Survey of Chemical Substances in Consumer Products

Survey no. 14 2002

Mapping of Chemical Substances Discharge when heating Clay

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1 Content

2 Introduction

May 2001 MILJØ-KEMI, Dansk Miljø Center A/S was assigned to carry out a project for the Danish Environmental Protection Agency (hereinafter named EPA) titles:

- ***Mapping of Chemical Substance Discharge when heating Clay.***

The project is part of a larger investigation of different consumer products titled:

- ***Mapping of Chemical Substances in Consumer Products.***

EPA had prepared a project proposal (2 April 2001, DS/12) that formed the background for contents and scope of the project.

The background of the project is that EPA wants to know whether there is an exposure risk of dangerous substances when heating clay in a regular oven and accordingly using it to ordinary cooking.

EPA wants to be informed of the different types of cay intended for oven hardening that are sold on the Danish market. Accordingly the clay must be analysed for content and an emission test at heating of the clay to 130°C and 200°C respectively must be carried out, in order to map a potential health risk when heating the products. Health and risk assessments are not included in this report.

Furthermore, EPA wants to include two types of clay that are not intended for oven hardening.

EPA's project leaders were Annette Orloff and Shima Dobel.

The products included in this report have been made anonymous.

3 Scope

3.1 Selection of products

3.1.1 Knowledge of the market

Danish trade organizations, manufacturers, and hobby commodity agents have been contacted in order to obtain information on the oven baking clay sold in Denmark.

3.1.2 Selection of products for the project

It did not prove necessary to make a selection of the products, as there are only a few manufacturers on the Danish market and they have all been included in the project.

The products in the project consisted of four types of clay for hardening i oven and two types of ordinary clay.

3.2 Chemical analyses

3.2.1 Content analysis

The chemical analyses performed on clay include the following chemical substances:

- Organic tin compounds
- Vinyl chloride
- Selected plastic softeners (phthalates, adipates, and citrates)
- Organic extractable substances.

The softeners included in the analysis have been chosen due to a specific demand contained in the standard EN71-5, of which it appears that PVC clay only may contain 30% of certain softeners (adipic acid polyesters, alkylsulphonic acid esters (C_{12}-C_{20}) of phenol, phthalic acid esters with straight chain aliphatic (C_6- and above) alcohols and mixtures of these esters, tributyl acetyl citrate, and tri-(2-ethylhexyl)-acetyl citrate).

Furthermore, a EU directive requires that the content of vinyl choride is below 1 mg/kg (EEC-directive 78/142/EEC), wherefore this directive must be included in the analysis scope.

3.2.2 Emission test

The emission test includes heating to 130°C and 200°C respectively, where the emission is collected on constant adsorbents and accordingly analysed for:

- Aldehydes
- Vinyl chloride
- Volatile organic compounds (VOC)
- Semi volatile organic compounds (SVOC)

4 Analytical methods

4.1 Content analyses

4.1.1 GC/MS screening (phthalates, adipates, citrates, and extractable substances)

Approximately 5 g of the product is taken and extracted with dichloromethane added internal standard by Soxhlet extraction for sixteen hours. A part sample of the extract is taken and analysed directly at combined gas chromatography and mass spectrometry (GC/MS), by scanning over a larger mass area. The content is calculated to relevant standards (phthalates, adipates, and citrates) or semi-quantitative to internal standards (others). The quantification is semi-quantitative for the components calculated to internal standard corresponding to a larger uncertainty (estimated 50-200%). As regards quantification to standards the uncertainty is estimated at 15-20%.

The analyses are carried out as double identification. The limit of detection is 4 mg/kg.

4.1.2 Quantification of phthalate compounds

Following detection and identification of phthalate compounds at GC/MS screening (see above) a gas chromatographically analysis with flame ionisation detection (GC/FID) based on quantification solely on the phthalate compounds. The content is calculated to the relevant standards. Unidentified phthalates are calculated to dipentyl phthalate. Uncertainty on quantification is estimated at 10-15%.

4.1.3 Organic tin compounds

A part sample of known weight and area is taken and extracted with acetic acid in methanol. The extract is shaken in aqueous media and derivatized at an extractive derivatization with sodium tetraethyl borat and pentane. Isooctane is added to the organic phase, concentrated, and analysed at combined gas chromatography and mass spectrometry (GC/MS) at selective ion monitoring of the substances in question. The content is calculated to relevant standards.

The analysis is carried out as double identification. The limit of detection depends on the single components and is stated below. The unit is µg organotin cation/kg.

Component	Limit of detection
Monobutyltin (MBT)	100
Dibutyltin (DBT)	50
Tributyltin (TBT)	50
Tetrabutyltin	100
Monooctyltin	100
Dioctyltin	100
Tricyclohexyltin	300
Triphenyltin	100

4.1.4 Vinyl chloride

Approximately 1 g sample is added dimethylformamide that is shaken thoroughly. The samples are filtered in a closed system and analysed directly at combined gas chromatography and mass spectrometry (GC/MS/SIM).

