A Novel Approach for Identifying Potential Interactions between Alcoholic Beverages and their Polyethylene Terephthalate (PET) Packaging Materials

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This paper attempts to present a novel approach that may prove useful in determining whether or not any interactions, particularly the levigation of some additives/compounds contained in the PET packaging materials into the alcoholic beverages occurs. The method consists in comparing the peak area resulting from HPLC analysis of a sample taken from an original PET bottle with that of the very same product sample taken from a glass bottle, both bottles having being stored in the original and glass bottles for a certain determined period of time. Should the case arises when the peaks overlay within the experimental errors, one may say that no interaction occurred and the package is very stable. However, if there is a significant difference in the peak area, particularly in the favour of the content stored in the PET bottle, than there is definitely the case of a levigation process from the packaging material into the alcoholic beverage.

Keywords: beverage-packaging interactions, PET, levigation, HPLC

The European legislation tends to cover more and more almost every possible field of activity, directly or indirectly related to human activity and is continuously expanding. Some of the European Directives refer to human exposure to substances originated from the potential interactions taking place between raw foods and the environmental conditions (as the environment represents one major factor which influences food quality), while others are related to food contact materials (FCM). The migration of different substances from the packaging materials into foods/beverages or vice-versa represents a controversial issue which stirs competent authorities and also the consumers interest. The concerns are related to the possibility that these additives may levigate or migrate into the foods and beverages and most of all, the concentration threshold of the migrating chemical compounds as they may endanger human health [1-4].

Various methods have been used over the years in order to establish whether or not any interaction between foods/beverages and their packaging materials takes place and to identify and speciate the migrating chemical compounds. Among the most used methods one may count different types of liquid chromatography (LC) techniques, such as: reverse-phase LC, used for the determination of di-ethylhexyl phthalate (DEPH) in polyvinyl chloride (PVC) raw materials (DEHP is the major plasticizer of most PVC materials) [5]. DEHP was also studied for its migration from the inner liner of beer bottle caps using HPLC as identifying method [6]. HPLC – GC was used for the fractionation of extracts from polypropylene (PP) films for screening potential migrants into food [7]. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and Atomic Fluorescence Spectrometry (AFS) have been compared for arsenic speciation in environmental samples, while HPLC-ICP-MS and HG-AFS were used for total antimony determination in liquid food simulants and in PET containers [8, 9] etc.

Another concern was related to the levigating BPA from the canned food and beverages and from polycarbonate baby bottles with repeated use as this additive is a carbon based synthetic compound acting as an endocrine disruptor and having harmful effects on human health [10, 11].

Even if the additives and the monomers used to obtain plastic packaging materials are tested extensively, the manipulation, the storing conditions (such as direct sunlight for example) along with so called "non-intentionally added substances" may also prove to be responsible for the above said interactions.

Polyethylene terephthalate (PET) is one of the polymers belonging to the family of polyesters, a semi-crystalline compound, manufactured by "polycondensation" of monoethylene glycol (MEG) with pure terephthalic acid (PTA) or dimethyl terephthalate (DMT). Even if apparently it represents one of the most appropriate packaging materials as it has been used to wrap a wide variety of products from food (meat, fruit) and drinks (fizzy soft drinks, waters, fruit juices, wine, beer and even alcoholic drinks) to pharmaceuticals, cosmetics etc, the use of PET as a food contact material represents a controversial issue [4,12].

PET has easily replaced glass over the years. This was especially due to its numerous advantages: it is not as heavy as the glass, it does not break so easily, it is cheaper, etc. Furthermore, the logistics involved in returning, processing and washing glass bottles for example, represents another major disadvantage of using this type of packaging.

As expected, there are also some drawbacks regarding the use of PET, most of them related to the chemical stability or better said instability of polyethylene terephthalate. The interactions between PET and food content represent a controversial topic, as polyethylene

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terephthalate undergoes various extraction and migration tests before being placed on the market, experiments which are required by the authorities in order to comply with the European legislation [1, 2]. Even if the results obtained during the tests are favourable, under certain conditions, as the ones above mentioned (direct sun light exposure), some interactions still may occur.

HPLC technique demonstrated over the time as being one of the most reliable and well-established solution for many research groups who resorted to this method [13-23]. In this particular case it proved to be a rapid, accurate, simple and economic testing method, a clear advantage over many other methods more expensive and too sophisticated leading to a limited applicability.

