Influence of a storage conditions on migration of bisphenol A from epoxy-phenolic coating to canned meat products

BRANISLAV STOJANOVIĆ[1], LJUBICA RADOVIĆ[2], DEJAN NATIĆ[3], MARGARITA DODEVSKA[3], GORDANA VRAŠTANOVIĆ-PAVIČEVIĆ[3], MILICA BALABAN[4], STEVA LEVIĆ[5], TANJA PETROVIĆ[5] and VESNA ANTIĆ[5*]

[1]Ministry of Defence, Republic of Serbia, Birčaninova 5, Belgrade, Serbia, [2]Military Technical Institute, Ratka Resanovića 1, Belgrade, Serbia, [3]Center for Food Analysis, Zmaja od Noćaja 11, Belgrade, Serbia, [4]University of Banja Luka, Faculty of Natural Sciences and Mathematics, Mladena Stojanovića 2, Banja Luka, Bosnia and Herzegovina, [5]University of Belgrade, Faculty of Agriculture, Nemanjina 6, Zemun, Serbia

***Corresponding author. E-mail:** vantic@agrif.bg.ac.rs

Abstract: Migration of bisphenol A (BPA) from epoxy-phenolic can coating into canned meat products, produced for the needs of the Serbian Armed Forces, was investigated in this work. The tinplate cans were made according to the special military demands, filled with the beef goulash or the meatballs in tomato sauce, and preserved by sterilization. The structure of internal can coating was analyzed by FTIR spectroscopy. The migration of BPA into content of the cans was investigated after storage under regular conditions in typical military facilities. The samples of beef goulash (BG) produced in 2010-2016, and the meatballs in tomato sauce (MB) produced in 2014-2017 were tested for the presence of BPA. Thereafter, the impact of storage temperature and degree of can damage on BPA migration was examined. Both meat products were thermostated on 20 and 40 °C, and BPA level was measured after 3, 6, 9 and 12 months of storage. The level of BPA was determined in the content of undamaged cans, and cans with lower and higher degree of damage. The BPA was extracted from food with acetonitrile and the extracts were purified by QuEChERS procedure. The level of BPA was determined by LC-MS.

Key words: BPA migration, canned food, can damage, storage temperature

RUNNING TITLE: BPA IN CANNED MEAT PRODUCTS

INTRODUCTION

Epoxy resins, whose elementary building block is bisphenol A (BPA), are commonly used to protect the interior of food and beverage cans against corrosion. The synthesis of BPA-type epoxy resins involves the condensation of BPA with 2-(chloromethyl)oxirane to yield soluble linear polymers of different molecular weight. Thermosetting products, used as the internal coating for food and beverage cans, are obtained by curing soluble epoxy polymer with phenolic type reactants.[1] Due to the possibility of multiple recycling, metal cans are increasingly being mentioned in the context of an environmentally acceptable way of food packaging. The cans can be recycled an infinite number of times, which helps to preserve the environment.

Food is usually contaminated with BPA through contact with food packaging materials that contain epoxy resins. BPA may remain unreacted when polymerization conditions or curing process is inadequate, and then the residual monomer can migrate from coating into foodstuffs.[2-4] Migration is particularly pronounced during storage and processing at elevated temperatures and thereafter consumers may routinely ingest trace amounts of BPA. BPA is an endocrine disruptor which interferes with the production, secretion, function and elimination of natural hormones, in a way that could be hazardous for health. For example, BPA is an oestrogenic xenobiotic that may affect the reproductive system of animals and is found to cause proliferation of breast cancer cells *in vitro*.[5] These considerations indicate the need of a continuous and accurate inspection of all possible sources of BPA, including food packaging.

The recent studies showed that canned food usually contains higher concentrations of BPA than foods sold in glass, paper or plastic containers.[6,7] By reviewing papers published to date, it seems that the smallest number refer to BPA in canned meat products, while more often are tested canned fish, seafood, vegetables and fruits.[8-17] In addition, it has recently reported a marked increase in urinary BPA levels in human who consumed canned foodstuff.[18] Food packaged in tinplate cans coated with epoxy resins is generally considered to be the predominant "source" of exposure to BPA.[19-20] Because of that, France officially passed a law suspending the production, trade and marketing of food cans containing BPA in December 2012. Such cans are banned at January 1, 2013 for food products intended for infants and on January 1, 2015 for all other products.[21] In January 2015, the European Food Safety Authority (EFSA) reduced the level of tolerable daily intake (TDI) for the BPA from 50 to 4 μg $(kg\ bw)^{-1}\ day^{-1}$ and set it as a temporary value (t-TDI), expecting the outcome of further scientific studies.[22] Thereafter, specific migration

limit (SML), which is the amount of BPA that can migrate from the plastic food contact material into the food, based on a specific risk assessment carried out by EFSA, is lowered from 600 to 50 μg kg^{-1} in February 2018, on the basis of new t-TDI value.[23] These reduced t-TDI and SML values require very careful, constant monitoring of BPA levels in canned food products.

