TECHNISCHE UNIVERSITÄT DRESDEN

Screening for Additives in PE and PP Food Contact Materials – Extraction and ^{1}H-NMR Analysis

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Background

The polyolefins PE and PP are important polymers for food contact materials (FCM). PP became a popular alternative to polycarbonate for baby bottles after the ban on the use of bisphenol A for this sensitive product. Antioxidants, antistatic agents, UV-stabilizers, lubricants, clarifier etc are frequently used as additives in the manufacture of PE/PP-articles and chromatographic screening methods may give insufficient results. A screening analysis by ^{1}H-NMR provides universal proton detection independent of molecular mass. Aim of this work was to develop a fast screening method to identify and quantifiy commonly used additives and potential NIAS in FCM made of polyolefins with the help of ^{1}H-NMR after extraction.

Summary

A fast screening method for identification and quantification of different additives (antioxidants, lubricants, clarifier etc.) for food contact materials (FCM) made of polyethylene (PE) and polypropylene (PP) was developed. After complete extraction by ultrasonication in deuterated chloroform (60 minutes) the extract is analysed via ^{1}H-NMR. Quantification is done by the internal standard Decamethylpentasiloxane. The method was applied to identify the additive composition of 12 different baby bottles made of PP. In addition, a ^{1}H-NMR database with spectra and specific information of 64 additives and potential NIAS was created with the help of AMIX®.

Extraction

After cryogenic milling the sample is extracted with deuterated chloroform (CDCl$_3$) and after centrifugation the extract is ready to be analysed by ^{1}H-NMR (Fig. 1). Decamethylpentasiloxane is added as internal standard for quantification (Fig. 2).
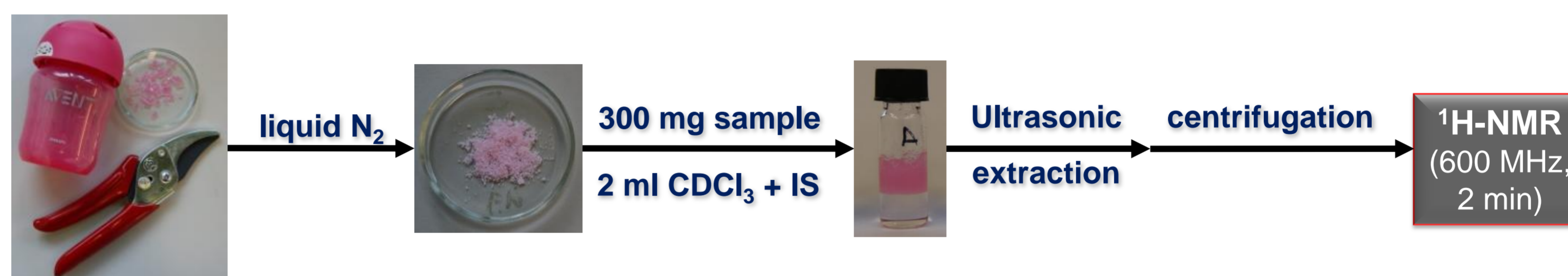

liquid N$_2$ · 300 mg sample · 2 ml CDCl$_3$ + IS · Ultrasonic extraction · centrifugation · ^{1}H-NMR (600 MHz, 2 min)

