ANALYSIS OF MIGRATION OF HARMFUL CONTAMINANTS FROM PET BOTTLES INTO DRINKABLES DURING STORAGE

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Abstract: *Plastic materials used in food packaging are made up of small molecules or monomers, together with their additives and can migrate into the product during packaging, manufacturing, filling and storage. Plastic water bottles are known to release harmful chemicals into the water they contain, especially when left in warm or hot environments. PET is the first choice for beverage packaging because of its possessing some superior properties viz. good mechanical and barrier properties,easy transport and processing, excellent clarity and light weight compared to metal and glass. In the present study, migration into 3% acetic acid, a soft drinks beverage and distilled water was followed during 10, 20 and 30 days of storage at different temperature such as sunlight temperature, refrigerator, car storage and room temperature. The overall migration value was affected by time and storage condition. Soft drink bottle A was observed with the highest average value of migration (17.70mg/l) in thirty days sunlight storage condition. Whereas the lowest average value of migration (0.51mg/l) was observed in Mineral water bottle D when stored for ten days in refrigerator. Critical evaluation of ANOVA revealed that significant difference was found at level of 5% due to treatments, days (10, 20 and 30) and their interaction in each category. pH was also affected by storage condition and difference in temperature. Lead and antimony were not detected in PET bottles at specified condition and storage. Therefore, PET Bottles are safe for storing water in refrigerator but not for long period of time.*

Key words: *PET, soft drinks, plastic containers, pH, food safety.*

Introduction

Drinking water is important for all living organisms especially for humans and due to the change of lifestyles in modern society, water bottled and soft drinks are most convenient for carrying and more hygienic than drinking from tap water. Plastic materials used in food packaging are made up of small molecules or monomers, together with their additives and can migrate into the product during packaging, manufacturing, filling and storage.Some heavy metals mainly antimonyused as a catalyst during plastic syntheses are among the most important contaminations and it may be present serious health hazards for human population. Polyethylene Terephthalate (PET) is the first choice for beverage packaging because of its possessing some superior properties viz. good mechanical and barrier properties,easy transport and processing, excellent clarity and light weight compared to metal and glass (Ewender et. al., 2003; Welle, 2011). Polyethylene terephthalate (PET) is formed by polymerization of ethylene glycol and terephthalic acid or terephthalic acid methyl ester with the present of antimony trioxide as catalyst (Duh, 2002) andin some cases, germanium and titanium oxides are also used as catalyst (Duh, 2002).PET is a long-chain thermoplastic polymer of the polyester family used in several applications for beverage packaging. PET homopolymer is synthesized from ethylene glycol (EG) and either from dimethyl terephthalate (DMT) or terephthalic acid (TPA) and all of which are derived from crude oil. For manufacturing of PET bottles, there are several degradation and decomposition reactions can occurs. High temp and presence of oxygen in PET melt process can promote thermo-mechanical and thermo-oxidative reactions (Romao*et. al.*, 2009a). The water sample stored in the bottles showed that higher formaldehyde and acetaldehyde levels after longer storage times. However, sunlight exposure has no effects on these compounds levels (Bach *et al.*, 2013; Wegelin*et al.*, 2001). Temperature and presence of CO_2 increased the release of formaldehyde, acetaldehyde and antimony in small amount (Ros-Chumillas*et al.*, 2007). The migration of acetaldehyde are undesirable taste and odor in water bottle are examined the relationship between the detection thresholds of this compound in carbonated mineral water. PET containers, with different acetaldehyde concentrations proved that the migration was related to the amount of acetaldehyde in the bottle wall and that it was directly dependents on temperature and storage time (Pepin *et al.*, 1983). It was observed that an increase of formaldehyde, acetaldehyde and acetone in carbonated water stored in PET bottles exposed over time to sunlight and ambient temperature (Wegelin.*et al.*, 2001; Nawrock*et al.,* 2002)). PET bottles are considered to be safe for drinking water, Juices, carbonated soft drinks and more sensitive beverages like beer, wine etc. PET also has good barrier properties towards moisture and oxygen (Ewender*et al.,* 2003). PET is also resistant to acidic beverage such as carbonated soft drinks and juices. Para-xylene is either oxidized to terephthalic acid or reacted with methanol to produce dimethyl terephthalate (Azapagic*et. al.*, 2003). PET materials do not degrade and are mostly recycled, so that it will not be decomposed. However, the development of natural additives as degradantand had introduced the additives (Hopewell *et. al.*, 2009). Bottles for mineral bottles and carbonated beverage drinks are largely made up from PE, PP and PET. However, PET packaging materials are preferred for bottling because of its high temperature, nontoxic, lack of influence on flavour, high mechanical strength, high transparency and also goodoxygen barrier properties.PET (polyethylene terephthalate) is increasingly used in bottles manufacturing for juices (Wegelin*et. al.,* 2001). Migration of substances into foodstuffs is a subject of increasing interest and an important aspect of food packaging.Due to the increasing importance of PET in food packaging an understanding of the migration properties of its residual compounds is important (Duh, 2002). The possible migration of Sb into food is of great concern due to its toxicity. A toxicological similarity between arsenic and Sb exists (Gebel, 1997).

