HAL
open science

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

Michael Kempf, Peter Schreier

▶ **To cite this version:**

Michael Kempf, Peter Schreier. Occurrence of 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate (Texanol®) in foods packed in polystyrene and polypropylene cups. Food Additives and Contaminants, 2009, 26 (04), pp.563-567. 10.1080/02652030802562920 . hal-00577349

HAL Id: hal-00577349

https://hal.science/hal-00577349v1

Submitted on 17 Mar 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

Journal:	*Food Additives and Contaminants*
Manuscript ID:	TFAC-2008-239.R1
Manuscript Type:	Original Research Paper
Date Submitted by the Author:	09-Oct-2008
Complete List of Authors:	Kempf, Michael; University of Wuerzburg, Chair of Food Chemistry Schreier, Peter; University of Wuerzburg, Chair of Food Chemistry
Methods/Techniques:	Simultaneous distillation-extraction, Chromatography - GC/MS
Additives/Contaminants:	Texanol, Migration, Packaging - inks
Food Types:	polysyrene packed foods, polypropylene packed foods

SCHOLARONE™
Manuscripts

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

S. Ramm, T. Feuerbach, M. Kempf and P. Schreier*

Lehrstuhl für Lebensmittelchemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Correspondence:

Prof. Dr. Peter Schreier
Universität Würzburg
Lehrstuhl für Lebensmittelchemie
Am Hubland
D-97074 Würzburg, Germany
Tel.: 0049-(0)931-8885481
Fax: 0049-(0)931-8885484
Email: schreier@pzlc.uni-wuerzburg.de

*To whom correspondence should be addressed: e-mail: schreier@pzlc.uni-wuerzburg.de

For Peer Review Only

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 µg kg^{-1} in polystyrene cups (average 25.1 µg kg^{-1}) and 0.9 to 45.7 µg kg^{-1} in polypropylene cups (average 10.8 µg 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 µg kg^{-1} and 0.9 µg 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®

For Peer Review Only

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;

http://mc.manuscriptcentral.com/tfac Email: fac@tandf.co.uk
For Peer Review Only

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 5-6mm^2 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.

http://mc.manuscriptcentral.com/tfac Email: fac@tandf.co.uk
For Peer Review Only

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)

http://mc.manuscriptcentral.com/tfac Email: fac@tandf.co.uk

A sample of curd, not containing TMPD-MIB, was spiked with six different concentrations (in the range of 0.1 to 5µg 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 µg kg^{-1} and 0.9 µg 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, repectively (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 µg kg^{-1} (average 25.1 µg kg^{-1}) and 0.9 to 45.7 µg kg^{-1} (average 10.8 µg 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 µg 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.

For Peer Review Only

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.

References

ANONYMUS. Texanol. CAS 25265-77-4. SIDS. 1996, Screening Information Data Set for High Production Volume Chemicals. http://toxnet.nlm.nih.gov/cgi-bin/sis/search/f?/temp/~pE2ami:19:BODY.

BARNES, K.A., WATSON, D.H. and SINCLAIR, C.R. (Eds.), 2007, Chemical migration and food contact materials. Boca Raton: CRC Press.

CHO, J.D. and HONG, J.W. 2004, UV-Initiated free radical and cationic photopolymerizations of acrylate/epoxide and acrylate/vinyl ether hybrid systems with and without photosensitizer. J. Appl. Polym. Sci. **93**, 1473–1483.

COE. Council of Europe. Resolution AP (2005) 2 on packaging inks applied to the non-food contact surface of food packaging materials and articles intended to come into contact with foodstuffs. [Internet]. 2005. [cited: 2008 May 14]. Available from: http://www.coe.int/t/e/social_cohesion/soc-sp/public_health/Food_contact/presentation.asp.