The present study is undertaken to investigate migration of BPA from epoxy-phenolic can coating into canned meat products, during different storage time period and temperature, and with intentionally caused dameges on the tested cans. The structure of uncured and cured resin, used as the can coating, was analyzed by FTIR spectroscopy. The cans were made of electrolytic tinplate (E5,6/5,6), produced according to the special requirements of the Serbian Armed Forces, and filled with two meat products, beef goulash (BG) and meatballs in tomato sauce (MB). The impact of the storage period, under the common, regular storing conditions, to BPA migration into tested food, was analyzed first. The samples of the BG as well as the MB, manufactured since 2010 onwards, were tested for the presence of BPA. After that, further experiment was set up to examine the impact of temperature, tin can damage and storage time to BPA migration. The meat products produced in 2016 were thermostated at 20 and 40 °C, and the samples were taken for BPA analysis after 3, 6, 9 and 12 months. The migration of BPA was determined in the canned food from undamaged cans, as well as from the cans with lower and higher degree of intentionally caused damage, at each storage temperature. After the can was opened, the food was homogenized and extracted with acetonitrile. The extract was purified by QuEChERS (Quick, Easy, Cheap, Effective, Rugged, Safe)-based procedure, and the concentrations of BPA were determined by LC-MS.

EXPERIMENTAL

Chemicals. Acetonitrile (ACN) and methanol, both of LC-MS grade, glacial acetic acid and ammonia (25 %), were all obtained from Merck. Dispersive SPE Multipacks (QuEChERS) were the products of Thermo Fisher Scientific. The bisphenol A standard [IUPAC name: 4,4'-(propane-2,2-diyl)diphenol], NaCl and $MgSO_4$, were obtained from Sigma Aldrich.

Empty cans. Tin cans used in this work were made of electrolytically coated tin plate and produced by the leading can producer in Serbia. The internal and external surface of tin plate was coated with protective epoxy-phenolic resin.

Liquid epoxy resin. The liquid, uncured sample of epoxy resin was obtained from the can producer and its structure was analyzed by IR spectroscopy.

Canned meat products. The samples of canned meat products (BG and MB) were manufactured for the needs of the Serbian Armed Forces, according to the Regulation on the quality of meat products,[24] in industrial facilities of various manufacturers. The weight of the products inside the cans was 400 g in both cases. The products were preserved by sterilization (BG 70 min at 120 °C, and MB 105 min at 118 °C), and stored in typical military facilities that provide prescribed microclimate requirements. Content of BPA was determined in both meat products, produced between 2010 and 2017.

Methods and measurements

Controlled damage of cans. Controlled damages were performed on the filled sterilized cans, using a Rockwell hardness device. The pressure force was constant, with the optimal depth of imprint, causing cracking of the coating, without perforation of the sheet. Two series with different degrees of mechanical damage were prepared: a series with a lower degree of damage (LDD), where cans were damaged with 6 stings (3 at the bottom and 3 on the lid), and a series with a higher degree of damage (HDD), where cans were damaged with 12 stings (6 on the body of the can, 3 on the bottom and 3 on the lid). The damage was induced using diamond impeller with a coupe shape and the angle of 120 °.

Storage under different conditions. The tested cans of particular product were with the same batch number, where BG was produced on 5th January 2016, and MB on 10th February 2016. The samples were stored at 20 °C and 40 °C (12 cans of BG + 12 cans of MB on each temperature). Undamaged (UND) and damaged canned food samples (LDD and HDD) were analyzed for the presence of BPA after 3, 6, 9 and 12 months of storage. After the expiration of a certain period of storage, the can has been opened and the contact between food and coating was stopped. In this marking, '0 day' was considered as the day of setting an experiment, *i.e.* the day of putting the cans in thermostats at predestined temperature (December 15, 2016). The content of BPA was also determined in both food products at '0 day'.

Extraction of BPA from canned meat products. After the can was opened, the sample was subsequently homogenized by electric chopper, and the portion of 10 g was taken for analysis. ACN (10 cm^3) and QuEChers Mylar Pouches (4 g $MgSO_4$ + 1 g NaCl), were added to the sample. The mixture was homogenized by Vortex (5 min at 3000 rpm). Supernatant (1.5 cm^3) was transferred to the centrifuge tube with the clean-up phase, which contained 150 mg anhydrous

$MgSO_4$, 50 mg PSA, and 50 mg endcapped C18, and homogenized 5 min at 3000 rpm. Supernatant (1 cm^3) was transferred to the tube, and the solvent was evaporated in the nitrogen stream. The residue was dissolved in 1 cm^3 mixture ACN/water (1:1) and 20 μL of this solution was injected to LC-MS. All glassware used for these experiments was rinsed with methanol and dried at 100 °C before use.

FTIR spectroscopy. FTIR spectra of cured resin sample acquired using a spectrometer IRAffinity-1 (SHIMADZU, Japan). Spectra were collected in the spectral range 4000-500 cm^{-1}, with the resolution of 4 cm^{-1}. Prior to analysis, the solid sample, scraped from the inner surface of the can, was mixed with KBr and compressed into pellets. The liquid, uncured resin sample (~10 μL) was analyzed after placing on the surface of blank KBr pellet.

