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DETERMINATION OF CARBONYL COMPOUNDS (ACETALDEHYDE AND FORMALDEHYDE) IN POLYETHYLENE TEREPHTHALATE CONTAINERS DESIGNATED FOR WATER CONSERVATION

Polyethylene terephthalate (PET) has in the last several years become the main packaging material for many food products, particularly carbonated beverages and bottled water, as well as for products of chemical industry (packaging of various hygiene maintenance agents, pesticides, solvents, etc.). The strength and permeability properties of PET are very good for packaging of beverages, its resistance to chemicals is high and it has a high degree of transparency. Acetaldehyde and formaldehyde are formed during the thermoforming of PET containers. After cooling, acetaldehyde and formaldehyde remain trapped in the walls of a PET bottle and may migrate into the water after filling and storage. Since there are no migration tests in Serbia prescribed for the determination of acetaldehyde and formaldehyde, the purpose of the paper is to test the quantitative contents of carbonyl compounds (acetaldehyde and formaldehyde) in PET containers of different volumes, made by various manufacturers of bottled mineral carbonated and noncarbonated water, and exposed to different temperatures. In this study, the migration of acetaldehyde and formaldehyde from PET bottles into mineral carbonated and noncarbonated water was determined by high performance liquid chromatography. Taking into consideration that formaldehyde and acetaldehyde have no UV active or fluorescent group, the chromatography was preceded by derivatization in a closed system (due to a low boiling point of acetaldehyde and formaldehyde), which transforms carbonyl compounds into UV active compounds.

Keywords: polyethylene terephthalate, formaldehyde, acetaldehyde, migration.

Polyethylene teraphthalate (PET) is increasingly being used as the packaging for drinking water. PET is obtained in the reaction of gradual polymerisation of teraphthalic acid (or dimethylteraphthalete) and ethylene glycol. The first level includes dimethylteraphthalete transesterification with ethylene glycol or esterification of terephthalic acid with ethylene glycol with the formation of bis(2-hydroxy-ethyl) terephthalate and small quantities of larger oligomers. The second level is the polycondensation of esters, bis(2-hydroxy-ethyl) terephthalate and formation of polyethylene teraphthalete (PET) which is processed into pellets or fibres [1].

Acetaldehyde and formaldehyde may occur as undesired by-products in the production of PET packaging, in the process of thermal decomposition of polyethylene teraphthalete, whereas the mechanism of forming of acetaldehyde is presented by the following equation [2, 3]:

$$\begin{aligned} &\text{\~{}}OOCC_6H_4COOCH_2CH_2OH \rightarrow \\ &\rightarrow \text{\~{}}OOCC_6H_4COOCH{=}CH_2 + H_2O \rightarrow \\ &\rightarrow \text{\~{}}OOCC_6H_4COOH + CH_3CHO \end{aligned} \quad (1)$$

If the production process is not strictly controlled in terms of precise maintenance of the temperature

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(which should not exceed 300 °C) and pressure during bottle blowing, or if the purity of raw materials is unsatisfactory, monomers could occur in a finished product. Due to the high volatility of acetaldehyde and formaldehyde, there is a great chance that migration from a PET bottle to the packed contents (drinking water) may occur and, consequently, this could lead to a change in taste and odour of the bottled drinking water. The minimum quantities of acetaldehyde that may be sensed in bottled drinking water range from 10 to 20 µg/kg. The presence of acetaldehydes in alcoholic and soft drinks which in themselves already contain acetaldehyde does not pose a problem, because the taste of acetaldehyde is disguised with the presence of additional aromas [1]. According to the Directive 2002/72/EEC, the permitted level of migrations of acetaldehyde from a PET bottle should not exceed 6 mg/kg, and formaldehyde 15 mg/kg [4].

