Survey of Chemical Substances in Consumer Products

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Mapping of chemical substances in air fresheners and other fragrance liberating products

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1 Content

2 Introduction

May 2002 Eurofins Danmark A/S was requested to carry out a project for the Danish EPA titled:

- *Mapping and exposure of chemical substances in air fresheners and other fragrance liberating products*

The Danish EPA (Danish EPA) had formulated a project (02/05/02), that forms the basis of the project content and scope.

The Danish EPA is interested in a mapping of which fragrances that is used in the products due to the population's increasing tendency to develop perfume allergy. EU's scientific committee on cosmetic products and non-food products has identified 24 specific fragrance ingredients as allergens that forms the background for the analyses.

Besides the quantification of the specific fragrance ingredients the project includes a qualitative analysis of solvents and a qualitative analysis for groups of other components that are able to liberate fragrances (assessed from chemical functional groups).

Manufacturers/retailers have had an opportunity of commenting on the report before publication. All comments are included in the report.

Project leaders at the Danish EPA were Anette Ejersted and Annette Orloff.

The products included in this project are anonymous in this report.

3 Mapping

3.1 Mapping of the market for air fresheners and other fragrance liberating products.

During recent years the tendency to develop perfume allergy in the population has been increasing. Among other things this may be attributed to the fact that a larger proportion of the population are using air fresheners in the home and in the car. Moreover, there are more product types and fragrance variants in the market than ever before.

In order to obtain an overview of the air freshener market the following stores/supermarkets that are typical dealers of products for the home and the car were contacted:

- FDB
- Dansk Supermarked
- Matas
- Århus Autosport

The above mentioned companies were asked to complete a questionnaire indicating all air fresheners that they market and the different fragrance ingredient types. In accordance with the Danish EPA solid blocks for the toilet (toilet freshener) were decided not to be included in the project. In the questionnaire name of manufacture, origin, and annual market share should be completed. From the information from the trades and the market air fresheners were generally divided into the following groups: suspending, electrical, spray, balls, gel plates for table or wall, and pressure can. Each group contains varying product amounts (the stated numbers are assessed from a general impression of the market based on the contact to the manufacture and supplier).

- Suspending – few manufactures (3-4), several fragrances (10-15)
- Electrical – several manufactures (5-8), several fragrances (5-10)
- Spray – few manufactures (2-3), several fragrances (5-10)
- Balls – few manufactures (2-3), many fragrances (10-15)
- Gel plates/pressure cans – several manufactures (5-8), several fragrances (10-15)

Nineteen air fresheners were selected covering the market within the different groups. The products were selected to represent the various areas of application and origin, and a certain sales volume.

The nineteen air fresheners can be divided into two main groups: home and car.

3.2 Car

Six products are used in the car. Three of these are suspending, two are electrical and connected to the car's ventilation installation, and one product is a spray for all auto textiles.

3.3 Home

Thirteen products are used in the home. Four of these are electrical (connected to plug) and applied in the entire house, three of the products are small balls for the vacuum cleaner (sucked into the vacuum cleaner), two are sprays for all rooms, and four products are mainly used in the bathroom. Including three gel types (where one product consists of a glass plate with gel), and a plastic pressure can.

3.4 Production and sales

The nineteen products are mainly produced in Spain, France, and Sweden. Single products are produces in Italy, United Kingdom, and Germany. Generally it is these countries that export air fresheners to the Danish market. Three main players dominate the market. Twelve products originate from these three producers - of which seven from one producer have been included in this project.

The manufacturers informed that 5% of the Danish population use air fresheners in the home or the car. For comparison Southern Europe e.g. Italy 70% of the population use air fresheners every day. A total of 1,608,850 air fresheners were sold in Danish groceries in 2001 for the home and the car. Petrol stations, auto equipment dealers, and garages are not included in the figure. Predominantly auto equipment dealers sell suspending of cardboard for the car. In 2001 approximately 500,000 pieces were sold in Denmark.

3.5 Exposure

Should 5% of the population use air fresheners approximately 268,000 persons would be in contact with air fresheners. If it is assumed that there are 3.5 persons in every household it corresponds to 76,000 households using air fresheners for their car and home. If the sales figures of approximately 2 mill. air fresheners are true (groceries and auto equipment dealers) it corresponds to air freshener using households in Denmark consuming approximately 26 air fresheners annually.