LC-MS. The HPLC was a Dionex ultimate 3000 (Thermo Fischer Scientific). The separations were performed with the Accucore-C18 column (2.6 μm diameter particles). The HPLC system was coupled to a mass spectrometer with an electrospray ion (ESI) source. The analytes were identified by their chromatographic characteristics and specific fragmentation patterns. In ESI-negative mode, the mobile phase was gradient mixture of 0.1 % ammonia in water and methanol. The oven temperature was 60 °C and the solvent flow-rate 0.5 mL min^{-1}.

Calibration curve, limits of detection and quantification. Quantification was performed based on matrix-matched calibration curve, made by spiking BPA with un-canned beef goulash. Five-point curve of 5, 10, 20, 50 and 100 ppb BPA was created. BPA was extracted as described above. Final solution (20 μL) was injected to LC-MS in triplicate. Correlation coefficient was >0.9976. The concentrations giving peak heights three and ten times the standard deviation of the baseline signal were defined as limit of detection (LOD) and limit of quantification (LOQ), respectively. LOD was determined to be 2 ppb, while LOQ was 5 ppb.

RESULTS AND DISCUSSION

The aim of this work was to investigate migration of BPA from packaging material to canned meat products which are in regular use in the diet of the Serbian Armed Forces. According to our knowledge, it was the first time to monitor BPA concentration in any food product in Serbia, regardless of whether it was produced for civilian or military use.

The production of cans in Serbia is in accordance with the standard,[25] which defines application of tin and lacquer on steel plate. The application of tin, as well as polymer coating

(lacquer), in cans used for the civilian market in Serbia, is usually about 2.8 g m^{-2}. For the needs of the Serbian Armed Forces, tin cans with this quality have been produced in a small number of cases, only if the products packed in such cans can be used within a calendar year. It has been noticed that cans for civilian needs usually begin to show corrosion after a year, which affects the change in the quality of the canned food. Since the Serbian Armed Forces possess high standards regarding the sustainability of canned food, which implies that their shelf life must be at least four years, additional requirements have been placed on the can suppliers in terms of the quality of tinplate and resulted cans. The application of tin must be twice as high as for civilian cans, with the quantity of tin of 5.6 g m^{-2}. In addition, the inner surfaces of the cans are coated by epoxy-phenolic, aluminized lacquer, with a minimum surface weight of 6 g m^{-2}, while the outer surface is coated with transparent lacquer with a minimum surface weight of 5 g m^{-2}. Canned products are strategically important for the Serbian Armed Forces, as a war reserved stock, and therefore their quality is given a high value, starting from the quality of empty cans to the final food product. On the other hand, it is very interesting to monitor the migration of toxic substances such as BPA into packaged meat content from these cans produced according to the specific standards, where in certain storage conditions a more intense emission of BPA can be expected, precisely because of the twice larger application of epoxy coating.

Structure of liquid and cured epoxy resin

Liquid, uncured resin sample, which is used to prepare coating on tinplate, was analyzed by FTIR spectroscopy in order to determine structure of polymer in detail. It was known from the can producer that the liquid sample is usually mixture of two components - a linear epoxy polymer and a phenolic component. The crosslinking of these components is taking place during the heating process at temperature about 200 °C. The FTIR spectrum was recorded immediately after opening the bottle with liquid resin, and again after solvent evaporation ("dried resin") in the air (Fig. 1-A and 1-B, respectively). The spectrum of cured epoxy-phenolic resin, scraped from the inner surface of the can, is shown in the Fig. 1-C.

It can be seen that all IR spectra do not show any other significant difference, except C=O band in dissolved liquid resin (Fig.1-A) at 1736 cm^{-1}, which disappeared after the solvent was evaporated. It was obvious that carbonyl band originated from the solvent.[1] The broad band at about 3380 cm^{-1}, seen in all IR spectra, is assigned to O-H stretching of hydroxyl groups originated from both epoxy and phenolic components. The bands at 1250 cm^{-1} and 1040 cm^{-1} correspond to

asymmetric and symmetric C-O-C vibrations. The 1,4-substitution of aromatic ring of epoxy component can be seen at 830 cm^{-1}. Bending bands of CH groups of oxirane ring (947 and 881 cm^{-1}) were also identified in all spectra, confirming the presence of epoxy groups in both liquid and cured polymer. The very low C-O deformation band of the terminal epoxy ring can be seen in IR spectra of liquid resin at 915 cm^{-1}, only when the image enlarges in that area. This suggests higher molecular weight of linear epoxy polymer. Symmetric C–H stretch of the epoxy ring is seen at 3056 cm^{-1}. The bands at 1610 and 1510 cm^{-1} are characteristic for aromatic ring from both epoxy and phenolic component.

