Fast Screening for Plasticisers in PVC – Extraction and ^{1}H-NMR Analysis

N. Kasprick[1], F. Brenz[1], G. Eisler[1], C. Conrad[1], T.J. Simat[1], M. Spraul[2]

[1]TU Dresden, Chair of Food Science and Food and Skin Contact Materials, Bergstr. 66, D-01069 Dresden, [2]Bruker Biospin GmbH, Silberstreifen 4, D-76287 Rheinstetten

Background and Aims

Soft PVC is widely used in food contact materials, toys and other products like wallpapers. The plasticiser content differs from 1 to 70 %. Due to the structural variety, chromatographic methods may reach their limits: The increased use of polymeric substances („polyadipates“) leeds to a need of derivatisation (e.g. transesterification). ^{1}H-NMR can be easily used to analyse plasticisers in soft PVC, because it is independent of molecular mass and has a very short measuring time (minutes).

Aim of this work was to develop a fast screening method to identify and quantifiy commonly used monomeric and polymeric plasticisers in soft PVC with the help of ^{1}H-NMR after extraction.

Summary

A fast screening method for identification and quantification of commonly used monomeric and polymeric plasticisers in soft PVC by ^{1}H-NMR was developed. Complete extraction was achieved by ultrasonication in deuterated chloroform within 60 minutes. The internal standards 1,2,4,5-Tetrachloro-3-nitro-benzene and Decamethylpentasiloxane are used for reliable quantification. ESBO and polyadipates were analysed without prior transesterification. Furthermore a ^{1}H-NMR database with spectra and specific informations of 75 plasticisers was created with the help of AMIX®. The plasticiser composition of food contact materials, toys etc. was analysed.

Extraction

The extraction with deuterated chloroform ($CDCl_3$) enables an immediate ^{1}H-NMR-measurement (Fig. 1). For quantification 1,2,4,5-Tetrachloro-3-nitrobenzene or Decamethylpentasiloxane is used as internal standard (Fig. 2).

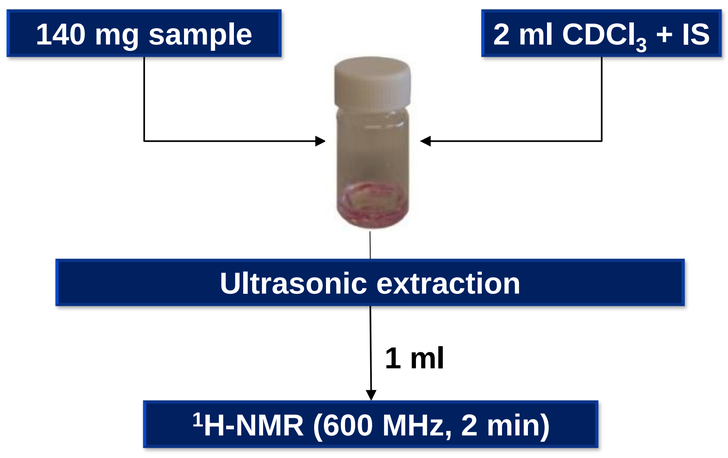

Fig. 1: Schematic procedure of the screening method

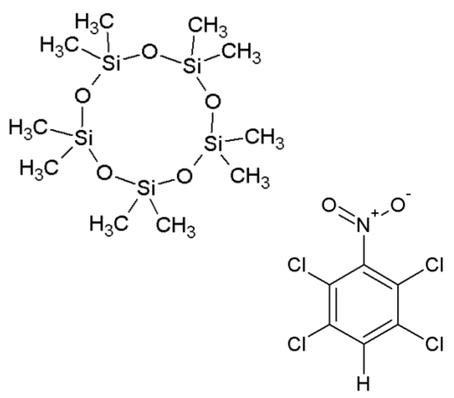

Fig. 2: Internal standards Decamethyl-pentasiloxane and 1,2,4,5-Tetrachloro-3-nitrobenzene

^{1}H-NMR database

Plastics with food contact	Toys	Pharmaceut. products
VO (EU) 10/2011[1]	VO (EG) 1907/2006[2]	EurPharm[3]

Reference substances

NMR measurements → Spectra processing (AMIX®) // Information research

Database

Dataset per substance

- Spectra
  - ^{1}H, ^{13}C , J-res, COSY, HSQC, HMBC, TOCSY
- Informations
  - name
  - name (IUPAC)
  - CAS number
  - molecular formula
  - molecular weight
  - log $k_{O/W}$
  - boiling point
  - vapour pressure
  - SML
  - producer

Evaluation

manually

- qualitative: table of signal shifts + comparison with reference spectra (AMIX®)
- quantitative: by internal standard

automatically (AMIX®)

Complete extraction of monomeric and polymeric plasticisers is achieved within 60 minutes. The LOD of the method depends on magnetic field strenght, probehead technology and proton number and multiplicity of the signals of the substance. For monomeric plasticisers LOD is 0.002 – 0.15 g/100g PVC and for the polyadipate backbone LOD was determined from 0.01 to 0.04 g/100g PVC.

