SMALL PARTICLES CONTAINING PHTHALIC ESTERS IN THE INDOOR ENVIRONMENT - A PILOT STUDY

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ABSTRACT
Many chemicals in polymeric materials have low vapour pressure. Hypothetically such chemicals are emitted and may stay as particles or be adsorbed onto dust particles and become air-borne. The aim of this pilot-study has been to validate the methods for measuring phthalates on particles in indoor environments. Sedimented dust from the child's bedroom in seventeen homes has been sampled using a Vacuu Mark sampler and a vacuum cleaner. The dust is collected on 90 millimetre cellulose filters, which are extracted and analysed by techniques such as HPLC and GCMS. First results have shown that phthalates and chemicals were extruded from the polymeric material. A co-variation between the amounts of the phthalate, DEHP on the filters and the type of interior decoration on walls and floors were found.

INDEX TERMS:
Dust, Phthalate, Emission, Indoor Environment, Particles, PVC-material

INTRODUCTION
Products based on polymeric materials are used in large amounts in indoor environments. Emissions of several of chemicals from polymeric materials have been reported in many papers. Studies of chemical emissions of volatile organic compounds, VOC, from PVC flooring materials have been investigated and reported by Rosell (1990), Gustafsson et al. (1993), Johnson et al. (1995) and Lundgren et al. (1999). These studies have shown that over the years low molecular weight chemicals have to some extent been exchanged for compounds with higher molecular weight with less ability to migrate in the material and giving less chemical emission than earlier. In a true sense several materials have become low emitting materials.

VOCs, specific for polymeric building materials have been measured for many years. However, the links between VOC from this materials and health effects especially respiratory symptoms for children have so far not been proven. Nevertheless, articles have recently been published indicating a correlation between the amount polymeric materials indoors and allergic reactions or reduced respiratory function among children, Öie (1997,1998), Jaakola (et al. 1993, et al. 1997, et al. 2000). Still, a verified link connecting polymeric material indoors to the respiratory tract of children is missing.

Differences in results between active and passive air sampling have been observed in our indoor sampling on the same premises. The active sampling has given higher concentrations of total volatile organic compounds, TVOC, and the GC-analysis has shown higher concentrations of semi-VOCs. This difference has been interpreted as an effect of particulates

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being trapped by active sampling but not adsorbed in passive sampling. Many chemical compounds in the polymeric materials have very low vapour pressure. This is specifically true for the plastisizers (Udhe et al. 2001).

The hypothesis is that these semi-VOCs and less volatile chemical compounds may be emitted from the material forming small particulates and/or adsorb onto dust particles and become air-borne and breathed due to the air movements in the occupied building. In the daily wear process many of these materials give off dust and particulates. The material itself, the migration and the molecular weight of the chemical compounds become governing factors for the wear process. If true, plastisizers, stabilizers and fillers in the polymeric material will be represented in the composition of the indoor dust particle fraction. We, therefore, wanted to measure the sedimented dust in apartments and analyse the chemical constituents present in the dust particles. The aim of this pilot-study has been to validate the method for measuring phthalates on dust in indoor environments.

METHODS AND MATERIALS

This study is a part of an on-going investigation on the impact of indoor environments on asthma and allergy among children, “Dampness in buildings and health”, where exposure measurements and clinical examinations will be made of 200 healthy children and 200 children with symptoms.

Several different analytical techniques were considered and screened. In the project the sampling would be performed by persons performing other physical investigations in the buildings and at the same time take several samples. For simplistic reason it was found best to use 90 millimetre filters mounted in cassettes that could be applied to an ordinary vacuum cleaner. The sampler is called Vacuu Mark Sampler.