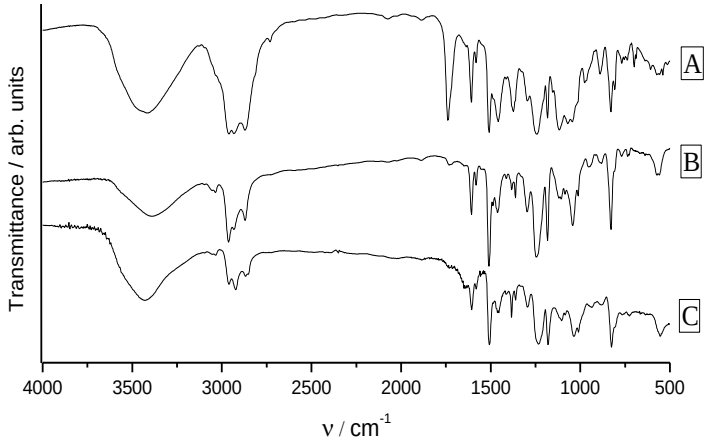

Fig. 1. IR spectra of dissolved uncured epoxy resin (A), uncured, dried resin (B), and cured resin scraped from the inner surface of the can (C)

Since the bands of oxirane ring at 3056, 947 and 881 cm^{-1} do not disappear from the spectrum of crosslinked resin, it is clear that the curing is accomplished via reaction of the secondary hydroxyl groups of the epoxy resin with the methylol groups of the resole (Fig. 2).[26] The band at 1120 cm^{-1} can be assigned to vibrations of secondary hydroxyl groups, and it can be seen in Fig. 1-B, when the image enlarges in that area. This band disappears during the curing process, and only the very tiny shoulder is noticeable in Fig. 1-C at 1120 cm^{-1}. The curing leads to the formation of ether bonds, which has already existed in linear epoxy polymer. The epoxy groups do not impart in that type of cure, and for that reason the higher molecular weight linear epoxy polymer is used in can coating formulations. Simplified curing process and the structure of cured epoxy-phenolic resin is shown in Fig. 2.

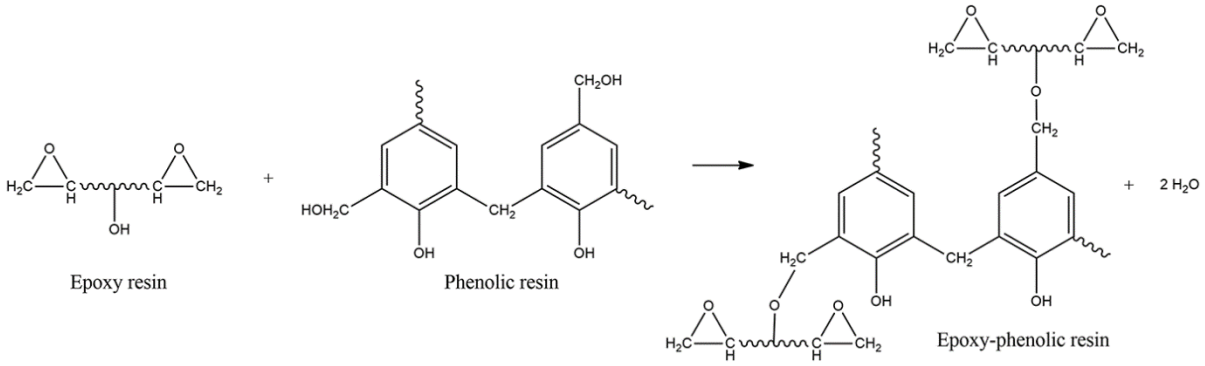

Fig. 2. Simplified curing process between epoxy and phenolic resin

Repeatability and recoveries

Repeatability of the applied method for determining BPA was tested out by measuring three replicates of one particular sample of the BG, as well as of the MB. Further, the samples of BG and the MB were spiked with a standard BPA solution to achieve concentration 20 μg kg^{-1} higher than previously determined for particular sample. The analyte was extracted and quantified, and recoveries were calculated. The results of repeatability, as well as recovery of BPA, with standard deviations (SD) and relative standard deviations (RSD), are given in Table S-I of the Supplementary material to this paper. The relative standard deviation was 7.5 % for the BG and 8.9 % for the MB. The proposed method was accurate and sensitive, characterized by very good recovery values. Recovery of BPA was slightly higher for the BG (82.1 %), than for the MB (78.7 %), although both values were entirely acceptable.