Up to now 75 plasticisers are implemented to the database (Tab. 1). A case oriented extension is recommended for future analysis because of possible new plasticisers.

Tab. 1: Plasticisers in the database

Group	Number	Group	Number
Phthalates	13	Glycerol ester	4
Adipates	5	Terephthalates	3
Sebacates	4	Trimellitates	2
Azelates	3	Polyadipates	13
Citrates	3	Other	25

Examples of qualitative and quantitative results

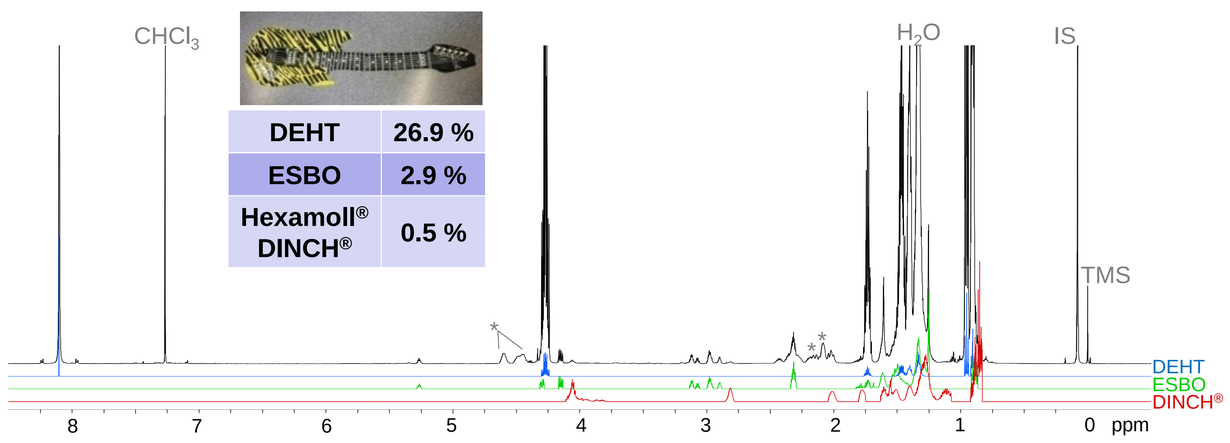

Fig. 3: ^{1}H-NMR-spectrum of the extract of PVC guitar (toy) with corresponding standard spectra from the database (IS = Decamethylpentasiloxane, *…PVC-oligomers)

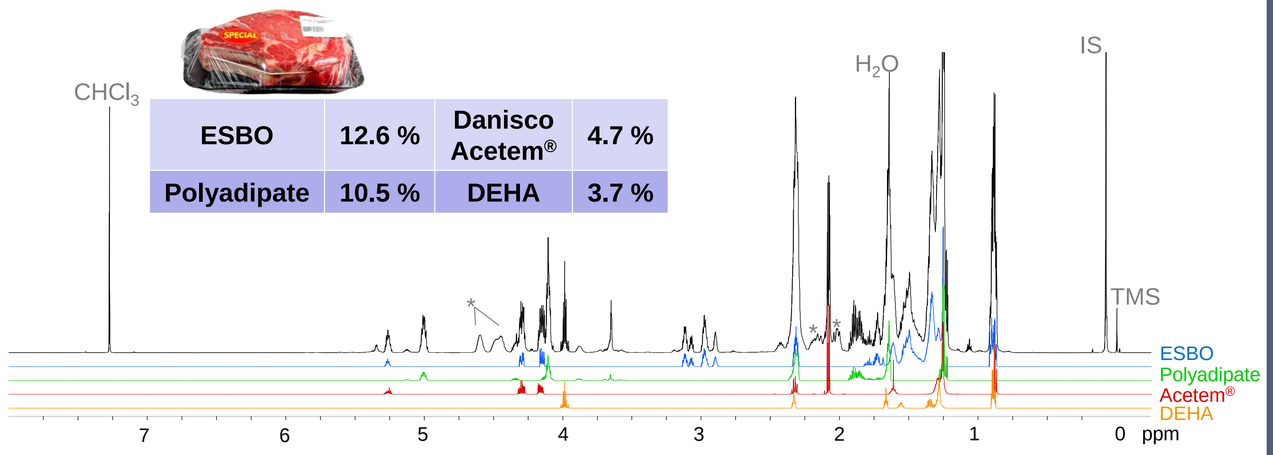

Fig. 4: ^{1}H-NMR-spectrum of the extract of a PVC foil with corresponding standard spectra from the database (IS = Decamethylpentasiloxane, *…PVC-oligomers)

