Pressurized Solvent Extraction
Decreasing the extraction time of different samples

Pressurized Solvent Extraction (PSE) of mineral oil hydrocarbons in cardboard and bisphenol A in canned food

Abstract

The BUCHI SpeedExtractor E-916 (Figure 1) is used for the fast extraction of mineral oil hydrocarbons (MOSH/MOAH) in cardboard and also for bisphenol A (BPA) in canned food. In comparison to reference methods the SpeedExtractor can extract MOSH/MOAH in 30 minutes instead of two hours. Up to six samples (E-916) are processed in parallel at elevated temperatures and pressures.

1. Introduction

Mineral oils are complex mixtures of hydrocarbons which can be classified as mineral oil saturated hydrocarbons (MOSH) and mineral oil aromatic hydrocarbons (MOAH). These contaminants are found in many food samples because of the migration from cardboard packaging made from recycled fibers [1, 2]. According to EFSA (European Food Safety Authority), MOAH should be absent from food because of potentional carcinogenic effects. For MOSH there is no fixed limitation level [3].

Bisphenol A (BPA) (Figure 2) is the raw material for the production of polycarbonate (PC). This plastic material is used, e.g. in baby bottles and coatings for different food containers. Because of endocrine disrupting effects PC should no longer be used for baby bottles [4]. Due to sterilization processes in canned food, BPA can be released from the PC coating and migrates into the food. Therefore the legal sum of migration level for BPA in food is a maximum of 0.6 mg/kg food [5].

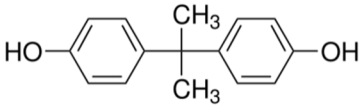

Figure 2: *Structural formula of bisphenol A*

2. Mineral oil residues in cardboard

For the extraction of mineral oil residues all parts which come in contact with the sample or extract must be pre-cleaned. By heating for at least 8 h at 450 °C, rinsing with n-hexane or cleaning in an ultrasonic bath using acetone and/or n-hexane for 5 min. Cardboard samples (length ~ 6 cm, width ~ 2 - 4 mm) are extracted with n-hexane to quantitatively transfer the mineral oil (Figure 3) into a measurable form.

Figure 3: *Extraction cell, two expansion elements and the sample, cut in strips [6]*

Figure 1: *SpeedExtractor E-916*

Using the SpeedExtractor E-916 the extraction is completed in 30 min compared to two hours with the reference method. Using the reference method the cardboard is extracted with a mixture of n-hexane : ethanol (1:1, v/v) and a clean-up step is necessary afterwards. In comparison the E-916 method requires no clean-up step after extraction or post-treament prior to analysis completely eliminating the Vortex-/centrifuge steps. In Figure 4 the comparison between the steps from extraction to analysis of the reference method and the extraction with SpeedExtractor is shown.

Reference method:	SpeedExtractor E-916:
1 g cardboard (cut in little pieces) + IS	1 g cardboard (cut in little pieces) + IS
↓	↓
+ 10 mL n-hexane : ethanol (1:1, v/v) (extraction: 2 h at RT)	n-hexane (extraction with E-916: 30 min at 60 °C)
↓	↓
3 mL extract + 6 mL H_2O	Injection
↓	
Vortex	
↓	
Centrifugation	
↓	
Injection	

Figure 4: *Comparison of the steps from the extraction of the cardboard sample to the injection for analysis – Left: the reference method, Right: the method with SpeedExtractor*

The quantification was performed with online LC-GC/FID (Brechbühler). Due to the high number of isomers present in mineral oil hydrocarbons, it is not possible to separate individual hydrocarbons by GC. For this reason GC traces are characterized by humps of unresolved peaks (Figure 5).