It was decided that the samples should be taken from non-plastic surfaces above the floor level containing sedimented dust. The vacuumed surfaces were window and floor sills and radiator heaters. Samples of the sedimented dust in 17 homes were taken in the bedroom of the child with the Vacuu Mark filter mounted to a vacuum cleaner. The caped holder including the filter, weighed before and after the sampling, was returned to the laboratory and extracted and analysed by techniques such as High Pressure Liquid Chromatography, HPLC and Gas Chromatographic analysis by Mass Selective detector, GCMS. The whole filter is transferred to a small jar and extracted twice by two millilitres of di-chloro methane and the whole extract is transferred to a 3-millilitre vial. Samples from the vial are then primarily transferred to GCMS equipment supplied with an auto-sampler for further analysis.

Initially, there was an intension to split the filter samples in several pieces so that several different analytical techniques would be used. The sample must be evenly distributed over the filter area for such a procedure. This condition has been tested by analysis of the filter surfaces by a time-of-flight mass-spectrometer with a secondary ion monitoring system, TOF-SIMS. The filter was cut in three sub-samples as described in fig 1. All fibrous dust was lifted from the filter surface by an adhesive mounted on a rod covering the surface. The sub-samples of filter material were then analysed in the TOF-SIMS equipment. The analysis of plastisizer was performed at two atomic mass units, 149 and 167 amu, specific for di-(octyl) phthalate, DOP and di-(ethyl-hexyl) phthalate, DEHP. Nine spot samples were taken on each sub-sample and the results averaged.

Before sampling in the seventeen homes a number of dust samples were taken in the same home but at different locations. The home had a simple type of wall-to-wall carpet in one bedroom and PVC flooring in the larger bedroom. Both rooms had wallpaper of printed-paper. Samples were taken on the floor in both bedrooms. Samples were also taken from a shelf and a windowsill and a doorsill in the larger bedroom. Another sample was taken from the dust in a computer set in the smaller bedroom. The two samples from each sampling point were split so that both TOF-SIMS analysis and extraction and GCMS analysis could be performed for each sampling point.

Preparation of sub-samples:

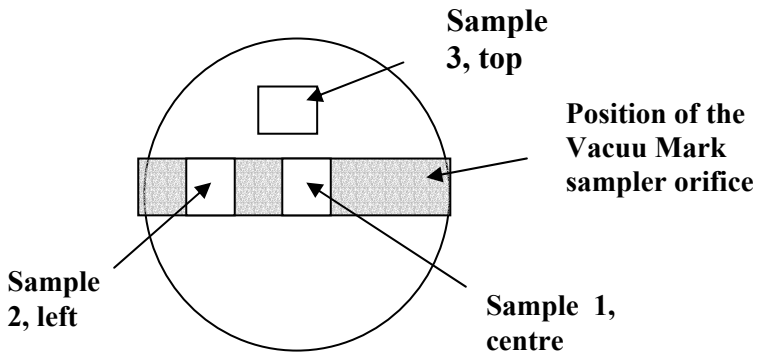

Figure 1. Analysis and preparation of sub-samples from Vacuu Mark filters

Table 1. Results of different analysis of test samples taken in one home

	Bedroom 1, PVC flooring	Bedroom 2, Wall-to-wall carpet	computer sample	Bedroom 1, Shelf sample	Zero filter
Sample weight, mg	170	470	80	70	< 5
GCMS intensity, TIC	1650	650	600	350	160
TOF-SIMS intensity, amu 149, ratio to C_3H_5	0.55	0.17	0.44	0.18	0.12
TOF-SIMS intensity, amu 167, ratio to C_3H_5	0.038	0.012	0.029	0.013	0.0078
Ratio MS/TOF-SIMS	3000	3800	1300	1900	1300
Ratio TOF-SIMS, amu 149/167	14	14	15	14	15

RESULTS

The signal in each spot of the sub-samples in figure 1 was normalised to one of the mass units specific for the filter material. The qualitative results from the three sub-samples were given as ratios 2930, 1920 and 4740 for samples 1 to 3 respectively. The background level for the pure filter was reported to ratio 650. From the analysis it was demonstrated the signal-to-noise ratio was three to eight. The individual analysis was variable in results and that the results between sub-samples are distinct. Thus, there is no even distribution of the phthalates over the filter surfaces and therefore not possible to analyse only part of the filter. The whole filter has to be taken into account. Even though fibrous material was removed from the filter surface there was phthalates enough left in the filter material for the analysis The result also suggests that phthalates are not only present adsorbed on the fibrous dust fraction but may exist as particulates.

