted in many advantages compared with traditional smoking processes, but the main advantage is the possibility of exact control of PAH concentrations in LSF. It was found that the use of commercially made LSF, UTP-1, in the smoking process lowered the PAH content by two orders compared to PAH contents in meat products smoked traditionally (Šimko *et al.*, 1992).

Many papers have reported the sorption of flavour compounds (carbonyls, alkylesters, sulphur compounds and alkylpyrazines) from foods by polyethylene packaging materials (Kwapong & Hotchkiss, 1987; Arora *et al.*, 1991; Nielsen *et al.*, 1991). Because the decrease of PAH concentrations in LSF has been shown to be a possible result of sorption processes into polyethylene packaging material (Šimko & Brunckovà, 1993), the aim of this study is to derive a rate equation of sorption as well as to calculate diffusion coefficients for individual compounds of the PAH group.

MATERIALS AND METHODS

Materials

The LSF, UTP-1, was obtained from the manufacturer (Slovenske lucobne zavody Hnusta, SR) in glass containers. Polyethylene bottles (volume 0·2 litre, i.d. 6·4 cm) were made from a low density polyethylene, type Bralen RA2-19, with a density of 922 kg/m^3 (Slovnaft Bratislava, Slovak Republic).

As four- and five-ring PAHs are the most carcinogenic compounds of this group, the following compounds were chosen for the experiment: pyrene (Py), benzo(*a*) anthracene (B*a*A), dibenzo(*a,c*) anthracene (DB(*a,c*)A), benzo(*e*)pyrene (B*e*P) benzo(*a*)pyrene (B*a*P) and dibenzo-(*a,h*) anthracene (DB(*a,h*)A).

The standard mixture solution was prepared by dissolving each compound in rectified methanol to give a total concentration of PAHs of 6 mg/litre.

Methods

First, the presence of the PAHs in LSF as well as in low density polyethylene bottles (LDPEBs) was established.

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The LSF, UPT-1, was then spiked with the standard mixture of PAHs at a level of 91·1 μg/kg. The spiked LSF was then filled into the LDPEBs, and PAHs were determined in both LSF and LDPEBs after 27, 68, 98, 116, 121·5, 141, 145·5 and 164 h storage. During the whole experiment the LDPEB were kept at a temperature of 24°C.

All determinations were performed in duplicate.

Extraction and high performance liquid chromatography (HPLC) analysis

Samples of LSF for HPLC analysis were prepared as follows: a well mixed sample (100 g) of LSF was transferred to a separating funnel and 100 ml of 20% (w/w) NaOH solution was added. The separating funnel was shaken for 2 min, 50 ml of hexane was added and the funnel was again shaken for 2 mins. The extraction of the water layer was repeated three times. The hexane layers were mixed and washed with 100 ml of water. The hexane layer was then separated, dried with anhydrous Na_2SO_4 and evaporated on a rotary vacuum evaporator to near dryness. The residue was dissolved in methanol and made up to 3 ml.

The LDPEBs were cut into small pieces (*c.* 1 cm × 1 cm) and put into Erlenmeyer flasks with 100 ml of hexane, shaken for 1 h, and sonicated for 20 min. After filtering, the hexane layer was evaporated to near dryness, and the residue was dissolved in methanol as described above.

HPLC was performed isocratically on a Separon SGX C_{18} reversed phase column (particle size 5 μm, length 30 cm, i.d. 3 mm; purchased from Tessek, Praha, Czech Republic) at ambient temperature. The mobile phase was a mixture of acetonitrile and water (3 : 1, v/v) with a flow rate of 1·15 ml/min.

The instrumentation consisted of a high pressure pump and syringe loop injector PK-1. The eluate from the column was directed to a Perkin-Elmer filter fluorescence detector, which operated at 310 nm excitation wavelength and 410 nm emission wavelength.

RESULTS AND DISCUSSION

The efficiency of the extraction procedure was tested by recovery studies. These were carried out after determination of PAHs in the 'blank' sample, using aliquots of LSF spiked with a PAH standard mixture at 104 μg/kg. As found, the recovery varied from 82 to 89% for each compound with a coefficient of variation of 0·4% at maximum. Under given experimental conditions the detection limits were as follows: Py 0·06, B*a*A 0·07, DB(*a,c*)A 0·05, B*e*P 0·02, B*a*P 0·04 and DB(*a,h*)A 0·06 μg/kg.

As seen from Table 1 row A, the LSF at the moment of its spiking by PAHs could not be used for food flavouring, as the Joint Expert Committee on Food Additives of FAO/WHO adopted a specification requiring a limit concentration of B*a*P in LSF of

Table 1. The changes in concentrations of PAHs (μg/kg) in LSF followed during the experiment. Rows A—measured values; rows B—values calculated by eqn (3)

Compound		Time of storage (h)										σ
		0	27	68	92	98	116	121·5	141	145·5	164	
Py	A	14·8	2·45	0·65	0·58	0·50	0·50	0·29	0·29	0·25	ND	0·33
	B	14·7	2·70	0·36	0·11	0·08	0·03	0·03	0·01	0·01	0·00	
B*a*A	A	26·8	8·23	3·40	1·54	1·79	1·43	1·03	0·99	0·75	ND	0·47
	B	26·5	9·12	3·09	1·64	1·41	0·88	0·74	0·46	0·41	0·24	
DB(*a,c*)A	A	17·8	3·55	0·78	0·67	0·47	0·43	0·25	0·16	0·13	ND	0·25
	B	17·8	3·80	0·64	0·23	0·17	0·08	0·06	0·03	0·02	0·01	
B*e*P	A	11·0	3·25	0·63	0·42	0·30	0·30	0·13	0·08	0·07	ND	0·09
	B	11·0	3·16	0·82	0·38	0·31	0·17	0·14	0·08	0·07	0·04	
B*a*P	A	10·2	2·25	0·44	0·32	0·26	0·21	0·16	0·08	0·07	ND	0·10
	B	10·1	2·34	0·44	0·17	0·13	0·06	0·05	0·02	0·02	0·01	
DB(*a,h*)A	A	10·7	2·20	0·43	0·31	0·24	0·23	0·10	0·06	0·06	ND	0·10
	B	10·6	2·29	0·39	0·14	0·11	0·05	0·04	0·02	0·01	0·01	
Total	A	91·1	21·9	6·33	3·83	3·54	3·11	1·96	1·67	1·32	ND	1·43
PAHs	B	90·7	24·0	5·56	2·37	1·91	1·01	0·80	0·41	0·35	0·18	

