Characterisation of Physicochemical Interactions between Benzo(a)Pyrene Contained in Vegetable Oil and Polyethylene Terephtalate

B. SKLÁRŠOVÁ[1], P. ŠIMKO[1]*, P. ŠIMON[2] and E. BELAJOVÁ[1]

[1]Food Research Institute, Bratislava, Slovak Republic, *E-mail: peter.simko@vup.sk;

[2]Department of Physical Chemistry, Faculty of Chemical and Food Technology,

Slovak Technical University, Bratislava, Slovak Republic

Abstract: Rapeseed oil was spiked with benzo(a)pyrene [BaP] solution at the level of 29.4 µg/kg, filled into polyethylene terephtalate [PET] cylindrical shape receptacles and the BaP concentrations were followed for during 97 h by HPLC. During this time, the BaP concentrations decreased to 22.9 µg/kg due to an interaction of BaP with PET. Using a modified kinetic equation, the diffusion coefficient for BaP in the oil was determined. Calculation of the area occupied by a BaP molecule on PET surface suggests that either the multilayer adsorption or the diffusion of BaP into PET bulk came into account as the decisive factors bringing about the decrease of BaP concentrations in the oil.

Keywords: polycyclic aromatic hydrocarbons; benzo(a)pyrene; polyethylene terephtalate; adsorption; packaging; kinetics

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) represent the largest class of known environmental carcinogens. Some of them, even though not carcinogenic, may act as synergists [1]. In a number of papers, remarkable high concentrations of PAHs in fats and oils have been reported. MORET *et al.* [2] analysed 51 samples of olive oils and determined the total PAHs concentrations from 2.94 to 143.12 µg/kg. PUPIN and TOLEDO [3] determined benzo(a)pyrene (BaP) in 40 olive oil samples available on Brasilian market. As found, BaP was present almost in all samples when the highest concentration reached the level of 164 µg/kg. STIJVE and HISCHENHUBER [4] tested 12 samples of vegetable oils. They determined the highest concentration of BaP in coconut oil (up to 581.7 µg/kg). HOPIA *et al*. [5] determined the concentrations of numerous PAHs in Finnish butters, margarines and vegetable oils, and some raw vegetable oil materials. Total PAHs concentrations in 25 samples varied from 0.17 (corn oil) to 4600 (crude coconut oil) µg/kg. It was concluded

that enormous PAHs concentrations in coconut oil could be brought about by direct drying of copra with smoke. Smokes, in general, are an important source of PAHs because they are formed during thermal combustion of wood under a limited access of oxygen [6]. With regard to the analytical findings as well as the harmful effect to health, Slovak food legislation has limited the maximum acceptable concentrations of BaP in vegetable oil to the level of 5 µg/kg in 1995 and International Olive Oil Council has recommended a value of 2 µg/kg as a maximum tolerable concentration of BaP in olive-pomace oil. When thinking about the interactions between foodstuff and packaging, the contamination of food by substances migrating from the polymer packaging is mostly intuitively considered. However, several papers have announced that the polymers could be used for removal of contaminants from foodstuff with regard to their ability to adsorb some organic contaminants from liquid media. In this way, PAHs concentrations were reduced in a liquid smoke flavour by two orders during 14 days [7]. The possibility of PAHs

removal from liquid smoke flavour by sorption into polyethylene was also studied by Guillén *et al*. [8]. As found [9], the rate-limiting step of the PAHs sorption from liquid into polyethylene is the diffusion in liquid media. PAHs are primarily adsorbed on the polyethylene surface, with subsequent migration into bulk polymer [10]. At present, the dominant plastic material used for vegetable oil and non-alcoholic drinks packaging is polyethylene terephtalate (PET). For packaging purposes, food industry uses-up 20% of total world production with an expected increase by 15% yearly in near future. Since there is no data available in the literature regarding the interaction of PET with BaP, the aim of this work is to study the possibility of using PET for the removal of PAHs contained in vegetable oil during static conditions.

EXPERIMENTAL

Oil. Refined rapeseed oil was obtained from Palma – Tumys Ltd., Bratislava, Slovak Republic.

PET receptacles. In the experiment, pre-bubbled PET receptacles of cylindrical shape were used with i.d. of 2.06 cm. The receptacles were also provided by Palma – Tumys Ltd. The company uses them for oil and fruit syrup packaging after blowing to volume of 2 l.

BaP. BaP of analytical grade was purchased from Promochem, Germany.

Solvents. Acetonitrile was of gradient grade (Merck, Germany), methanol of UV purity (Lachema, Czech Republic), chloroform for analysis (Lachema, Czech Republic), cyclohexane for analysis (ITES, Slovak Republic).

Experiment. First of all, the oil was analysed for the presence of BaP. Subsequently, 100 g of the oil was spiked with PAHs solution in 2 l volume glass flask and left to evaporate the solvent spontaneously. To accelerate the evaporation, the oil was mixed up occasionally. Then, roughly 900 g of the oil was added and the content of the flask was mixed thoroughly. At this stage, the sample of spiked oil was taken to determine the initial BaP concentration. The receptacles were then filled with the spiked oil and placed into a polystyrene box to protect them from the light and to maintain the constant temperature of 18.3°C. Samples for analysis were taken after 1, 3, 5, 7, 11, 14, 24, 49, and 73 hours by a glass pipette from a couple of receptacles. To maintain equal conditions during the whole experiment, a new

couple of receptacles were taken for each analysis. Sample preparation as well as HPLC conditions are described in Šimko *et al*. [14].