Materials and Methods

The research “Analysis of migration of harmful contaminants from Pet Bottles into Drinkables during Storage” was conducted at the research lab of “FICCI, New Delhi, India – 110077.

Collection of samples-

Four samples of Pet bottleswerecollected from local market of Dwarka, New Delhi-110077. All the sample were collected freshly in sterile container and stored at ambient temperature until analyze.Fourth samples were randomly selected such as1**.** Soft drink A - Total 12 bottles (BN-466)2**.** Soft drink B- Total 12 bottles (BN470)3. Drinking water C- Total 12 bottles (BN-2988) and 4. Drinking water D - Total 12 bottles (BN-0201) with capacity of bottles of Soft drink A andSoft drink B were 600 ml each and Drinking water C and Drinking water D were 1000ml each.

Reagent and Equipment-

There was various equipment’s and reagents used during research work such aselectric oven, water bath, electric hot plate, analytical balance, glass beakers, stainless steel evaporating dish, stainless steel tongs, measuring cylinder(100ml), pH meter, simulant (acetic acid, 3%), distilled water, ICP-OES.

Flow Chart of Pet Bottles

Collected bottles from single outlet, Dwarka (stored in)

Flow Chart for Making Metal Sample

Weight 0.5 gm of sample

↓

↓

Bring bottles to room temperature

↓

Empty the bottles

↓

Wash the bottles thoroughly with clean water (3 times)

↓

Dry the bottles at room temperature

↓

Labelling

All the samples were kept at four different conditions namely- exposed to sunlight(40 °C kept in oven), refrigeration temperature (5°C), room temperature (25°C-30°C) and inside a closed car for 30 days and were tested after 10 days of intervals.

Add SuperApure HNO_3 (8ml)

↓

Digestion (to remove organic substances)

↓

Volume makeup with milieq water up to (50ml)

↓

Centrifuge (5 min.)

↓

Run ICP-OES

Preparation of migration test of different storage condition and time duration.

Selection of sample

Minimum triplicate samples representing the batch were selected. Representative samples were of sufficient size to convert into 2 pouches of size 125 mm width and 200 mm length with 1000 cm surface area coming in contact.

Preparation of Test Specimen

The bottles used were carefully rinsed with water (25-30” (Z) to remove extraneous materials prior to actual migration test.

Simulant Quantity

Equal to nominal filling capacity or at least 1 ml/cm^{2}of contact area.

Method of analysis.

Determination of overall migration of constituents of plastics materials and articles intended to come in contact with food stuffs by Migration IS9845:1998. Determination of pH by prescribes electrometric and colorimetric methods of IS 3025(PART 11). Determination of lead and antimony by ICP-OES (*Inductively Coupled Plasma -optical emission spectrometry) by AOAC 999.10*

Result and Discussion

This study was conducted to investigate the pet bottles in different types such as soft drink bottles and mineral water bottles. The results obtained from the analysis are presented and discussed on overall migration, determination of lead and antimony and statistical analysed byICP-OES *(Inductively Coupled Plasma -optical emission spectrometry*) of Pet bottles.

Table: Average migration (harmful contaminants, plasticizer) data for different parameters of control and experiments in (mg/l)

Condition of Temperature	**Days**		
	10	**20**	**30**
1. Average of data of migration in soft drink bottle A			
Sunlight	14.00	14.71	17.70
Refrigerator	6.70	8.51	11.00

