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Short Communication

Investigation of carbonyl compounds (acetaldehyde and formaldehyde) in bottled waters in Iranian markets

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Abstract

The contamination of water bottles has become a very serious problem attracting more and more concerns due to the possibility of acetaldehyde and formaldehyde migration from PET bottles. Therefore, the study aims to assess the extent of acetaldehyde and formaldehyde migration from polyethylene terephthalate bottles of different manufacturers into bottle contents in relation to the storage time and at room temperature sold in Iranian markets. Twenty typical brands of PET-bottled water samples were purchased from supermarkets and shops in Iran between April and May 2015. In this study, the levels of formaldehyde and acetaldehyde were determined using a high performance liquid chromatograph (HPLC). All bottled water samples in Iranian supermarkets and shops had detectable levels of formaldehyde and acetaldehyde. Minimum and maximum levels of formaldehyde and acetaldehyde in this study varied between 12-45 µg/l and 25-120 µg/l, respectively. The average levels of formaldehyde and acetaldehyde in Iranian bottled waters were 28.6 µg/l and 61.3 µg/l, respectively. Overall, it could be stated that the bottled waters, available in Iran, are safe for the human consumption, as regards the levels of formaldehyde and acetaldehyde.

Introduction

Safe drinking water is important for human (Dehghani *et al*., 2013; Fazlzadeh *et al*., 2017; Derakhshani *et al*., 2017). Bottled water consumption has grown at a high rate over the past thirty years worldwide (Ferrier, 2001). The pollution of water bottles has become a very serious problem attracting more and more concerns. Therefore, its quality assessment is of primary importance. Nowadays, polyethylene terephthalate (PET), a semi-crystalline polymer belonging to the family of polyesters, has been extensively used for food and beverages packaging due to its light, tough and transparent characteristics. Despite these properties, water in PET bottles may contaminate with the material's components (Kim *et al*., 1990). However, very little attention has been concentrated on potential changes in quality of these waters after long term storage in plastic bottles. The widespread use of PET packaging of drinking water is a cause for concern as release of the pollutants from PET materials into water is associated with health risk issues (Dąrowska *et al*., 2003). Formaldehyde (CH_2O) is highly toxic and can potentially cause deleterious effects in all animals. For example, an ingestion of 30 mL of a solution containing formaldehyde 37% can cause death in human(Tang *et al*., 2009). Acetaldehyde and formaldehyde, the most relevant carbonyl compounds, are highly volatile and can migrate from bottles into water after filling and storage and, consequently, this could lead to a change in taste and odour of the bottled drinking water (Nawrocki *et al*., 2002). The formation route of acetaldehyde can be shown as below (Valentina *et al*., 2014):

$$OOCC_6H_4COOCH_2CH_2OH \rightarrow OOCC_6H_4COOCH{=}CH_2 + H_2O \rightarrow OOCC_6H_4COOH + CH_3CHO$$

Trace levels of acetaldehyde have been reported in water stored in PET containers (Feron *et al.,* 1991). The International Agency for Research on Cancer (IARC) has classified acetaldehyde as a possible carcinogen. Taste and odour thresholds of formaldehyde in water are 50 and 25 mg/l, respectively (Verschueren, 1983). Many researchers have studied the influence of thermo-oxidative and chemical degradation of PET containers (Zhang and Ward, 1995; Paci and La Mantia, 1999; Wang *et al*., 2000). Due to the degradation almost all

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polymers under environmental factors as sunlight (UV light) and temperature, therefore, the storage conditions of the bottled waters need to be controlled (Gijsman *et al.*, 1999). The Directive 2002/72/EEC has recommended that the level of migration of formaldehyde in water stored in PET bottles should not exceed 15 mg/kg, and acetaldehyde 6 mg/kg (Petersen and Jensen, 2010). In this study, the levels of formaldehyde and acetaldehyde were determined by a high performance liquid chromatograph (HPLC). Due to the absence of UV active or fluorescent group in acetaldehyde and formaldehyde, it is necessary to conduct derivatization and convert them into UV active or fluorescent compounds. For the purpose of the experiment, PET bottles (0.5 and 1.5 L) of different brands of bottled water were used. To date, no studies have been done regarding formaldehyde and acetaldehyde levels in bottled water in Iran. Therefore, the study aims to assess the extent of acetaldehyde and formaldehyde migration from polyethylene terephthalate bottles of different manufacturers into bottle contents in relation to the storage time (30 days) at room temperature 15-30ºC sold in Iranian supermarkets and shops.

Materials and Methods

Twenty typical brands of PET-bottled water samples were purchased from supermarkets and shops in Iran between April and May 2015. The samples were coded as 1 to 20 corresponding to the brands. After collection, the bottles were kept at room temperature for 30 days. A summary of the results of formaldehyde and acetaldehyde levels is shown in Table 1. The volume of the bottle samples was in range of 0.5 -1.5 L. Determination of acetaldehyde and formaldehyde content is generally carried out using HPLC (Series 200, Perkin Elmer). Sample preparation and then determination of levels of acetaldehyde and formaldehyde were carried out according to Redžepović *et al.* (2012). Initially, 100 mL of a sample (water) was derivatised under acidic conditions, (pH 3) with 6 mL, 2,4-dinitrophenylhydrazine 70% solution. The container is immediately sealed and placed on a heater with a magnetic stirrer at 40ºC, 550 rpm, for 1 h. After derivation, dinitrophenylhydrazines were extracted with solid and liquid extraction on column Supelco SPA -C18 (SPE-C18). After that, the column was conditioned with 10 mL of citrate buffer at pH 3, and then the saturated sodium chloride sample prepared previously, and transferred to the column. Finally, the levels of acetaldehyde and formaldehyde were read from a calibration curve at the wavelength of 360 nm.