For Peer Review Only

COE. Council of Europe. Policy statement concerning packaging inks applied to the non-food contact surface of food packaging materials and articles intended to come into contact with foodstuffs. [Internet]. 2006. [cited: 2008 May 14]. Available: http://www.rotoflex.ch/uploads/media/Resolution_AP-2005-2_ON_PACKAGING_INKS_mit_Tech_Doc_1_und_3.pdf. Accessed: 14. May 2008.

COMMISSION REGULATION (EC) No. 2023/2006 on good manufacturing practice for materials and articles intended to come into contact with food; published in the Official Journal of the European Communities on 29 December 2006 (OJ No. L 384 29.12.2006).

DIBT. Deutsches Institut für Bautechnik. Gesundheits- und Umweltkriterien bei der Umsetzung der EG-Bauprodukten-Richtlinie (BPR). [Internet]. 2004. [cited: 2008 May 08]. Available: http://www.dibt.de/de/Data/Aktuelles_Ref_II_4.pdf. Accessed: 08. May 2008.

DIRECTIVE 2007/19/EC. Commission Directive of 2 April 2007 amending Directive 2002/72/EC relating to plastic materials and articles intended to come into contact with food and Council Directive 85/572/EEC laying down the list of simulants to be used for testing migration of constituents of plastic materials and articles intended to come into contact with foodstuffs. http://ec.europa.eu/food/food/chemicalsafety/foodcontact/legisl_list_en.htm

EFSA. Opinion of the Scientific Panel on food additives, flavourings, processing aids and materials in contact with food (AFC) on a request related to a 12th list of substances for food contact materials. 2006, EFSA Journal 395 to 401, 1-21.

ELSS, S., GRÜNEWALD, L., RICHLING, E. and SCHREIER, P. 2004, Occurrence of 2-ethylhexanoic acid in foods packed in glass jars. *Food Additives and Contaminants*, **21**, 811-814.

EUROPEAN COMMISSION. Food Contact Materials. Annex I. Substances listed in EU directives on plastics in contact with food. Updated version of 10th April 2008 (reference no. PM.95020).

FANTONI, L. and SIMONEAU, C. 2003, European survey of contamination of homogenized baby food by epoxidized soybean oil migration from plasticized PVC gaskets. *Food Additives and Contaminants*, **20**, 1087–1096.

GALLAGHER, M., DALTON, P., SITVARIN, L. and PRETI, G. 2008, Sensory and analytical evaluations of paints with and without Texanol. *Environmental Science & Technology,* **42**, 243–248.

For Peer Review Only

GALLART-AYALA, H., MOYANO, E. and GALCERAN, M.T. 2008, Liquid chromatography/tandem mass spectrometry (highly selective selected reaction monitoring) for the analysis of isopropylthioxanthone in packaged food. *J. Chromatogr. A,* **1208**, 182-188.

HAMMARLING, L., GUSTAVSSON, H., SVENSSON, K., KARLSSON, S. and OSKARSSON, A. 1998, Migration of epoxidized soya bean oil from plasticized PVC gaskets into baby food. *Food Additives and Contaminants*, **15**, 203-208.

LIN, C.C. and CORSI, R.L. 2007, Texanol® ester alcohol emissions from latex paints: Temporal variations and multi-component recoveries. *Atmospheric Environment*, **41**, 225–3234.

PETERSEN, J.H. and BREINDAHL, T. 2000, Plasticizers in total diet samples, baby food and infant formulae. *Food Additives and Contaminants*, **17**, 133–141.

SCHWENK, U. and BECKER, A. 1972, Reactions of isobutyraldehyde. IV. 1- and 3-Isobutyrate of 2,2,4-trimethyl-1,3-pentanediol. Liebigs Ann. Chem., **756**, 162-169.

SKJEVRAK, I., BREDE, C., STEFFENSEN, I.L., MIKALSEN, A., ALEXANDER,J., FJELDAL, P. and HERIKSTAD, H. 2005, Non-targeted multi-component analytical surveillance of plastic food contact materials: Identification of substances not included in EU positive lists and their risk assessment. *Food Additives and Contaminants*, **22**, 1012–1022.

For Peer Review Only

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).