Car storage	11.00	11.50	16.50
Room temperature	10.38	11.49	14.10
2. Average of data of migration in soft drink bottle B			
Sunlight	10.30	10.95	14.50
Refrigerator	4.20	5.30	7.90
Car storage	7.81	9.70	12.10
Room temperature	7.05	8.31	10.27
3. Average of data of migration in Mineral water bottle C			
Sunlight	3.00	4.00	5.10
Refrigerator	1.01	1.56	2.60
Car storage	3.00	3.54	4.10
Room temperature	2.01	2.48	3.10
4. Average of data of migration in Mineral water bottle D			
Sunlight	2.60	3.71	4.80
Refrigerator	0.51	0.66	2.21
Car storage	2.10	2.59	3.21
Room temperature	1.53	2.10	2.71
5. Average of data of pH in soft drink bottle A			
Sunlight	5.42	5.35	5.40
Refrigerator	5.59	5.45	5.37
Car storage	5.65	5.45	5.26
Room temperature	5.59	5.37	5.32
6. Average of data of pH in Soft drink bottle B			
Sunlight	5.58	4.37	5.32
Refrigerator	5.56	5.49	5.25
Car storage	5.75	5.48	5.37
Room temperature	5.66	5.57	5.23
7. Average of data of pH in Mineral water bottle C			
Sunlight	6.65	6.42	6.74
Refrigerator	6.45	6.67	6.69
Car storage	6.50	6.16	6.16
Room temperature	6.77	6.32	6.25
8. Average of data of pH in Mineral water bottle D			
Sunlight	6.55	6.41	6.54
Refrigerator	6.68	6.94	6.78
Car storage	6.79	6.34	6.38
Room temperature	6.65	6.33	6.62
Determination of Lead and Antimony			
At All Temperatures	ND	ND	ND

ND=not detected

Average data of migration in soft drink bottlesand Water pet Bottles (mg/lit.) in different Temperatures and Storage time.

Average data regarding effect of time and storage condition on migration of harmful contaminants and plasticizers in soft drink bottle A can be observed from the table. The highest average value of migration (17.70mg/l) was observed in thirty days sunlight storage condition. Whereas the lowest average value of migration (6.70mg/l) was observed in ten days in refrigerator.

Critical evaluation of ANOVA revealed that significant difference was found at level of 5% due to treatments, days (10, 20 and 30) and their interaction.

Average data regarding effect of time and storage condition on migration of harmful contaminants and plasticizers in soft drink bottle B can be observed from the table. The highest average value of migration (14.50 mg/l) was observed in thirty days sunlight storage condition. Whereas the lowest average value of migration (4.20mg/l) was observed in ten days in refrigerator.

Critical evaluation of ANOVA revealed that significant difference was found at level of 5% due to treatments, days (10, 20 and 30) and their interaction.

Average data regarding effect of time and storage condition on migration of harmful contaminants and plasticizers in Mineral water bottle C can be observed from the table. The highest average value of migration (5.10mg/l) was observed in thirty days sunlight storage condition. Whereas the lowest average value of migration (1.01mg/l) was observed in ten days in refrigerator.

Critical evaluation of ANOVA revealed that significant difference was found at level of 5% due to treatments, days (10, 20 and 30) and their interaction.

Average data regarding effect of time and storage condition on migration of harmful contaminants and plasticizers in Mineral water bottle D can be observed from the table. The highest average value of migration (4.80mg/l) was observed in thirty days sunlight storage condition. Whereas the lowest average value of migration (0.51mg/l) was observed in ten days in refrigerator.

Critical evaluation of ANOVA revealed that significant difference was found at level of 5% due to treatments, days (10, 20 and 30) and their interaction.

All the values observed for overall migration of harmful contaminants into drinkables fall under the limit. According to FSSAI's Food Safety and Standards (Packaging) Regulations, 2017, All packaging materials of plastic origin shall pass the prescribed overall migration limit of 60mg/kg or 10mg/dm2 as per IS 9845 with no visible colour migration.

