

Survey of Chemical Substances in Consumer Products

Survey no. 17, 2002

Analysis of perfluorooctanesulfonate compounds in impregnating agents, wax and floor polish products

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1 Preface

This project is part of a larger study of different consumer products entitled:

"Survey of chemical substances in consumer products"

The Danish EPA have wished to have a chemical analysis of selected products carried out for their content of perfluorooctanesulfonate (PFOS compounds). In this study impregnating agents, wax and other floor polishes purchased from retail outlets in the Autumn of 2001 have been chosen as the basis. Impregnating agents, wax and other floor polishes were chosen because the survey "Survey of Perfluorooctanesulfonate and Similar Compounds in Consumer Products - Phase 2" carried out with data from the Danish Products Data Register showed that PFOS compounds were used in such products.

21 products, which are kept anonymous in the report, have been analysed. The 21 products have been analysed for six different PFOS compounds and in three of the products PFOS compounds were found.

The Danish EPA have been informed by several retailers and manufacturers of the analysed products that they previously used PFOS compounds in their products, but after the phasing out of the compounds, they have substituted the PFOS compounds with other compounds. Manufacturers who have produced products used in this study containing PFOS compounds, have stated that the products have either been removed from the market or that new products will no longer contain PFOS compounds.

2 Summary

In the present study 21 different consumer products are tested for the content of perfluorosulfonates. Thirteen products were impregnating agents for shoes and textile and 8 products were wax and floor polish.

The products were tested for the following compounds; perfluorobutanesulfonate; perfluorohexanesulfonate; perfluorooctanesulfonate, perfluorodecane-sulfonate; perfluorooctanesulfonamide and ethyl-perfluorooctanesulfonamide. The detection limit was 1 µg/ml for all compounds.

In 3 out of 21 purchased consumer products a content of perfluorooctanesulfonate (PFOS) compounds was found.

One of the impregnating agents contained 212 µg/ml perfluorodecane-sulfonate. Another impregnating agent contained 3.5 µg/ml perfluorooctanesulfonamide.

One of the wax and polish products contained 9 µg/ml ethyl-perfluorooctanesulfonamide.

The analysis was performed at the National Environmental Research Institute, Department of Environmental Chemistry.

3 Sammenfatning

I undersøgelsen er 21 forskellige forbrugerprodukter testet for indhold af perfluorsulfonat forbindelser. Af disse 21 forbrugerprodukter er 13 imprægneringsmidler til sko og tøj. De sidste 8 er voks og polish midler til gulve.

Produkterne er undersøgt for følgende stoffer; perfluorobutansulfonat; perfluorohexansulfonat; perfluorooktansulfonat, perfluorodecansulfonat; perfluorooktansulfonamid og ethyl-perfluorooktansulfonamid, med en detektionsgrænse på 1 µg/ml.

Der er i 3 ud af 21 undersøgte forbrugerprodukter påvist et indhold af perfluorooktanylsulfonat (PFOS) forbindelser.

Et af imprægneringsmidlerne indeholdt 212 µg/ml perfluorodecansulfonat. Et andet imprægneringsmiddel indeholdt 3,5 µg/ml perfluorooktansulfonamid.

Et af voks og polish midlerne til gulve indeholdt 9 µg/ml ethylperfluorooktansulfonamid.

Undersøgelsen er udført på Danmarks Miljøundersøgelser, Afdeling for Miljøkemi.

4 Background and purpose

Within the last couple of years several investigations has shown a content of perfluorooctanysulfonates (PFOS) in the environment. A survey of the workers at 3M in USA showed PFOS-compounds in the blood of the employed. 3M was previously the major manufacturer of PFOS-compounds, but the company decided to discontinue the production in may 2000. This decision was partly due to the findings of PFOS-compounds in the blood of the workers.

Following studies have shown that PFOS-compounds are persistent in the environment and propensity to bioaccumulate in both human and animal tissue.

Mammals and birds (with the sea as main food source) have been found to contain PFOS-compounds. The data available so far indicates that PFOS-compounds are widely distributed in the environment, including the arctic region.