Furthermore, the producers informed that the fragrance durability for air fresheners vary from 2-3 weeks to 10-11 weeks depending on type. Thus it may be concluded that 268,000 persons are actually exposed to air fresheners all year round and that these often have several air fresheners in the house, e.g. in the bathroom, living room, and in the car.

Generally the producers inform that the market for air fresheners is increasing. Several consumers have shown an interest in products with a more appealing appearance (e.g. glass plate with gel or electric air fresheners) and that can provide a constant fragrance over a longer period. These fragrances are generally of a better quality sensuously than the cheap and traditional formats.

3.6 Selected products

The selected products for the project are stated in the table.

Lab no	Product description	Fragrance
1	Fragrance balls for vacuum cleaner – vacuum cleaner deodorant	Freesia
2	Glass plate with gel	White flowers
3	Stick up for living room. Stick to the wall fragrance strength may vary.	Lavender
4⋆	Electric air freshener for the entire house – the product is connected to the plug - adjustable	Vanilla & Orchid
5	Electric air freshener connected to the car's ventilation system - adjustable	No information
6⋆	Auto suspending (cardboard)	Flower
7	Auto suspending	No information
8	Fragrance remover, spray for textile	No fragrance
9	Electric air freshener for the entire home – the product is connected to the plug	Purity
10⋆	Electric air freshener for the entire home – adjustable	Vanilla-Lily
11	Electric air freshener for the entire home that drives away tobacco and liberates fragrance.	"After Tobacco"
12	Air freshener connected to the car's ventilation system and fragrance liberating – adjustable	"After Tobacco"
13	Fragrance gel in plastic container	Violet
14	Fragrance sticks for vacuum cleaner – vacuum cleaner deodorant	Flower
15	Fragrance freshener for the bathroom – pressure adjustable	Romantic Bouquet
16	Fragrance balls for vacuum cleaner – vacuum cleaner deodorant	Tutti Frutti
17	Spray for living room.	Flower
18	Auto suspending (cardboard)	Skogsfrisk
19	Mini spray bathroom – pressure adjustable	Marine

⋆ Product no longer on the market

4 Analytical methods

4.1 Sample preparation

The samples represent different states wherefore the sample preparation has been determine for every single sample.

Material	Procedure
Liquid	Density is determined after which the sample is measured
Gel and cardboard	The sample is weighed
Balls	The sample is cut and accordingly weighed
Spray	The sample is injected into a glass flask and accordingly weighed.

Packaging, suspending, or other kind of decorative packaging is not included in the analysis.

4.2 Specific fragrance ingredients

Approximately 1 g of the sample is taken and dissolved in 50 ml dichloromethane. The mixture is shaken in a sealed glass container on ultra sound for 30 minutes, after which the sample stands over night at room temperature. The extract is analysed at combined gas chromatography and mass spectrometry (GC/MS). The single components are identified based on their retention time and mass spectrum. The amount of the selected components is determined from the intensity of selective ions that are compared with standard curves of pure compounds dissolved in dichloromethane.

The result is given as a sum at cis/trans isomer occurrence.

It proved impossible to procure an analytical standard of known purity for the fragrance ingredients hydroxymethylpentylcyclohexencarboxaldehyde. Thus the concentration of the single peaks in the chromatogram was calculated from their share of the total area in the chromatogram.

The fragrance ingredients are given in the below mentioned table with specific CAS no, and limits of detection.

	CAS no.	Limit of detection	Danish classification
Amyl cinnamal*	122-40-7	2	
Amylcinnamyl alcohol	101-85-9	4	
Benzyl alcohol	100-51-6	1	Xn R20/22
Benzyl salicylate	118-58-1	1	
Cinnamyl alcohol*	104-54-1	3	
Cinnamal*	104-55-2	1	
Citral	5392-40-5	4	Xi R38 R43
Coumarin	91-64-5	1	
Eugenol*	97-53-0	2	
Geraniol*	106-24-1	1	
Hydroxycitronellal*	107-75-5	2	
Hydroxymethylpentyl-cyclohexenecarboxaldehyde	31906-04-4	10	
Isoeugenol*	97-54-1	2	
Anisyl alcohol	105-13-5	2	
Benzyl benzoate	120-51-4	1	Xn R22
Benzyl cinnamate	103-41-3	1	
Citronellol	106-22-9	6	
Farnesol	4602-84-0	10	
Hexyl cinnamaldehyde	101-86-0	3	
2-methyl-3-(4-tert-butylbenzyl)propionaldehyde	80-54-6	3	
d-Limonene	5989-27-5	2	R10; XI R38 R43 N R50/53
Linalool	78-70-6	2	
Methyl heptine carbonate	111-12-6	2	
3-Methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one	127-51-5	2	

* part of the fragrancemix, physicians use to test against perfume allergy

4.3 Solvents - qualitatively

A part sample is extracted with DMF (Dimethylformamide) added internal standards. 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. All identifications of substances are made from the mass spectrum by comparing with mass spectra in a data library. The spectra that represent the best match are assessed by ”scientific judgement” in each case.