The analyses are carried out as double identification. The limit of detection is 0.03 mg/kg.

4.2 Emission analysis

A sample consisting of 3 cubes of clay each containing 1 x 1 x 1 cm corresponding to 7-10 g sample. The samples are heated in a climate chamber with controlled temperature and inlet of atmospheric air with a flow of 5.0 l/min ± 0.01 l/min. The air humidity is 50% ± 5% and the temperature is 23°C ± 2°C. The test is carried out two times at 130°C (corresponding to the prescribed conditions) and 200°C (corresponding to worst case) respectively.

The emission from the products is collected on Tenax-TA, Chromosorb 106, Spherocarb, and aldehyde (DNPH coated tubes) tubes in series over a period of 30 minutes. Thus the emitted volatile and semi-volatile compounds are collected.

The tests are repeated for both temperatures using XAD II-tubes to collect the higher boiling compounds. The test is carried out under the same conditions with the exception of the test with the two types of clay not intended for oven hardening. The samples generated condensate at the heating of these tests due to the water liberation from the samples¸ wherefore the exposure time was reduced to 5 minutes for these samples.

During the test the oven hardening clay developed aerosols at 200°C, wherefore a filters were placed before and after the XAD II-tube to ensure complete collection.

The exposed tubes are desorbed thermally and eluted with an elution fluid. The specific procedures are stated below. The test was carried out as double identification.

4.2.1 Analysis for volatile organic components (VOC) in air

The exposed Tenax-TA and Chromosorb 106-tubes are thermally desorbed and analysed directly at combined gas chromatography and mass spectrometry (GC/MS) by scanning over a larger mass area. The content is calculated to relevant standards. The content is either calculated to relevant external standards (vinyl chloride, nonyl phenol, adipates, citrates, and phthalates), or by using the relative response factor (charts) or semi-quantitatively to internal standards (toluene or C_{30}). It is specifically stated in the table with results which components are calculated to internal standards. The quantification is semi-quantitative for these components corresponding to a larger uncertainty (estimated 50-200%). Uncertainty is estimated at 15-20% for quantification to standards or use of relative response factors.

The limit of detection is 0.1 mg/kg for all four types of oven hardening clay and 1 mg/kg for the non-oven hardening clay.

4.2.2 Analysis for semi-volatile organic components (SVOC) in air

The exposed XAD-II tubes are desorbed at extraction with dichloromethane and accordingly analysed at combined gas chromatography and mass spectrometry (GC/MS). The content is either calculated to relevant external standards (vinyl chloride, nonyl phenol, adipates, citrates, and phthalates), or by using the relative response factor (charts) or semi-quantitatively to internal standards (toluene or C_{30}). It is specifically stated in the table with results which components are calculated to internal standards. The quantification is semi-quantitative for these components corresponding to a larger uncertainty (estimated 50-200%).

The limit of detection is 0.2 mg/kg.

4.2.3 Vinyl chloride in air

The exposed SP-tubes are thermally desorbed and analysed at combined gas chromatography and mass spectrometry (GC/MS-SIM).

The limit of detection is 0.01 mg/kg.

4.2.4 Aldehydes

The exposed aldehyde tubes (DNPH coated) are desorbed at elution with acetonitrile and analysed at liquid chromatography with UV detection (HPLC/UV). The content is calculated to relevant standards.

The limit of detection is 0.1 mg/kg.

5 Results

5.1 Mapping

5.1.1 Market contact

Following have been contacted:

- Four foreign manufacturers
- Fourteen hobby distributors wholesale and retail
- Six larger supermarket chains
- One industrial organization (FFFH)

Furthermore, the Internet has been searched including sites from the Forbrugerinformationen (Consumer Information), Öko Test, Consumer Safety, Grøn Information (Green Information), and Chemical Awareness.

5.1.2 Selection of products

Market contact indicated that only four types of clay for oven hardening are sold on the Danish marker. All types of clay consist of PVC mass. According to EPA two ordinary types of clay have been included in the test meaning types that are not meant for oven hardening.

The selection of the products was made in co-operation with Anette Orloff of the Danish Environmental Protection Agency.

Table 1 stated name, description, and manufacture/supplier. A table with additional information is enclosed as appendix A.

In connection with the preparation of this report the supplier of 4 informed us that the import of the product had ceased.

Table 1. Products included in the project.

Description	Manufacture/supplier
Clay mass for oven baking	Panduro Hobby
Clay mass for oven baking	Danmore Hobby ApS
Clay mass for oven baking	Kreativ Hobby A/S
Clay mass for oven baking	Vestergaard ApS
Soft dough - not for oven baking	Top Toy A/S
Traditional dough - not for oven baking	Top Toy A/S

5.2 Content analysis results

5.2.1 Organic tin compounds

The results for organic tin compounds are stated in table 2.The limit of detection is stated in section 4.1.2.