The Danish Environmental Agency (Danish EPA) conducted in May 2001 a survey of the use of PFOS-compounds in chemical products in Denmark. This survey was based on informations in the Danish Product Register. The survey showed that the PFOS-compounds are used as surface active compounds (surfactants) in a wide range of different chemical products, typically in products that demand compounds with a high chemical or thermal stability. Examples are fire fighting foams and lubricants.

The survey also showed that the PFOS-compounds are used as water- and dirt- repellent and as floating agent. The PFOS-compounds may therefore also be found in some types of products for impregnating of textiles and footwear, glue, paint and floor polish.

The survey was based on the OECD list (made by USA and Canada) of 175 perflouro-compounds which might degraded to perfluoroktylsulfonate. Countries that try to make a general view of the use of PFOS-compounds are asked to use this list.

In the light of the results from the survey the Danish EPA chose to investigate the occurrence of PFOS-compounds in two types of consumer products; wax and polish for floors and impregnating agents for footwear and textile on the Danish marked.

A list of 45 consumer products was made by market survey of the retail outlets in Roskilde. In corporation with the Danish EPA 21 products from the list were selected for chemical analysis.

The selected products are described in Table 1. The ingredient list, where labelled on the product, is also included in Table 1.

Table 1. Overview of the analysed products

Product description - Application	Product Category	Labelled ingredient list	DMU Reg. No.
Impregnating agent - for leather and textile	Aerosol spray	Aerosol propellant : Air	01-1321
Impregnating agent - for leather and textile	Aerosol spray	Aerosol propellant: propane/butane Impregnating agent: fluorcarbon resin	01-1322
Impregnating agent - Anti colouring for socks	Aerosol spray	Contains 30 –100 % isopropanole	01-1323
Impregnating agent - for leather, skin and textile	Aerosol spray	Aerosol propellant: propane/butane Solvents: butylacetate, heptane and ethylacetate Impregnating agent: fluorcarbon	01-1324
Impregnating agent - for textile	Spray flask		01-1325
Impregnating agent - for tents, sleeping bags etc.	Spray flask		01-1326
Impregnating agent - for textile	Aerosol spray		01-1327
Impregnating agent - for leather and textile	Aerosol spray		01-1328
Impregnating agent - for leather and textile	Aerosol spray		01-1329
Impregnating agent - for shoes	Aerosol spray	Aerosol propellant: butane/propane 30-40% Solvent: heptane 40-50% Impregnating agent: Polymer fluorcarbon 1-5 %	01-1330
Impregnating agent - for leather and textile	Aerosol spray		01-1331
Wash and care agent – for vinyl, cork linoleum etc.	Liquid agent with wax / polish	Contains less than 5% nonionic tensides	01-1332
Wash and care agent - for vinyl, linoleum, asphalt and parquet	Liquid agent with wax / polish	Wax, polymer, persevering agent and water	01-1333
Wash and care agent - for marble, floortiles, vinyl and linoleum	Liquid agent with wax	Water suspension of wax, polymers, metal coupled acrylpolymers and plasticizers	01-1334
Wash and care agent - for tiles, marble, floortiles etc.	Liquid agent with wax		01-1335
Polish wax - for parquet, linoleum and vinyl	Liquid wax		01-1336
Oil for care of wooden floor	Oil	Vegetable oil compounds, isoparaffins and drying agents	01-1337
Oil for care of wooden floor	Oil		01-1338
Polish wax – for wood	Wax	Bees' wax, carnaubarwax and candelillawax	01-1339
Impregnating agent - for wash of textile	Liquid		01-1340
I Impregnating agent - for wash of textile with down	Liquid		01-1346

5 Method of analyses

The samples were analysed for the following substances by the use of LC/MS/MS; perfluorobutansulfonate, perfluorohexansulfonate, perfluorooktansulfonate, perfluorodecansulfonate, perfluorooktansulfonamide and ethylperfluorooktansulfonamide. The structures of the substances are given in appendix A.

The limit of detection was less than 1 µg/ml product for all target substances.