The analyses are carried out as true double determination.

5 Results

5.1 24 specific fragrance ingredients

The result of the analyses for the 24 specific fragrance ingredients is stated in table 1. The limit of detection for the single components varies from 1 mg/kg to 10 mg/kg. The specific limits of detection are stated in the method description.

Table 1. Results for analyses for 24 specific fragrance ingredients in air fresheners and other fragrance liberating products. Two results indicate double determination. The results are given in mg/kg.

	1		2		3		4		5	
Amyl cinnamal	3100	2900	-	-	-	-	-	-	1700	1800
Amylcinnamyl alcohol	-	-	-	-	-	-	-	-	-	-
Benzyl alcohol	370	340	480	500	-	-	-	-	1300	1200
Benzyl salicylate	2100	1900	-	-	-	-	-	-	1300	1200
Cinnamyl alcohol	-	-	-	-	-	-	-	-	-	-
Cinnamal	-	-	-	-	-	-	-	-	-	-
Citral	83	80	-	-	-	-	1800	2000	-	-
Coumarin	15	15	-	-	300	290	-	-	1600	1700
Eugenol	-	-	-	-	15	11	12	12	2800	2900
Geraniol	430	390	-	-	510	410	-	-	1900	2000
Hydroxycitronellal	2300	2000	-	-	-	-	2600	2600	400	440
Hydroxymethylpentyl-cyclohexenecarboxaldehyde	890	660	-	-	-	-	9600	8700	320	310
Isoeugenol	-	-	-	-	-	-	-	-	-	-
Anisyl alcohol	-	-	-	-	-	-	-	-	-	-
Benzyl benzoate	10000	9000	-	-	-	-	-	-	8200	8500
Benzyl cinnamate	190	170	-	-	-	-	-	-	-	-
Citronellol	1600	1400	13000	12000	540	430	-	-	1900	2000
Farnesol	-	-	-	-	-	-	-	-	-	-
Hexyl cinnamaldehyde	4900	4400	-	-	-	-	9400	10000	1800	1900
2-methyl-3-(4-tert-butylbenzyl)propionaldehyde	770	650	6200	5400	-	-	10000	11000	450	520
d-Limonene	110	79	9500	8200	-	-	280	300	6200	6400
Linalool	22000	19000	6100	5500	1800	1500	10000	13000	6100	6400
Methyl heptin carbonate	-	-	-	-	-	-	-	-	-	-
3-Methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one	1300	1200	-	-	-	-	4200	4200	-	-
Total sum	50000	44000	35000	31000	3100	2700	49000	52000	36000	37000
Total sum (weight%)	5.0	4.4	3.5	3.1	0.31	0.27	4.9	5.2	3.6	3.7

-: Means less than the limit of detection

Table 1, continued. Results for analyses for 24 specific fragrance ingredients in air fresheners and other fragrance liberating products. Two results indicate double determination. The results are given in mg/kg.

