Survey of Chemical Substances in Consumer Products

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Mapping of chemical substances in earplugs

Phase 2: Analysis of substances

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1 Content

2 Introduction

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

Mapping of chemical substances on earplugs

The Danish Environmental Protection Agency had formulated a project that formed the basis on the content and scope of the project.

Present project is a follow-up on a former project (carried out in 2001 by another sub-contractor than Eurofins Danmark) where the Danish Environmental Protection Agency had purchased 34 different products of earplugs that were all sold in retail or over the Internet.

As earplugs are in close contact with skin over a longer period of time the Danish Environmental Protection Agency partly wanted to collect product information from suppliers and/or manufactures in order to map the content of chemical substances by means of chemical analyses.

Before hand the Danish Environmental Protection Agency had determined the scope of analyses wherefore the analytical programme was determined.

Project leaders for the Danish Environmental Protection Agency were Shima Dobel and Anette Ejersted.

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

The manufacturer of product no. 15 has informed the Danish Environmental Protection Agency that this product is no longer in sale. Instead two other earplugs are sold which do not contain tributhyltin (TBT) and dibuthyltin (DBT).

The manufacturer of product no. 26 has informed the Danish Environmental Protection Agency that no antimon is used in the procuction of their products. The concentration fund is very low and close to the detection limit. This gives no concern for health effects.

3 Scope

3.1 Products

A total of 34 types of earplugs had been purchased for the former project. One of which had been omitted for a new type wherefore this was included in the project instead. Another type was deleted and not replaced. Eurofins Danmark was unable to get into contact with the supplier of a third kind of earplug (foreign supplier). The two latter kinds were therefore not included in the further investigation.

One supplier could inform that three types of earplugs were produced from the exact same material, and the same applies to four other types of earplugs. Only one type has been analysed from this group, however, the result applies to the entire group. Appendix A states identical numbers for the two groups, as it is visible which products that are produced from identical material. These decisions are made in accordance with the Danish Environmental Protection Agency.

The project includes earplugs that are produced from the following materials:

- Polyurethane foam (PUR)
- PVC
- Silicone
- Silicone rubber
- Cotton
- Elastomers
- Siloxan

The material for the single products and a description of the product is stated in the below mentioned table.

Table 1. Short description of the products included in the project. The laboratory no of the single products
(or mixtures) is used in all other result tables.

Lab. no	Product description	Material
1	Fitted disposable earplug (rounded cylinder shaped)	PUR
2	Fitted plug for strap (round)	PUR
3	Fitted plug with or without strap (cylinder shaped)	PVC
4	Fitted plug (cylinder shaped)	PUR
5	Fitted six-sided earplug	PUR
6	Fitted expanding plug (cylinder shaped)	PVC
7	Fitted expanding plug (rounded cylinder shaped	PUR
8	Fitted plug (comforter shaped)	PVC
9	Fitted expanding plug (rounded cylinder shaped)	PUR
10	Fitted, two-coloured plug (rounded cylinder shaped)	PUR
11	Fitted plug (rounded cylinder shaped)	PUR
12	Fitted two-coloured plug in string (metal detectable)	PUR
13	Fitted, two-coloured plug for strap (semi-round with holder)	PVC
14	Mixed sample consisting of soft fitted (rounded cylinder shaped) plug + plug for strap + semi-round plug with injection handle	PUR
15	Fitted plug preventing water percolation (Christmas tree shaped)	PVC
16	Fitted plug with string (Christmas tree shaped)	PVC
17	Fitted earplug in string (toadstool shaped)	Silicone rubber
18	Fitted earplug (toadstool shaped)	Silicone rubber
19	Fitted earplug in string (Christmas tree shaped)	TPE (thermal plastic elastomers)
20	Non-fitted plug with injection cover (Christmas tree shaped)	Silicone
21	Mixed sample consisting of plug for swimming + music + "ordinary" noise + metal detectable (Christmas tree shaped)	Silicone rubber
22	Disposable plug (rounded cylinder shaped)	Down + PE
23	Ear ball	Cotton
24	Non-fitted earplug preventing water percolation	High vulcanised elastomers
25	Non-fitted plug	Silicone
26	Individually fitted plug	Vinyl polydi-

		methyl siloxane
27	Pressure reducing earplug (Christmas tree shaped)	Silicone

3.2 Analyses

The determined analytical programme includes the following analyses:

- Organic tin compounds
- Phthalates
- Antimony
- Brominated flame retardants
- Isocyanates and amines

The organic tin compounds are included as some of these compounds may be used as stabilators in PVC and catalyst at production of PUR. Phthalates are used as e.g. softeners of PVC. Antimony may be used as flame-retardants in plastic in shape of antimony trioxide. The brominated flame-retardants are used as flame-retardants in all types of plastic. Isocyanates form the basis for a production of polyurethane and isocyanates may be transformed to corresponding amines.