5.1 Sample preparation

The aerosol cans were placed in a liquid nitrogen container to freeze the contents. Then they were opened to enable the propellant gases to evaporate. After the content of the opened cans had reached room temperature, the liquid contents were transferred to glass bottles. The aerosol cans were weighted before and after the opening see Table 2. The low percentage liquid for 01-1324 and 01-1327 (69 and 48%) is partly due to losses during evaporation of the propellant (which produced excessive foam).

Sample 01-1328 has a relatively low percentage of liquid as sample 01-1324 and 01-1327. A possible explanation could be that this sample just contains less liquid and more propellant.

The content of propellant gases is for the other cans between 3 and 36 weight % of the total contents of the cans.

One ml (or 1 g for the wax products) was diluted to 100 ml with methanol. The two floor care products (01-1337 and 01-1338) were diluted in acetone to avoid precipitation. Internal standard was added before the dilution.

The two wax samples (01-1336 and 01-1339) were first dissolved in 10 ml dichloromethane and then internal standard was added, followed by making up to 100 ml with acetone, this caused a slight precipitation.

All samples were analysed in duplicates. In cases where the content in the samples was above 100 µg/ml, a further dilution was made and the samples were reanalysed.

Table 2: Content in the aerosol cans all weights are given in gram.

DMU product-number	Total weight of the aerosol can	Weight of the empty can	Weight of the liquid and the propellant gas	Liquid content	Liquid content in % of the total content
01-1321	161,3	43,3	117,9	114,2	97
01-1322	234,2	71,6	162,6	129,5	80
01-1323	121,6	50,2	71,4	53,6	75
01-1324	200,0	66,0	134,0	92,5	69
01-1327	246,1	77,4	168,7	80,8	48
01-1328	244,6	74,1	170,6	109,2	64
01-1329	200,4	64,3	136,2	110,2	81
01-1330	203,6	66,6	137,0	114,1	83
01-1331	196,5	66,1	130,5	116,8	90

5.2 LC/MS/MS analysis

The analysis were performed on a API 2000 LC/MS/MS system (PE Sciex, Canada) with the use of a reverse phase C18-column and a water/methanol gradient.

The quantification was done by the use of MS/MS to avoid interference on the analytical results from other substances in the samples. The ion traces of the selected mother/daughter ions are showed for the lowest standard level (10 ng/ml) in appendix B. With a 100 times dilution of the samples, this corresponds to a 1µg/ml contents in the samples.

5.3 Uncertainty of measurements and blank values

The combined uncertainty of the dilution and the LC/MS/MS analysis is about 5%. The additional step of evaporation of the propellant gases in the aerosol spray products means that the uncertainty of measurement is increased to about 10%. The possible evaporation of the PFOS compound with the propellants is considered negligible as the evaporation was performed at room temperature.

The partly participation of the polish wax sample (01-1336 and 01-1339) means that the uncertainty of measurement is higher for these samples (25 to 50%).

No problems with blank values were observed during this study.

6 Results

The Results of the chemical analysis are reported in Table 3. Three of the analysed samples contained PFOS-compounds.

As the product has in this investigation only been analysed for six PFOS-compounds, it is possible that some of the products may contain other perfluorinated substances.

Fluorocarbon substances were listed on the declaration in 3 of the investigated aerosol impregnation sprays products (01-1322, 01-1324 and 01-1330). On two of the products it was stated that they contain polymer fluorocarbon (teflon like) substances.

It is also likely that similar substances might be found in the products where no ingredients were labelled.

Table 3: The contents of PFOS compounds in the analysed samples with findings. All results are given in µg/ml (as the sodium salt for the sulfonates).

DMU Reg. No.	01-1324 Impregnating agent - for leather, skin and textile		01-1326 Impregnating agent - for tents, sleeping bags etc.		01-1332 Wash and care agent – for vi- nyl, cork lino- leum etc.	
Perflurobutansulfonat	-	-	-	-	-	-
Perflurohexansulfonat	-	-	-	-	-	-
Perflurooctansulfonat	-	-	-	-	-	-
Perflurodecansulfonat	-	-	212	211	-	-
Perfluro-octansulfonamid	3	4	-	-	-	-
Ethyl-Perfluro-octansulfon- amid	-	-	-	-	9	10

- Indicates that the concerned substance not has be found in the sample with a limes of detection on 1 µg/ml. All concentrations have been corrected for the internal standard.