Table 2. Results for organic tin compounds. The results are stated in μg organotin cation/kg. Two results per product indicate double identification.

	Clay – for oven baking								Dough – not for oven baking			
	3		2		1		4		5		6	
Monobutyltin (MBT)	-	-	-	-	-	-	-	-	-	-	-	-
Dibutyltin (DBT)	-	-	-	-	-	-	-	-	-	-	-	-
Tributyltin (TBT)	-	-	-	-	-	-	-	-	-	-	-	-
Tetrabutyltin	-	-	-	-	-	-	-	-	-	-	-	-
Monooctyltin	-	-	-	-	-	-	-	-	-	-	-	-
Dioctyltin	-	-	-	-	-	-	-	-	-	-	-	-
Tricyclohexyltin	-	-	-	-	-	-	-	-	-	-	-	-
Triphenyltin	-	-	-	-	-	-	-	-	-	-	-	-

-: Means less than the limit of detection.

5.2.2 Organic extractable compounds

Table 3 contains the result of the vinyl chloride analysis and the organic extractable substances from the GC/MS screening. Some components could be identified at the screening and others are stated with a component name in brackets, where the component name presents the most viable estimate. Other components are stated with a group designation as e.g. aliphatic hydrocarbons. The detected phthalate compounds are stated in table 4.

Table 3. Results of the vinyl chloride and GC/MS-screening of clay. With the exception of vinyl chloride internal standard has been used for calculation. Uncertainty of the semi-quantitative results is 50-200% as stated in the method description. The results are calculated to internal standards and relevant standards. The results are stated in mg/kg. Two results per product indicate double identification.

	Clay - for oven baking								Dough – not for oven baking			
	3		2		1		4		5		6	
Vinyl chloride	-	-	-	-	-	-	-	-	-	-	-	-
Benzene	-	-	-	-	-	-	-	-	-	-	-*	-*
Hexanol	21	17	-	-	-	-	-	-	-	-	-	-
Benzaldehyde	-	-	-	-	-	-	23	28	-	-	-	-
Benzoic acid	-	-	-	-	-	-	-	-	-	-	4200	3700
Ethyl glycol	-	-	-	-	31	18	270	310	-	-	-	-
Benzyl chloride	-	-	-	-	-	-	59	74	-	-	-	-
Benzyl alcohol	-	-	-	-	-	-	650	780	-	-	-	-
Penta methyl heptane	28	23	-	-	-	-	-	-	-	-	-	-
Ethyl hexanol	17	13	9,3	9,8	15	36	330	430				
Octanol	360	330	-	-	-	-	-	-	-	-	-	-
Ethyl hexane acid	-	-	9000	8800	-	-	-	-	-	-	-	-
Decanal	-	-	-	-	47	34	-	-	-	-	-	-

-: Means less than the limit of detection.
*: Sample 6 has been analysed separately to a benzene standard.

Table 3. Continued. Results of the vinyl chloride and GC/MS-screening of clay. With the exception of vinyl chloride internal standard has been used for calculation. Uncertainty of the semi-quantitative results is 50-200% as stated in the method description. The results are calculated to internal standards and relevant standards. The results are stated in mg/kg. Two results per product indicate double identification.

	Clay - for oven baking								Dough – not for oven baking			
	3		2		1		4		5		6	
Dimethylethyl cyclo hexanol	12	11	-	-	-	-	-	-	-	-	-	-
Cyclodecan	460	400	-	-	300	260	-	-	-	-	-	-
Phthalate acid anhydrid	-	-	-	-	-	-	-	-	-	-	13	11
Piperonal	-	-	-	-	-	-	-	-	-	-	130	100
Hydroxymethoxy benzaldehyde	-	-	-	-	-	-	-	-	-	-	870	720
Chloroctane	-	-	-	-	-	-	43	55	-	-	-	-
Tetradecene	-	-	-	-	-	-	19	26	-	-	-	-
Undecanol	37	27	-	-	32	27	-	-	-	-	-	-
Chlordodecane	-	-	-	-	-	-	330	450	-	-	-	-
Hexyl octyl ether	32	31	-	-	-	-	-	-	-	-	-	-
Decene	-	-	330	450	150	120	-	-	-	-	-	-
Dodecanoic acid	45	50	-	-	-	-	-	-	-	-	-	-
Hexyl benzoic acid ester	18	24	-	-	-	-	-	-	-	-	-	-
Cyclododecane	-	-	-	-	38	31	-	-	-	-	-	-
Chlortetradecane	-	-	28	53	-	-	58	58	-	-	-	-
Heptadecane	-	-	-	-	-	-	260	240	-	-	-	-
Dodecanamide	75	120	-	-	-	-	-	-	-	-	-	-
Benzyl benzoate	-	-	-	-	-	-	10	6	-	-	-	-
Tetradecanoic acid	2600	3300	-	-	-	-	-	-	-	-	-	-
Aliphatic benzoic acid ester	120	140	-	-	-	-	-	-	-	-	-	-
C_{16}, alcohol, unsaturated or cyclic	270	300	720	690	1300	1000	76	100	-	-	-	-
Chlorhexadecane	-	-	-	-	-	-	200	200	-	-	-	-
Ethylhexyl decanoic acid ester	15	16	-	-	-	-	-	-	-	-	-	-
Hexadecanoic acid	1000	160	-	-	97	85	59	100	-	-	-	-
Octadecanol	590	630	1300	1500	2900	2400	45	110	-	-	-	-
Octadecanoic acid	370	860	14	22	72	80	83	130	-	-	-	-
Methyl octadecanoic acid ester	-	-	-	-	-	-	13	14	-	-	-	-
Docosane	250	250	-	-	150	130	42	40	-	-	-	-
Dicyclohexyl-1,2-benzene dicarboxylic acid ester	-	-	-	-	220	180	-	-	-	-	-	-
Diethylhexyladipate (DEHA)	-	-	-	-	-	-	38	40				

