Investigation of the acetaldehyde content of PET raw materials, PET preforms and PET bottles

Alexandra Mauer, Frank Welle

Fraunhofer Institute for Process Engineering and Packaging (IVV), Giggenhauser Straße 35, 85354 Freising, Germany,
email: welle@ivv.fraunhofer.de, phone: ++49 8161 491 724

Introduction

Polyethylene terephthalate (PET) bottles are widely used for beverage packaging. However for the application of PET bottles as packaging material for mineral water, the acetaldehyde content of the bottle wall should be minimized. Acetaldehyde is a thermal degradation product of the PET polymer by the reaction of the vinyl end groups. If acetaldehyde migrates into the bottled water, it might influence the organoleptic properties of the bottled water. The organoleptic threshold concentration of acetaldehyde in mineral water is in the range of 10 to 20 µg l^{-1}. Due to this low threshold limit, the concentration of acetaldehyde in the bottle wall as well as in the raw materials (pellets, preforms) need to be controlled. One inherent problem of the quantitative acetaldehyde determination is its high volatility (boiling point of acetaldehyde: 21 °C). For example, grinding of the PET material might lead to the loss of acetaldehyde during sample preparation and results in too low determined bottle wall concentrations. This would lead to an underestimation of the acetaldehyde migration into bottled mineral water. On the other hand, due to the reaction of the PET vinyl end groups with water dissolved in the hygroscopic PET polymer acetaldehyde might be regenerated during analysis.
Aim of the study was the development of a quantitative determination method for acetaldehyde in PET bottles, preforms and pellets without a grinding step.

Method

1.0 g of the PET sample was sealed into a 22 ml headspace vial and analyzed by headspace gas chromatography with flame ionization detector (FID). Gas chromatograph: Perkin Elmer AutoSystem XL, column: ZB 1, length: 30 m, inner diameter: 0.25 mm, film thickness: 0.25 µm. Temperature program: 50 °C (4 min), rate 20 °C min^{-1}, 320 °C (15 min), pressure: 50 kPa Helium, split: 10 ml min^{-1}. Headspace autosampler: Perkin Elmer HS 40 XL, oven temperature: 200 °C, needle temperature: 210 °C, transfer line temperature: 210 °C, equilibration time: 1 h, pressurization time: 3 min, injection time: 0.02 min, withdrawal time: 3 min. The moisture content of the investigated PET samples was determined with the Moisture Analyzer BMA 600 (Berghof, Germany). In order to increase the moisture content in the headspace vials, water was injected with a microliter syringe just before sealing.

Results

Method of choice for the determination of acetaldehyde is static headspace gas chromatography. For that purpose, the PET sample was heated in a closed vial in order to establish the equilibrium between the sample and the headspace vapor at the equilibration temperature of 200 °C. At this temperature, acetaldehyde was regenerated by the reaction of the PET end groups with moisture. Therefore most of the acetaldehyde determination methods are using equilibration temperatures of 150 °C. The low temperatures, however, are also resulting in a low detector response. This increases the uncertainty of the quantification method. Figure 1 shows the dependency of the acetaldehyde concentration in the vapor phase with increasing moisture content in the vial at different temperatures. As a result, the relative increase of acetaldehyde during equilibration is nearly independent from the equilibration temperature. At moisture levels of more than 1%, the regeneration of acetaldehyde shows a saturation effect.