Influence of a storage period on BPA content under regular conditions

Content of BPA was determined in cans of BG and MB, produced between 2010 and 2017, and stored in the manner described in Experimental part. This is the first time that BPA was determined in any type of food produced in Serbia, although a very small number of papers dealing with BPA in meat products are published in the world at large. Results closest to this area are from campaign "Toxic Cash Receipts", conducted in our country, where results from 33 samples have demonstrated that thermal papers for fiscal receipts imported to Serbia are contaminated with BPA, as well as cardboard packaging made of recycled paper, while tested plastic containers for food did not contain BPA.[27]

The cans were checked before opening and it was found that there was no any kind of damage on them. The results, presented in Table I, showed that BPA was detected in all 11 samples,

with levels ranging from 3.2 μg kg^{-1} to 64.8 μg kg^{-1} for BG (average 26.2 mg kg^{-1}), and with levels from 21.3 μg kg^{-1} to 31.2 μ kg^{-1} for MB (average 25.6 μg kg^{-1}). Much higher oscillations were observed in samples of BG in comparison with the samples of MB, with the lowest BPA value of 3.2 μg kg^{-1}, which is below the limit of quantification (LOQ = 5 ppb). The highest BPA value of 64.8 μ kg^{-1} was found in the sample of BG from 2014, and this value is above the new migration limit of BPA from food contact plastics to food, which has been strengthened 12-fold by new regulative, from 600 to 50 μg kg^{-1}.[27] According to this latest Commission Regulation, "food contact plastics" and "food contact varnished or coated materials and articles" which were lawfully placed on the market before September 6, 2018, may remain on the market until stocks are exhausted. Regardless of this Regulation, the product with highest BPA value expired in April 2018, so certainly it is not further in diet of solders of the Serbian Armed Forces. The sample of BG from 2015 contained the level of BPA of 44.0 μg kg^{-1}, which is near the permitted limit of 50 μg kg^{-1}, while all other samples contained less than 31.2 μg kg^{-1}, and this is why they are completely safe for consumption, in terms of BPA content.

The correlation between the level of BPA and the time of storage cannot be found for obtained results. Given that all samples are stored under the same conditions, it is clear that the migration of BPA to canned meat products depends in the first place on the quality of polymer coating, *i.e.* the amount of residual BPA monomer and degree of crosslinking of epoxy-phenolic resin. BPA may remain unreacted when polymerization conditions or the curing process is insufficient. Since the cans are manufactured in the same factory, with the same quality requirements, the variation in the properties of the coating of different batches are probably the outcome of very fine differences in the quality of the starting material or the curing process. As result, cans with coating of different "potential" to release BPA into foods are produced.

Other authors reported very diverse results in terms of the content of BPA in canned food, sometimes of the same level of magnitude as in our work, but sometimes much higher values in comparison with our results, far above the new SML of 50 μg kg^{-1}. For example, BPA concentrations ranged from 10 to 29 μg kg^{-1} found in canned foods, among which canned meat products were tested.[10] In contrast, BPA in foods and beverages from Turkish markets was up to 1858 μg kg^{-1}.[14] In general, BPA average levels in the present study are on lower part on scale in comparison with those reported in previous studies for canned food samples. As a result, we can say that BPA is not a risk factor for soldier health in Serbia at the present time, although, in view

of the latest European regulation, constant monitoring of the content of BPA in the canned foodstuffs will be necessary.

Table I. BPA content in the samples of BG and the MB, stored in typical military facilities

Date of production	Storage period y/m/d*)	Best before	BPA, μg kg^{-1}
Beef goulash (BG)			
15.09.2010.	6y/6m/00d	14.09.2014.	22.4
23.09.2011.	5y/5m/23d	22.09.2015.	6.2
26.10.2012.	4y/4m/20d	25.10.2016.	3.2
13.04.2013.	3y/11m/02d	12.04.2017.	24.6
19.04.2014.	2y/10m/27d	18.04.2018.	64.8
04.12.2015.	2y/2m/16d	03.12.2019.	44.0
05.01.2016.	0y/11m/10d	04.01.2020.	18.0
Meatballs in tomato sauce (MB)			
12.06.2014.	3y/0m/03d	11.06.2018.	24.2
02.07.2015.	2y/7m/18d	01.07.2019.	25.5
10.02.2016.	0y/10m/05d	09.02.2020.	21.3
13.02.2017.	0y/4m/02d	12.02.2021.	31.2

*) y/m/d = year/month/day

Migration of BPA under different storage conditions – influence of can damage, temperature and storage time

In order to examine BPA migration into food in more detail, cans filled with BG and MB were stored between 3 and 12 months, at two different temperatures, which imitated regular room storage conditions (20 °C) and drastic storage conditions (40 °C), such as warm summer season and places in Serbia. For each storage period, at given temperature, the food from undamaged can (UND), can with lower degree of damage (LDD) and can with higher degree of damage (HDD) was analyzed. The results are presented in Fig. 3. The content of BPA at "0 day" amounted 18.0 μg kg^{-1} for BG and 21.3 μg kg^{-1} for MB. These quantities of BPA migrated to food from the coating of the cans before the experiment was set, *i.e.* during can sterilization and previous storing under regular conditions in typical military facilities. Before setting the experiment, the cans of BG were stored 11 months and 10 days, while the cans of MB were stored 10 months and 5 days under regular storing conditions. The migration level of BPA in the BG was determined to be between 17.0 μg kg^{-1} (6 months at 20 °C, UND can) and 32.9 μg kg^{-1} (6 months at 40 °C, LDD can). When