-: Means less than the limit of detection.
*: Sample 6 has been analysed separately to a benzene standard.

Table 3 continued. Results of the vinyl chloride and GC/MS-screening of clay. With the exception of vinyl chloride internal standards have been used for calculation. Uncertainty of the semi-quantitative results is 50-200% as stated in the method description. The results are calculated to internal standards and relevant standards. The results are stated in mg/kg. Two results per product indicate double identification.

	Clay - for oven baking								Dough – not for oven baking			
	3		2		1		4		5		6	
Aliphatic hydrocarbons	130	110	200	140	120	70	700	790	-	-	-	-
Aliphatic alcohols	3.3	2.0	170	250	1900	1500	280	370	-	-	140	230
Aliphatic ethers	33	41	-	-	78	68	-	-	-	-	-	-
Aliphatic esters	15	14	110	110	120	120	24	22	-	-	-	-
Aliphatic hydrocarbons, unsaturated, cyclic, or alcohol	200	250	5500	5400	40	26	3500	4300	190000	160000	16000	13000
Aromatic compounds	4.7	2.2	170	120	100	83	27	26	-	-	-	-
Phenol compounds	-	-	1100	790	-	-	-	-	-	-	-	-
Unidentified components	490	650	1700	1500	1400	1000	4100	4000	-	-	28	14

-: Means less than the limit of detection.
*: Sample 6 has been analysed separately to a benzene standard.

Table 4 states the phthalate compounds detected in the GC/MS screening. Accordingly the samples are analysed at GC/FID with a view to quantification of the phthalates.

Table 4. Analytical results of phthalate compounds detected at the GC/MS screening. Calculated to phthalate standards. The results are stated in mg/kg. The two results per product states double identification.

	Clay - for oven baking								Dough – not for oven baking			
	3		2		1		4		5		6	
Dimethyl phthalate	-	-	-	-	-	-	-	-	-	-	-	-
Diethyl phthalate	-	-	-	-	-	-	-	-	-	-	-	-
Dibutyl phthalate	-	-	-	-	43	200	91	120	-	-	-	-
Diisobutyl phthalate	-	-	-	-	-	-	-	-	-	-	-	-
Dipropyl phthalate	-	-	-	-	-	-	64	67	-	-	-	-
Diisopropyl phthalate	-	-	-	-	-	-	-	-	-	-	-	-
Dipentyl phthalate	-	-	-	-	-	-	-	-	-	-	-	-
Diisopentyl phthalate	-	-	-	-	-	-	-	-	-	-	-	-
Diphenyl phthalate	-	-	-	-	-	-	-	-	-	-	-	-
Butylbenzyl phthalate	-	-	-	-	-	-	37000	37000	-	-	-	-
Diethylhexyl phthalate (DEHP)	-	-	-	-	600^	580^	21	18	-	-	-	-
Dicyclohexyl phthalate	-	-	-	-	-	-	-	-	-	-	-	-
Butylcyclohexyl phthalate	-	-	-	-	-	-	-	-	-	-	-	-
Diheptyl phthalate	41000	43000	15000	15000	-	-	-	-	-	-	-	-
Diisoheptyl phthalate	-	-	-	-	-	-	-	-	-	-	-	-
Di-n-octyl phthalate	87000	90000	-	-	170	150	-	-	-	-	-	-
Diisoocty phthalate	-	-	-	-	-	-	-	-	-	-	-	-
(Di(2-ethylhexyl) iso phthalate)*	-	-	-	-	-	-	140000	130000	-	-	-	-
Octyldecyl phthalate	63000	65000	-	-	470	440	-	-	-	-	-	-
Diisodecyl phthalate	-	-	-	-	-	-	-	-	-	-	-	-
Didecyl phthalate	-	-	-	-	-	-	-	-	-	-	-	-
Di-n-nonyl phthalate	-	-	-	-	-	-	-	-	-	-	-	-
Diisononyl phthalate	-	-	97000	99000	-	-	-	-	-	-	-	-
Unidentified phthalates	23000	24000	48000	49000	230000	230000	700	700	-	-	130^^	61^^

