

TNO Report

Greenpeace UK
Attn. Mr M. Strutt
Canonbury Villas
LONDON
N1 2PN
Engeland

TNO-MEP
Laan van Westenenk 501
PO Box 342
7300 AH Apeldoorn
The Netherlands
Telephone: +31 55 549 34 93
Fax: +31 55 549 33 90
Internet: www.mep.tno.nl

Subject: The determination of additives in food products

Report no. : TR 2003/725
Order no. : 33076-033
File no. : 52003303
Date : 11 december 2003
Pages : 9

Issued by:
Department Environmental Quality

All rights reserved.
No part of this publication may be reproduced and/or published by print, photoprint, microfilm or any other means without the previous written consent of TNO.

In case this report was drafted on instructions, the rights and obligations of contracting parties are subject to either the Standard Conditions for Research Instructions given to TNO, or the relevant agreement concluded between the contracting parties. Submitting the report for inspection to parties who have a direct interest is permitted.

Ing. R. Geenen
(Author)
Date:

Dr. R.J.B. Peters
(Co-ordinator)
Date:

© 2003 TNO

The Quality System of the TNO Environment, Energy and Process Innovation has been certified in accordance with ISO 9001.

TNO Environment, Energy and Process Innovation is a recognised contract research institute for industry and government with expertise in sustainable development and environmentally oriented process innovation.

The Standard Conditions for research instructions given to TNO, as filed at the Registry of the District Court and the Chamber of Commerce in The Hague shall apply to all instructions given to TNO.

1. Introduction

In an earlier study the presence of nonylphenol in foil used to wrap meat products was shown (see TNO report TR 2003/549: “The determination of nonylphenol and organotin compounds in packed meat products”, 01 October 2003). In addition it was shown that this compound could be found in the top layer of the food product directly beneath the wrapper, indicating at least some migration of this compound into the food product. In addition, some phthalates were found in the same top layer of the food product. These probably also originate from the wrapper, since these phthalates are used as additives in the wrapper materials.

This study focuses on the presence of alkylphenols and alkylphenol ethoxylates in the foil used to wrap a food product, and in the top layer of that food product directly beneath the foil. In addition a GC/MS screening is performed on these samples to identify any other compounds or additives present in the sample.

2. Samples

In total five wrapped fresh meat products (turkey and chicken), three fresh cheese products (brie) were collected by Greenpeace UK in various shops, and send to the TNO laboratory where they were received on November 11, 2003. The samples were cooled during transport and stored in a refrigerator (only the food products) until analyses. The TNO codes of the samples and their description are as follows:

<i>Description:</i>	<i>TNO-MEP code</i>
Tesco Turkey Breast Fillet (4330810.08)	52003303-001
Sainsbury's Fresh British Turkey Breast Fillets (Mo644)	52003303-002
Sainsbury French Brie	52003303-003
Tesco Continental Brie	52003303-004
Marks & Spencer Oakham White Mini Chicken	52003303-005
Waitrose French Brie	52003303-006
Waitrose Fresh Turkey Breasts	52003303-007
Asda Turkey Escalopes	52003303-008

3. Methods

3.1 Sub-sampling

Sub-samples were prepared from the food products. These include the following:

- A sub-sample of the foil or wrapper in which the meat is packed.
- A sub-sample of the food directly underneath the foil, typically a slice of 2-3 mm thick.

Depending on the type of analysis a sub-sample of 1 or 5 grams was used for analysis.

3.2 Analyses of food wrap

The sub sample of the food wrap was cut into small pieces and soxhlet extracted overnight with dichloromethane. The extract was concentrated and brought to a final volume of 100 ml with dichloromethane. This extract was analysed directly for the determination phthalates and the screening with gas chromatography coupled with mass spectrometry (GC/MS). For the determination of

alkylphenols and alkylphenol ethoxylates, a part of this extract was evaporated to dryness under nitrogen. The residue was re-dissolved in methanol, filtered through a 0.45 µm filter and analysed with liquid chromatography coupled with mass spectrometry (LC/MS).

3.3 Analyses of food products

For the meat and brie samples a steam distillation was applied to isolate alkylphenols and alkylphenol ethoxylates. The extraction liquid for the steam distillation was a solution of sodium chloride and hydrochloric acid in water. A mixture of n-heptane and iso-octane was used for the in-situ solvent extraction in the steam distillation apparatus. After distillation the organic phase is isolated, dried, concentrated to a small volume and split into equal aliquots. One aliquot was used for the GC/MS screening. A second aliquot was concentrated under nitrogen to near dryness. The residue was re-dissolved in methanol and analysed with LC/MS for alkylphenols and alkylphenol ethoxylates.