Fig. 1: Schematic procedure of the screening method (note: only the body of the baby bottles was analysed)
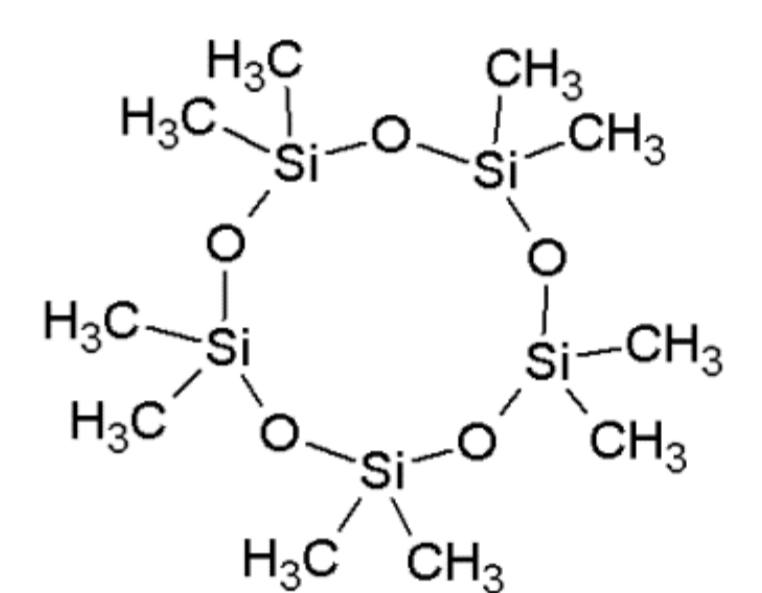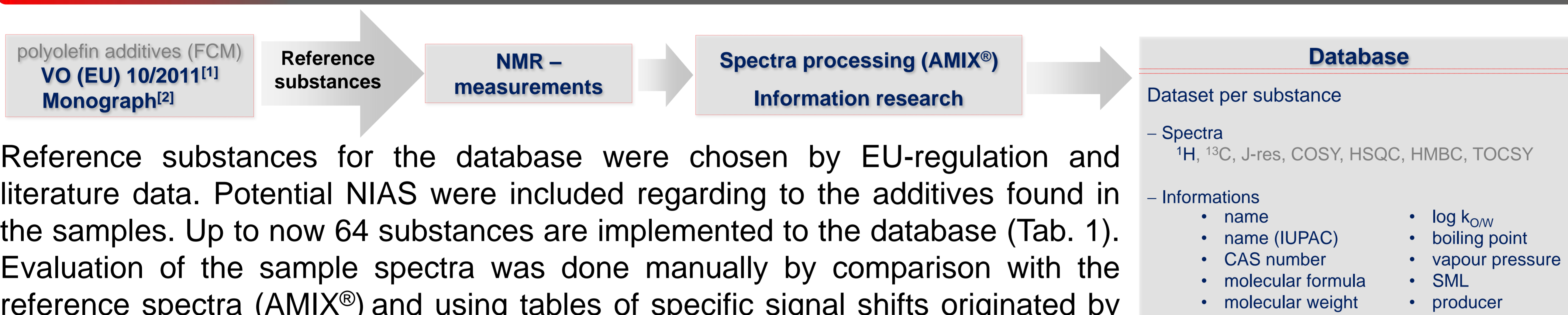
Fig. 2: IS Decamethylpentasiloxane

Complete extraction of antioxidants, lubricants and nucleating agents (clarifier) was 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 the investigated additives and NIAS the LOD is 10 – 100 mg/kg polyolefin.

^{1}H-NMR database

polyolefin additives (FCM) VO (EU) 10/2011[1] Monograph[2] → Reference substances → NMR – measurements → Spectra processing (AMIX®) Information research → Database

Reference substances for the database were chosen by EU-regulation and literature data. Potential NIAS were included regarding to the additives found in the samples. Up to now 64 substances are implemented to the database (Tab. 1). Evaluation of the sample spectra was done manually by comparison with the reference spectra (AMIX®) and using tables of specific signal shifts originated by the authors.

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

Tab. 1: Substances in the database

Group	Number
Antioxidants	24
UV-stabilizer	10
Antistatic agents	2
Lubricants	11
Clarifier	5
Other (e.g. NIAS)	12

Results

Additive composition

All main additives in the baby bottles could be identified. Especially the aromatic region is fully explained (s. Fig 3). In addition, characteristic signals of unsaturated PP-oligomers were detected.