No calibration of the response intensity was performed for either of the two methods (TOF-SIMS method and the extraction and GCMS analysis method) used in table 1. Therefore the precise amount of the phthalates has not been determined. Still, several conclusions may be drawn from the table. The solid surface analysis by TOF-SIMS and analysis of the extract by GCMS demonstrate similar trends between samples. When GCMS intensity is decreasing the same happens to TOF-SIMS signal. The ratio between GCMS and TOF-SIMS is reasonably constant considering that GCMS is an analysis of the total extract from the filter, while the TOF-SIMS is an analysis of phthalates in the filter material. There is a good agreement for the samples not taken from the floor such as the computer sample and the shelf sample and also the zero filters. The two floor samples have slightly higher response for GCMS than for TOF-SIMS. The ratio between the two atomic mass units, amu, 149 and 167 used in the analysis in the TOF-SIMS demonstrate good agreement. The signals from the zero filters indicate that both methods have a background to take into account. As should be expected there was a significant difference between samples directly from the PVC flooring as compared to the sample from shelf and sills.

A large amount of dust was found in the bedroom having wall-to-wall carpet but a distinctly smaller fraction of di-(ethyl-hexyl) phthalate, DEHP, was present compared the other samples, but still DEHP was present in significant amount in the bedroom having wall-to-wall carpet. Thus, it may be concluded that the used procedures are sensitive enough to detect phthalate in the samples from dust and particulates. It seems possible to distinguish different types of surfaces by the different amounts of phthalate present. The contribution from the surface of a material containing plastisizer is higher than from surrounding dust. The task to sample dust in a child's bedroom in seventeen homes having different wall and floor material seemed meaningful. The results concerning phthalates in the dust samples from these homes are presented in table 2.

DISCUSSION

The analysis of samples from the seventeen homes have so far mainly concerned di-(ethyl-hexyl) phthalate in the extracts. DEHP was detected in all samples analysed in the study. Other types of phthalates have been found in individual samples but the number of samples is still too small for a thorough analysis. Identified are two types of di-(butyl)-phthalates, DBP 1 and DBP 2, di-(hexyl) phthalate, DHP, di-(butyl-benzyl) phthalate, BBP and di-(ethyl-hexyl) phthalate. In the present analysis only a few physical characteristics of the seventeen homes have been considered. A more complete analysis should follow in the main project.. There seems to be a small artefact of di-(butyl) phthalate in the analysed filter including a filter having been at the sampling spot but not opened. The lid to the filter holder is the suspected source.

The first three samples in table 2 are taken in homes reporting wooden parquet flooring and wallpaper of only paper in the child's bedroom. The second set of data in table 2 has linoleum flooring and wallpaper of paper. The third group was declared as either having PVC flooring or having vinyl wallpaper or a painted top coating on the wallpaper. The fourth group have PVC flooring and either vinyl wallpaper or a painted top coating on the wallpaper. The amount of dust sampled in each home varied a lot. It was therefore necessary to correlate the amount of phthalate found to the amount of dust found. More dust would have been preferable for decreasing the uncertainty in the determination of amount of dust. The number of data points for each category is in reality too small for a proper statistical analysis.

Table 2. Results of the analysis of phthalates in dust samples from the child's bedroom in 17 homes.

