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**Occurrence of 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol[®])
in foods packed in polystyrene and polypropylene cups**

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Abstract

After simultaneous distillation-extraction (SDE) of foods packed in polystyrene cups (n=77) as well as in polypropylene cups (n= 42) from 61 different suppliers, analyses performed by coupled capillary gas chromatography-mass spectrometry (HRGC-MS) indicated the presence of the diastereomers of 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (TMPD-MIB; Texanol[®]), a known coalescent of paints and printing inks. The contaminant was found in 55 and 50% of the polystyrene and polypropylene packed samples, respectively. Amounts ranged from 1.2 to 64.5 $\mu\text{g kg}^{-1}$ in polystyrene cups (average 25.1 $\mu\text{g kg}^{-1}$) and 0.9 to 45.7 $\mu\text{g kg}^{-1}$ in polypropylene cups (average 10.8 $\mu\text{g kg}^{-1}$). Texanol's[®] origin from the printed plastic cups was indicated by their separate HRGC-MS analysis, showing amounts in the higher ng g^{-1} range. In addition, the presence of two pairs of enantiomers both found to be racemic by enantioselective multi-dimensional gas chromatography-mass spectrometry (enantio-MDGC-MS) excluded it being of natural origin. The detection of overall procedure (DLOP) and the reliable quantification limit (RQL) were 0.2 $\mu\text{g kg}^{-1}$ and 0.9 $\mu\text{g kg}^{-1}$, respectively. As the diester, 2,2,4-trimethyl-1,3-pentandiol diisobutyrate (TXIB), is on the EU list of regulated substances (restricted to be used in single-use gloves only) with a migration limit of 5 mg/kg in food and the diester is known to be metabolised rapidly by hydrolysis, the observed migration of the monoester Texanol[®] at the ng g^{-1} level can be considered to pose no risk of adverse effects.

Keywords: contamination, migration, polypropylene, polystyrene, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate, TMPD-MIB, Texanol[®]

Introduction

High-quality food currently offered in a global market requires adequate packaging. There is no doubt that present-day food packaging materials are fulfilling their primary role of ensuring the microbiological safety of our packaged food, and maintaining quality and nutritional value (Barnes *et al.* 2007). However, concerning chemical migration, especially of printing ink constituents and plasticizers, questions of safety may arise, as in recent years several cases of undesirable migration have been reported. Hence, harmful compounds from plastic gaskets, i.e. material for sealing the metal lids of glass jars, such as epoxidized soybean oil (ESBO) (Hammarling *et al.* 1998; Fantoni and Simoneau 2003), plasticizers other than ESBO (Petersen and Breindahl 2000), and 2-ethylhexanoic acid (2-EHA) (Elss *et al.* 2004) were detected in food. The latest event to hit the headlines concerned the notification of the Italian competent authorities in 2005 that liquid baby milk contained 2-isopropylthioxanthone (ITX), a known photoinitiator in UV curing inks (Cho and Hong 2004). ITX was present in certain cartons, due to the printing process applied to rolls of packaging. Since then, the contaminant has been found in various food samples (Gallart-Ayala *et al.* 2008).

The European Commission reacted by the GMP regulation 2023/2006 (Commission Regulation 2006). In the 4th Amendment to the Plastics Directive (Directive 2007/19/EC), one of the significant novelties introduced includes the functional barrier doctrine for plastics. For this a layer reducing the migration of non-listed substances to a "non-detectable" level of <10 µg kg⁻¹ is demanded. This cut-off for the performance of a functional barrier does not remove the need for an individual substance to be listed. Set-off substances are mentioned (almost in passing and only once) in the Directive as an aid to the printing industry. However, printing inks are not regulated by the Commission and Directive 2007/19 is for plastics only. For substances originating from other materials including inks the general provisions of the framework directive apply which requires that producers perform their own risk assessment.

In this paper, we report about the occurrence of a “non-listed” contaminant that has not been described before as a migrant from plastic food contact materials (Skjevrak *et al.* 2005), i.e. 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (TMPD-MIB, Texanol[®]) (COE 2005;

2006). This ester that consists of two isomers (Figure 1) has been found in many of our routine analyses of food packed in printed plastic cups and was then extensively investigated in various commercial foods packed in polystyrene (n=77) and polypropylene cups (n=42).

Materials and Methods

Chemicals

2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate (TMPD-MIB, Texanol®) and solvents were purchased from Sigma-Aldrich (Steinheim, Germany). Solvents were of HPLC grade purity, other solvents were re-distilled before use.