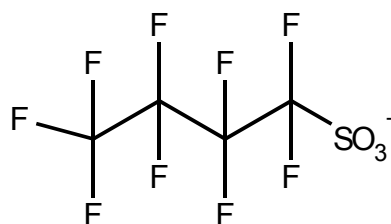


Figure 1. Perfluorobutansulfonate, CAS [29420-43-3] (potassium salt)

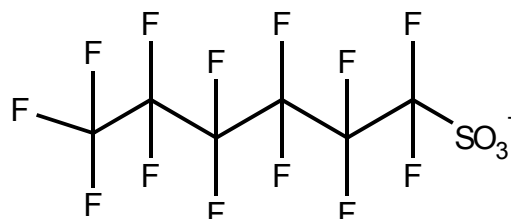


Figure 2. Perfluorohexansulfonate, CAS [432-50-7] (Acid fluoride)

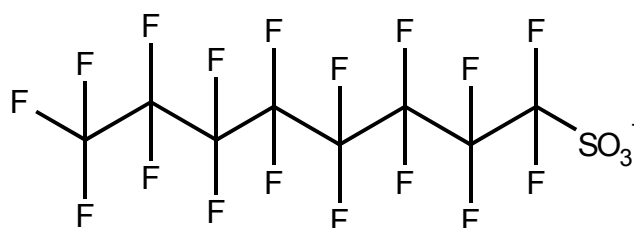


Figure 3. Perfluorooctansulfonate, CAS [2795-39-3] (Potassium salt)

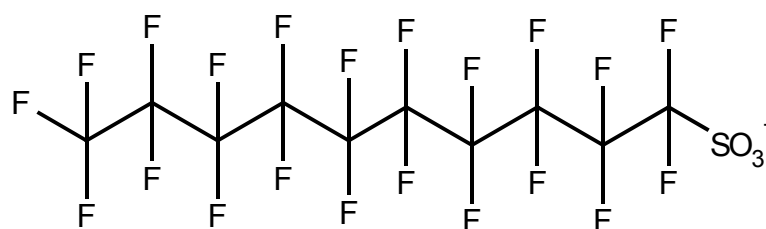


Figure 4. Perfluorodecansulfonate, CAS [67906-42-7] (ammonium salt)

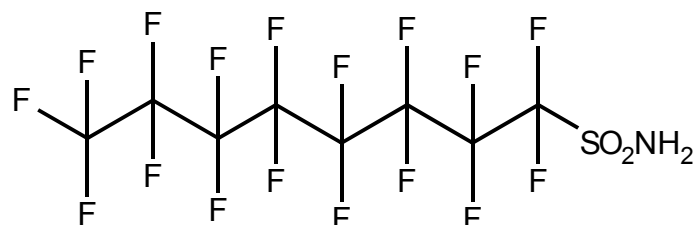


Figure 5. Perfluorooctansulfonamide

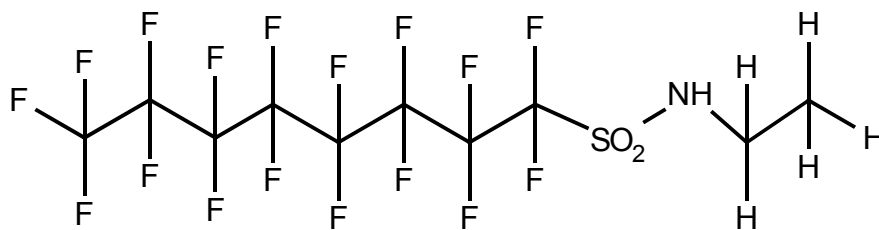


Figure 6. Ethyl-perfluorooctylsulfonamide, CAS [4151-50-2]

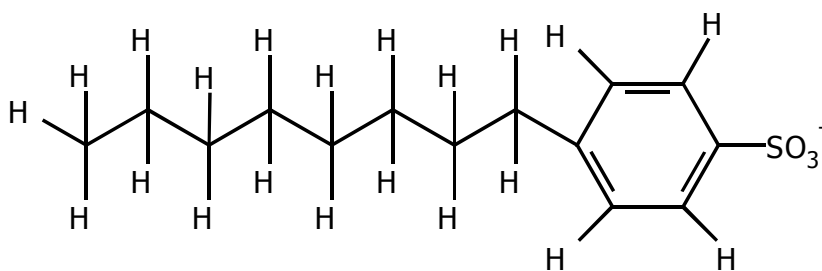


Figure 7. Internal standard, 4-Octylbenzenesulfonate, [6149-03-7]

Ion traces of the selected mother /daughters for the analysed PFOS compounds (10 ng/ml standard).