The samples had a similar additive composition (Fig. 4). All baby bottles contained antioxidants, mostly IF®168 and IN®1010. A clarifier (Millad® NX8000, 3988i type) was found in all transparent samples and mono fatty acid esters of glycerol as antistatic/mould release agent were detected in some bottles.
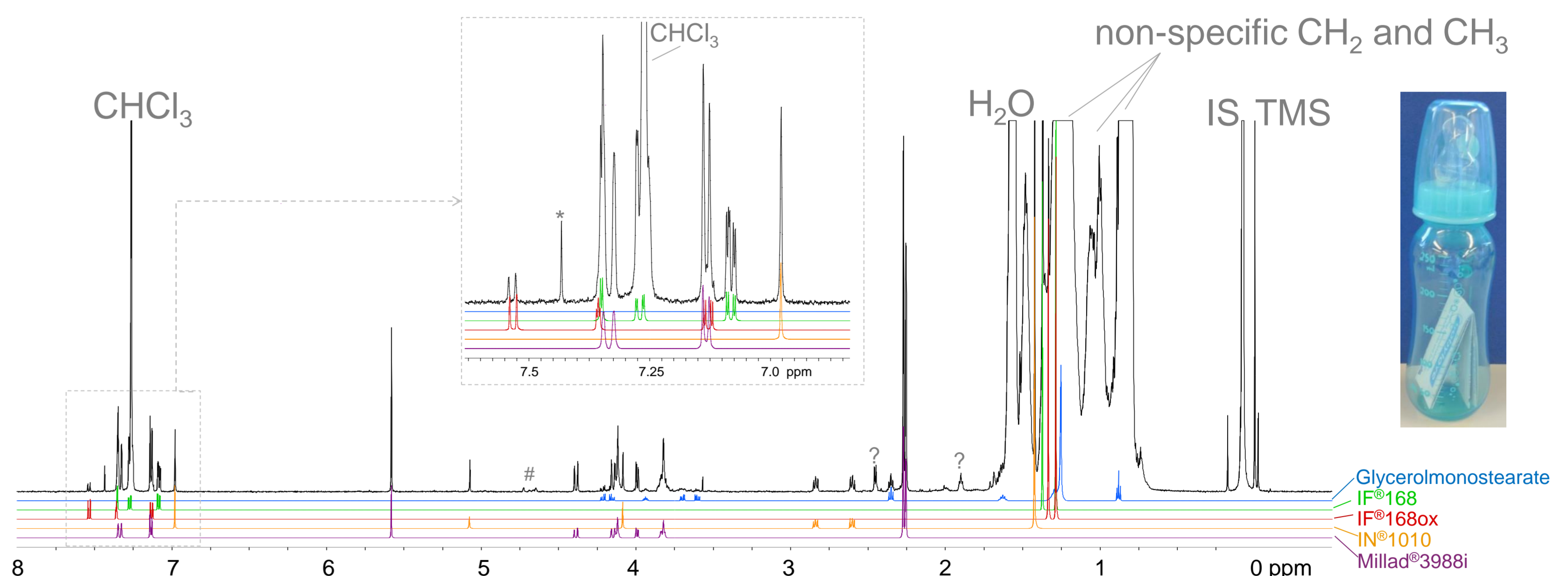

Fig. 3: ^{1}H-NMR-spectrum of the extract of a baby bottle (PP) with corresponding standard spectra from the database (* … ^{13}C-satellite of CHCl$_3$; # … signal of unsaturated PP-oligomers)
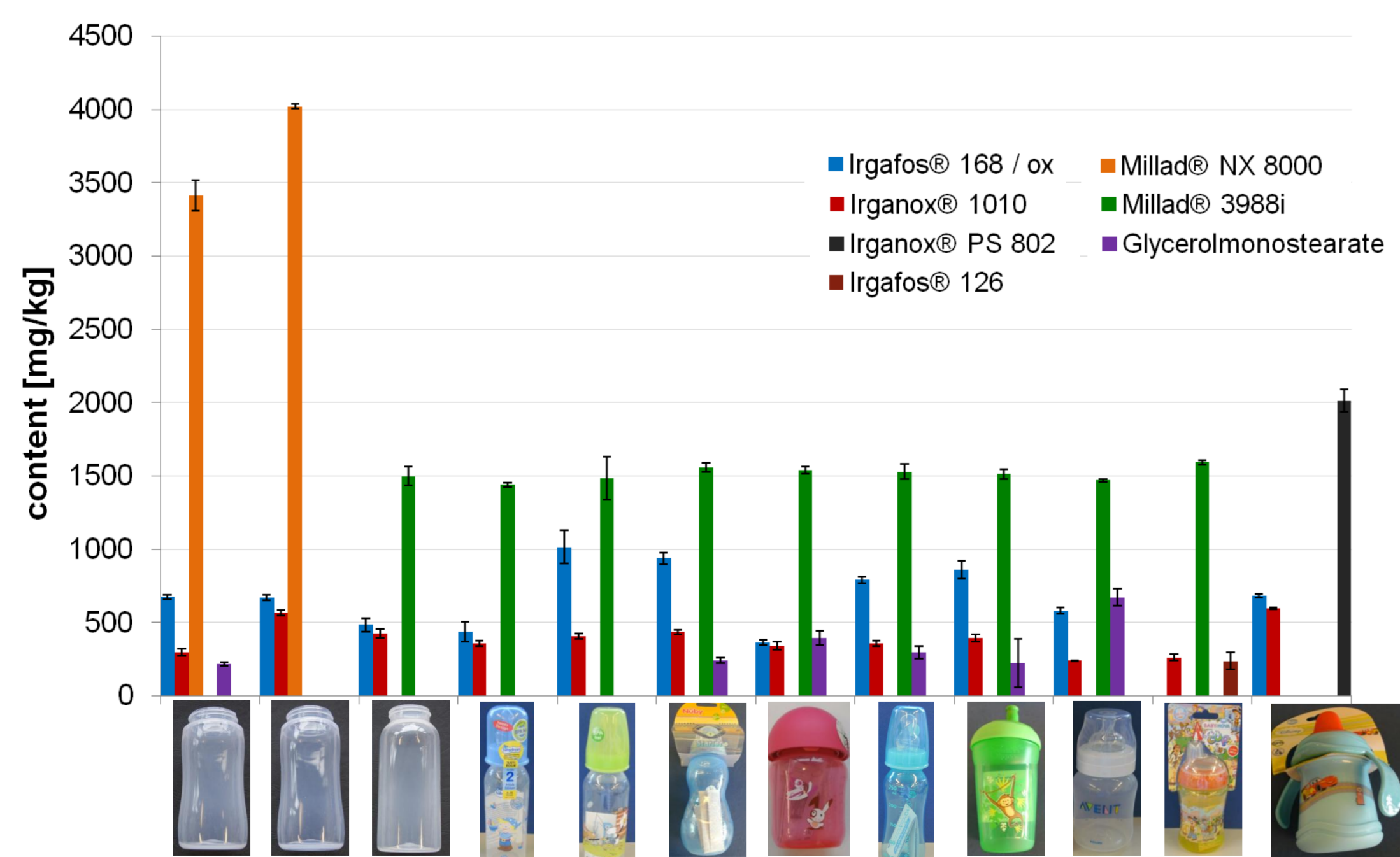