-: Means less than the limit of detection.
*: Means that the component has been quantified as an unidentified phthalate as the external standar was not available. The identification of the component is made by GC/MS using the mass spectrum.
^: Means three peaks are quantified together as they could not be separated by. GC/FID. The three peaks are dicyclohexyl phthalate, DEHP and an unidentified phthalate. The unidentified phthalate and DEHP each equal 2/5 of the sum.
^^: Means that the sample is not re-analysed at GC/FID, meaning that the values states the result of the GC/MS screening. The values are therefore defective with an uncertainty described in the chapter on methods.

Phthalate compounds are identified at GC/MS by means of external standards. Furthermore, several compounds of unidentified phthalates have been detected. A total content of up to 24% phthalate has been detected:

	Clay - for oven baking				Dough – not for oven baking	
	3	2	1	4	5	6
Sum of phthalates	22%	16%	23-24%	17%	< 0.0005%	0.006-0.01%

Besides phthalates only one softener was detected – diethylhexyl adipate (DEHA) that was found in minor amounts in 4.

At the following analysis phthalates corresponding to a technical phthalate mixture sent to MILJØ-KEMI, Dansk Miljø Center A/S has been detected in product 3. According to the manufacturer's information the technical CAS no is 68515-51-5.

5.3 Emission test

Due to two separate emission tests with following analysis there may be higher deviation between the double identifications than seen at the content analyses.

5.3.1 Test at 130°C

Table 4 states the components detected at the collection of air during the heating test of the products to 130°C. The identifiable components are stated by name, whereas components with less identification security are stated by name in parenthesis with the best estimate. Other components are stated as groups.

The result is stated as mg substance emitted per kg sample. All emission tests are carried out as double identification.

Table 5. Vinyl chloride and VOC/SVOC collected from the emission test performed at 130°C. The results are stated at mg substance emitted per kg sample. Information regarding the calculation is stated as a footnote, the others are calculated using the relative response factors (charts). Uncertainty of the semi-quantitative results is 50-200% as stated in the method description. The Two results per product indicate double identification.

	Clay for oven baking								Dough not for oven baking			
	3		2		1		4		5		6	
Vinyl chloride#	-	-	-	-	-	-	-	-	-	-	-	-
Benzaldehyde	-	-	-	-	-	-	4.0	2.3	-	-	-	-
Ethyldi glycol*	-	-	-	-	-	-	14	8.5	-	-	-	-
Benzyl alcohol	-	-	-	-	-	-	80	50	-	-	-	-
Octanol	1.1	5.2	-	-	-	-	-	-	-	-	-	-
Ethylhexanol	0.30	-	-	-	0.91	0.43	30	17	-	-	-	-
Undecanol*	-	-	-	-	-	-	-	2.1	-	-	-	-
Decanal*	-	-	-	-	3.8	1.7	-	-	-	-	-	-
Undecene*	0.49	2.6	-	-	1.9	0.72	-	-	-	-	-	-
Undecane	0.28	1.9	-	-	-	0.63	-	-	-	-	-	-
Ethyl hexanoic acid*	-	-	22	73	11	-	-	-	-	-	-	-
Nonanol*	-	-	0.67	3.1	-	-	-	-	-	-	-	-
Cyclodecane*	-	9.2	-	-	15	5.4	-	-	-	-	-	-
Ethylnonene*	-	-	-	-	-	-	1.8	1.0	-	-	-	-
C_{12}-C_{17}*	-	-	-	-	-	-	-	-	320	360	890	590
Tridecane	0.24	2.2	-	-	-	-	-	-	-	-	-	-
Tetradecane	-	1.8	0.16	0.59	-	-	-	-	-	-	-	-
(Diheptylether)*	-	-	1.1	4.7	-	-	-	-	-	-	-	-
Pentadecane	0.30	2.8	-	-	-	-	2.8	2.5	-	-	-	-
(Methyloctanol)*	-	-	0.33	2.1	-	-	-	-	-	-	-	-
Heptadecane*	-	-	-	-	-	-	-	1.9	-	-	-	-
Butylbenzyl phthalate#	-	-	-	-	-	-	3.1	4.6	-	-	-	-
Diisooctyl phthalate, Diisononyl phthalate, Diisodecyl phthalate#	¤	0.39	0.23	0.75	-	-	-	-	-	-	-	-
Nonylphenol#	¤	0.66	1.7	6.0	2.1	1.5	-	-	-	-	-	-
(Glycerol tricaprylate) ^	¤	4.1	3.8	3.5	3.1	2.9	3.6	4.0	-	-	-	-
Unknown phthalates^	-	-	1.9	1.4	2.7	1.7	3.8	5.2	-	-	-	-
Unknown^	0.7	2.8	12	15	34	23	7.4	8.6	-	-	-	-
Sum of others^	¤	57	43	77	30	16	79	49	9.0	10	57	35

-: Means less than the limit of detection
¤: No replicate analysis
#: Calculated to external standard
*: Calculated to toluene
^: Calculated to C_{30}

5.3.2 Test at 200°C

Table 5 states the components detected at the collection of air during the heating test of the products to 200°C. This temperature simulates "worst case scenario". The identifiable components are stated by name, whereas

components with less identification security are stated by name in parenthesis with the best estimate. Other components are stated as groups.
The results are stated as mg substance emitted per kg sample. All emission tests are carried out as double identification.