In accordance with the Danish Environmental Protection Agency the analysis for isocyanates and amines was exclusively performed on PUR foam products.

4 Analytical methods

4.1 Sample preparation

All samples are cut into small pieces (2-3 mm).

Earplugs made from one material were cut entirely. If the earplug consisted of several types of material only the part that contacts the ear is included in the final test. I.e. the "handle", metal clips, wires, or similar are not included in the analysis.

4.2 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 derived at extractive derivation with sodium tetraethylborate and pentane. The organic phase is added isooctane concentrated and analysed at combined gas chromatography and mass spectrometry (GC/MS) at selective ion monitoring of the compounds in question. The content is calculated to relevant standards.

The analysis is carried out in double determination. The limit of detection varies from 0.002 to 0.010 mg/kg depending on the single component. The specific limits of detection are stated in the table. Uncertainty is 10-15%RSD.

4.3 Brominated flame retardants

4.3.1 Tetrabromobisphenol A (TBBP A)

Principle:
A part sample is extracted with acetonitrile (mobile phase) and analysed accordingly by means of liquid chromatography with UV detection (HPLC/DAD).

The analyses are carried out as true double identification.

The limit of detection is 10 mg/kg, however, the limits of detection have been increased for the products 3, 5, 6, and 13 due to interference from other components in the products at the applied analytical conditions (wavelength). These products are stated in the table of results.

Uncertainty is 10-15%RSD.

4.3.2 Other brominated flame retardants

Principle:
A part sample is extracted with toluene at Soxhlet extraction. The extract is purified on aluminium oxide column and analysed at combined gas chromatography and mass spectrometry (GC/MS). Quantification is carried out at isotopic dilution technique.

The analyses are carried out as true double identification. Uncertainty is 10-15% RSD.

The analysis included the following compounds:

	Limit of detection (mg/kg)
Brominated diphenyl ether (PBDPE)	
4,4'-DiBDPE	1
Total DiBDPE	1
2,4,4'-TriBDPE	1
3,4,4'-TriBDPE	1
Total TriBDPE	1
2,4,4',6-TetraBDPE	1
2,3',4',6-TetraBDPE	1
2,2',4,4'-TetraBDPE	1
2,3',4,4'-TetraBDPE	1
3,3',4,4'-TetraBDPE	1
Total TetraBDPE	1
2,2',4,4',6-PentaBDPE	2
2,3',4,4',6-PentaBDPE	2
2,2',4,4',5-PentaBDPE	2
2,2',3,4,4'-PentaBDPE	2
Total PentaBDPE	2
2,2',4,4',5,6'-HexaBDPE	2
2,2',4,4',5,5'-HexaBDPE	2
Total HexaBDPE	2
2,2',3',4,4',5,6'-HeptaBDPE	2
2,3',3',4,4',5,6'-HeptaBDPE	2
Total HeptaBDPE	2
Total OctaBDPE	10
Total NonaBDPE	10
DecaBDPE	20
Brominated biphenyl (PBB)	
Total TetraBB	1
Total PentaBB	1
Total HexaBB	2
Total HeptaBB	2
Total OctaBB	2
Total NonaBB	10
Total DecaBB	20
Hexabromocyclododecan (HBCD)	20

4.4 Antimony

Principle:
A part sample (approximately 0.25 g) is opened with sulphuric acid and nitric acid in microwave. The extract is filtered and the dissolved metals are determined accordingly on ICP-spectrophotometer (Inductively Coupled Plasma).

The limit of detection is 30 mg/kg. Uncertainty is 10%RSD.

4.5 Phthalates

Principle:
A part sample is taken and extracted with dichloromethane added internal standards. A part sample of the extract is taken and analysed directly at combined gas chromatography and mass spectrometry (GC/MS) with a view to identification of phthalates, and gas chromatography with flame ionisation detection (GC/FID) for quantification. It was not possible to quantify phthalates on GC/FID as the chromatogrammes contained inferring components, making a more specific detection necessary. Thus the components could exclusively be quantified at GC/MS. The content is calculated to relevant phthalate standards i.e. the components that are identified at the analysis. The unidentified phthalates are quantified as DEHP (Diethylhexylphthalate). The analyses are carried out as true double determination.