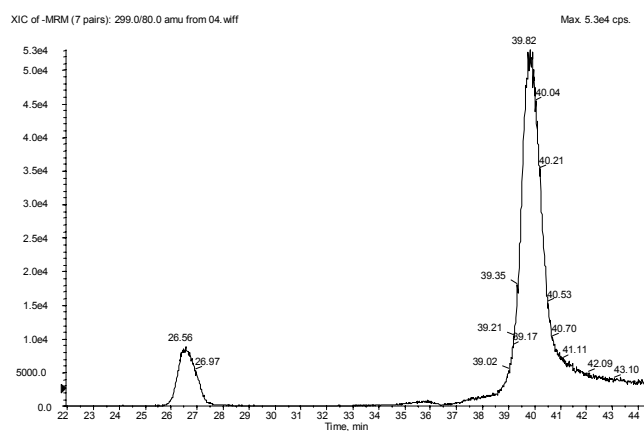


Figure 1. The mother /daughter (299/80) ion trace for Perfluorobutansulfonate, notice it is the first peak.

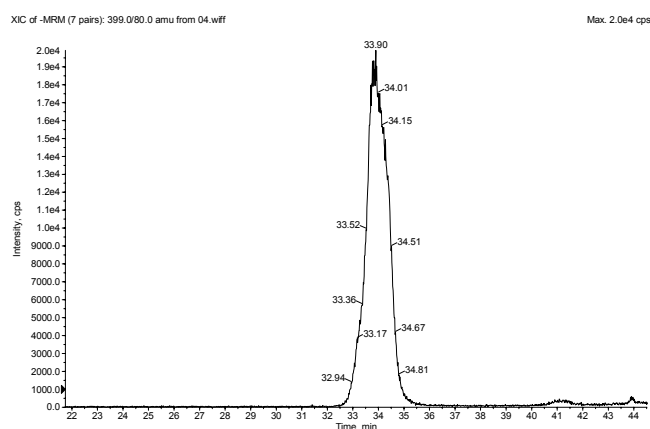


Figure 2. The mother /daughter (399/80) ion trace for Perfluorohexansulfonate.

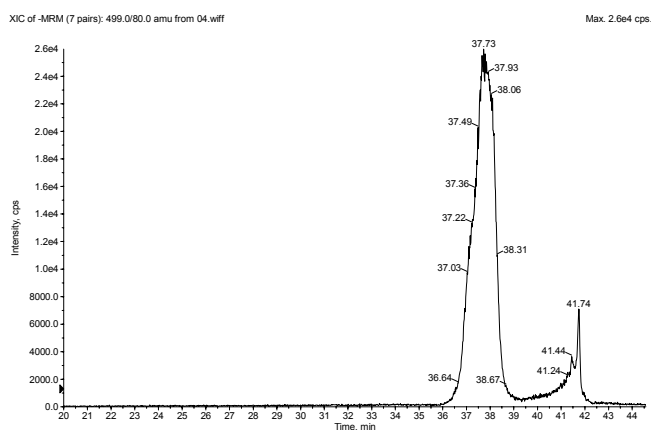


Figure 3. The mother / Daughter (499/80) ion trace for Perfluorooctansulfonate.