It should be noted that the figures from 5 and 6 are the results of a five-minute exposure respectively, whereas the others have been exposed for thirty minutes. The difference is cause by return water from the two products that effected the development of condensated water when exposed for more than five minutes. The results may therefore be underestimated.

Table 6 Vinyl chloride and VOC/SVOC collected from the emission test at 200°C. Results are stated in mg substance emitted per kg sample. Information regarding the calculation is stated as a footnote, the others are calculated using the relative response factors (charts). Uncertainty of the semi-quantitative results is 50-200% as stated in the method description. Two results per product indicated double identification.

	Clay for oven baking								Dough not for oven baking			
	3		2		1		4		5		6	
Vinyl chloride#	-	-	-	-	-	-	-	-	-	-	-	-
(Chlorobutan)*	-	-	-	-	-	-	12	21	-	-	-	-
Benzene	4.9	7.2	-	-	4.7	9.0	130	210	-	-	-	-
Butanone	11	20	9.3	3.8	39	35	-	-	-	-	23	21
(Methylbutanone)*	-	3.4	2.5	-	-	-	-	-	-	-	-	-
(Pentanone)*	-	-	-	-	7.7	6.4	-	-	-	-	5.2	5.2
Pentanal	15	12	9.3	5.6	27	26	10	-	-	-	18	18
Hexanone	-	-	5.3	3.8	10	8.7	5.9	-	-	-	-	-
(Hexanol)*	11	17	-	-	-	-	-	-	-	-	-	-
Hexanal	11	10	3.4	2.4	16	15	15	8.5	-	-	10	7.0
Hydrobutanoic acid*	-	-	-	-	6.0	4.7	-	-	-	-	-	-
Heptanone*	6.8	5.7	3.6	4.9	12	11	5.7	3.9	-	-	7.7	6.3
Heptanal	6.9	6.8	4.1	2.7	22	24	3.9	-	-	-	9.4	9.3
Benzaldehyde	-	-	-	-	-	-	32	31	-	-	-	-
(Heptanol)*	-	-	4.6	3.3	-	-	-	-	-	-	-	-
Nonane	-	-	-	-	-	-	-	-	-	-	4.0	5.2
Methylheptanone	-	-	-	-	-	-	-	-	-	-	-	3.4
(Octanone)*	-	-	2.1	1.3	10	10	3.6	-	-	-	4.5	4.6
Ethyldi glycol*	-	-	-	-	-	-	41	32	-	-	-	-
Benzyl chloride*	-	-	-	-	-	-	140	190	-	-	-	-
(C_9-alkane)*	-	-	-	-	-	2.7	12	21	-	-	-	-
(C_{10}-alkane)*	-	-	-	-	-	6.2	-	-	-	-	-	-
(C_{11}-alkane)*	-	-	-	-	-	3.0	-	-	-	-	-	-
Benzyl alcohol	-	-	-	-	-	-	230	210	-	-	-	-
Octanal	13	16	4.5	2.2	12	12	-	-	-	-	10	11
Octanol*	40	50	-	-	-	-	-	-	-	-	-	-
(Chloroctane)*	4.2	6.3	-	-	-	-	-	-	-	-	-	-
(Octanoic acid)*	9.4	18	-	-	11	10	-	-	-	-	-	-
Ethylhexanol	6.4	7.9	1.5	1.8	2.9	3.8	110	120	-	-	-	-
Decane	-	-	-	-	7.4	7.5	-	-	-	-	3.7	4.9
(Decanal)*	7.5	9.3	-	-	-	-	-	-	-	-	-	-

-: Means less than the limit of detection.
#: Calculated to external standard
*: Calculated to toluene

Table 6 continued. Vinyl chloride and VOC/SVOC collected from the emission test at 200°C. Results are stated in mg substance emitted per kg sample. Information regarding the calculation is stated as a footnote, the others are calculated using the relative response factors (charts). Uncertainty of the semi-quantitative results is 50-200% as stated in the method description. Two results per product indicated double identification.