The limit of detection is 10 mg/kg. Uncertainty is 10-15%RSD.

4.6 Isocyanates and amines

Principle:
The sample is extracted with water-free toluene and added dibutylamine (DBA) for derivation of possible diisocyanates. Ethylchlorformiate is added before analysis for derivation of the diamines. The diamines are thus determined as carbamates. The analyses are carried out at combined liquid chromatography and mass spectrometry (LC/MS). The analyses are carried out as true double determination.

The limit of detection is 0.05 mg/kg. Uncertainty is 10-15%RSD.

5 Results

5.1 Product designation

The product description in table 1 corresponds to the product numbers in all tables.

5.2 Organic tin compounds

The result of the analyses for the eight organic tin compounds is stated in table 1. The limit of detection for the single components is stated in the table.

Table 2. Results for analyses for organic tin compounds in earplugs. Two results indicate double determination. The results are given in mg/kg.

	LOD	2		3		5		6		7	
Monobutyltin (MBT)	0.005	-	-	-	-	41	34	44	73	-	-
Dibutyltin (DBT)	0.005	0.017	0.028	0.051	0.051	1300	1300	1100	1200	0.013	0.019
Tributyltin (TBT)	0.002	0.002	0.006	0.005	0.005	0.26	0.27	3.3	3.6	0.011	0.024
Tetrabutyltin	0.01	-	-	-	-	<0.050*	<0.050*	<0.050*	<0.050*	-	-
Monooctyltin	0.01	-	-	-	-	<0.050*	<0.050*	<0.050*	<0.050*	-	-
Dioctyltin	0.01	-	-	-	-	0.16	0.16	0.13	0.12	-	-
Tricyclohexyltin	0.01	-	-	-	-	<0.050*	<0.050*	<0.050*	<0.050*	-	-
Triphenyltin	0.01	-	-	-	-	<0.050*	<0.050*	<0.050*	<0.050*	-	-

-: Means less than the limit of detection
LOD: i.e. the limit of detection
*: increased limit of detection due to interference

Table 2, continued. Results for analyses for organic tin compounds in earplugs. Two results indicate double determination. The results are given in mg/kg.

	LOD	8		9		10		11		12	
Monobutyltin (MBT)	0.005	0.16	0.16	-	-	-	0.005	-	-	-	-
Dibutyltin (DBT)	0.005	4.5	4.8	0.006	0.006	-	-	0.014	0.011	0.017	0.013
Tributyltin (TBT)	0.002	0.039	0.038	0.003	0.007	-	-	0.003	0.006	0.006	0.006
Tetrabutyltin	0.01	<0.050*	<0.050*	-	-	-	-	-	-	-	-
Monooctyltin	0.01	<0.050*	<0.050*	-	-	-	-	-	-	-	-
Dioctyltin	0.01	<0.050*	<0.050*	-	-	-	-	-	-	-	-
Tricyclohexyltin	0.01	<0.050*	<0.050*	-	-	-	-	-	-	-	-
Triphenyltin	0.01	<0.050*	<0.050*	-	-	-	-	-	-	-	-

-: Means less than the limit of detection
LOD: i.e. the limit of detection
*: increased limit of detection due to interference

Table 2, continued. Results for analyses for organic tin compounds in earplugs. Two results indicate double determination. The results are given in mg/kg.

	LOD	13		14		15		16		17	
Monobutyltin (MBT)	0.005	73	51	0.007	0.012	10	9.4	14	14	<0.020*	<0.020*
Dibutyltin (DBT)	0.005	800	560	0.029	0.030	3.6	3.5	11	11	<0.020*	<0.020*
Tributyltin (TBT)	0.002	0.77	0.61	-	0.002	0.015	0.011	0.020	0.024	<0.010*	<0.010*
Tetrabutyltin	0.01	<0.050*	<0.050*	-	-	<0.050*	<0.050*	<0.050*	<0.050*	<0.050*	<0.050*
Monooctyltin	0.01	0.30	0.27	-	-	<0.050*	<0.050*	<0.050*	<0.050*	<0.050*	<0.050*
Dioctyltin	0.01	1.2	0.85	-	-	0.048	0.061	<0.050*	<0.050*	<0.050*	<0.050*
Tricyclohexyltin	0.01	<0.050*	<0.050*	-	-	<0.050*	<0.050*	<0.050*	<0.050*	<0.050*	<0.050*
Triphenyltin	0.01	<0.050*	<0.050*	-	-	<0.050*	<0.050*	<0.050*	<0.050*	<0.050*	<0.050*

-: Means less than the limit of detection
LOD: i.e. the limit of detection
*: increased limit of detection due to interference

Table 2. continued. Results for analyses for organic tin compounds in earplugs. Two results indicate double determination. The results are given in mg/kg.