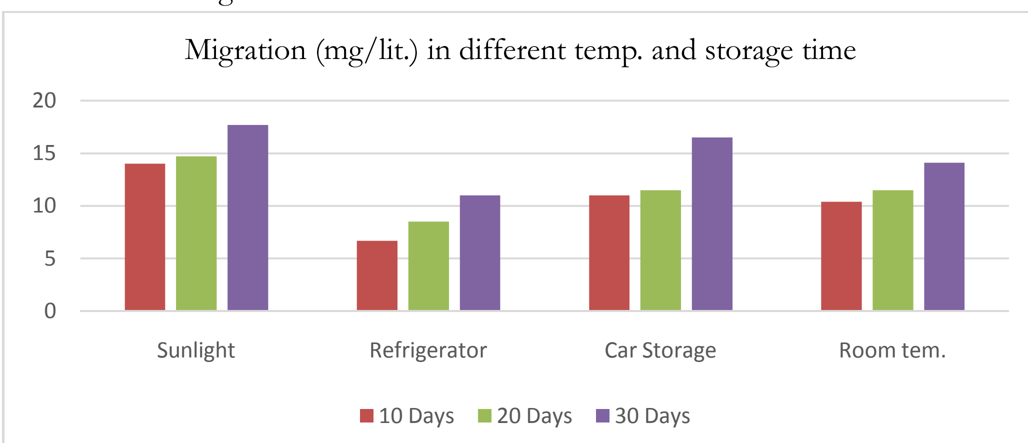

Fig. 1 Migration (mg/lit.) soft drink A bottles of different days and temperature

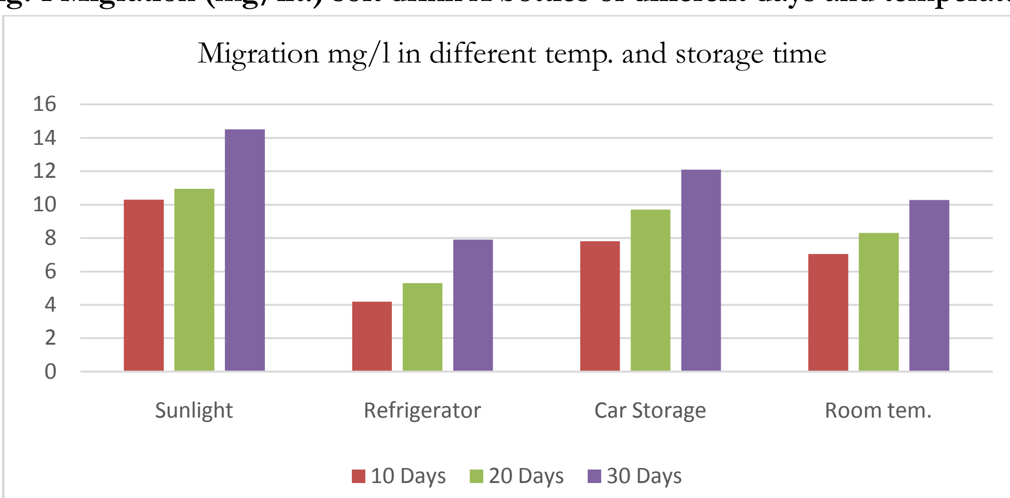

Fig. 2 Migration (mg/lit.) soft drink Bbottles of different days and temperature

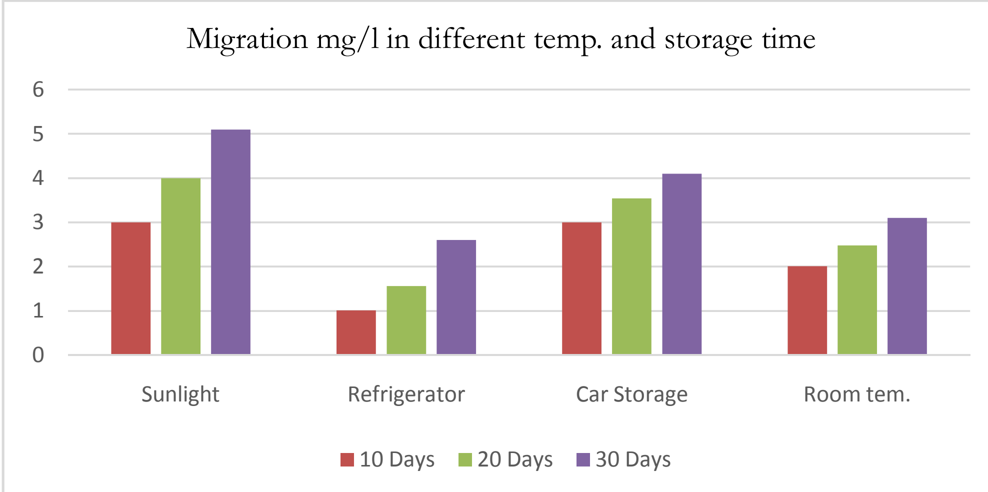

Fig. 3 Migration (mg/lit.) drinking waterCbottles of different days and temperature