	Clay for oven baking								Dough not for oven baking			
	3		2		1		4		5		6	
(Nonanon)*	3.3	6.3	3.0	-	-	6.5	4.3	-	-	-	6.5	6.0
Nonanal	13	15	5.5	3.8	15	15	6.8	5.6	-	-	11	12
Octyloxirane*	-	-	1.5	1.1	-	-	-	-	-	-	-	-
Undecene*	4.9	5.2	-	-	4.9	4.9	-	-	-	-	-	-
Undecane	3.6	4.1	1.4	0.93	3.7	4.1	-	-	-	-	4.9	6.7
Ethyl hexanoic acid*	-	-	430	470	240	88	98	45	-	-	-	-
(Methylindene)*	-	-	-	-	-	-	4.1	4.5	-	-	-	-
Nonanol*	-	-	11	8.4	-	-	-	-	-	-	-	-
(Furfural)*	-	-	-	-	-	-	-	-	9.5	10	-	-
(Octanoic acid)*	-	-	13	25	-	-	21	16	8.6	14	17	15
Cyclodecane*	29	29	-	15	45	-	-	-	-	-	-	-
(Dodecene)*	-	-	4.5	-	-	-	-	-	-	-	-	-
(decen-on)*	-	-	-	-	7.6	14	-	-	-	-	-	-
Dodecane	4.0	5.2	4.3	-	2.7	2.7	-	-	-	-	-	-
C_{12}-C_{17}*	-	-	-	-	-	-	-	-	1600	1900	9700	9700
(Ethyldihydro-(3H)-furanon)*	-	-	-	-	4.2	4.3	-	-	-	-	-	-
(Dihydropropyl-(3H)-furanon)*	-	-	-	-	5.7	5.5	-	-	-	-	-	-
(Butyldihydro-(3H)-furanon)	-	-	4.1	-	3.5	-	5.0	-	-	-	-	-
Tetrahydropropyl-(2H)-pyranon	-	-	-	-	-	-	5.2	-	-	-	-	-
Phthalic acid anhydride*	15	29	11	15	9.4	-	17	15	-	-	-	-
(3H)-isobenzo-furanon*	-	-	-	6	-	-	-	-	-	-	-	-
Ethylnonene*	-	-	-	-	-	-	71	66	-	-	-	-
(Decanoic acid)*	7.5	14	13	25	16	21	23	19	6.9	12	-	-
Decanal*	-	-	-	-	30	29	3.0	-	-	-	4.3	4.0
(Undecanal)*	4.3	4.9	-	-	4.0	4.7	-	-	-	-	-	-
(Undecanol)*	-	-	4.5	5.8	-	73	34	31	-	-	-	-
(Tetradecene)*	-	-	-	-	7.6	15	4.3	4.2	-	-	-	-
Tridecane	6.8	7.4	2.1	-	-	2.1	-	-	-	-	7.2	11
Tetradecane	3.5	3.8	2.1	2.4	-	-	2.0	1.8	-	-	9.2	10
Tetradecanoic acid*	69	41	-	-	34	-	-	-	-	-	-	-
(Hexyldihydro-(3H)-furanon)*	-	-	3.7	-	-	-	5.9	-	-	-	-	-
Chlorododecane*	-	-	37	7.6	-	-	59	55	-	-	-	-
(Dodecanal)*	-	-	-	-	2.5	2.6	2.9	-	-	-	-	-
Pentadecane	5.7	5.2	1.7	3.5	-	-	8.4	7.9	-	-	-	-

-: Means less than the limit of detection.
#: Calculated to external standard
*: Calculated to toluene

Table 6 continued. Vinyl chloride and VOC/SVOC collected from the emission test at 200°C. Results are stated in mg substance emitted per kg sample. Information regarding the calculation is stated as a footnote, the others are calculated using the relative response factors (charts). Uncertainty of the semi-quantitative results is 50-200% as stated in the method description. Two results per product indicated double identification.