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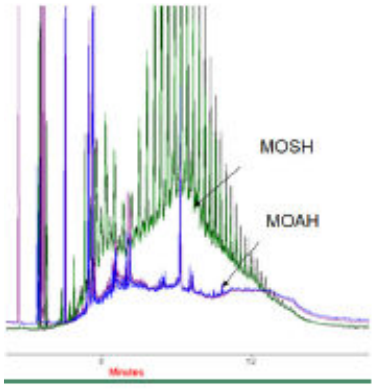

Figure 5: *LC-GC profile of MOSH and MOAH characterized by humps [6]*

3. Bisphenol A in canned food

The homogenized preserved food samples (beans, poultry soup stew, ravioli and artichokes) were freeze-dried prior to extraction. The extraction with the SpeedExtractor E-916 is done with acetonitrile : water (1:1, v/v) and lasts 1 h 15 min. Effective extraction is achieved with only three cycles. This was verified with a post-extraction in which no BPA was detected. Before the quantification with LC-MS/MS (Thermo TSQ Quantum Ultra AM) an aliquot of each extract was filtered through a 0.45 µm PTFE syringe filter. As an example, in Figure 6 the total ion current (TIC) from the artichoke sample is shown. On average all samples had a BPA content far below the legal sum of migration level.

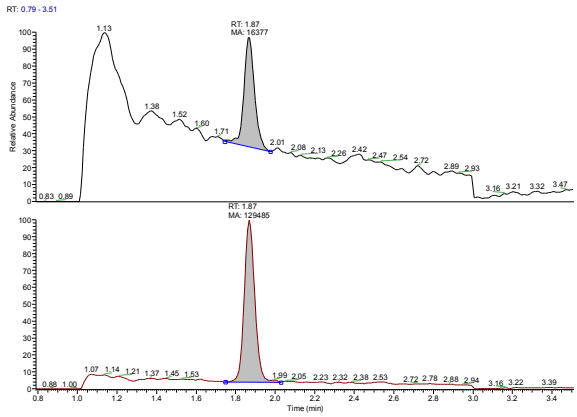

Figure 6: *Both chromatograms show the total ion current (TIC) from the artichoke sample. The upper chromatogram shows the native bisphenol A mass trace and the lower chromatogram the TIC of the internal standard $^{13}C_{12}$-bisphenol A. The internal standard (deuterated BPA) acts like the native BPA which means it has the same chemical properties and the same retention time but a different mass.*

4. Conclusion

The extraction of mineral oil contamination from cardboard can be performed by PSE using the SpeedExtractor E-916. Since the extraction is done with n-hexane, a solvent change and the following clean-up step is not necessary. The extracts can be injected directly into the online LC-GC/FID system. The results obtained with the SpeedExtractor E-916 show good correlation with those obtained using the reference method.

The determination of bisphenol A in preserved food samples using the SpeedExtractor E-916 provides reliable and reproducible results. The level of bisphenol A in the post-extractions was below the LOQ, therefore extraction yields can be considered as complete.

5. Acknowledgement

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6. References

[1] Rapid and sensitive solid phase extraction- large volume injection-gas chromatography for the analysis of mineral oil saturated and aromatic hydrocarbons in cardboard and dried food: S. Moret, L. Barp, G. Purcaro, L. Conte, Journal of Chromatography A, 1243 (2012) 1-5

[2] Is recycled newspaper suitable for food contact materials? Technical grade mineral oils from printing inks: M. Biedermann, K. Grob, Eur.Food Res. Technol. 230 (2010) 785-796

[3] Scientific Opinion on Mineral Oil Hydrocarbons in Food: European Food Safety Authority, EFSA Journal 2012; 10(6):2704

[4] COMMISSION DIRECTIVE 2011/8/EU of 28 January 2011 amending Directive 2002/72/EC as regards the restriction of use of Bisphenol A in plastic infant feeding bottles

[5] COMMISSION DIRECTIVE 2004/19/EC of 1 March 2004 amending Directive 2002/72/EC relating to plastic materials and articles intended to come into contact with foodstuffs

[6] Optimisation of pressurized liquid extraction (PLE) for rapid and efficient determination of MOSH and MOAH in cardboard and foods. S. Moret; presentation at ExTech 2012 (Messina)

7. Additional resources

- Application Note No. 99/2013 Mineral oil contamination in cardboard (http://www.buchi.com/en/content/mineral-oil-contamination-cardboard)
- Application Note No.119/2013 Determination of Bisphenol A in preserved food (http://www.buchi.com/en/content/determination-bisphenol-preserved-food)