For the purpose of determining concentrations of formaldehyde and acetaldehyde, one should use spectrophotometric and chromatographic methods. Considering that the spectrophotometric methods are non-specific and usually determine the sum of carbonyl compounds solution [5], whereas nowadays, chromatographic methods are more often used (HPLC and GC) [6-9].

In this paper, the level of concentration of formaldehyde and acetaldehyde has been determined by the chromatographic method, using a high performance liquid chromatograph (HPLC). Considering that acetaldehyde and formaldehyde have no UV active or fluorescent group, it is necessary to conduct derivatization and translate them into UV active compounds or fluorescent compounds. 2,4-dinitrophenylhydrazine (DNPH) was used as a reagent for derivatisation [8].

The reaction equation of DNPH is shown in Figure 1.

Due to the very low boiling points of formaldehyde (-21 °C) and acetaldehyde (20.1 °C), the derivatization should be conducted in a closed system [10].

The purpose of the study was to determine concentrations of acetaldehyde and formaldehyde in PET bottles of different manufacturers of carbonated and noncarbonated mineral water in the Republic of Serbia. For the purpose of the experiment, PET bottles (0.33 and 2 L) of different manufacturers of bottled water were used. PET bottles filled with carbonated and noncarbonated mineral water were obtained from local stores. The level of acetaldehyde and formaldehyde migration was assessed in relation to the storage time (1 day, 15 days, 3 months, 6 months and 8 months), exposure to the sunlight, presence of carbon dioxide, and application of different polyethylene caps.

EXPERIMENTAL

Sampling and sample preparation

Migration tests were conducted on bottled carbonated and noncarbonated mineral water in PET bottles of different volumes (0.33 and 2 L) bought in local stores, with different dates of filling.

The method of determining the contents of acetaldehyde and formaldehyde in the water

100 mL of a sample (water) is derivatised in acid environment pH 3 (adjustment is performed with 6 M of hydrochloric acid) with 6 mL, 70% of 2,4-dinitrophenylhydrazine (DNPH) solution. The container is immediately sealed and positioned on a heating device with a magnetic stirrer at 40 ºC, 550 spins/min, for 1 h.

The resulting derivatives, dinitrophenylhydrazines, are then extracted from the solution with solid and liquid extraction on column Supelco SPA - C18 (SPE-C18). The column is conditioned with 10 mL of citrate buffer pH 3, and then the sample in which sa-

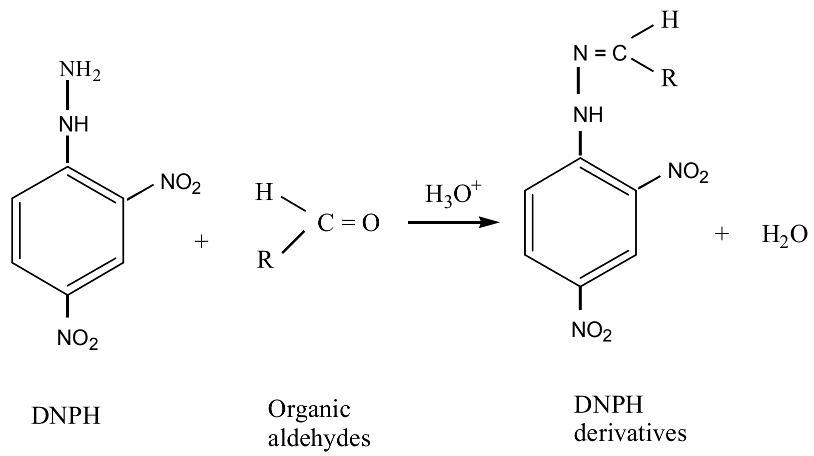

Figure 1. DNPH derivative of organic aldehydes.

turated sodium chloride (10 mL) was previously added, is quantitatively transferred to the column. Elution of derivatives on SPE-C18 column is performed with 8 mL of acetonitrile (HPLC purity, Merck) in a measuring container of 10 mL in which the sample volume is raised to the notch with acetonitrile (HPLC purity, Merck). Such a sample is transferred to a vial (1.5 mL in volume) and then analysed on a high performance liquid chromatography (HPLC) device. The concentration of acetaldehyde and formaldehyde in eluted volumes are read from a calibration curve at the wavelength of 360 nm [8].