Samples

A large variety of different product groups, liquid as well as solid foodstuffs (in particular, milk products such as yogurt, curd, cream whey, and cheese, as well as, additionally, fruit preparation, jams and marmelades), packed in printed polystyrene (PS) (n = 77) and polypropylene (PP) cups (n = 42) from 61 German suppliers were purchased from local supermarkets. The cups were partly directly printed, partly exhibited printed plastic or paper sleeves. Several “not printed” cups – unprinted, unlabeled, blank cups just sealed with printed aluminium top covers – were also among the samples. Best before dates ranged from June 2007 to April 2009.

Sample preparation

Solid products (350-600g pooled from identical batches, diluted 1+2 with distilled water) and liquids (400-600 ml, thinned 1+1 with distilled water) were subjected to traditional Likens-Nickerson simultaneous distillation-extraction (SDE) over 2h using a pentane-diethyl ether mixture (1+1, v/v). The extract was dried over anhydrous sodium sulphate, filtered, carefully concentrated to 1ml using a Vigreux column (45°C) and after adding 2-methyl-1-pentanol (100µg) as external standard subsequently analysed by capillary gas chromatography-mass spectrometry (HRGC-MS).

Upon removal of the content one representative cup was cut into small pieces (about 5-6mm² surface) and used for subsequent SDE, employing 1000ml distilled water. For checking purposes, a following Soxhlet extraction with diethyl ether and n-pentane (1+1, v/v) under reflux was accomplished for 6h.

Capillary gas chromatography-mass spectrometry (HRGC-MS)

HRGC-MS was carried out with an Agilent GC 6890 series gas chromatograph with split injection (220°C, 1:20) directly coupled to an HP Agilent 5973 Network mass spectrometer (Agilent Technologies, Inc., Palo Alto, CA, USA). The GC was equipped with a J&W DB-Wax (30m × 0.25mm) fused silica capillary column coated with a 0.25µm film (J&W Scientific Products GmbH, Cologne, Germany), temperature program running 3min isothermal at 50°C, then raised at 4°Cmin⁻¹ to 250°C. The temperature of connecting parts was 220°C; electron ionisation energy was 70eV. Identification was carried out by comparison of linear retention indices and mass spectral data (recorded by full scan in the EI mode) of the samples with that of authentic TMPD-MIB.

Enantioselective multidimensional gas chromatography-mass spectrometry (enantio-MDGC-MS)

A double oven MDGC system (oven I, Fisons GC 8160; oven II, Fisons GC 8130) (Thermo Electron, Dreieich, Germany) equipped with split injection (200°C, 1:20) and a moving column switching system (MCSS) was coupled to a Fisons MD 800 mass spectrometer (Thermo Electron, Dreieich, Germany). Pre-separation was performed using a J&W DB-Wax fused silica capillary column (30m × 0.25mm i.d., d_f = 0.25µm), temperature program started at 100°C and raised at 10°C min⁻¹ to 240°C. Enantiomeric separation was performed using a modified cyclodextrin phase: 30% 2,6-O-dimethyl-3-O-pentyl-β-cyclodextrin in OV 1701 (25m × 0.25mm i.d., d_f = 0.25µm; Mega, Milano, Italy), temperature program started at 80°C, held for 70min and raised at 0.5°C min⁻¹ to 200°C. Identification of TMPD-MIB was performed by comparison of linear retention indices and mass spectral data of the samples with that of authentic reference compound.

Calibration and expression of results

Texanol was quantified by means of a calibration curve (peak area divided by external standard area versus analyte concentration divided by external standard concentration) constructed with standard solutions in distilled water at eight calibration levels ranging from 0.45 to 52.25 µg l⁻¹ Texanol[®] and each of 100 µg 2-methyl-1-pentanol as external standard. The SDE extracts were concentrated by a Vigreux column (45°C) to a defined volume of 1ml. Calibration equation, $y = 1.2106x + 0.0206$. $R^2 = 0.9974$.

Detection limit of overall procedure (DLOP) and reliable quantification limit (RQL)

A sample of curd, not containing TMPD-MIB, was spiked with six different concentrations (in the range of 0.1 to 5 $\mu\text{g kg}^{-1}$) of Texanol[®] and analysed with the above mentioned procedure. The results indicated a detection of overall procedure (DLOP) and the reliable quantification limit (RQL) with signal-to-noise ratios of 3:1 and 7:1 at 0.2 $\mu\text{g kg}^{-1}$ and 0.9 $\mu\text{g kg}^{-1}$, respectively.