Py: pyrene; B*a*A: benzo(*a*)anthracene; DB(*a,c*)A: dibenzo(*a,c*)anthracene; B*e*P: benzo(*e*)pyrene; B*a*P: benzo(*a*)pyrene; DB(*a,h*)A: dibenzo(*a,h*)anthracene. ND: not detectable.

10 μg/kg. The concentrations of PAHs, however, started to decrease as a consequence of PAHs sorption on LDPE packaging material. The rate of sorption was so high that after 164 h none of the compounds were detectable in LSF (Table 1, row A).

As the LSF was not mixed during the experiment, it is possible that the factor limiting the rate of PAH drop in LSF is the diffusion into the packaging. Because LDPEB had a cylindrical shape, we used the relationship derived for diffusion in a cylinder (Cranck, 1976):

$$\frac{n_t}{n_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4}{a^2 . \alpha_n^2} \exp(-D\alpha_n^2 . t) \qquad (1)$$

where n_t is the amount of diffused substance, which left the LSF as a consequence of the diffusion into the LDPEB at time t, and n_∞ is the amount of substance, which corresponds to infinite time. D is the diffusion coefficient, a is the radius of the cylinder, and α_n are the roots of the equation:

$$J_0(a \cdot \alpha_n) = 0 \qquad (2)$$

where J_0 is the zero-order first-class Bessel function.

In the experiment it was not the amount of substance sorbed into the LDPEB, but the amount left in the cylinder that was determined. Therefore, after recalculation of the amount of substance to the concentration, eqn (1) was modified to the form:

$$c_t = c_0 - \sum_{n=1}^{\infty} \frac{4}{a^2 . \alpha_n^2} \exp(-D\alpha_n^2 . t) \qquad (3)$$

where c_0 and c_t are concentrations at time $t = 0$ and t.

Diffusion coefficients of PAHs (Table 2) were obtained by the nonlinear least squares method by minimizing the sum of squares of differences between the concentrations of PAHs measured experimentally and those calculated by eqn (3) (row B, Table 1). The minimization was carried out by the simplex method (Nelder & Mead, 1965). Minimized parameters were c_0 and D. The parameter c_0 was minimized, because the error of determination of this concentration in trace analysis is usually relatively high, and might affect all values of concentrations calculated. In calculations, the first 20 terms of eqn (3) were taken into account. The values α_n were taken from tables (Abramowitz & Stegun, 1964). The agreement between experimental and calculated values of PAH concentrations is very good as can be seen from Table 1 and as is demonstrated by the low values of standard deviations (σ), in the right-hand column of Table 1.

Table 2. The values of diffusion coefficients calculated by eqn (1) for individual and sum of PAHs

Compound	Values of diffusion coefficients, $D \times 10^2$ (m^2/h)
Py	8·7
B*a*A	4·6
DB(*a*,*c*)A	7·7
B*e*P	5·8
B*a*P	7·2
DB(*a*,*h*)A	7·6
Sum of PAHs	6·3

Abbreviations: see Table 1.

Table 3. The total amounts of PAHs in LSF and LDPEBs determined in both during experiment

Time of experiment (h)	Total amounts of PAHs (ng) in	
	LSF	LDPEB
0	1 274·7	ND
27	295·3	881·1
68	88·6	1 067·4
92	53·6	1 055·7
98	49·6	1 114·8
116	43·5	1 095·7
121·5	27·4	1 122·6
141	23·3	1 138·8
145·5	18·5	1 163·8
164	ND	1 187·3

ND: not detectable.

By numerical solution of eqn (3) for known values of the diffusion coefficient and given initial concentration c_0, it is possible to calculate the time at which PAH concentration decreases to a required value c_t. This means that, by eqn (3), it is possible to predict the time necessary for lowering PAH concentrations to the level acceptable by law. For example, if $c_0 = 10{\cdot}2$ μg of B*a*P per kg of LSF, it can be calculated that the acceptable concentration, $c_t = 9{\cdot}90$ μg/kg, will be reached within 51 mins of the experiment.

The evidence for diffusion as well as sorption processes of PAHs into LDPEBs is shown in Table 3, where the total amounts of PAHs determined in both LSF and LDPEB are compared. As follows from the table, the amounts of PAHs 'lost' in LSF during the experiment were possible to recover from the LDPEB.

The results obtained lead to the following conclusions:

1. The concentrations of PAHs in LSF can be decreased by proper choice of packaging materials.
2. The elimination of PAHs is a complex process involving the diffusion of PAHs into a solution followed by the sorption on the wall and eventual subsequent diffusion inside the packaging material.
3. Equation (3) makes it possible to calculate the time of interaction between LSF and packaging material which is necessary for reaching the concentration c_t.
4. This 'passive way' of elimination of contaminants from the food chain might offer a solution to the problems caused by the presence of PAHs in foods or food additives.

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