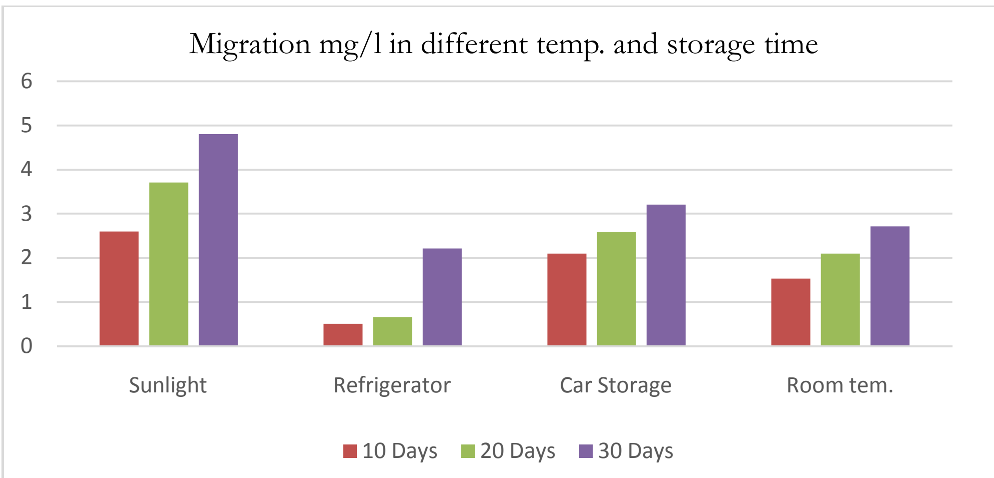

Fig. 4 Migration (mg/lit.) drinking waterDbottles of different days and temperature

Average data of pH in soft drink bottles and water PET bottles in different Temperatures and Storage time

The soft drink **A** bottles pH of different days decreasing significantly on the migration of 10 days 20 days and 30 days of storage and different condition of temperature. It was observed that the Sunlight data 5.42, 5.10 and 4.91, Refrigerator data 5.59, 5.35 and 5.22, Car storage data 5.59, 5.38 and 5.23 and Room temperature data 5.59, 5.41 and 5.32. There was significant different among the days. At all temperature, lead and antimony were not detected.

The soft drink **B** bottles pH of different days decreasing significantly on the migration of 10 days 20 days and 30 days of storage and condition of temperature. It was observed that the Sunlight data 5.58, 5.20 and 4.93, Refrigerator data 5.56, 5.49 and 5.35, Car storage data 5.75, 5.42 and 5.21 and Room temperature data 5.65, 5.57 and 5.23. There was Significant different among the days. At all temperature, lead and antimony were not detected.

The drinking water **C** bottles pH of different days decreasing significantly on the migration of 10 days 20 days and 30 days of storage and different condition of temperature. It was observed that the Sunlight data 6.74, 6.65 and 6.42, Refrigerator data 6.69, 6.67 and 6.45, Car storage data 6.50, 6.16 and 6.00 and Room temperature data 6.77, 6.32 and 6.25. There was significant different among the days. At all temperature, lead and antimony were not detected.

The drinking water **D** bottles pH of different days decreasing significantly on the migration of 10 days 20 days 30 days of storage and different condition of temperature. It was observed that the Sunlight data 6.55, 6.54 and 6.41, Refrigerator data 6.94, 6.78 and 6.68, Car storage data 6.79, 6.38 and 6.34 and Room temperature data 6.65, 6.62 and 6.33.There was Significant different among the days. At all temperature, lead and antimony were not detected.

Conclusion

The aim of the research was to check the overall migration of harmful contaminants in PET bottles. Bottles were kept at different temperature and specified conditions. It was seen that exposure to sunlight, in car storage and room temperature storage plasticizer to a slight increase in migration of harmful contaminants in all the four samples. Refrigeration storage had no significant effect on migration of harmful chemicals relative to control in the bottle samples. It is apparent that PET bottles kept in sunlight and in- car storage has higher migration. As migration takes place pH also decreased. pH decrease was maximum in soft drink bottle A and B bottles. Drinking water C and D bottle showed only a slight decrease in the pH. It can be suggested that exposure to sunlight and in-car storage are not appreciable practice for water storage in PET bottles, making it apparent by the study that Soft drink bottle A and B bottles have higher overall migration level. Although All the values observed for overall migration of harmful contaminants into drinkables fall under the limit. According to FSSAI's Food Safety and Standards (Packaging) Regulations, 2017, All packaging materials of plastic origin shall pass the prescribed overall migration limit of 60mg/kg or 10mg/dm2 as per IS 9845 with no visible colour migration.

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