RESULTS AND DISCUSSION

Total changes in BaP concentrations in the rapeseed oil are shown in Figure 1. As follows from Figure 1, BaP concentration started to decrease immediately after filling the PET receptacles by rapeseed oil until equilibrium between liquid and
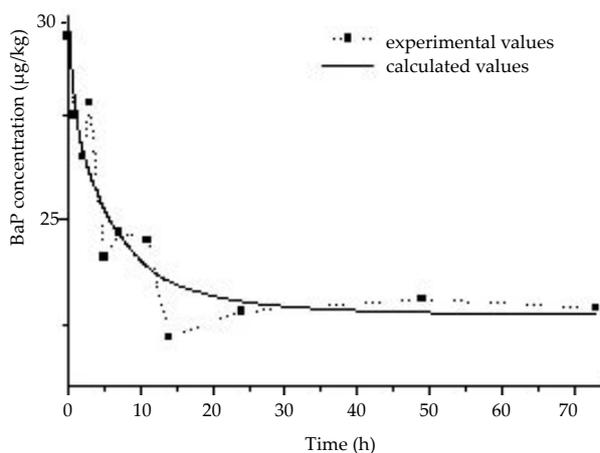

Figure 1. Changes of total BaP concentrations in rapeseed oil stored in PET receptacles

solid phases was reached. As the spiked samples were not stirred during the experiment, it is reasonable to assume that the factor limiting the rate of BaP concentration decrease is the diffusion in liquid media. Because the PET receptacles were of cylindrical shape, we therefore used for quantitative description the relationship derived for the diffusion in a cylinder [11]:

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

where: n_t – amount of diffused BaP, which has left the sample as a consequence of the diffusion into PET

t – time

n_∞ – amount of BaP corresponding to infinite time

D – the diffusion coefficient

a – radius of the cylinder

α_n – roots of the equation

$$J_0\left(a\,\alpha_n\right) = 0 \qquad (2)$$

where: J_0 – the zero-order first-class Bessel function

In the experiments, not the amount of BaP adsorbed on PET was measured, but their residual concentration in the liquid media. After recalculation of the amount of BaP to their concentration, eq. (1) can be modified into the form

$$c_t = c_\infty + (c_0 - c_\infty) \sum_{n=1}^{\infty} \frac{4}{a^2 \alpha_n^2} \exp\left[- D \alpha_n^2 t\right] \qquad (3)$$

where: c_0 – the initial concentration,
$\quad\quad\quad c_t$ – concentration at time t
$\quad\quad\quad c_\infty$ – equilibrium concentration

Diffusion coefficient of BaP was calculated by the non-linear least squares method by minimising the sum of squares of differences between the concentrations of BaP measured experimentally and those calculated by eq. (3). The minimisation was carried out by the simplex method. The minimised parameters were c_∞, $c_0 - c_\infty$ and D. In the calculations, the first 20 terms of eq. (3) were taken into account. The values of α_n were taken from tables [12]. The values of minimised parameters are: c_∞ = 22.75 µg/kg, $c_0 - c_\infty$ = 7.00 µg/kg and D = 2.51 × 10^{-2} cm²/hr. The agreement between experimental and calculated values is fairly good as it can be seen from Figure 1. Elucidation of the mechanism of the BaP adsorption on PET could be facilitated when calculating the area occupied by BaP molecule, A. If a monomolecular layer is assumed, it can be very simply derived that, for the adsorption in the cylinder, A is given by the formula

$$A = \frac{2M}{N_A (c_0 - c_\infty) a \rho} \qquad (5)$$

where: M – molar mass of the PAH
$\quad\quad\quad N_A$ – Avogadro number
$\quad\quad\quad \rho$ – the density of the matrix

Assuming that a molecule is of a circular shape, the diameter of a molecule adsorbed on PET surface would be 4.17 nm. This value is much greater than the dimension of BaP molecule which indicates the monomolecular adsorption of BaP onto PET surface. Eq. (3) makes possible to calculate the time necessary for a decrease of the BaP concentration from the initial value to a value desired. The values of diffusion coefficients are transferable to another geometry of containers, what could be used for removal of these contaminants without employing traditional extraction procedures in food industry. As mentioned [13], there are three main routes of human exposure to BaP – food 80%, air 19.7% and drinking water 0.2%. As the experiments have demonstrated, the use of PET for food packaging could be also useful in preventive human health protection. This fact was especially underlined two years ago when serious problems appeared in Czech Republic and Slovak Republic with over-limit concentrations of BaP in olive oils packed in glass bottles. If producers had used PET packaging materials, they could have avoided serious troubles associated with banning the sale and returning the oils back to the country of origin. The results of this study lead to the implication that the used PET bottles could act as a conceal source of BaP, and for this reason their reuse, or recyclation should be being carried out only at the control for presence of these compounds in PET bulk.

CONCLUSIONS

Summarising the results and findings obtained in this work, the following conclusions could be postulated:

1. The BaP concentration in liquid media can be reduced on the basis of interaction between BaP contained in liquid phase and PET as a solid phase.

2. The rate of decrease in BaP concentration describes the modified kinetic equation using calculated diffusion coefficients.

3. The equation makes possible to calculate the BaP concentration at any time during the interaction as well as to predict final equilibrium concentrations.

4. This way of BaP elimination could be useful especially in cases, where the usage of organic compounds is impossible, improper, or banned by legislation, respectively.

5. It seems, that the dominant influence on BaP removal from liquid media is the interaction of π-electrons between aromatic rings of BaP molecules and PET polymer.

6. A measure of the distribution of PAHs between PET and liquid phase is a ratio $\beta = (c_0 - c_\infty)/c_\infty$. The higher is the value of β, the greater part of the PAH interacted with PET. The value of β determined in this paper is 0.307 which is very close to the value of 0.213 obtained in Šımко *et al*. [14] for a much higher concetration range and a slightly higher temperature. This indicates that the adsorption of BaP onto PET is an equilibrium process.

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