

Development and application of a SBSE-TD-GC/MS-method for the determination of plasticizers and antioxidants in beverages

Upon contact of food with the primary packaging, substances, such as plastic additives, can migrate from them into the food. Plasticizers, especially phthalates, are used to achieve or improve specific properties of plastics. Some phthalates affect reproduction in mammals or have the potential to disrupt the endocrine system in humans. Therefore low TDI-values (tolerable daily intake) apply to them, for example 0.05 mg/kg bw/day for di-(2-ethylhexyl)-phthalate (DEHP) or 0.01 mg/kg bw/day for dibutylphthalate (DBP). Antioxidants are used to increase resistance of polyolefines, e.g. polyethylene (PE), to oxygen, high temperatures and UV-radiation.

To safely identify and quantify contamination of beverages with plasticizers and antioxidants, a routine capable SBSE-TD-GC/MS-method (stir bar sorptive extraction with thermodesorption and GC/MS-determination) was developed in cooperation with the Faethe Labor GmbH, Paderborn. Analytes were extracted from a beverage sample by stirring them with a PDMS-coated (polydimethylsiloxane) magnetic stir bar (Twister®, Gerstel). Then the Twister® was thermally desorbed and the desorbate was analyzed with GC/MS. A particular problem was the ubiquitous presence of phthalates, which led to contamination of working material and necessitated special cleaning measures. Limits of detection of the method are between <0.01 and 0.13 µg/L. The simultaneous extraction of up to 15 samples on a multipoint magnetic stirrer makes high sample throughput possible. Comparing this method with published SPE-methods (solid phase extraction) for analysis of phthalates reveal for many substances lower or at least the same limits of detection.

Analysis of mineral waters stored in glass and PET bottles (polyethylene terephthalate) showed in some cases contamination by DEHP of up to 17 µg/L and with DINCH (di-iso-nonyl-1,2-cyclohexanedicarboxylic acid) to about 50 µg/L. The sources of these relatively high concentrated impurities are obviously metal screw caps with injected sealing compound. Mineral waters from PET bottles with PE-screw cap contained 2,4-di-tert-butylphenol in concentrations up to 0.84 µg/L. This compound is a hydrolysis product of the antioxidant Irgafos 168 which is incorporated in the PE matrix. The analytical method developed was also applied to samples of fruit juices (apple and orange). Typical packagings for these beverages are carton packages. Packaging specific contaminations (manufacturer dependent) could be found, such as the antioxidants 2,4-di-tert-butylphenol or butylated hydroxytoluol. Further it was found that these substances apparently migrate more easily into orange juice than in apple juice because orange juice was contaminated at higher levels.

In addition, PET materials containing different additives, such as oxygen scavengers or acetaldehyde scavengers were analyzed. For this purpose, PET was directly thermally desorbed and the desorbate was analyzed by GC/MS. Besides PET-typical signals the chromatograms also showed signals, which were assigned to certain additives. In PET material from used bottles of fruit juice, aroma compounds could be identified. Chromatographic data were evaluated by means of the chemometric software Pirouette lite®, so that unknown PET-samples could be assigned to already known PET-specifications.