	6		7		8		9		10	
Amyl cinnamal	750	750	-	-	-	-	660	640	-	-
Amylcinnamyl alcohol	-	-	-	-	-	-	50	17	-	-
Benzyl alcohol	460	290	-	-	12	11	-	-	50000	50000
Benzyl salicylate	5000	5400	-	-	4.2	4.1	6500	6700	500	520
Cinnamyl alcohol	320	320	-	-	-	-	-	-	-	-
Cinnamal	35	33	-	-	-	-	-	-	-	-
Citral	-	-	-	-	-	-	450	530	1800	2400
Coumarin	1400	1400	-	-	-	-	-	-	54	53
Eugenol	160	170	-	-	-	-	360	390	-	-
Geraniol	460	460	-	-	-	-	2200	3100	1400	1200
Hydroxycitronellal	460	450	-	-	-	-	-	-	-	-
Hydroxymethylpentyl-cyclohexenecarboxaldehyde	-	-	-	-	-	-	37000	36000	29000	29000
Isoeugenol	-	-	-	-	-	-	110	120	-	-
Anisyl alcohol	-	-	-	-	-	-	-	-	-	-
Benzyl benzoate	4600	4400	17	7,7	-	-	670	720	4200	4100
Benzyl cinnamate	-	-	-	-	-	-	490	500	-	-
Citronellol	-	-	-	-	-	-	190	280	18000	18000
Farnesol	-	-	-	-	-	-	-	-	-	-
Hexyl cinnamaldehyde	4200	4200	-	-	34	35	21000	22000	8200	8000
2-methyl-3-(4-tert-butylbenzyl)propionaldehyde	490	470	-	-	-	-	26000	27000	1300	1300
d-Limonene	140	140	-	-	-	-	7000	7000	13000	12000
Linalool	3900	3800	-	-	-	-	36000	37000	22000	21000
Methyl heptin carbonate	-	-	-	-	-	-	13	27	14	3.5
3-Methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one	2900	2900	-	-	-	-	1800	2000	14000	13000
Total sum	25000	25000	17	7.7	50	51	140000	140000	160000	160000
Total sum (weight%)	2.5	2.5	0.0017	0.0008	0.0050	0.0051	14	14	16	16

-: Means less than the limit of detection

Table 1, continued. Results for analyses for 24 specific fragrance ingredients in air fresheners and other fragrance liberating products. Two results indicate double determination. The results are given in mg/kg.

	11		12		13		14		15	
Amyl cinnamal	-	-	-	-	-	-	-	-	-	-
Amylcinnamyl alcohol	-	-	-	-	-	-	-	-	-	-
Benzyl alcohol	-	-	-	-	840	830	82	73	-	-
Benzyl salicylate	13000	13000	21	22	-	-	790	740	-	-
Cinnamyl alcohol	-	-	-	-	27	19	-	-	-	-
Cinnamal	-	-	-	-	10	16	-	-	-	-
Citral	-	-	19000	25000	-	-	240	200	-	-
Coumarin	-	-	12000	13000	57	59	25	24	-	-
Eugenol	-	-	8100	9000	-	-	250	240	120	93
Geraniol	-	-	-	-	-	-	8100	8900	-	-
Hydroxycitronellal	-	-	-	-	-	-	-	-	-	-
Hydroxymethylpentyl-cyclohexenecarboxaldehyde	8200	8800	16000	16000	-	-	61000	60000	-	-
Isoeugenol	-	-	-	-	-	-	-	-	26	23
Anisyl alcohol	-	-	-	-	-	-	-	-	-	-
Benzyl benzoate	27	23	290	300	-	-	8400	8100	460	450
Benzyl cinnamate	-	-	-	-	-	-	-	-	-	-
Citronellol	1700	1700	980	1100	-	-	-	-	2900	2700
Farnesol	-	-	-	-	-	-	-	-	-	-
Hexyl cinnamaldehyde	7500	7300	110	120	-	-	-	-	1600	1600
2-methyl-3-(4-tert-butylbenzyl)propionaldehyde	9500	9600	-	-	-	-	-	-	2800	2700
d-Limonene	10000	10000	28000	29000	-	-	820	650	41	46
Linalool	22000	22000	36000	39000	1100	1500	11000	11000	1500	1400
Methyl heptin carbonate	-	-	-	-	-	-	270	270	-	-
3-Methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one	5700	5800	12000	13000	-	-	11000	11000	-	-
Total sum	78000	78000	130000	140000	2000	2400	100000	100000	9500	9000
Total sum (weight%)	7.8	7.8	13	14	0.20	0.24	10	10	0.95	0.90

-: Means less than the limit of detection

Table 1, continued. Results for analyses for 24 specific fragrance ingredients in air fresheners and other fragrance liberating products. Two results indicate double determination. The results are given in mg/kg.