Results and discussion

As a representative example, figure 2A shows the total ion chromatogram (TIC) for a HRGC-MS separation of a typical TMPD-MIB-containing yogurt extract. In figure 2B the TIC of the extract obtained from the packaging material (PS cup) is shown. As expected, two peaks were observed for the isomers of TMPD-MIB in about 60:40% relation for 2,2,4-trimethyl-1,3-pentanediol-1-isobutyrate and 2,2,4-trimethyl-1,3-pentanediol-3-isobutyrate, respectively (Schwenk and Becker 1972). The result shown from figure 2B clearly indicates their origin from the packaging material.

One might conclude a “natural” origin for TMPD-MIB, however, our enantio-MDGC-MS analyses distinctly indicated its synthetic origin, i.e. each a racemic mixture was obtained for both the synthetic reference and the analytes under study. A representative example of the enantio-MDGC-MS analysis is shown in figure 3.

HRGC-MS analysis showed, in total, the presence of TMPD-MIB in 55 and 50% of polystyrene and polypropylene packed samples under study, respectively. Amounts ranging from 1.2 to 64.5 $\mu\text{g kg}^{-1}$ (average 25.1 $\mu\text{g kg}^{-1}$) and 0.9 to 45.7 $\mu\text{g kg}^{-1}$ (average 10.8 $\mu\text{g kg}^{-1}$) in polystyrene and polypropylene cups, respectively, were found (figure 4A/B). Only 10% of the packaging materials were investigated; in these cases, amounts ranging from 150 to 680 $\mu\text{g kg}^{-1}$ were found. As no exact quantification was performed for the TMPD-MIB analysis of cups, these amounts cannot be used in a balance study comparing them with the quantities found in food samples under study. The analysis of TMPD-MIB in the cups can therefore only be taken to be indicative of its source in the foods.

TMPD-MIB is a common coalescing agent in latex paints and belongs to the group of high production volume chemicals. Assessment and conclusions from previous screening information (Anonymus 1996) indicates low level environmental exposure to a high number of consumers as well as low order of toxicity. More recent data focus on the emission as influence on indoor air quality (Lin *et al.* 2007). Furthermore, in human sensory experiences it was investigated that TMPD-MIB is one of the compounds responsible for paint odour and its persistence in indoor air (Gallagher *et al.* 2008). However, since the data are inadequate for assessment, no threshold for TMPD-MIB in indoor air is determined (DIBT 2004).

Considering the above mentioned amounts of TMPD-MIB in the food samples under study, their presence in food could be considered undesirable but it is not likely to present a health risk at the levels reported. As the diester, 2,2,4-trimethyl-1,3-pentandiol diisobutyrate (TXIB), is on the EU list of regulated substances (restricted to be used in single-use gloves only) with a migration limit of 5 mg/kg food (European Commission 2008) and the diester is known to be metabolised rapidly by hydrolysis (EFSA 2006), the observed migration of the monoester Texanol[®] in the ppb level can be considered to pose no risk of adverse effects.

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Legends

Figure 1. Two isomers of TMPD-MIB: esterified with secondary alcohol (A) and with primary alcohol (B)

Figure 2. HRGC-MS separation (total ion chromatogram, TIC) of an SDE extract from a typical yogurt sample (A) and that of the corresponding polystyrene cup (B). St, standard; two isomers of Texanol[®] (X).

Figure 3. Enantio-MDGC-MS separation of a TMPD-MIB reference with its two isomers (A) and TMPD-MIB isolated and cut from a yogurt sample out of a polystyrene cup (B). Enantio-MDGC-MS conditions (cf. the Materials and methods).

Figure 4. Amounts of TMPD-MIB in extracts of foods packed in polypropylene cups (A) and in polystyrene cups (B). The average (AV) is given at the end of each row. In (A) sample numbers 1–26: directly printed; 27–37: printed plastic sleeve and 38–42: printed paper sleeve. In (B) sample numbers 1–46: directly printed; 47–54: printed plastic sleeve; 56–74: printed paper sleeve and 75–77: without printing. Samples containing traces (amount < RQL = 0.9 $\mu\text{g kg}^{-1}$) of TMPD-MIB (polypropylene: 5, 19, 35–37 and polystyrene: 13, 14, 17, 18, 20–23, 27, 39, 41, 60, 62–64) are not listed in the charts.