Results and Discussion

Table 1 shows the levels of formaldehyde and acetaldehyde in bottle samples. All bottled water samples in Iranian supermarkets and shops had detectable levels of formaldehyde and acetaldehyde. As can be seen from the table, unexpectedly high amounts of acetaldehyde were observed in the samples S5 and S19, for bottled water stored for 30 days in 0.5 L PET containers at room temperature. According to the results given in Table 1, it may be concluded that in the same bottle, the level of acetaldehyde in bottled water is higher than the level of formaldehyde. Minimum and maximum levels of formaldehyde and acetaldehyde in this study varied between 12-45 µg/l and 25-120 µg/l, respectively (Table 1). The highest level of formaldehyde was found for S19. However, several studies have clearly reported levels of formaldehyde and acetaldehyde in bottled water. These contaminants may originate from bottle materials, background contamination, water processing steps, cap-sealing resins, recycled PET, etc. It is also reported that presence of heterotrophic bacteria in bottle waters, can decompose and therefore change the levels of formaldehyde and acetaldehyde. The levels of formaldehyde and acetaldehyde in Japanese PET bottles ranged from 10.1- 27.9 µg/l, and from 44.3–107.8 ug/l, respectively, while the North American waters ranged from 13.6- 19.5 µg/l and from 41.4-44.8 µg/l, respectively (Mutsuga *et al.*, 2006). According to the present study, the average levels of formaldehyde and acetaldehyde in Iranian bottled waters were 28.6 µg/l and 61.3 µg/l, respectively after 30 days storage at room temperature. In a study, levels of aldehydes in water were reported in a range of <0.5 to 59 µg/l and <0.5 to 260 µg/l for formaldehyde and acetaldehyde in mineral bottled waters, respectively (Sugaya *et al.*, 2001). Moreover, level of acetaldehyde in carbonated water after a storage period of 10 days at 40ºC was <2 µg/l (Ceretti *et al.*, 2010). The levels of formaldehyde and acetaldehyde in bottled water in Serbia in 2012 were in a range of 1.34-39.17 µg/l and 1.62-222 µg/l, respectively (Ozlem, 2008). Temperature and duration of storage of the bottles are critical factors for the migration of acetaldehyde. High levels of migration can occur at 40ºC. Therefore, bottled waters should not be kept under the influence of sunlight, especially during the summer months (Ozlem, 2008). The similar results were also obtained in two other studies (Wegelin *et al.*, 2001) after about 6 months of sunlight exposure. Furthermore, another study (Lorusso *et al.*, 1985; Nawrocki *et al.*, 2002)

Table 1. Levels of formaldehyde and acetaldehyde in bottle samples

Samples	Bottle volume (L)	Bottle color	Formaldehyde (μg/L)	Acetaldehyde (μg/L)
S1	0.5	colorless	14	36
S2	0.5	colorless	23	56
S3	0.5	colorless	35	64
S4	1.5	colorless	12	25
S5	0.5	colorless	45	103
S6	0.5	colorless	27	43
S7	1.5	colorless	33	76
S8	1.5	colorless	41	80
S9	1.5	colorless	16	39
S10	0.5	colorless	18	51
S11	0.5	colorless	28	44
S12	0.5	colorless	34	64
S13	0.5	colorless	26	66
S14	0.5	colorless	37	93
S15	0.5	colorless	42	52
S16	1.5	colorless	13	43
S17	1.5	colorless	16	33
S18	0.5	colorless	35	81
S19	0.5	colorless	54	120
S20	0.5	colorless	23	57

also showed that storage conditions enhanced the process of release of formaldehyde and acetaldehyde into water. Formaldehyde and acetaldehyde in many studies dominate as likely to cause organoleptic changes, but they mostly are below migration limits (SML) (2002/72/EEC) which is consistent with the results of the present study. Throughout this study, we have made it clear that formaldehyde and acetaldehyde migrated into water from PET bottles.

Conclusion

There are different types of materials in PET bottles such as monomers, olygomers, and additives (UV stabilisers, antistatic agents, fillers, etc.) and during the storage period passes from the packaging wall into the water. Formaldehyde and acetaldehyde are among toxic materials in PET walls. For this reason, it is important to determine the levels of these migrants and their toxic effect on consumers' health (Barnes *et al*., 2006). This study demonstrates the levels of formaldehyde and acetaldehyde in twenty brands of bottled waters in Iran. However, more studies should be carried out to further explore the other important organic compounds like THMs, HAAs, VOCs, etc., in bottled waters in the country. Packaging materials should be considered with precaution, because they might contaminate drinking water with substantial levels of different contaminants including formaldehyde and acetaldehyde, to the extent that they may be above standards of drinking water. Overall, the comparison between PET samples regarding their formaldehyde and acetaldehyde concentration is very difficult, due to the variety of parameters leading to the migration of contaminants including storage period, water type, temperature, disinfectants, sunlight exposure, the process of bottling, the thickness of bottle wall and even environmental pollution. Thus, there is a need to frequently monitor the contaminants in bolted waters. Therefore, alternative materials for packing including coated aluminium and stainless steel bottles is recommended for the production of containers of food and beverages. Overall, it could be stated that the bottled waters, available in Iran, are safe for the human consumption, as regards the levels of formaldehyde and acetaldehyde.

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