HPLC separations were performed on an Agilent 1100 series HPLC (USA) including a degasser G1379 A, binary G1312 pump, ALS G1313A, COLCOM G1316A and DAD G1315B. The column used was commercially available particle size 5 μm: Spherisorb ODS - 2.5 μm, 124 mm×4 mm (Hewlett Packard, USA). The mobile phase of acetonitrile: water 60:40 (v/v) with a flow rate at 1 mL/min, temperature of column 35 °C and UV detection at 360 nm were used.

Evaluation method

Linearity

Based on the linearity parameters (Table 1), it can be concluded that the linearity of the calibration curve of formaldehyde and acetaldehyde has been achieved in the range from 1.5 to 300 μg/L in two calibration ranges - lower (1.5-60, 1.5, 7.5, 15, 30 and 60 μg/L) and higher (7.5-300; 7.5, 15, 75, 150 and 300 μg/L) with a correlation coefficient that meets the validation criteria (> 0.9990).

Figure 2 presents a chromatogram of acetaldehyde and formaldehyde.

Accuracy and repeatability

In 800 mL of distilled water, 0.8 mL of standard DNPH-formaldehyde and DNPH-acetaldehyde in the concentration of 15 μg/mL were added. Six aliquotes were measured and analysis was conducted using the method, and the expected concentrations of formaldehyde and acetaldehyde in the prepared sample reached 15 μg/L.

A relative standard deviation of repeatability for formaldehyde and acetaldehyde (Table 2) meets the validation criterion (*RSD* ≤ 20%), whereas for formaldehyde it is 4.878%, and for acetaldehyde 2.604%. The accuracy of the method is within the required limits of 80-120%, whereas for formaldehyde it is 89.24% and for acetaldehyde 92.99%.

Limit of detection and quantitation

A limit of detection, *i.e.*, limit of method quantitation has been defined as a threefold, *i.e.*, tenfold value of the standard deviation of the results of the blank test analysis (Table 3).

RESULTS AND DISCUSSION

The purpose of this study was to determine the concentration of migrants, carbonyl compounds (acetaldehyde and formaldehyde) from PET containers to the packed carbonated and noncarbonated mineral water. The stated migrants may cause chemical and sensory changes in packed drinking water in PET bottles [12].

Migration of formaldehyde and acetaldehyde to packed carbonated mineral water

In studying the migration of formaldehyde and acetaldehyde used for the packing of carbonated mineral water, PET bottles of different volumes (0.33

Table 1. Linearity parameters for formaldehyde (FA) and acetaldehyde (AA) in two calibration ranges lower (1.5-60 μg/L) and higher (7.5-300 μg/L)

Analyte	Range	Equation	Correlation coefficient
FA	1.5-60 μg/L	A = 1.66697345*Amt + 0.0618378	0.99997
AA	1.5-60 μg/L	A = 1.00626839*Amt - 0.2929327	0.99993
FA	7.5-300μg/L	A = 1.71464253*Amt - 4.2994569	0.99991
AA	7.5-300μg/L	A = 1.2722231*Amt - 3.1696415	0.99991