Sample No	Sum, μg Phthalates	DBP1	DBP2	DHP	BBP	DEHP	Fraction DEHP in dust	Dust, mg
6989	76.9	0	9.1	0	3.4	64.4	0.287	224
13606	6.4	0	0	0	3.8	2.6	0.252	10
12834	31.8	0	1.9	0	2.8	27.1	0.362	75
4661	16.2	0	1.9	0	1.4	12.9	0.069	186
9184	99.2	26.9	17.2	0	15.3	39.8	0.267	149
8520	12.8	1.6	3.5	0	2.2	5.5	0.267	38
6101	135.1	0	33.3	0	9	92.8	0.839	110
10018	111.4	1.3	1.3	8.1	5.5	95.2	0.868	111
13991	7.8	0.3	1	0	3.9	2.6	0.085	31
12112	17.7	1.7	1.1	0	2.2	12.7	0.256	50
12460	9.3	0.7	0	0	2.1	6.5	0.157	41
5337	22.7	0.7	1.2	0	4.5	16.3	0.163	100
3898	34.2	1.1	2.1	0	4.7	26.3	0.509	52
2778	11.2	0	0	0	1.5	9.7	1.043	9
1863	20.9	1.3	0	0	4.3	15.3	1.195	13
95	11	0	0	0	0	11	0.112	98
6469	66.3	0.4	4.7	0	0	61.2	1.304	47

However, in figure 2 the fraction of μg of DEHP in mg of dust has been plotted against the type of interior decorations reported at the sampling. The fraction of DEHP is higher in the dust samples from homes having PVC compared to those not having PVC in the bedrooms. Most interesting is the much higher fraction of DEHP found in homes having the flooring material and the wall material contain PVC or plastics in the child's bedroom. Phthalates are present even if there were no plastic material immediately identified in the child's bedroom. Many homes have for instance PVC flooring in the bathroom and the kitchen and may therefore have indications of phthalates in the dust in the bedroom.

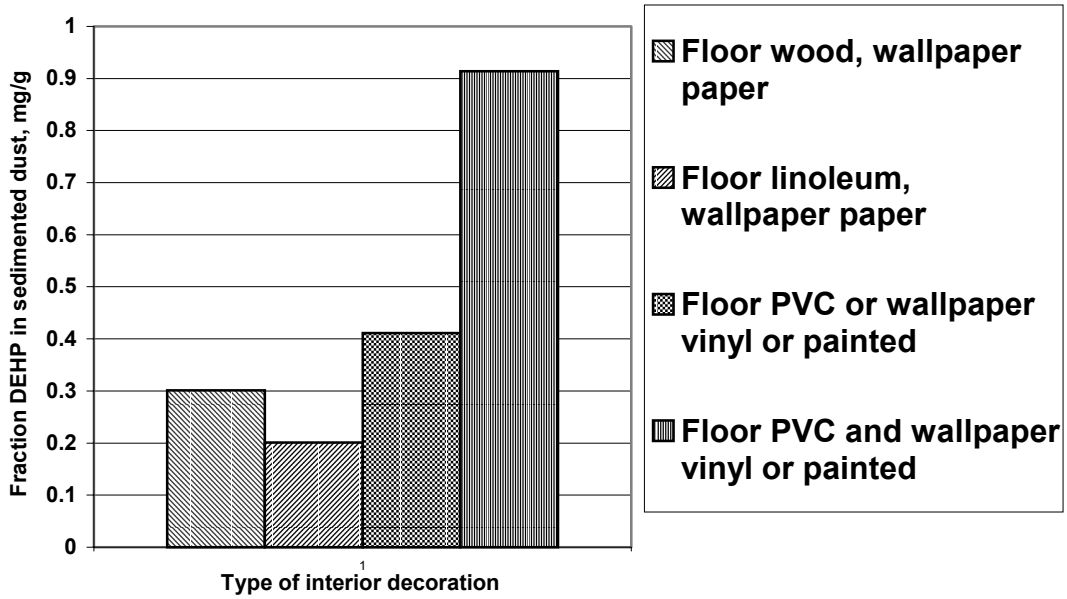

Figure 2. Fraction DEHP in sedimented house dust.

CONCLUSIONS

Based on the data presented in this paper

- it seems possible to perform meaningful sampling and analysis of the amount of plastisizers present in sedimented dust samples from homes.
- The amount of plastisizer in the dust is normally low but significant,
- There may be a distinct difference between houses having high fractions of interior decorations from materials containing plastisizers and those having a low fraction.
- At least 100 mg of dust is preferable for a good analysis of sedimented dust.

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