Figure 1

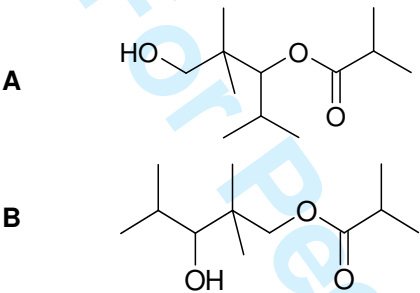


Figure 2

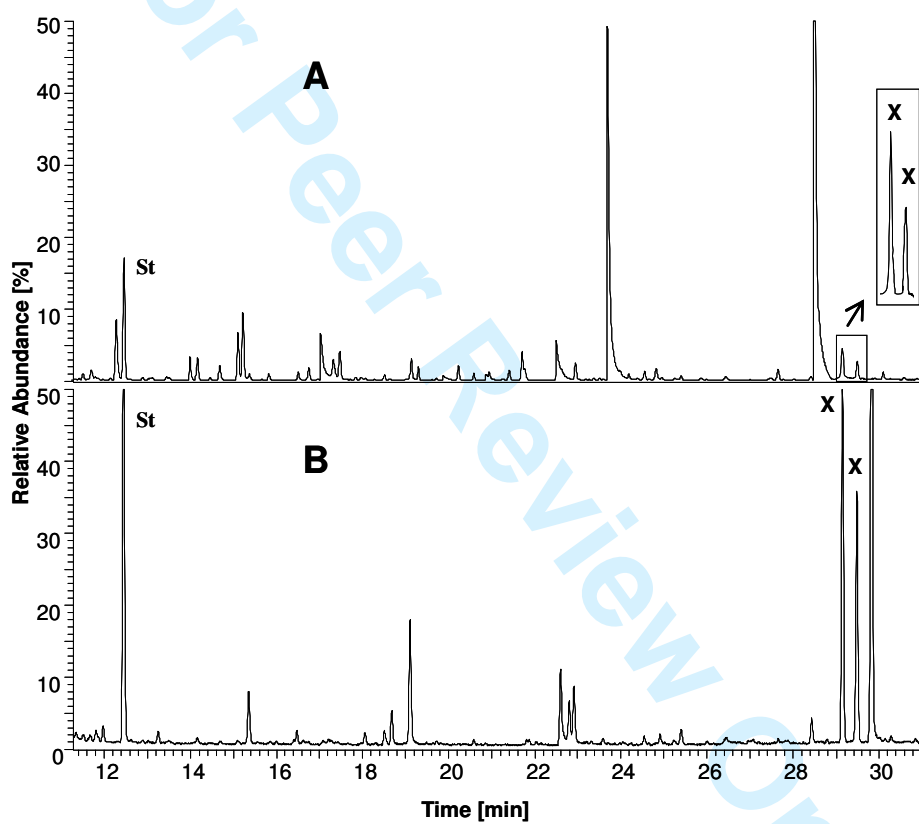


Figure 3

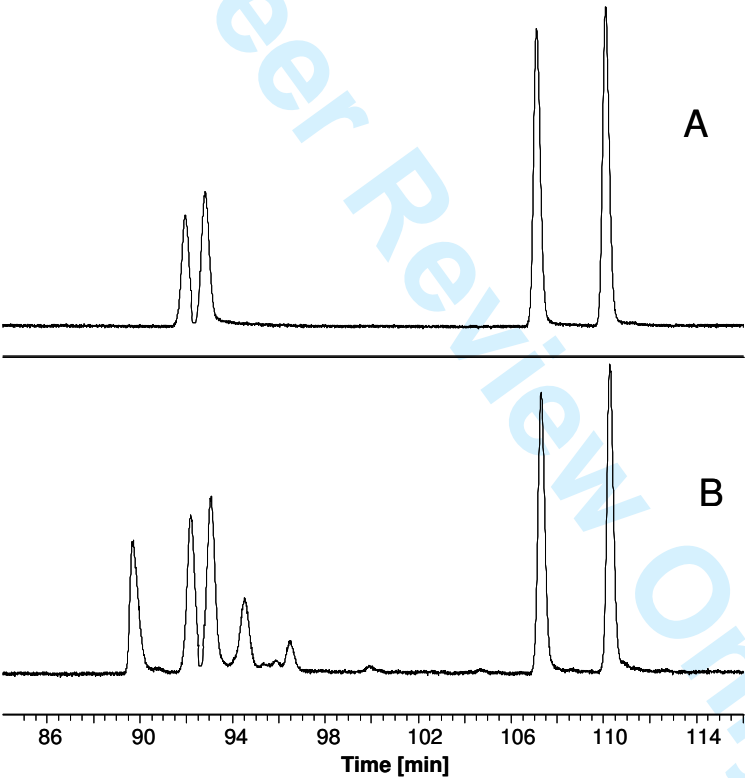


Figure 4