4. Results

4.1 Alkylphenols and alkylphenol ethoxylates

The results of the alkylphenol and alkylphenol ethoxylates are presented in table 1 for the wraps and in table 2 for the food products. The specific compounds that were determined are bisphenol-A, octyl- and nonylphenol, and the octyl- and nonylphenol ethoxylates.

Bisphenol-A was found only in two of the food wraps (3303-001 and -002).

Octylphenol was found in none of the samples, which is not surprising since it is much less used than nonylphenol. Nonylphenol was found in five out of the eight wrap materials in a maximum concentration of 62 mg/kg. Nonylphenol ethoxylates were found in only one of the food wraps (3303-004) in a concentration of 49 mg/kg.

In the top layers of the food products bisphenol-A and nonylphenol were detected in those cases where these compounds were also present in the wrap material. For nonylphenol we found that the concentrations in the top layer of the meat products are roughly 1% of the nonylphenol concentration in the wrap material. For the cheese products this is roughly 0.1%, indicating a possible lower migration into these products, presumably as a consequence of the crust of these products.

An exception is nonylphenol ethoxylate. While this compound was only found in one sample of the wrap material, it is found in comparable concentrations in all food samples but one (3303-001). The reason for this is not clear. Method blank samples do not show any nonylphenol ethoxylates.

4.2 GC/MS screening

4.2.1 GC/MS screening wrapping materials

A GC/MS screening was applied to all wrap materials and the top layer food samples. Table 3 presents the results for the wrap materials. To make a distinction between major and minor compounds, and indicative concentration of the compounds, expressed in mg/kg is given in table 3, based on peak areas in chromatograms and a uniform response factor. These indicative concentrations should be interpreted with care since they may be wrong by a factor of two or even more. In general the GC/MS analysis reveals one or more major compounds (often the plasticizer applied) and some other compounds present at low concentrations, and probably impurities of the major additive.

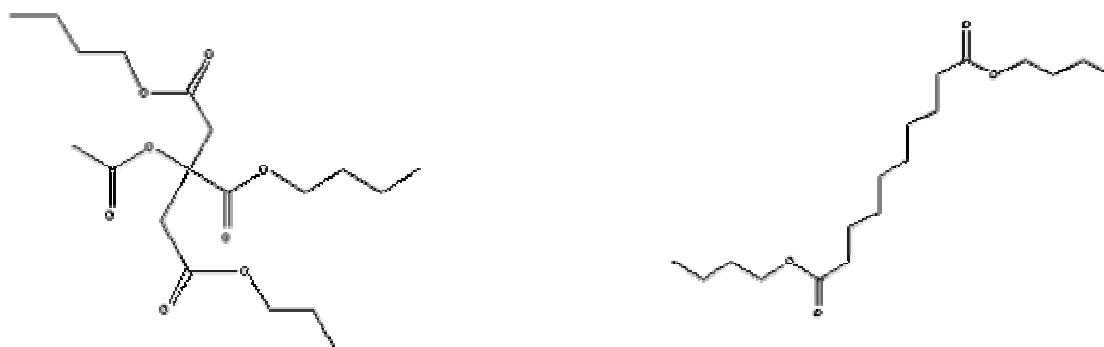
Four of the materials, 3303-001, -002, -005 and -008 contain di-iso-octyl adipate as a plasticizer. The concentrations are very comparable and range from 83000 to 96000 mg/kg. This fact, and the fact that the other compounds found in these samples are more or less the same, suggests that these four samples are one and the same material.

Sample 3303-003 contains a very different type of plasticizer, tributyl acetylacrylate, common name Citrfole®BII (see structure on the left), often used in medical and pharmaceutical applications. The concentration was 36000 mg/kg.

Sample 3303-004, according to the Greenpeace information a non-PVC wrap, does not seem to contain any plasticizers other than the low amounts of plasticizers like dibutyl phthalate that were found in all the samples. However, from table 1 we know that this is the only sample containing nonylphenol ethoxylate. This, or similar compounds, are not detected using GC/MS.

Sample 3303-006 contains another type of plasticizer, decanedioic acid dibutyl ester, better known as dibutyl sebacate (see structure on the right), a less common plasticizer. The concentration was 31000 mg/kg. Again, other plasticizers are present at low concentrations and surprisingly dichloro- and trichlorobenzene were also identified in this sample. It is unclear why these compounds are present in this material, even as impurities.

Finally sample 3303-007, also a non-PVC wrap according to Greenpeace, only seems to contain low amounts of some plasticizers that are probably just impurities.