the samples of BG were stored at 20 °C, very small variations in the BPA level observed, with the maximum value of 21.0 μg kg^{-1} (12 months, HDD can). During the storage of BG at 40 °C, a slight increase in BPA level was noticed in the period between 3 and 6 months; then a plateau was observed between 6 and 9 months, with almost no change in the BPA level; and finally, a slight decrease in the BPA level was seen between 9 and 12 months (Fig. 3). The migration level of BPA in the MB was between 21.0 μg kg^{-1} (3 month at 20 °C, HDD can) and 38.0 μg kg^{-1} (6 months at 40 °C, HDD can). It seems from Fig. 3 that the level of BPA increases slowly, but constantly at 20 °C in the samples of MB. Migration of BPA was generally lower at 20 °C in comparison with 40 °C, in both food products. During the storage MB at 40 °C, an increase in BPA level was seen between 3 and 6 months; then a moderate decrease was observed between 6 and 9 months; and finally, a plateau was reached between 9 and 12 months.

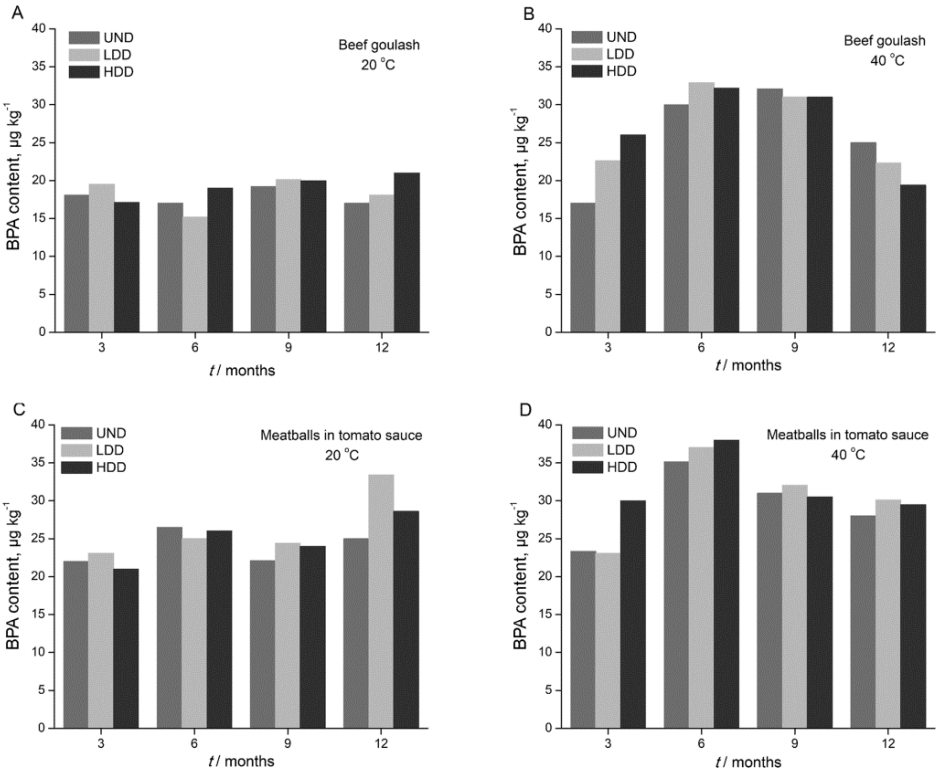

Fig. 3. Migration of BPA to BG and MB samples, during storage at 20 °C and 40 °C

The BPA level was appreciably higher in MB than in the BG at all times of storage at 20 °C. It can be assumed that migration of BPA to MB is more pronounced because this food is more acidic in comparison with BG. The more acidic environment in the MB acts more aggressively on

the epoxy-phenolic inner coating, which leads to faster migration of BPA monomers into food. It can also be noted that an increase in pH values during storage (12 months) leads to a slight decline in the BPA level, which is in line with the previous assumption. These results are presented in the Fig. S-1 of the Supplementary material. Moreover, Sadeghi *et al.* have suggested that food acidity affects the extraction of BPA, in way that increase of pH value leads to decrease of extraction recovery.[16] The degree of damage of the cans was of little significance regarding to migration of BPA. It can be concluded from presented results, that migration of BPA from can coating to food will be increased during the storage in warm places, bearing in mind that the level of BPA will be higher in more acidic food. Some authors reported that most of the BPA migrated during the sterilization process, while the storage time is of little significance at temperatures between 25 and 35 °C.[9] Our results show an unambiguous connection between the migration of the BPA and the increased storage temperature of 40 °C. Migration of BPA to tested food resulted in levels below the new European legislation limit of 50 μg kg^{-1}. Both meat products can be considered completely safe for nutrition in terms of BPA content, so there is no reason for consumers to change their consumption pattern.