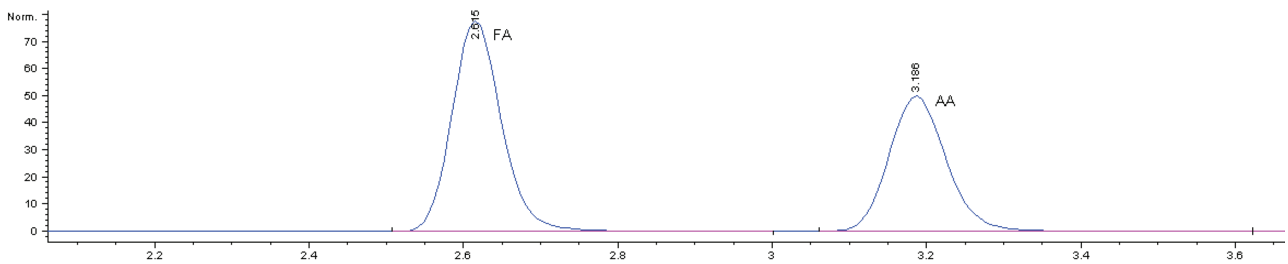

Figure 2. Renowned chromatogram of formaldehyde - FA (retention time 2.615 min) and acetaldehyde - AA (retention time 3.185 min).

Table 2. Parameters of accuracy and repeatability of the method for formaldehyde and acetaldehyde

Parameters of accuracy and repeatability	Formaldehyde, FA	Acetaldehyde, AA
Standard deviation of repeatability, s_r / μg L^{-1}	0.750	0.396
Relative standard deviation of repeatability, $RStDev_r$	4.878	2.604
Systematic deviation, bias%	-10.76	-7.01
Recovery, Rec%	89.24	92.99

and 2 L) were used. The time of water preservation was one whole day (24 h) or three months. In nine PET bottles of 2 L (samples from O1-1 to O1-9), mineral water was stored for one day (24 h). In PET bottles of 2 L, samples A1-1, A1-2, and in PET bottles of 0.33 L (samples from B1-1 to B1-7), mineral water was stored for three months. The obtained results are presented in Table 4.

Table 3. Limit of detection and limit of quantitation, in μg/L (ppb), of the method for formaldehyde and acetaldehyde

Parameter	FA	AA
Limit of detection, *LOD*	0.3	0.3
Limit of quantitation, *LOQ*	1	1

Based on the data referred to in Table 4, one could notice that already after 24 hours, the storage of mineral water in PET bottles of 2 L (O1-1 to O1-9) results in the migration of formaldehyde and acetaldehyde to water. In one bottle, the concentration of formaldehyde is always lower in comparison to the concentration of acetaldehyde. After three months of storage of mineral water in PET bottles of 2 L (A1-1 and A1-2), concentrations of both migrants significantly increased. In this case, the concentration of formaldehyde is lower in comparison to the concentration of acetaldehyde.

The largest concentration of acetaldehyde is in the mineral water stored for three months in the bottles of 0.33 L (from B1-1 to B1-7). It is four times higher than the concentration of acetaldehyde in mineral water which was also stored for three months but in the bottles of 2 L (A1-1 and A1-2), and about thirty times higher than the concentration of acetaldehyde in mineral water held in the bottles of 2 L (O1-1 from O1-8) which was stored for one day, Table 4.

In addition, the concentration of formaldehyde in mineral water stored in the bottles of 0.33 L (from B1-1 to B1-7) is about three to four times higher than the concentration of formaldehyde in carbonated mineral

Table 4. Concentrations of migrants, formaldehydes and acetaldehydes, from PET bottles to carbonated mineral water; marked with O - mineral water was stored in 2 L PET bottles for one day (24 h); marked with A - mineral water was stored in 2L PET bottles for three months; marked with B - mineral water was stored in 0.33 L PET bottles for three months (each value is the mean of three trails)

Sample	Water volume, L	Storing period, day	Concentration, μg/L	
			FA	AA
O1-1	2	1	1.34	1.82
O1-2	2	1	1.45	1.62
O1-3	2	1	1.27	1.78
O1-4	2	1	1.47	2.09
O1-5	2	1	1.28	2.18
O1-6	2	1	1.73	1.99
O1-7	2	1	1.78	2.22
O1-8	2	1	1.55	2.16
O1-9	2	1	1.52	222
A1-1	2	90	8.61	13.94
A1-2	2	90	12.38	17.68
B1-1	0.33	90	35.36	60.90
B1-2	0.33	90	35.23	53.57
B1-3	0.33	90	39.17	64.85
B1-4	0.33	90	26.56	59.80
B1-5	0.33	90	22.56	55.86
B1-6	0.33	90	32.03	82.06
B1-7	0.33	90	28.25	78.05

water held in the 2 L bottles (A1-1 and A1-2) after three months, and about twenty-three times higher than the concentration of formaldehyde in carbonated mineral stored in the bottles of 2 L (O1-1 to O1-8) for one day.