4.2.2 GC/MS screening food products

A GC/MS screening was applied to the top layers of the food directly beneath the wrap. Table 4 presents the results of these analyses. As in table 3, indicative concentrations in mg/kg are added. Please note the remark in 4.2.1 concerning the interpretation of these values. Not surprisingly, the GC/MS analysis shows aldehydes and alkanolic acids for the meat products and alkanolic acids for brie products as the major compounds. The concentrations for these compounds are not representative for the sample since they originate from partial hydrolysis of fats in the sample and the clean-up method will remove these compounds as far as possible.

Di-iso-octyl adipate was detected in samples 3303-001, -002, -005 and -008, and often one or two more phthalates were identified in the same samples. These are the same samples in which di-iso-octyl adipate was found in the wrap material, indicating a migration of this compound to the food product itself. The indicative concentrations of di-iso-octyl adipate in the top layer samples ranged from 10 to 35 mg/kg, which is 0.01% to 0.05% of the concentration in the wrap material. Of course it should be noted that this indicative concentration is found in the top layer only, and that it is not representative for the whole product.

Dibutyl sebacate, found in the wrapping material of sample 3303-006, could be identified in the top layer of the brie product in a concentration of about 2 mg/kg. In the same way, tributyl acetylcitrate, present in the wrapping of sample 3303-003, was found in the brie product in an concentration of about 2 mg/kg. Based on the observations in this study meat products appear to be a little bit better in extracting these plasticizers from the wrapping material than a cheese like brie. This difference is probably caused by the crust that covers the brie. On the other hand it should be kept in mind that these are only a limited number of observations and certainly tributyl acetylcitrate may behave differently from the more classical plasticizers.

5. Conclusions

This study showed the presence of nonylphenol and phthalates in both, the wrap, and the top layer of food directly beneath the wrap material. This indicates that migration of these compounds from the wrapper to the food takes place. As an indication the concentration of the compounds in the top layer of meat products, relative to the wrap material was roughly 1% for nonylphenol and 0.02% for phthalates or adipates. For the cheese products this migration appears to be lower by a factor of 10.

Table 1. Project 52003303: Alkylphenol and alkylphenol ethoxylate concentrations in wrappers and pyjamas

TNO code	GP code	Product description	BPA mg/kg	OP mg/kg	NP mg/kg	OPEO mg/kg	NPEO mg/kg
52003303-001	1	Tesco Turkey Breast Fillet: wrap	0.61	<0.5	<0.5	<2	<2
52003303-002	2	Sainsbury Fresh British Turkey Breast Fillets: wrap	0.50	<0.5	55	<2	<2
52003303-003	3	Sainsbury French Brie: wrap	<0.5	<0.5	1.3	<2	<2
52003303-004	4	Tesco Continental Brie: wrap	<0.5	<0.5	5.9	<2	49
52003303-005	5	Marks & Spencers Oakham White Mini Chicken: wrap	<0.5	<0.5	58	<2	<2
52003303-006	6	Waitrose French Brie: wrap	<0.5	<0.5	<0.5	<2	<2
52003303-007	7	Waitrose Fresh Turkey Breasts: wrap	<0.5	<0.5	<0.5	<2	<2
52003303-008	8	Asda Turkey Escalopes: wrap	<0.5	<0.5	62	<2	<2

Table 2. Project 52003303: Alkylphenol and alkylphenol ethoxylate concentrations in food products

TNO code	GP code	Product description	BPA mg/kg	OP mg/kg	NP mg/kg	OPEO mg/kg	NPEO mg/kg
52003303-001	1	Tesco Turkey Breast Fillet: toplayer meat	0.001	<0.001	0.07	<0.005	<0.005
52003303-002	2	Sainsbury Fresh British Turkey Breast Fillets: toplayer meat	0.002	<0.001	0.59	<0.005	0.06
52003303-003	3	Sainsbury French Brie: toplayer brie	<0.001	<0.001	<0.001	<0.005	0.06
52003303-004	4	Tesco Continental Brie: toplayer brie	<0.001	<0.001	0.009	<0.005	0.06
52003303-005	5	Marks & Spencers Oakham White Mini Chicken: toplayer meat	<0.001	<0.001	0.34	<0.005	0.06
52003303-006	6	Waitrose French Brie: toplayer brie	<0.001	<0.001	<0.001	<0.005	0.06
52003303-007	7	Waitrose Fresh Turkey Breasts: toplayer meat	<0.001	<0.001	<0.001	<0.005	0.07
52003303-008	8	Asda Turkey Escalopes: toplayer meat	<0.001	<0.001	0.34	<0.005	0.07

Table 3. Project 52003303. Results of GC/MS screening wrap materials of food products