	16		17		18		19	
Amyl cinnamal	-	-	-	-	15000	16000	-	-
Amylcinnamyl alcohol	-	-	-	-	-	-	-	-
Benzyl alcohol	310	310	-	-	380	410	-	-
Benzyl salicylate	-	-	-	-	15000	16000	-	-
Cinnamyl alcohol	-	-	-	-	-	-	-	-
Cinnamal	-	-	-	-	-	-	47	63
Citral	-	-	-	-	25000	26000	-	-
Coumarin	15	15	-	-	-	-	-	-
Eugenol	2100	2000	57	53	7100	7500	3100	3400
Geraniol	-	-	-	-	-	-	6400	6300
Hydroxycitronellal	-	-	450	440	-	-	-	-
Hydroxymethylpentyl-cyclohexenecarboxaldehyde	-	-	-	-	-	-	61000	62000
Isoeugenol	-	-	32	31	-	-	-	-
Anisyl alcohol	-	-	-	-	-	-	-	-
Benzyl benzoate	3100	3100	470	440	310	320	-	-
Benzyl cinnamate	-	-	-	-	-	-	-	-
Citronellol	-	-	-	-	-	-	8300	8400
Farnesol	-	-	-	-	-	-	-	-
Hexyl cinnamaldehyde	-	-	120	110	39	39	2900	2900
2-methyl-3-(4-tert-butylbenzyl)propionaldehyde	-	-	-	-	10000	10000	11000	12000
d-Limonene	720	700	47	49	8400	8700	7200	7200
Linalool	-	-	-	-	970	990	21000	21000
Methyl heptin carbonate	-	-	-	-	-	-	-	-
3-Methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one	-	-	240	220	-	-	5100	5200
Total sum	6300	6100	1400	1300	83000	86000	130000	130000
Total sum (weight%)	0.63	0.61	0.14	0.13	8.3	8.6	13	13

-: Means less than the limit of detection

Summed values up to 16% were detected. The products with the highest values (13-16%) are all liquid. The product with the second lowest value (0.005%) is a product that removes fragrance and does not liberate fragrance, which may explain the low value. The lowest value comes from a fragranceed product; however, the fragrance ingredients are not included in the 24 specific fragrance ingredients.

When products from the same manufacture are compared there is no conjunction as to the detected components and their values. However, samples 11 and 12, both fragranced with "after tobacco", indicate a certain conjunction i.e. they might contain the same technical raw material.

5.2 Solvents – qualitative

Results of the analyses for solvents are stated in table 3. Identification of the substances is marked with an x, as there are no quantitative analyses.

Table 3. Results for analyses for solvents in air fresheners and other fragrance liberating products. Two results indicate double determination.

Component	1		2		3		4		5	
Ethylacetate									x	x
Isopropanol									x	x
Ethanol									x	x
Isoamylacetate										
Isoamylbutyrate										
Hexane acid ethylester										

x: Quantitative identification of the component

Table 3, continued. Results for analyses for solvents in air fresheners and other fragrance liberating products. Two results indicate double determination.

Component	6		7		8		9		10	
Ethylacetate										
Isopropanol					x	x				
Ethanol										
Isoamylacetate										
Isoamylbutyrate										
Hexane acid ethylester										

x: Quantitative identification of the component

Table 3, continued. Results for analyses for solvents in air fresheners and other fragrance liberating products. Two results indicate double determination.

Component	11		12		13		14		15	
Ethylacetate										
Isopropanol									x	x
Ethanol							x	x	x	x
Isoamylacetate							x	x		
Isoamylbutyrate										
Hexane acid ethylester										

x: Quantitative identification of the component

Table 3, continued. Results for analyses for solvents in air fresheners and other fragrance liberating products. Two results indicate double determination.

Component	16		17		18		19	
Ethylacetate								
Isopropanol								
Ethanol							x	x
Isoamylacetate	x	x						
Isoamylbutyrate	x	x						
Hexane acid ethylester							x	x

x: Quantitative identification of the component

Solvents could be detected in six of the products. Two of which are fragrance products for the vacuum cleaner and the remaining products are all liquid for different purposes.

6 Summary and conclusion

6.1 Specific fragrance ingredients

At least one of the 24 components that EU's scientific committee has identified as allergens were detected in all samples. Single components were detected from trace levels (3.5 mg/kg) to large content (62,000 mg/kg corresponding to 6.2 weight%). The total content of the detected components varied from 10 to 162,000 mg/kg corresponding to 0.001 to 16 weight%.

Five products have a total content of ≥ 10% of which four of these products originate from the same supplier. There is no general conclusion for the remaining products as the single products within identical product types vary some.

The total content for the vacuum cleaner products vary from 0.6% to 10%. Auto suspending products varied from the lowest content of 0.001% to 8.4%. Auto products connected to the ventilation system detected content from 3.7% to 14%.

Gel products are used for wall suspending (pressed for fragrance liberation) and for surface placement. These products represent the lowest content from 0.2% to 3.3%.

The liquid samples detected the highest content from 0.9% to 16%.

6.2 Solvents

Solvents could be detected in six products. Two of which are fragrance products for the vacuum cleaner and the remaining products are all liquid used for different purposes.