Evaluation of non-intentionally added substances (NIAS) in PET bottles

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Introduction

Polyethylene terephthalate (PET) is widely used in beverage packaging for mineral water and soft drinks. Some non-intentional added substances (NIAS) in PET beverage bottles are related to degradation products of the polymer as well as impurities from additives and colorant masterbatches. In addition, PET oligomers can be considered as NIAS as well. For the evaluation of NIAS a migration threshold limit of 10 µg/l is typically applied. Such concentration is very low compared to other specific migration limits (SML) and therefore NIAS determination and evaluation in food (simulants) is challenging. This is especially due to the fact that NIAS are in the nature of things non-intentionally added and it remains incompletely known up to now which NIAS occur in PET bottles in day by day production. This presents a risk for preform manufacturers and bottling companies. Non-target analytical screening methods in the migration solutions with detection limits of 10 µg/l (or lower) are labor-intensive, time consuming and expensive. For production control of PET preforms migration tests with such long storage times are not useful.
Aim of the study was to develop a fast detection and evaluation method for NIAS in PET preforms and bottles.

Method

PET preform material was rasped into strangs of about 0.2 mm thickness. PET bottles were cut into pieces of about 0.5x0.5 cm. Subsequently 1.0 g of PET material were weighed into a headspace vials and analysed by headspace gas chromatography. Gas chromatograph: Perkin Elmer AutoSystem XL. Column: DB 1, length 30 m, inner diameter 0.25 mm, film thickness 0.25 µm. Temperature program: 50 °C (4 min), rate 20 °C/minute, 320 °C (hold for 15 min), pressure: 50 kPa helium, split: 10 ml/min. Headspace Autosampler: Perkin Elmer HS 40 XL, oven temperature 200 °C, needle temperature 210 °C, transferline temperature 210 °C, equilibration time 60 min, pressurizing time 3 min, injection time 0.02 min, withdrawel time 1 min. For NIAS identification, headspace GC is coupled with mass spectrometry (MS). The molecular volume of determined NIAS were calculated from free "molinspiration" program [1].

Results

Headspace gas chromatography (GC) presents the method of choice for PET preform or bottles testing towards NIAS. Subsequently the molecular volume of the NIAS was calculated, from which the diffusion coefficient can be predicted. The prediction model for the diffusion coefficient D_P in PET has been published [2]. For compliance evaluation it is important that migration is overestimated by the applied modeling parameters up to a certain limit. This means that the calculated migration should be in any case higher than the real migration into food under given storage conditions. However, if the migration is too overestimated the very low migration limit of 10 µg/l limit risks to be exceeded only due to the overestimative character of the migration modelling. A diffusion coefficient overestimation of 20% has been identified most appropriate for compliance evaluation. By use of the diffusion coefficient in PET, the migration of the determined NIAS into food can be calculated. For production control, however, it is preferred to calculate the maximum concentration of NIAS interrelating with the migration limit of 10 µg/l under given migration conditions (Figure 1). This can be considered as a translation of the 10 µg/l SML into maximum concentration (QM) values within the PET bottles.
Figure 1 shows the dependency of the molecular volume of NIAS and its maximum bottle wall concentration to reach the maximum permissible migration level of 10 µg/l. This correlation was established for a bottle volume of 1 l with an inner surface area of 600 cm^2 for a storage time of 365 d at room temperature (25 °C). The thickness of the bottle wall was 200 µm. Similar curves can be established for any other storage conditions and preform weights. As expected, small molecules with their corresponding high diffusion coefficients are the most critical NIAS in PET. For example, the concentration of acetaldehyde (molecular volume of 47 $Å^3$) in the PET bottle wall should be below 1 mg/kg, otherwise the SML of 10 µg/l is exceeded which is coincidentally also the organoleptic threshold limit for acetaldehyde in natural mineral water. On the other hand, NIAS with molecular volumes above 150 $Å^3$ need concentrations above 100 mg/kg in the PET bottle wall in order to exceed the SML of 10 µg/l after storage for one year at room temperature.

NIAS in the concentration ranges of 100 mg/kg in PET preforms are extremely rare and for shorter storage times as 365 d the maximum bottle wall concentration increases accordingly. The intentionally added substance 2-aminobenzamide has a molecular volume of 125 $Å^3$. For beverages, 2-aminobenzamide is approved in PET bottles up to a migration level of 50 µg/l. As the migration is directly proportional to the concentration in the PET bottle, a concentration of 420 mg/kg is applicable for storage times of 365 d at room temperature.

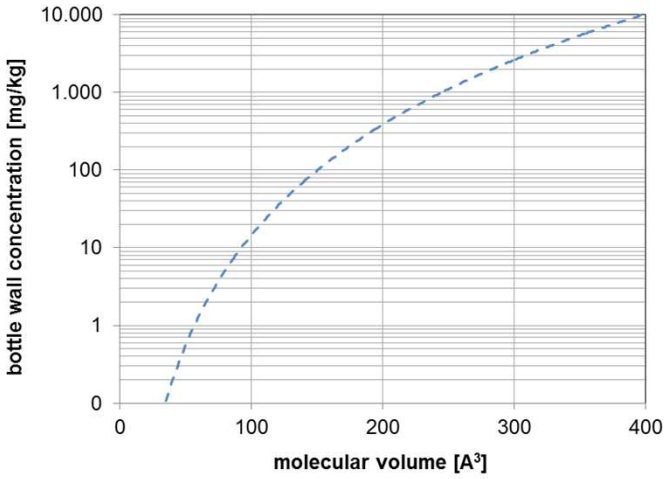

Figure 1: Interrelation between the bottle wall concentration and the molecular volume of NIAS corresponding to a migration of 10 µg/l after storage for 365 d @ 25 °C (1 l in contact with 6 dm^2)

Conclusions

By screening PET preforms or bottles as a production control by use of headspace GC allows:

- determination of the concentration of any NIAS in the PET bottle
- calculation of the molecular volume of the determined NIAS and prediction of the diffusion coefficient in PET
- comparison of the calculated maximum concentrations in the PET bottle wall (according to the foreseeable contact conditions) with the actual determined concentration levels as pass/fail criteria.

By use of this procedure, NIAS in PET preforms and bottles are evaluated with a concomitant combination of material tests on the PET material and migration modelling. Experimental migration tests are not necessary any longer. Material tests on preforms have the advantage that the concentration of migration relevant substances in PET is at least a factor of 1000 higher than in the concentration in food (simulants) after migration tests. Therefore, the applied analytical screening tests on preforms are much easier to validate and less expensive. In addition, analysis of the PET preforms or bottles require no storage time for the migration test. Therefore the results are available within hours instead of 10 d. The method described within this study is an effective control test for determination of any migration relevant NIAS in PET preforms and bottles during production. The headspace GC method combined with its migration modelling is recommended to be applied in order to ensure conformity with the European Regulation 10/2011 in a fast way.

References

[1] http://www.molinspiration.com/cgi-bin/properties
[2] F. Welle., A new method for the prediction of diffusion coefficients in poly(ethylene terephthalate). Journal of Applied Polymer Science 2013, 129(4), 1845-1851.

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