	LOD	20		21		22		23		24	
Monobutyltin (MBT)	0.005	-	-	0.050	0.084	<0.050*	0.053	-	-	<0.050*	<0.050*
Dibutyltin (DBT)	0.005	0.017	0.028	4.8	3.5	<0.020*	<0.020*	<0.010*	<0.010*	0.081	0.030
Tributyltin (TBT)	0.002	-	-	0.014	0.011	<0.010*	<0.010*	-	-	-	-
Tetrabutyltin	0.01	-	-	<0.050*	<0.050*	<0.050*	<0.050*	-	-	-	-
Monooctyltin	0.01	-	-	<0.050*	<0.050*	<0.050*	<0.050*	-	-	-	-
Dioctyltin	0.01	-	-	<0.050*	<0.050*	<0.050*	<0.050*	-	-	-	-
Tricyclohexyltin	0.01	-	-	<0.050*	<0.050*	<0.050*	<0.050*	-	-	-	-
Triphenyltin	0.01	-	-	<0.050*	<0.050*	<0.050*	<0.050*	-	-	-	-

-: Means less than the limit of detection
LOD: i.e. the limit of detection
*: increased limit of detection due to interference

Table 2, continued. Results for analyses for organic tin compounds in earplugs. Two results indicate double determination. The results are given in mg/kg.

	LOD	25		26		27	
Monobutyltin(MBT)	0.005	-	-	<0.020*	<0.020*	0.011	0.020
Dibutyltin (DBT)	0.005	0.009	0.011	<0.020*	<0.020*	1.9	3.4
Tributyltin (TBT)	0.002	-	-	<0.010*	<0.010*	0.028	0.023
Tetrabutyltin	0.01	-	-	<0.050*	<0.050*	-	-
Monooctyltin	0.01	-	-	<0.050*	<0.050*	-	-
Dioctyltin	0.01	-	-	<0.050*	<0.050*	-	-
Tricyclohexyltin	0.01	-	-	<0.050*	<0.050*	-	-
Triphenyltin	0.01	-	-	<0.050*	<0.050*	-	-

-: Means less than the limit of detection
LOD: i.e. the limit of detection
*: increased limit of detection due to interference

Organic tin compounds could not be detected over the limit of detection in products 1, 4, 18, and 19 thus these products are omitted from the table

Some samples showed large amounts of total amount of organic tin. Samples 3, 6, and 13 all contained amounts of approximately 0.1 weight% total.

The samples with the highest content are all the PVC produced samples (samples 3, 6, 8, 13, 15, and 16), whereas all PUR products showed no content or a content of maximum 0.03 mg/kg. Two products of silicone

rubber and silicone (samples 21 and 27) showed a total amount of organic tin from 1.9 to 4.8 mg/kg.

5.3 Brominated flame retardants

The specific components included in the analysis are stated in the analytical method description.

No brominated flame retardants over the limit of detection are detected in any of the samples.

5.4 Antimony

The result of the antimony analyses is stated in table 3. The limit of detection for antimony is 30 mg/kg.

Antimony was detected in two products, whereas the other products did not contain antimony above the limit of detection.

Table 3. Results for anitmony analyses of earplugs. Two results indicate double determination. The results are given in mg/kg.

	3		6		26	
Antimony	21000	28000	35	35	35	37

-: Means less than the limit of detection

Antimony was detected in product no 3, 6, and 26 of which the two with the highest content were PVC produced and the last sample was made from silicone. Sample 3 showed the highest amount of antimony of 2.5% (average).

Antimony over the limit of detection could not be determined in all other products.

5.5 Phthalates

The result of the analyses for phthalates is stated in table 4. The analysis includes all esters of 1,2-benzendicarboxyl acids. The table states the content of the detected phthalates. The limit of detection is 10 mg/kg.

Table 4. Results for the analyses for phthalates in earplugs. Two results indicate double identification. The results are given in mg/kg.