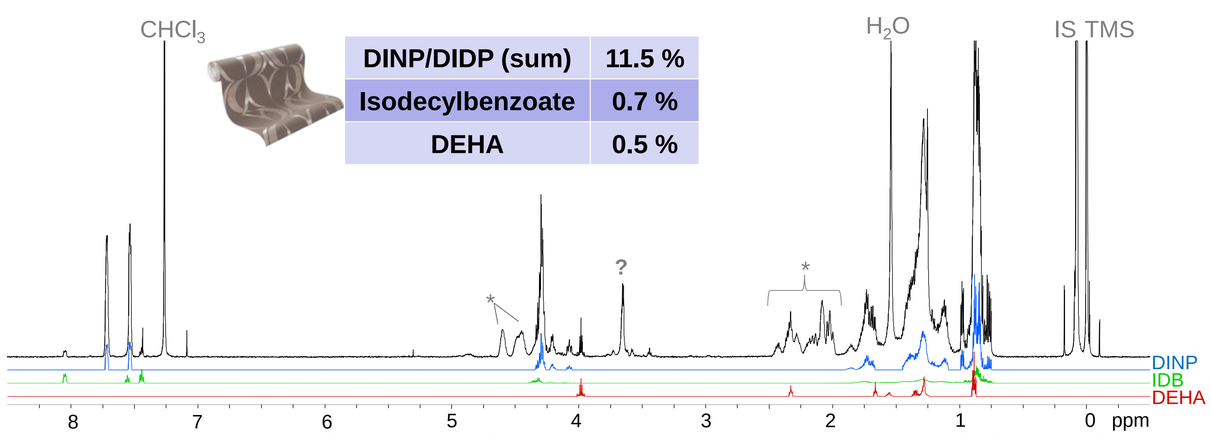

Fig. 5: ^{1}H-NMR-spectrum of the extract of a PVC wallpaper with corresponding standard spectra from the database (IS = Decamethylpentasiloxane, *…PVC-oligomers)

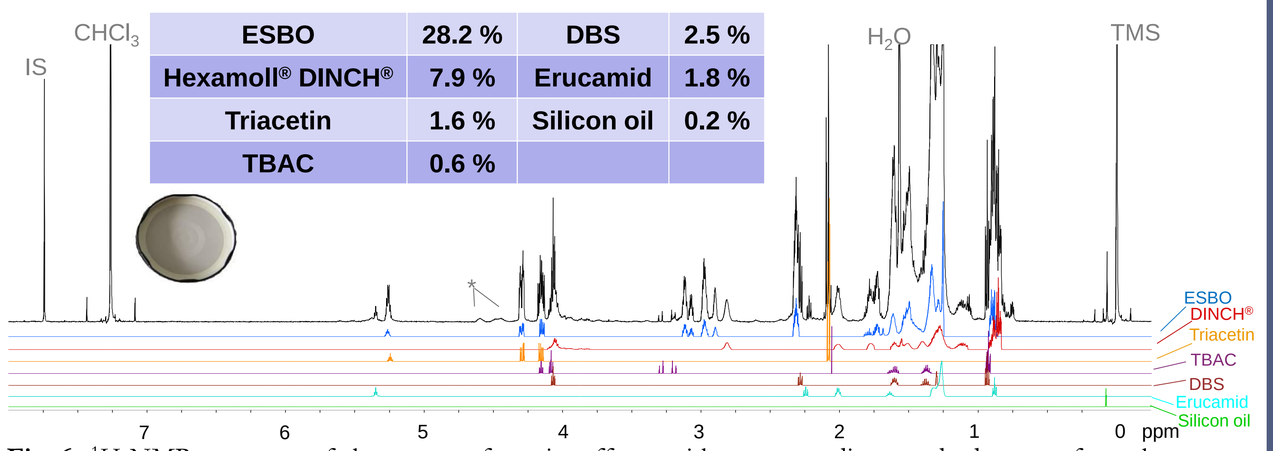

Fig. 6: ^{1}H-NMR-spectrum of the extract of a twist-off cap with corresponding standard spectra from the database (IS = 1,2,4,5-Tetrachloro-3-nitrobenzene, *…PVC-oligomers)

Acknowledgement: We like to thank the Bruker Biospin GmbH for the ^{1}H-NMR-measurements and providing the software AMIX® and Topspin®.

Literature: [1] Commission Regulation10/2011 on plastic materials and articles intended to come into contact with food
[2] Regulation (EC) No 1907/2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH)
[3] Pharmacopoeia Europaea, 3.1.13 Plastics Additives, 6. Edition, 2nd amendment, p. 4857-4860