TNO-code	Greenpeace code	Product Description	Compounds identified in GC-MS screening	mg/kg (indication)
52003303-001	1	Tesco Turkey Breast Fillet: wrap	di-iso-octyl adipate di-butyl phthalate di-(2-ethylhexyl) phthalate di-(2-ethylhexyl) adipate	85000 100 350 300
52003303-002	2	Sainsbury Fresh British Turkey Breast Fillet wrap	di-iso-octyl adipate di-butyl phthalate di-(2-ethylhexyl) phthalate di-(2-ethylhexyl) adipate tridecanoic acid octadecenoic acid butylated hydroxytoluene benzophenone typical cluster of 4 unidentified peaks (isomers)	92000 100 150 200 250 200 100 100 550
52003303-003	3	Sainsbury French Brie wrap	tributyl acetylcitrate di-butyl phthalate decanedioic acid, dibutyl ester 1-propene-1,2,3-tricarboxylic acid, tributyl ester butylated hydroxytoluene	36000 100 100 250 200
52003303-004	4	Tesco Continental Brie wrap	di-butyl phthalate erucylamide	200 550
52003303-005	5	Marks & Spencer Oakham White Mini Chicken wrap	di-iso-octyl adipate di-butyl phthalate di-(2-ethylhexyl) adipate typical cluster of 3 unidentified peaks (isomers) typical cluster of 4 unidentified peaks (isomers) butylated hydroxytoluene	83000 100 150 1600 1100 100
52003303-006	6	Waitrose French Brie wrap	decanedioic acid, dibutyl ester di-iso-octyl adipate di-butyl phthalate dichlorobenzene trichlorobenzene hexadecanamide	31000 100 150 150 100 350
52003303-007	7	Waitrose Fresh Turkey Breast wrap	cycloalkanes butylated hydroxytoluene di-butyl phthalate butylbenzyl phthalate	1500 100 100 100
52003303-008	8	Asda Turkey Escalopes wrap	di-iso-octyl adipate di-(2-ethylhexyl) adipate di-butyl phthalate tridecanoic acid octadecenoic acid typical cluster of 4 unidentified peaks (isomers) butylated hydroxytoluene	96000 200 100 200 100 500 100

Table 4. Project 52003303. Results of GC/MS screening in top layers food products

TNO-code	Greenpeace code	Product Description	Compounds identified in GC-MS screening	mg/kg (indication)
52003303-001	1	Tesco Turkey Breast Fillet: toplayer meat	benzophenone	4
			hexadecanal	60
			octadecanal	30
			tetradecanoic acid	2
			hexadecanoic acid	70
			9,12-octadecadienoic acid	40
			di-butyl phthalate	2
			di-iso-octyl adipate	35
52003303-002	2	Sainsbury Fresh British Turkey Breast Fillet: toplayer meat	benzophenone	4
			hexadecanal	60
			octadecanal	10
			tetradecanoic acid	2
			hexadecanoic acid	20
			9-octadecenoic acid	10
			9,12-octadecadienoic acid	9
			di-iso-octyl adipate	10
52003303-003	3	Sainsbury French Brie toplayer brie	hexanoic acid	9
			octanoic acid	25
			decanoic acid	170
			dodecanoic acid	170
			tetradecanoic acid	300
			hexadecanoic acid	400
			9-octadecenoic acid	400
			tributyl acetyl/citrate	2
52003303-004	4	Tesco Continental Brie toplayer brie	hexanoic acid	10
			octanoic acid	5
			decanoic acid	30
			dodecanoic acid	40
			tetradecanoic acid	90
			hexadecanoic acid	130
			9,12-octadecadienoic acid	30
			52003303-005	5
nonanal	3			
2-nonenal	3			
2-decenal	5			
hexadecanal	6			
octadecanal	2			
di-butyl phthalate	2			
benzylbutyl phthalate	3			
52003303-006	6	Waitrose French Brie toplayer brie	hexanoic acid	10
			octanoic acid	20
			n-decanoic acid	150
			dodecanoic acid	250
			tetradecanoic acid	450
			n-hexadecanoic acid	250
			9-octadecenoic acid	80
			dodecanedioic acid dibutyl ester	2
52003303-007	7	Waitrose Fresh Turkey Breast toplayer meat	hexadecanal	80
			9-octadecanal	15
			n-hexadecanoic acid	5
			9-octadecenoic acid	20
			9,12-octadecadienoic acid	20

Table 4 (continued). Project 52003303. Results of GC/MS screening in top layers food products

TNO-code	Greenpeace code	Product Description	Compounds identified in GC-MS screening	mg/kg (indication)
52003303-008	8	Asda Turkey Escalopes toplayer meat	hexadecanal	120
			9-octadecanal	15
			dodecanoic acid	6
			tetradecanoic acid	10
			9-hexadecenoic acid	170
			n-hexadecanoic acid	100
			9-octadecenoic acid	10
			9,12-octadecadienoic acid	140
			di-isoctyl adipate	20
			di-n-octyl phthalate	2