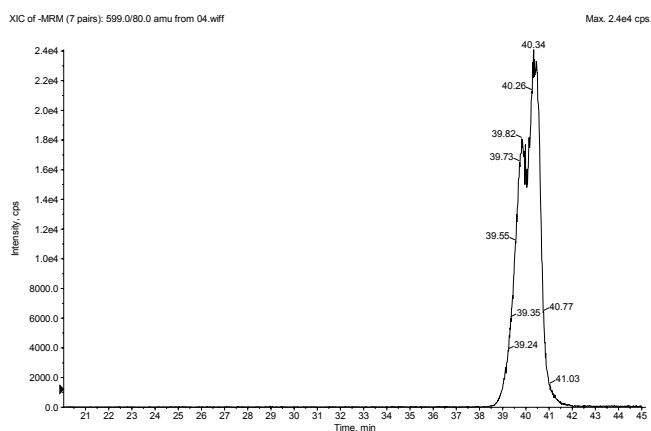


Figure 4. The mother / daughter (599/80) ion trace for Perfluorodecansulfonate.

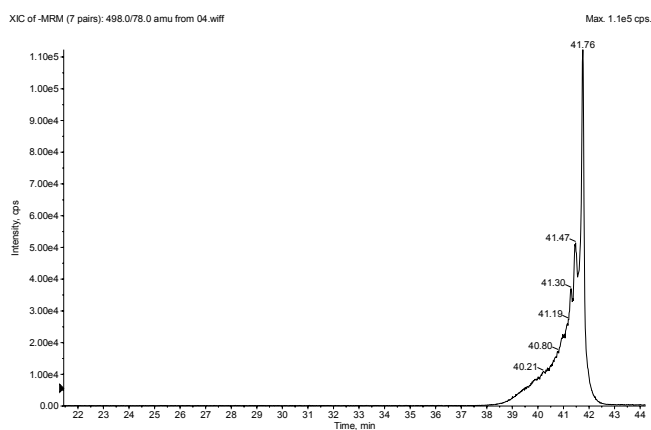


Figure 5. The mother / daughter (498/78) ion trace for Perfluorooctansulfonamide.

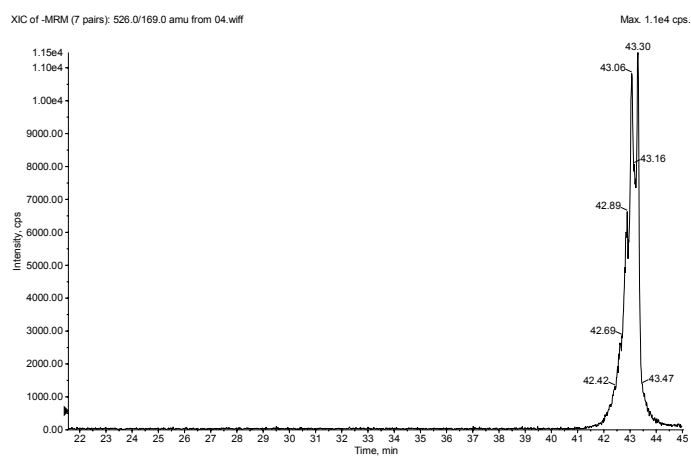


Figure 6. The mother / daughter (526/169) ion trace for Ethylperfluorooctylsulfonamide.

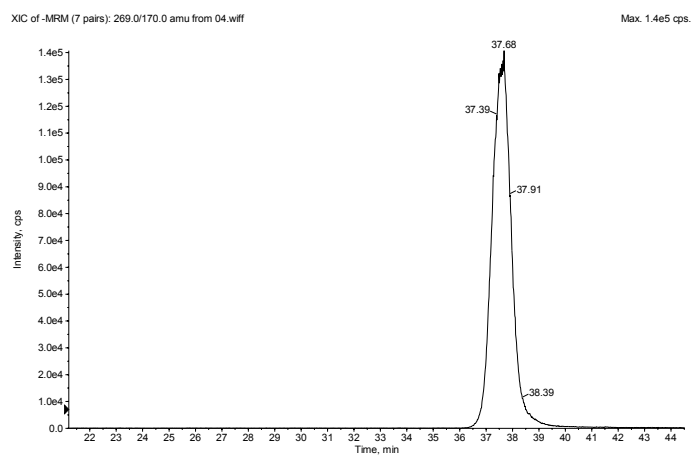


Figure 7. The mother / daughter (269/170) ion trace for 4-Octylbenzensulfonate.