Various influences on the migration of formaldehyde and acetaldehyde in packaged carbonated and noncarbonated mineral water

The following part of the study determined the migration of formaldehyde and acetaldehyde to packaged carbonated and noncarbonated mineral water of the same manufacturer M in the bottles of different volumes (0.33 and 2 L), polypropylene caps (Z-1, Z-2 and Z-3), dates of packaging and storage conditions (atmosphere conditions or exposure to the sunlight 5 days prior to the analysis - air temperature between 20-38 °C). The obtained results are presented in Table 5.

Based on the data referred to in Table 5, it may be noticed that in the same bottle, the concentration of formaldehyde in mineral water is always lower than the concentration of acetaldehyde. This is consistent with previous experiments (results presented in Table 4). The concentration of formaldehyde is higher in the mineral water held in PET bottles of 0.33 L (C1-1, C1-3, C1-4, C1-5 and C1-6, C1-8 and C1-10) than the concentration in the mineral water held in PET bottles of 2 L (C1-7 and C1-9). In addition, it has been noticed that the concentration of formaldehyde in the carbonated mineral water in the bottles which were exposed to the sunlight for 5 days (C1-3, C1-4 and C1-5) is higher than the concentration in the mineral water in the bottles with noncarbonated water (C1-1 and C1-2) which were also exposed to the sunlight. These points to the fact that the concentration of carbon dioxide and UV radiation contributes to the migration of formaldehyde and acetaldehyde from PET bottles to mineral water, which is in compliance with previous studies [6]. It is possible that the pressure which CO_2 makes to the walls of PET bottles incites the migration of formaldehyde and acetaldehyde from a PET bottle.

The unexpectedly large migration of acetaldehyde to mineral water was obtained in the samples C1-8 and C1-10, carbonated mineral water stored for 8 months in 0.33 L PET bottles.

It is known that acetaldehyde and formaldehyde may migrate from polypropylene caps [6]. In terms of the impact of different polypropylene caps (Z-1, Z-2 and Z-3), it may be stated that the three different polypropylene caps have no significant effect on the migration of formaldehyde and acetaldehyde to mineral carbonated and noncarbonated water (Table 5).

Micro-organisms and beverages

While microbiological tests have not been carried out in this work, their importance should not be ignored [9].

A bottled drink constitutes a unique system which can inhibit or enhance the growth of microorganisms. Micro-flora, if present, will enter a dormant stage during which their chances of survival are related to their immediate surroundings. Following this lag stage, during which specific micro-flora may adapt to their new environment and start to grow, there is a burst of species-dependent activity, during which the population doubles repeatedly at a a steady rate. Since a bottled drink is a closed system, waste products and diminishing nutrients will serve to slow down the growth and eventually bring it to a standstill, when the death rate increases and all activities stop. At this point the product, although perhaps not a health hazard, has been spoiled and can no longer

Table 5. Concentrations of migrants, formaldehydes and acetaldehydes, from PET bottles to noncarbonated and carbonated mineral water. PET bottles were exposed to different temperatures in different time spans and sealed with different polypropylene caps Z-1, Z-2 and Z-3