CONCLUSIONS

This was the first time to examine content of BPA in canned food produced in Serbia. This issue has been widely discussed in many other countries, but to our best knowledge there is a lack of data in Serbia, where tinplate cans are manufactured and widely used in the food industry. The samples of the BG and the MB, produced for needs of the Serbian Armed Forces, were tested to the presence of BPA. The cans were made by the special requirements, with application of tin and epoxy-phenolic coatings which were twice as high as for the civilian market. The level of BPA was ranged from 3.2 to 64.8 μg kg^{-1}, after regular storage in typical military facilities. No correlation between storage time and BPA level was found, indicating that migration of BPA mostly depends on the quality of the coating on the inner surface of the can. The experiments of storing at different temperatures and with different degrees of can damage showed that migration of BPA was generally lower at 20 °C in comparison with 40 °C, for both food products. The BPA level was higher in the MB than in the BG at both temperatures, for almost all storage periods. It is obvious that migration of BPA from the inner epoxy-phenolic coating to food will be more pronounced during the storage in warm places, and when the food is more acidic. The degree of can damage

was of little significance regarding to migration of BPA. Results from our work show an unambiguous connection between the migration of BPA and the increased storage temperature of 40 °C. The found levels of BPA are below the new SML limit of 50 μg kg^{-1}. Both canned meat products can be considered completely safe for nutrition of solders of the Serbian Armed Forces in terms of BPA content. However, there is continuous need of an accurate monitoring of canned food as possible source of BPA.

SUPPLEMENTARY MATERIAL

The Table S-I and Fig. S-1 are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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И З В О Д

УТИЦАЈ УСЛОВА СКЛАДИШТЕЊА НА МИГРАЦИЈУ БИСФЕНОЛА А ИЗ ЕПОКСИ-ФЕНОЛНИХ ПРЕВЛАКА У КОНЗЕРВИСАНЕ ПРОИЗВОДЕ ОД МЕСА

БРАНИСЛАВ СТОЈАНОВИЋ, ЉУБИЦА РАДОВИЋ[1], ДЕЈАН НАТИЋ[2], МАРГАРИТА ДОДЕВСКА[2], ГОРДАНА ВРАШТАНОВИЋ-ПАВИЧЕВИЋ[2], МИЛИЦА БАЛАБАН[3], СТЕВА ЛЕВИЋ[4], ТАЊА ПЕТРОВИЋ[4] и ВЕСНА АНТИЋ[4]

Министарство одбране-Република Србија, Бирчанинова 5, Београд, Србија, [1]Војнотехнички институт Ратка Ресановића 1, Београд, Србија, [3]Центар за испитивање намирница, Змаја од Ноћаја 11, Београд, Србија, [4]Природно-математички факултет, Универзитет у Бањој Луци, Младена Стојановића 2, Бања Лука, Босна и Херцеговина, [4]Универзитет у Београд – Пољопривредни факултет, Немањина 6, Земун, Србија

У овом раду је испитана миграција бисфенола А (BPA) из епокси-фенолне превлаке којом је обложена метална лименка, у конзервисане производе од меса, произведене за потребе Војске Србије. Лименке су произведене од белог лима према специјалним војним захтевима, напуњене говеђим гулашем или ћуфтама у парадајз сосу, и конзервисане стерилизацијом. Структура унутрашње превлаке на лименци је испитана FTIR спектроскопијом. Миграција BPA у садржај конзерве је испитана након складиштења при регуларним условима у типичним војним објектима. Узорци говеђег гулаша (BG), произведени у периоду 2010-2016, и ћуфти у парадајз сосу (MB) произведених у периоду 2014-2017, су тестирани на присуство BPA. Затим је испитан утицај температуре складиштења и степена оштећења конзерви на миграцију BPA у садржај конзерви. Оба производа од меса су термостатирана на 20 и 40 °C, и садржај BPA је мерен после 3, 6, 9 и 12 месеци складиштења. BPA је одређен у садржају неоштећених конзерви, као и конзерви

са већим и мањим степеном оштећења. BPA је из хране екстрахован ацетонитрилом а екстракти су пречишћени QuEChERS процедуром. Садржај BPA је одређен LC-MS методом.