	1		2		3		4		5	
Diethylphthalate	11	8	11	15	-	-	35	27	-	-
Dibutylphthalate	-	-	-	-	-	-	180	190	-	-
Benzylbutylphthalate	-	-	-	-	-	-	-	-	-	-
Diisooctylphthalate	-	-	-	-	86000	75000	-	-	-	-
Diethylhexylphthalate	-	-	-	-	-	-	-	-	1600	4000
Diisodecylphthalate	-	-	-	-	-	-	-	-	-	-
Unidentified phthalates	-	-	-	-	3500	3400	-	-	-	-

-: Means less than the limit of detection

Table 4, continued. Results for the analyses for phthalates in earplugs. Two results indicate double identification. The results are given in mg/kg.

	6		9		10		11		12	
Diethylphthalate	-	-	31	28	14	15	23	20	-	-
Dibutylphthalate	-	-	-	-	-	-	-	-	-	-
Benzylbutylphthalate	-	-	-	-	-	-	-	-	-	-
Diisooctylphthalate	73000	82000	-	-	-	-	-	-	-	-
Diethylhexylphthalate	-	-	-	-	-	-	-	-	21000	5100
Diisodecylphthalate	6600	11000	-	-	-	-	-	-	-	-
Unidentified phthalates	2400	2500	44	49	-	-	-	-	-	-

-: Means less than the limit of detection

Table 4, continued. Results for the analyses for phthalates in earplugs. Two results indicate double identification. The results are given in mg/kg.

	13		14		15		16		17	
Diethylphthalate	-	-	-	-	-	-	-	-	13	7.9
Dibutylphthalate	-	-	-	-	860	480	-	-	-	-
Benzylbutylphthalate	-	-	-	-	1900	1200	-	-	-	-
Diisooctylphthalate	110000	160000	-	-	7800	11000	3300	8000	-	-
Diethylhexylphthalate	12000	10000	31	26	-	-	-	-	-	-
Diisodecylphthalate	-	-	-	-	9800	8400	9400	8500	-	-
Unidentified phthalates	860	850	-	-	-	-	-	-	-	-

-: Means less than the limit of detection

Table 4, continued. Results for the analyses for phthalates in earplugs. Two results indicate double identification. The results are given in mg/kg.

	18		19		21	
Diethylphthalate	-	-	520	600	-	-
Dibutylphthalate	-	-	-	-	-	-
Benzylbutylphthalate	-	-	-	-	-	-
Diisooctylphthalate	-	-	-	-	-	-
Diethylhexylphthalate	880	700	-	-	270	56
Diisodecylphthalate	-	-	-	-	-	-
Unidentified phthalates	-	-	-	-	28	48

-: Means less than the limit of detection

Phthalates over the limit of detection could not be detected for the products no 7, 8, 20, 22, 23, 24, 25, 26, and 27, thus they are omitted from the table.

Sample 12 showed a big difference on the double determinations. As it solely applies to DEHP (diethylhexylphthalate) and not all other detected components (verification of GC/MS chromatogramme) it may be caused by the fact that the sample consists of two different colours of foam and thus two parts that may contain different amounts of DEHP despite the supplier's information that the materials are similar.

Three samples (no 3, 6, and 13) showed a total content of phthalates of 8-17%. All three samples are produced from PVC. Two other PVC products (no 15 and 16) showed a total phthalate amount of 1.3 – 2.1%. The latter PVC product did not show phthalates.

Phthalates could not be detected in all other products or only in amounts owed to an impurity from the raw material used for production of earplugs.

5.6 Isocyanates and amines

The result of the nine isocyanate and amine compounds is given in table 5. The analysis is exclusively performed on earplugs produced from polyurethane foam and sample 3 as it was presumed to be a PUR product from the beginning of the analysis. The limit of detection is 0.05 mg/kg for all components.

Table 5. Results for analyses for isocyanates and amines in earplugs. Two results indicate double identification. The results are given in mg/kg.

	1		4		7		9		10	
Hexamethylenediisocyanate (HDI)	-	-	-	-	-	-	-	-	-	-
Toluenediisocyanate (2,6-TDI)	-	-	-	-	-	-	-	-	-	-
Toluenediisocyanat (2,4-TDI)	-	-	-	-	-	-	-	-	-	-
4,4'-Methylenediphenyl-diisocyanate(MDI)	-	-	-	-	-	-	-	-	-	-
"Hydrogenerated" 4,4'-Methylenediphenyl-diisocyanat (HMDI)	*	*	0.14	0.12	0.11	0.14	*	*	*	0.045
Toluenediamine (2,6-TDA)	-	-	0.36	0.49	-	-	-	-	-	-
Toluenediamine (2,4-TDA)	-	-	0.25	0.32	-	-	-	-	-	-
Methylenediphenyldiamine (MDA)	-	-	-	-	-	-	-	-	-	0.067
"Hydrogenerated" Methylene-diphenyldiamine (HMDA)	-	-	4.1	4.2	0.68	0.57	-	-	4.5	4.2

-: Means less than the limit of detection
*: Detected in trace amounts

Table 5, continued. Results for analyses for isocyanates and amines in earplugs. Two results indicate double identification. The results are given in mg/kg.