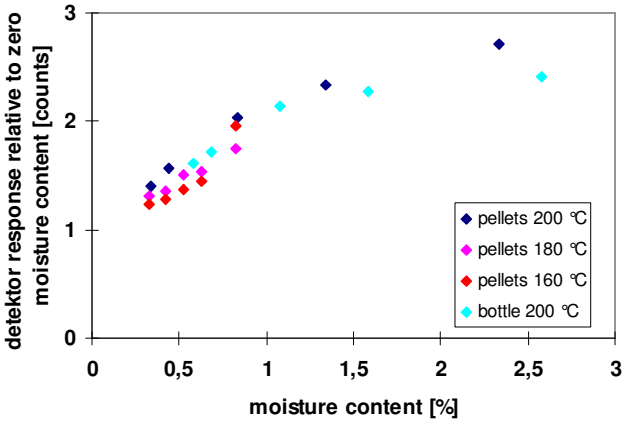

Figure 1: Influence of the moisture content of a PET pellet sample (and bottles made thereof) on the detector response (FID) at different equilibration temperatures

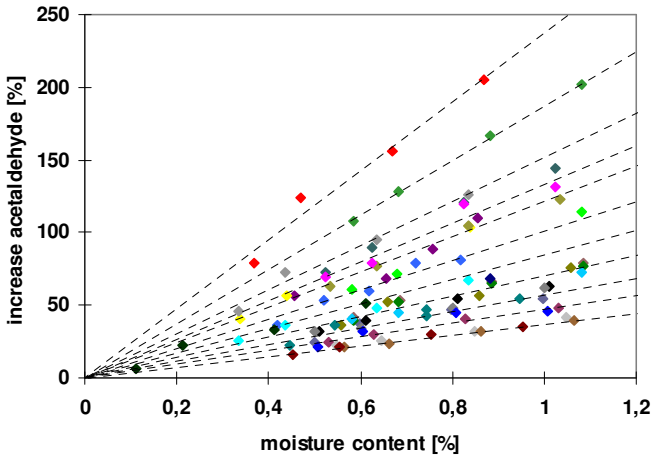

Figure 2: Correlation between the increase of acetaldehyde of 24 different PET materials (pellets, recyclates, bottles and preforms) during equilibration (1 h at 200 °C) versus the moisture content in the headspace vial

The moisture content of 49 PET preforms lots taken from several manufacturing sides over 15 months are determined between 0.33% and 0.74%. Additionally, the moisture content of pre-dried PET pellets was determined to about 0.12% (one sample).
The results in Figure 1 show, that it should be possible to extrapolate the acetaldehyde concentration to a zero moisture level, if the headspace is spiked with certain water concentrations. Unfortunately, there exists no consistent acetaldehyde re-generation potential for different PET materials (Figure 2). However, each investigated material follows the linear behaviour with increasing moisture content.

Conclusions

For a certain PET material the moisture influence is independent from the equilibration temperature. Therefore, headspace gas chromatography at equilibration temperatures of about 200 °C are suitable conditions for the quantitative determination of acetaldehyde in PET samples. Increasing the equilibration temperatures from 160 °C to 200 °C increases the detector response within this study by a factor of about 7. This increases the sensitivity and reproducibility of the applied method.
The results of this study show clearly, that the moisture content of the PET sample should be taken into account. The comparison between PET samples regarding their acetaldehyde concentration is very difficult, because the moisture content of PET samples varies between 0.12% and 0.74% and the generation of acetaldehyde in the PET samples during equilibration is completely different for the investigated PET materials. However, from the linear correlation of the detector response with the moisture content in the headspace vials, the acetaldehyde concentration can be extrapolated to a zero moisture content. This fictive zero moisture level correlates with the acetaldehyde concentration in the PET sample without a thermal process during analysis. For a comparison of the acetaldehyde concentration in PET materials, these zero levels are more suitable, because it considers the re-generation of acetaldehyde during headspace analysis into account.
As an overall conclusion, exact quantification of the acetaldehyde in PET samples with static headspace gas chromatography is impossible, if the moisture content and the re-generation behaviour is not known. However, static headspace gas chromatography might be used for production control (e.g. same PET material, similar moisture levels of the preforms) on basis of relative concentrations.

Poster presentation at the 4th international Symposium on Food Packaging, 19-21 November 2008, Prague

Fraunhofer Institut Verfahrenstechnik und Verpackung