This paper describes an innovative approach in the use of High Performance Liquid Chromatography (HPLC) for identifying any possible potential interactions between foods/beverages and their packaging materials, namely between polyethylene terephthalate (PET) bottles and alcoholic drink contents, particularly vodka in this case, as there is an increased need to develop simple and reliable methods for the analysis of food products quality markers. The vodka was chosen due to the fact that the concentration of the alcohol is high enough and it is more likely that it may extract various additives included in the above said polyethylene terephthalate bottles. Once these additives leaked into the water-alcohol mixture, they will be definitely transferred into the consumer body. As mention above, one underlines that the purpose of this paper was to demonstrate whether or not the water-alcohol mixture extracts these additives, regardless if they are approved or not for human consumption or if they are below or above the established safe threshold. No investigation was carried out to demonstrate if these leaked substances are toxic or not and if they could endanger the humanhealth or not as these are a separate issue.

Experimental part

Materials and method

For performing the experiments one has used commercially acquired vodka of 37.5% alcohol by volume, bottled in polyethylene terephthalate (PET), identified as such on the bottom of the bottle.

Initially one has taken three sealed bottles of vodka: one was kept in its original polyethylene terephthalate bottle, one was cut into pieces of known surface area and were inserted into a volumetric flask containing the very same amount of vodka as in the first one and the third bottle was transferred into a glass volumetric flask considered as a reference sample.

The reason for doing that is that all the bottles of vodka may have extracted initially a certain amount of additives. By storing the vodka into a glass bottle, the levigation process is stopped and this sample can be regarded as a reference sample.

The experiments were conducted using the three samples of vodka after they were left for three months at room temperature, 22 ± 3°C (the first sample, S_1, was taken from the original polyethylene terephthalate bottle, the second sample was taken from the volumetric flask containing the pieces of the polyethylene terephthalate bottle, S_2, while the third, S_3, was taken from the glass volumetric flask).

The experiments were carried out in three replicated experiments for each considered sample (a total of nine experiments) using high performance liquid chromatography (HPLC).

The experimental layout consisted of Jasco PU -1580 Intelligent HPLC Pump, Jasco DG-980-50-3 Line Degasser and Jasco UV-1575 Intelligent UV-VIS Detector. The data obtained were further processed using the related software – BORWIN Chromatography Software.

The pump was set on constant flow (CF) mode, with a 0.750 mL. min^{-1} flow, while the maximum pressure was set at 300 $kgfcm^{-2}$.

The wavelength of the UV-Vis detector was set at 210 nm. This wave length was chosen by running a set of preliminary experiments and scanning a wide range of wave length, so that one should obtain the maximum peak height/peak area for the second peak, corresponding to the migrating additives mixture.

The eluent used for all experiments was distilled water obtained through a Millipore filtration system and the retention time was set at ten minutes.

Results and discussions

The main idea was to see if maintaining three months the alcohol kept in the original PET bottle and the alcohol kept in a volumetric flask containing the polyethylene terephthalate pieces extracts or not any additives/substances from the packaging material.

Should the case arise when no additives substances are extracted, one should see some overlapping peaks, within the experimental errors, otherwise one should see differences in the peak heights/areas, the highest/largest one being the sample S_1, taken from the original polyethylene terephthalate bottle, and the lowest/smallest one being S_3, the reference sample taken from the glass volumetric flask (as it will contain only substances extracted initially before being transferred into the glass bottle), while S_2, the sample taken from the flask containing the pieces of the polyethylene terephthalate bottle, being in the middle.

The chromatograms obtained for samples S_1, S_2 and S_3 are depicted in figure 1.

As one may see in the chromatogram, the first peak was automatically identified and attributed to the ethyl alcohol (this was also verified by separately injected HPLC grade ethylic alcohol and comparing the HPLC standard with the experimental results). By comparing the peak heights/areas for the first peak it resulted that within the experimental errors these overlap for all three samples S_1, S_2 and S_3. However, the second peaks have been attributed to the migrating compounds/additives from PET into vodka.

The height of the peak does not necessarily mean that an important amount of compounds are extracted into vodka, but the fact that these compounds are more sensitive at 210 nm, as it resulted from the initial scanning of the wave length.

The peak areas are calculated automatically using the associated software.

One of the drawbacks associated with this method is that due to experimental inherent errors there are very small differences in peak height/area even in the case of alcohol, when, theoretically they should be almost the same, as the alcohol concentration is identical.

This problem was sorted out with an ingenious normalisation procedure explained in details below.