Sample ID	Carbonated	Polypropylene caps	Water volume, L	Storing period day	Exposure to the sunlight for 5 days	Concentration, µg/L	
						FA	AA
C1-1	No	Z-2	0.33	240	Yes	33.33	56.88
C1-2	No	Z-1	0.33	180	Yes	27.17	37.41
C1-3	No	Z-2	0.33	15	Yes	40.33	53.98
C1-4	No	Z-1	0.33	15	Yes	37.69	53.69
C1-5	Yes	Z-3	0.33	15	Yes	35.14	54.38
C1-6	Yes	Z-2	0.33	15	Yes	33.13	51.78
C1-7	Yes	Z-2	2	240	No	32.06	56.87
C1-8	Yes	Z-2	2	240	No	30.72	47.88
C1-9	Yes	Z-2	0.33	240	No	35.13	92.98
C1-10	Yes	Z-2	0.33	240	No	35.42	108.82

serve its intended function [13]. It is very important to stress that the aldehydes are easy digestible and bacteria present in the non-carbonated water can be responsible for the significant decrease in aldehyde concentration.

CONCLUSION

Plastic packaging contains molecules of a smaller molecular mass, monomers and olygomers, as well as additives (fillers, UV stabilisers, antistatic agents, etc.). Polymer additives and remaining parts of monomers or olygomers are not chemically linked to a polymer molecule, which enables them to freely move inside a polymer. For this reason, it is important to determine potential migrants and their toxic effect on consumers' health. Acetaldehyde and formaldehyde occur as a result of degradation of polyethylene terephthalate and remain trapped in PET walls, but it is possible to keep acetaldehyde and formaldehyde in PET bottles at low levels during production processes by controlling the critical stages of the production process [7].

Migration of acetaldehyde and formaldehyde from a PET bottle to bottled drinking water grows in time. Migration of acetaldehyde from a PET bottle to bottled drinking water dominates over the migration of formaldehyde. In all the cases the concentrations of acetaldehyde and formaldehyde are always considerably lower than the permitted level of migration from PET packaging (according to the Directive 2002/72/EEC) [4].

Generally speaking, it may be said that the results obtained in the study comply with the results of the studies conducted in other countries, where concentrations of acetaldehyde and formaldehyde in bottled carbonated and noncarbonated water and soft drinks were determined in Poland [6], Thailand [8], Japan [9] and Turkey [7].

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NAUČNI RAD

ODREĐIVANJE KARBONILNIH JEDINJENJA (ACETALDEHIDA I FORMALDEHIDA) U AMBALAŽI OD POLIIETILENTEREFTALATA NAMENJENOJ ZA ČUVANJE VODE

Poletilen-tereftalat (PET) je u poslednjih nekoliko godina postao glavni materijal za pakovanje mnogih prehrambenih proizvoda, naročito za gazirana pića i flaširane vode, kao i za proizvode hemijske industrije (za pakovanje raznih sredstava za održavanje higijene, pesticida, rastvarača i dr). Acetaldehid i formaldehid nastaju u toku termoformiranja PET ambalaže. Posle hlađenja acetaldehid i formaldehid ostaju zarobljeni u zidu PET boce i mogu migrirati u vodu posle punjenja i skladištenja. S obzirom da kod nas nisu propisani migracioni testovi za određivanje acetaldehida i formaldehida, cilj ovog rada je bio da se ispita kvantitativni sadržaj karbonilnih jedinjenja (acetaldehida i formaldehida) u PET ambalaži različitih zapremina, različitih proizvođača flaširane mineralne gazirane i negazirane vode, izložene različitim temperaturama. Karbonilna jedninjenje su određivana obrnuto-faznom tečnom hromatografijom pod visokim pritiskom (RP-HPLC). S obzirom da formaldehid i acetaldehid nemaju UV aktivnu ili fluorescentnu grupu, hromatografskim određivanjima prethodi derivatizacija u zatvorenom sistemu (zbog niskih tački ključanja formaldehida i acetaldehida), čime se karbonilna jedinjenja prevode u UV aktivna jedinjenja.

Ključne reči: polietilen tereftalat, formaldehid, acetaldehid, migracija.