	11		12		14	
Hexamethylenediisocyanate (HDI)	-	-	-	-	-	-
Toluenediisocyanate (2,6-TDI)	-	-	-	-	-	-
Toluenediisocyanat (2,4-TDI)	-	-	-	-	-	-
4,4'-Methylenediphenyl-diisocyanate(MDI)	-	-	-	-	-	-
"Hydrogenerated" 4,4'-Methylenediphenyl-diisocyanat (HMDI)	*	*	*	*	0.040	0.041
Toluenediamine (2,6-TDA)	-	-	-	-	-	-
Toluenediamine (2,4-TDA)	-	-	-	-	-	-

Methylenediphenyldiamine (MDA)	-	-	-	-	-	-
"Hydrogenerated" Methylene-diphenyldiamine (HMDA)	-	-	-	-	-	-

-: Means less than the limit of detection
*: Detected in trace amounts

Products 2, 3, and 5 did not detect isocyanates and amines over the limit of detection. Traces of the compounds could not be determined, thus the products are omitted from the table.

The isocyanate compound (HMDI) is found above the limit of detection in four PUR products. Likewise three of these products showed the corresponding amine (HMDA).

Furthermore, one product showed the amines 2,4-TDA and 2,6-TDA. The detection could indicate that there has been a presence of 2,4-TDI and 2,6-TDI respectively. The isocyanate compounds may be transformed at hydrolysis into amine compounds. The hydrolysis occurs in the product when the isocyanate is subjected to water. Thus the detection of an amine will indicate that the corresponding isocyanate present merely earlier i.e. closer to the production date.

6 Summary and conclusion

6.1 Organic tin compounds

With the exception of five products (sample numbers 1, 4, 18, 19, and 26) organic tin compounds have been detected in all 27 samples.

PVC produced samples (no 3, 6, 8, 13, 15, and 16) contain the largest total amounts of organic tin varying from 4.7 mg/kg to 1,300 mg/kg corresponding to maximum 0.1 weight%. The main part of the amount is allocated to MBT, TBT, and especially DBT, however, for some products also with detection of mono and dioctyltine. These findings indicate that organic tin compounds are used as PVC stabilisers.

The polyurethane foam products where organic tin compounds were detected the presence exclusively consisted of TBT and especially DBT. The amounts varied from 0.002 to 0.51 mg/kg. The findings indicated that DBT is used as catalyst in PUR production and that TBT may be a contamination of the raw material.

The other detected components were generally found in silicone and rubber products.

6.2 Brominated flame retardants

Brominated flame retardants could not be detected in the products.

6.3 Antimony

Antimony was detected in three types of earplugs in varying amounts from 35 mg/kg to 28,000 mg/kg corresponding to a maximum weight of 2.8 weight%. The three products were produced of PVC and silicone respectively. Antimony may be added flame retardant in form of antimony trioxide.

6.4 Phthalates

Phthalates could be detected in sixteen samples of which five samples (no 3, 6, 13, 15, and 16) had the largest total content over 1 weight% with the largest content of 17%. These earplugs are all PVC produced. The latter PVC product did not show phthalates over the limit of detection. Phthalates are used as softener for PVC thus the results were expected.

One PUR foam product showed phthalates of a content of up to 2%. Phthalates could not be detected in the remaining products or only in amounts originating from impurities at production of the earplugs.

6.5 Isocyanates and amines

The analysis for isocyanates and amines is exclusively performed on PUR products and sample 3 as it was presumed to be a PUR product from the beginning of the analysis.
The isocyanate HMDI was detected in four products and traces were detected in additional four products. The corresponding amine (HMDA) was detected in three of four products with HMDI.

The content of the other amines (2,4-TDA and 2,6-TDA) may indicate that the corresponding isocyanates are included in the production and transformed at e.g. hydrolysis.

The amount of isocyanate monomer in PUR products depends on the hardening of the product, and the subsequent storage, where factors as air availability, humidity, light, and temperature are of utmost importance.