The peak normalization procedure is carried out initially on ethanol, considered as standard substance from vodka, and consists in calculating a normalization factor, as follows:

$$f_{i,1} = \frac{A_{i,1}}{A_{3,1}} \quad (1)$$

where: i represents the samples number, $f_{i,1}$ is the normalization factor of S_1 in relation to sample S_3 and $A_{i,1}$

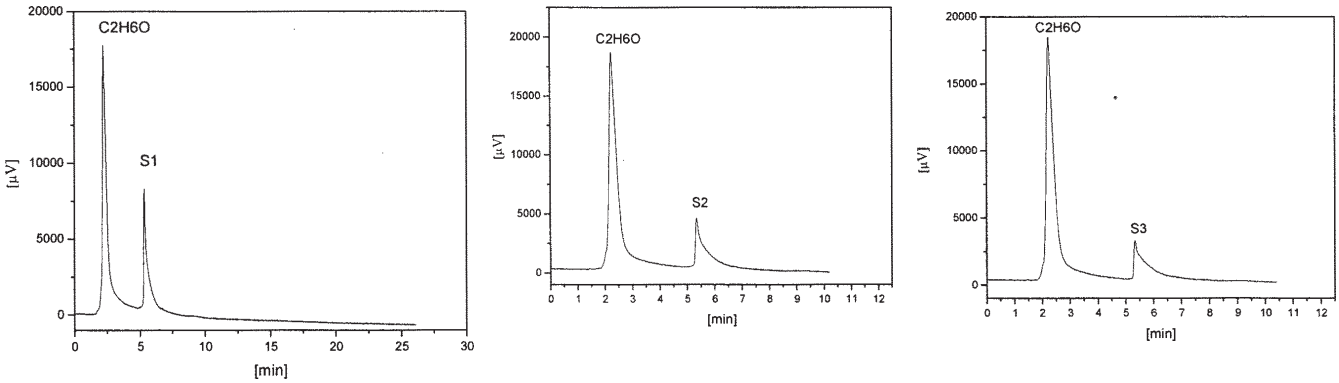

Fig. 1. Chromatograms obtained for sample S_1, S_2 and S_3

Table 1
CENTRALIZED DATA FOR THE NORMALIZATION FACTOR AND THE CORRECTED PEAK AREA

Sample number	First peak area [V·s]	Second peak area [V·s]	$f_{i,1}$	$Ac_{2,i}$ [V·s]
S_1	0.388	0.083	0.974	0.082
S_2	0.394	0.065	0.989	0.066
S_3	0.398	0.060	1	1
S_1	0.387	0.077	0.957	0.080
S_2	0.392	0.068	0.970	0.070
S_3	0.404	0.060	1	1
S_1	0.388	0.080	0.866	0.092
S_2	0.382	0.073	0.852	0.086
S_3	0.448	0.050	1	1

Table 2
AVERAGED AREA OF SECOND PEAK, STANDARD DEVIATION AND RELATIVE STANDARD DEVIATION OF THE SECOND PEAK FOR EACH SAMPLE

	S_1	S_2	S_3
Area average [V·s]	0.080	0.069	0.057
SD [V·s]	0.003	0.004	0.006
RSD [%]	3.750	5.857	10.129

represents the recorded area of the first peak corresponding to the sample (S_i), while $A_{3,1}$ is the recorded area of the first peak corresponding to S_3.

Once this normalisation factor is calculated, one may now calculate equivalent areas of second peak using the equation:

$$A_{i,2c} = \frac{A_{i,2}}{f_{i,1}} \quad (2)$$

where: $A_{i,2}$ is the equivalent area of the second peak corresponding to S_1 or S_2 and $f_{i,1}$ is the normalization factor of S_i in relation to sample S_3.

The processed results containing the area of three replicates for the first and second peaks, the normalisation factor and the normalised area, and their standard deviation are presented in table 1.

As the main interest is focused on the second peak, one has calculated also the average aria and the standard deviation for the second peak (table 2).

As one can see, the highest normalised peak area for the second peak corresponds to S_1, the sample taken from the original polyethylene terephthalate bottle, while the smallest normalised peak area corresponds to S_3 - the sample taken from the glass volumetric flask, S_2 being in the middle. The differences are more than 40% between S_1 and S_3, and cannot be explained by experimental errors, especially now when the experimental values were normalised, confirming that certain additives/compounds levigate from the PET bottle into the water-alcohol mixture.

The method presented above may supply valuable preliminary information about the levigation processes and if used in conjunction with standards for known additives may be used also for speciation and quantitative identification of the levigated compounds.

Conclusions

The novel approach presented above and consisting in comparing the peak area resulting from HPLC analysis of a sample taken from an original PET bottle with that of the same product sample taken from a glass bottle (both samples being stored in the original and glass bottles for 3 months) was tested for a commercially available vodka.

The method proved that the resulting HPLC peaks do not overlay and there is a significant difference in the peak area, particularly in the favour of the content stored in the PET bottle and hence the conclusion that there is definitely the case of some levigation from the packaging material into the alcoholic beverage.

Starting from the experimental chromatograms one has calculated the average of the peak area, the standard deviation emphasising that the novel approach of using HPLC proved to be a reliable method in evaluating the potential interactions between the packaging materials and the beverages content.

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