REFERENCES

1. C. A. May, *Epoxy resins - chemistry and technology*, 2nd Edition, Marcel Dekker, Inc., New York, USA, 1988 (ISBN 08247-7690-9)
2. T. Geens, T.Z. Apelbaum, L. Goeyens, H. Neels, A. Covaci, *Food Addit. Contam. Part A.* **27** (2010) 1627 (https://doi.org/10.1080/19440049.2010.508183)
3. X. L. Cao, C. Perez-Locas, G. Dufresne, G. Clement, S. Popovic, F. Beraldin, R.W. Dabeka, M. Feeley, *Food Addit. Contam.Part A.* **28** (2011) 791 (https://doi.org/10.1080/19440049.2010.513015)
4. G. O. Noonan, L. K. Ackerman, T. H. Begley, *J. Agric. Food Chem*. **59** (2011) 7178 (https://doi.org/10.1021/jf201076f)
5. J. R. Rochester, *Reprod. Toxicol.* 42 (2013) 132 (https://doi.org/10.1016/j.reprotox.2013.08.008)
6. C. Liao, K. Kannan, *J. Agric. Food Chem*. **61** (2013) 4655 (https://doi.org/10.1021/jf400445n)
7. C. Liao, K. Kannan, *Food Addit. Contam. Part A.* **31** (2014) 319 (https://doi.org/10.1080/19440049.2013.868611)
8. E. M. Munguia-Lopez, E. Peralta, A. Onzalez-Leon, C. Vargas-Requena, H. Soto-Valdez, *J. Agric. Food Chem.* **50** (2002) 7299 (https://doi.org/10.1021/jf0257502)
9. A. Goodson, W. Summerfield, I. Cooper, *Food Addit. Contam.* **21** (2004) 1015 (https://doi.org/10.1080/02652030400011387)
10. B. M. Thomson, P. R. Grounds, *Food Addit. Contam. Part A.* **22** (2005) 65 (https://doi.org/10.1080/02652030400027920)
11. J. Sajiki, F. Miyamoto, H. Fukata, C. Mori, J. Yonekubo, K. Hayakawa, *Food Addit. Contam.***24** (2007) 103 (https://doi.org/10.1080/02652030600936383)
12. S. C. Cunha, C. Cunha, A. R. Ferreira, J. O. Fernandes, *Anal. Bioanal. Chem.* **404** (2012) 2453 (https://doi.org/10.1007/s00216-012-6389-5)
13. S.C. Cunha, J.O. Fernandes, *Food Control* **33** (2013) 549 (https://doi.org/10.1016/j.foodcont.2013.03.028)
14. S. Sungur, M. Koroglu, A. Ozkan, *Food Chem.* **142** (2014) 87 (https://doi.org/10.1016/j.foodchem.2013.07.034)
15. S. Errico, M. Bianco, L. Mita, M. Migliaccio, S. Ross, C. Nicolucci C. Menale, M. Portaccio, P. Gallo, D. G. Mita, N. Diano, *Food Chem.* **160** (2014) 157 (https://doi.org/10.1016/j.foodchem.2014.03.085)

16. M. Sadeghi, Z. Nematifar, N. Fattahi, M. Pirsaheb, M. Shamsipur, *Food Anal. Methods* **9** (2016) 1814 (https://doi.org/10.1007/s12161-015-0357-6)
17. S. N. El Moussawi, R. Karama, M. Cladière, H. Chebib, R. Ouaini, V. Camel, *Food Addit. Contam. Part A.*, 35 (2018) 377 (https://doi.org/10.1080/19440049.2017.1395521)
18. J. C. Hartle, A. Navas-Acien, R. S. Lawrence, *Environ. Res.* **150** (2016) 37 (https://doi.org/10.1016/j.envres.2016.06.008)
19. M. Lorber, A. Schecter, O. Paepke, W. Shropshire, K. Christensen, L. Birnbaum, *Environ. Int.* **77** (2015) 55 (https://doi.org/10.1016/j.envint.2015.01.008)
20. S. C. Cunha, R. N. Alves, J. O. Fernandes, S. Casal, A. Marques, *Food Chem.* **232** (2017) 501 (https://doi.org/10.1016/j.foodchem.2017.04.006)
21. French Republic, Law No 2012-1442 for the Suspension of the Manufacture, Import, Export and Marketing of All-Purpose Food Packaging Containing Bisphenol A, *J Off de la République Française*, JORF n° 0300:20395 (https://www.legifrance.gouv.fr/eli/loi/2012/12/24/AFSX1240700L/jo/article_1)
22. EFSA CEF Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids, Scientific Opinion on the risks to public health related to the presence of bisphenol A (BPA) in foodstuffs: Executive summary, *EFSA J.* **13** (2015) 397 (https://efsa.onlinelibrary.wiley.com/doi/pdf/10.2903/j.efsa.2015.3978)
23. Commission Regulation (EU) 2018/213 of 12 February 2018 on the use of bisphenol A in varnishes and coatings intended to come into contact with food and amending Regulation (EU) No 10/2011 as regards the use of that substance in plastic food contact materials, *Official Journal of the European Union, L41/6-L41/12* (https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32018R0213&from=EN)
24. Official Gazette of RS, No. 94/15 of 17 November 2015: *Regulation on the quality chopped meat, semi-products from meat and products from meat* (http://www.mpzzs.gov.rs/download/Pravilnici/4827015.0064.34-1.pdf)
25. Standard SRPS EN 10202 (2007): *Cold reduced tinmill products - Electrolytic tinplate and electrolytic chromium/chromium oxide coated steel* (http://www.iss.rs/rs/standard/?natstandard_document_id=15966)
26. A. M. Motawie, E. M. Sadek, *Polym. Adv. Technol.* **10** (1999) 223 (https://doi.org/10.1002/(SICI)1099-1581(199904)10:4<223::AID-PAT865>3.0.CO;2-7)
27. Safer chemicals alternative (ALHem, Civil Society Organization Belgrade), *Toxic Cash Receipts: Presence of Bisphenol A (BPA) in thermal paper and some of food contact materials* (2017) (http://www.alhem.rs/wp-content/uploads/2015/12/TOXIC-RECEIPT-REPORT.pdf)