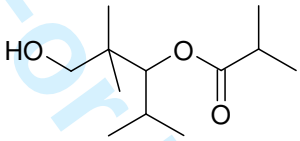
Figure 3. Enantio-MDGC-MS separation of a TMPD-MIB *reference with its two isomers (A) and* TMPD-MIB *isolated and cut from a yogurt sample out of a polystyrene cup (B). Enantio-MDGC-MS conditions (cf. the Materials and methods).*

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* $= 0.9\ \mu g\ kg^{-1}$*) 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.*

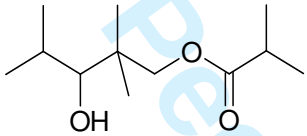
For Peer Review Only

Figure 1

A

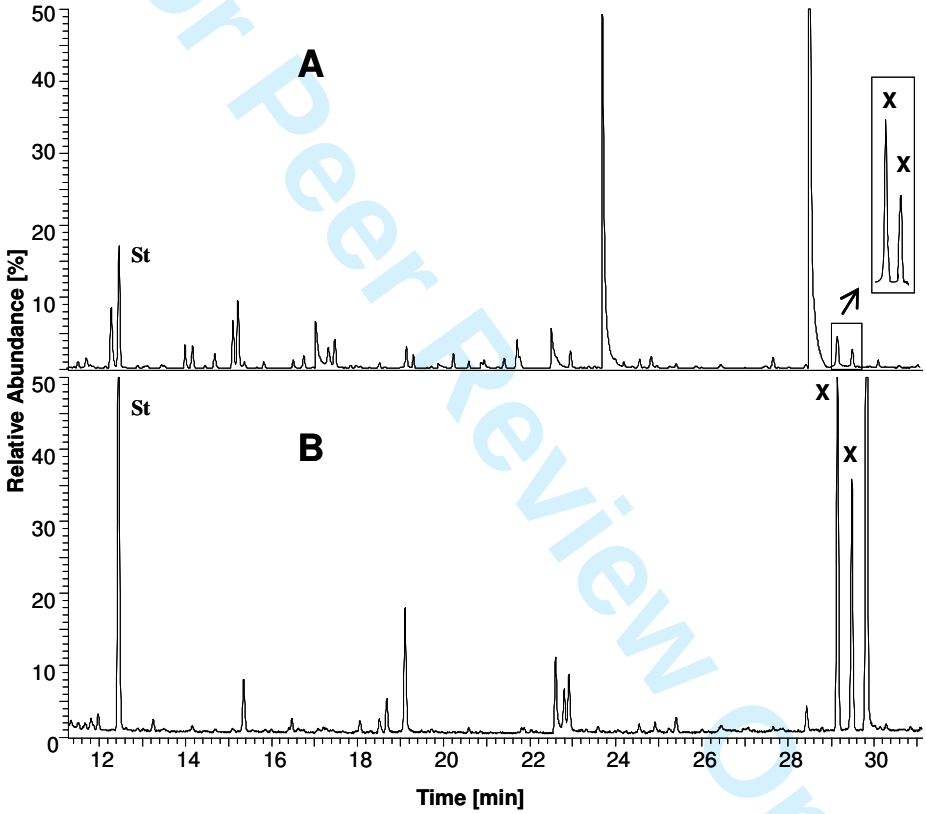


B



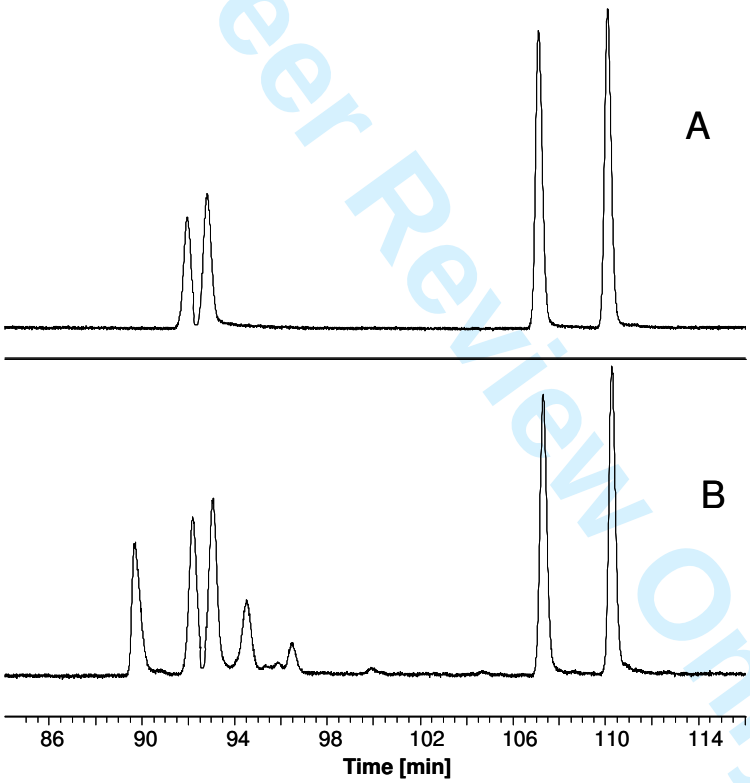
For Peer Review Only

Figure 2



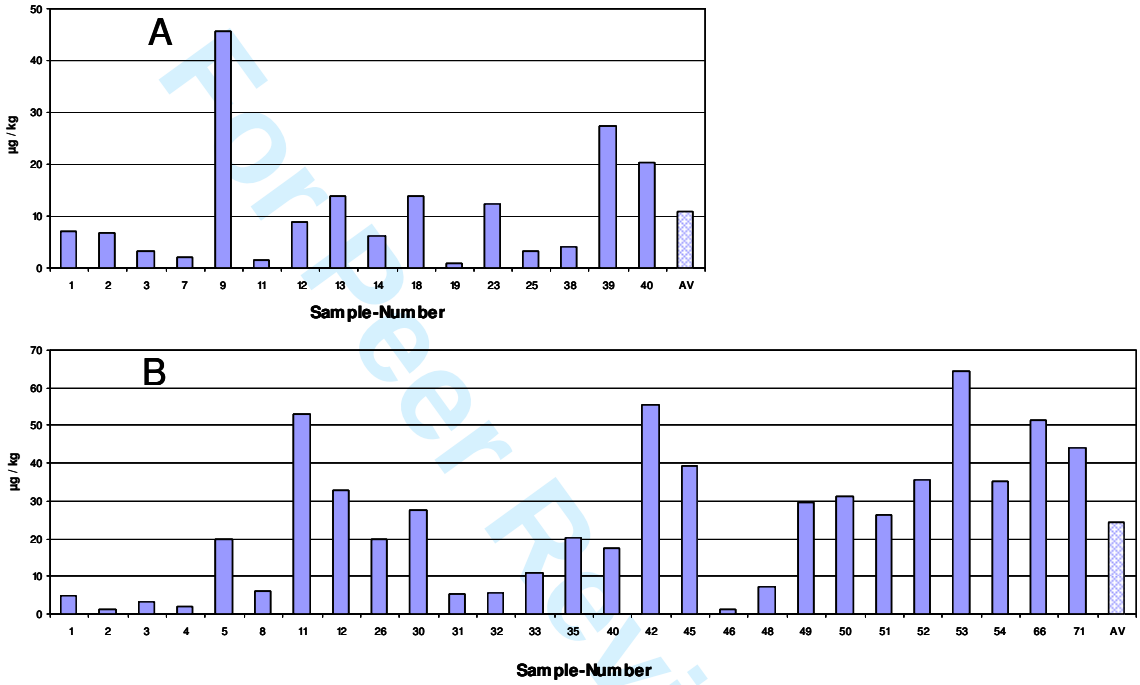
For Peer Review Only

Figure 3



For Peer Review Only

Figure 4



For Peer Review Only