

Sample Preparation of PET Preforms

Plastic bottles from PET have become a common part of everyday life. The main advantages of PET over glass are its considerably lower weight and its breaking resistance. However, PET is not gas-tight which results in a shorter shelf life of carbonated beverages.

In the last few years, two further disadvantages of PET have been widely discussed in the press:

- Contamination with antimony: In the production of PET, antimony is used as a catalyst. Very small amounts of antimony are deposited in the plastic, thus diffusing into the beverage. The German Drinking Water Ordinance (DWO) stipulates a limit of 5 µg/l for antimony. However, the DWO does not make a difference between the different manifestations of antimony.
- When PET gets warm, acetaldehyde is produced which may diffuse into the beverage. Acetaldehyde is considered harmful to health. There is no limit value due to the fact that acetaldehyde in food can also be of natural origin. However, there is a limit of 6 mg/l for the amount which is allowed to diffuse from the package to the beverage.

So far, the amounts of antimony as well as acetaldehyde detected in beverages have been far below the limit values. As even very small amounts (>0.1 mg/l) of acetaldehyde can be tasted, the beverage industry initially used PET bottles solely for soft drinks with a very strong characteristic flavor. Thanks to modifications in the production process of PET bottles the concentration of acetaldehyde has been reduced to a point where the taste of the beverage is no longer impaired in any way. It is however recommended not to leave PET bottles in the sun too long, as warmth accelerates the diffusion process.

Another topic of discussion are estrogen-like substances in PET bottles. So far, there has been no definite proof for this as PET normally does not contain these substances and they have not yet been detected as a degradation product like in polycarbonate packaging, for example. It is however possible that the sealing gaskets of the bottle caps contain bisphenol A, particularly if

the bottle is filled with carbonated beverages. The EU threshold value for migration burden with bisphenol A is 0.6 mg/l.

Production

PET bottles are produced in two steps. First, the so-called PET preform is produced by injection molding. PET preforms have thick walls and are relatively small (a preform for a 1.5 l bottle is about 13 cm in height) which makes them easy to transport and store. The beverage producer then warms and inflates the preform.

Analysis

Due to the fact that water from PET bottles is also used for the preparation of baby food, these are subjected to regular checks. As the bottles are supplied in the form of preforms to the beverage producer/bottler, investigation usually focuses on the preforms which are processed and analyzed for this purpose. The typical method for the detection of antimony is atomic emission spectroscopy (ICP-OES or ICP-MS) for which approximately 1 g of sample is digested and analyzed. But first of all, a representative sample needs to be obtained. For this, several preforms are pre-ground in a cutting mill SM 300 with parallel section rotor and a 6 mm sieve. In a second step, the pre-ground material is pulverized to a fineness below 500 microns in the ultra centrifugal mill ZM 200 with a 0.5 mm ring sieve. From this sample, 1 g is extracted for microwave digestion.

It is basically easier to grind plastics if they are cooled. PET has a glass transition temperature of 74 °C, i.e. beyond that temperature plastic gets elastic and is more difficult to grind. During the grinding process in the ZM 200, this temperature may be achieved. Therefore, it is recommendable to embrittle the sample with liquid nitrogen before grinding or to mix it with dry ice.

The acetaldehyde content is analyzed by gas chromatography. The sample preparation process is the same as for the antimony analysis, however, it should be taken into account that acetaldehyde is a volatile substance (boiling point 20 °C). Therefore, it is important to cool the sample during processing,

which can be done with the CryoMill. The CryoMill achieves grind sizes below 500 microns. A few grams of the ground sample are then filled into an Autosampler vial and heated. The gaseous acetaldehyde surrounding the sample is injected on the chromatographic column (headspace technique).

The detection of estrogen substances is done with High Pressure Liquid Chromatography. As these substances are not volatile, the sample preparation can be carried out with the SM 300 and ZM 200 as described for antimony. With a particle size of less than 500 microns, the sample is then digested and analyzed.