	Clay for oven baking								Dough not for oven baking			
	3		2		1		4		5		6	
Methylundecane*	-	-	-	-	-	-	98	-	-	-	-	-
Dimethylundecane	-	-	-	-	-	-	-	-	-	-	7.2	4.8
Cyclododecane*	-	-	2.5	-	15	21	-	-	-	-	-	-
Dodecanoic acid*	5.5	7.4	3.9	-	5.7	7.5	5.2	3.1	-	-	-	-
Cyclotetradecane*	-	-	-	-	-	-	15	12	-	-	-	-
Chlortetradecane*	-	-	-	-	-	-	21	19	-	-	-	-
(Pentadecanon)*	2.9	3.4	-	-	-	-	-	-	-	-	-	-
Hexadecane	-	-	-	-	-	-	3.9	3.2	-	-	-	-
(Heptadecene)*	-	-	-	-	-	-	27	23	-	-	-	-
Heptadecane*	-	-	-	-	4.7	15	71	66	-	-	-	-
Dibutyl phthalate#	-	-	6.0	5.6	-	0.37	4.0	5.3	-	-	-	-
Dipentyl phthalate#	6.0	3.2	-	0.49	-	-	4.0	5.1	-	-	-	-
Butylbenzyl phthalate#	**	**	2.6	2.6	-	0.95	930	1000	-	-	-	-
Diethylhexyladipate (DEHA)#	-	-	-	-	-	-	-	-	-	-	0.2	0.2
Diethylhexyl phthalate (DEHP)#	***	***	21	23	2.5	2.8	4.6	0.5	-	-	-	-
Di-n-octyl phthalate#	***	***	210	230	0.7	9.9	**	**	-	-	-	-
Diisodecyl phthalate+Dinonyl phthalate#	¤	¤	600	580	4.9	18	-	-	-	-	-	-
Nonylphenol#	7.5	3.2	150	130	12	22	8.1	11	-	-	-	-
Cyclotetradecane^	9.8	9.3	-	-	-	-	-	-	-	-	-	-
Hexadecanoic acid	92	82	-	-	-	-	-	-	-	-	-	-
Heptadecanol^	15	13	-	-	-	-	-	-	-	-	-	-
Ethylhexanoic acid decyl ester^	-	-	81	63	-	-	-	-	-	-	-	-
Pentadecanal^	-	-	-	-	-	-	3.5	6.2	-	-	-	-
(Tetradecadien) ^	-	-	-	-	-	-	7.3	10	-	-	-	-
(Glycerol Tricaprylate) ^	-	-	96	76	89	110	88	120	92	78	99	86
Unknown phthalates^	3000	3100	1200	1100	835	710	2400	2700	-	-	-	-
C_{10}-C_{14} multi component*	-	-	-	-	-	-	-	-	-	-	420	460
Alkane*	12	12	-	-	6.8	7.5	-	-	-	-	8.9	18
Unknown*	440	380	340	260	220	330	700	800	150	120	160	160
Sum of others*	220	220	2000	1700	250	570	100	56	49	110	380	14

-: Means less than the limit of detection.
¤: Means that the limit of detection is increased to 1.0 mg/kg due to interference
**: Means that the limit of detection is increased to 4.0 mg/kg due to interference.
***: Means that the limit of detection is increased to 9.0 mg/kg due to interference.
#: Calculated to external standard
*: Calculated to toluene
^: Calculated to C_{30}

Diisodecyl phthalate and diisononyl phthalate are summarized in table 5 as they could not be separated chromatographically.

5.4 Result evaluation

Generally, the detected components in the products from the content analysis correspond with the detected components in the emission. However, there are differences between the results of the content analysis and the emission test for single components. This is caused by different conditions during treatment: the emission primarily contains the most volatile compounds from the products and the compounds that are formed and released during heating at oxidation and hydrolysis.

Now and then components are detected in the emission that cannot be detected in the content analysis due to interference from other components. At the emission the distribution in the concentration between the different components according to their chemical/physical parameters, primarily vapour pressure and diffusion coefficient. In some cases this changed distribution can reveal components present in minor amounts.

6 Summary and conclusion

6.1 Content analysis

No content of organic tin compounds or vinyl chloride were detected in the products.

The screening for organic substances in the products indicated several different substances whereof the majority could be identified specifically.

The non-baking products contained less than 0.01 per cent phthalates. The oven baking PVC products contained phthalates in levels from 16% to 24%.

Generally the two products are very different. The oven baking products contained a large amount of different components: unsaturated and saturated hydrocarbons, chlorinated hydrocarbons, cyclic and aromatic hydrocarbons, alcohols, acids, phthalates etc. The two products that were not intended for oven baking only contained single volatile and semi-volatile components besides hydrocarbons.

6.2 Emission test

There is a good conformity between the content of the components in the products and the components detected at the emission test.

Vinyl chloride was not detected from at products at the emission test.

The test performed at 200°C detected most substances, generally the same substances detected at the content analysis: aldehydes, ketones, unsaturated hydrocarbons, chlorinated hydrocarbons, alcohols, acids, phthalates etc. At the test performed at 130°C, which is the prescribed temperature for baking clay, a minor amount of the substances detected from the 200°C test was detected. Furthermore, all substances are possible in minor amounts.

The two non-baking products contained aldehydes, ketones, and alkenes at 200°C and at 130°C only alkenes were detected in the emission.

7 Appendix A: Table of purchased products

Product name	Product-description	Name and address of the store where the product was purchased	Purchase date
1	Clay for oven baking	Directly at the importer	15/8-01 + 20/9-01
2	Clay for oven baking	Terapi-Hobby Bøgekildevej 24 DK-8361 Hasselager Phone: 86 28 34 11	20/9-01
3	Clay for oven baking	Panduro Hobby as Badstuegade 5 DK-8000 Århus C Phone: 86 18 22 22	20/9-01
4	Clay for oven baking	Kreativ Hobby Mads Bjerresvej 10 DK-7500 Holstebro	20/9-01
5	Soft dough – not intended for oven baking	TOYS R'US Århus	
6	Traditional dough – not intended for oven baking	TOYS R'US Århus	