Fig. 4: Qualitative and quantitative additive composition of the samples (mono fatty acid esters of glycerol calculated as glycerolmonostearate)

Legend: Irgafos® 168 / ox · Millad® NX 8000 · Irganox® 1010 · Millad® 3988i · Irganox® PS 802 · Glycerolmonostearate · Irgafos® 126

Potential NIAS

The ^{1}H-NMR screening provides information regarding potential NIAS (Fig. 5). Further analysis is recommended, because NIAS were below LOD of ^{1}H-NMR.

Millad® NX8000 CAS 882073-43-0 SML: 5 mg/kg (incl. sum of hydrolysis products) → 4-Propylbenzaldehyd CAS 28785-06-0

Millad® 3988i CAS 135861-56-2 SML:60 mg/kg → 3,4-Dimethylbenzaldehyd CAS 5973-71-7 Not listed in [1]

Irgafos® 126 CAS 26741-53-7 SML: 0.6 mg/kg

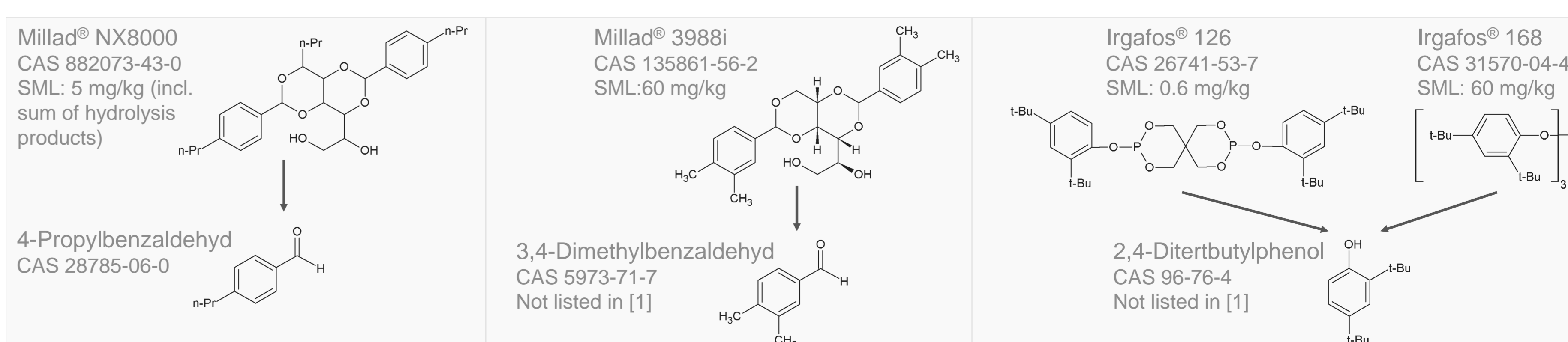Irgafos® 168 CAS 31570-04-4 SML: 60 mg/kg → 2,4-Ditertbutylphenol CAS 96-76-4 Not listed in [1]

Fig. 5: Detected additives and selected potential NIAS

Literature: [1] Commission Regulation10/2011 on plastic materials and articles intended to come into contact with food
[2] Van Lierop, B., Castle, L., Feigenbaum, A., Boenke, A. (1998): Spectra for the Identification of Additives in Food Packaging. Kluwer Academic Publishers. Dordrecht. 1st Edition