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Occurrence of Chlorinated Paraffins in Bavarian House Dust Samples

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Abstract— **House dust samples from Bavaria were examined for chlorinated paraffins using gas chromatography-mass spectrometry in ECNI mode. Middle-chain chlorinated paraffins (MCCPs) were detected in all studied samples. The concentrations of MCCPs varied between 4.12 µg/g and 237.54 µg/g. Short-chain chlorinated paraffins (SCCPs) were detected in 9 out of 11 studied samples. As compared to MCCPs, concentrations of SCCPs were on average 29 fold lower.**

Keywords-component; polychloro alkanes; occurrence;, house dust; determination

I. INTRODUCTION

Chlorinated paraffins (CPs), also known as polychlorinated n-alkanes (PCA), are complex mixtures consisting of thousands of isomers which are also not possible to be completely separated by HR-GC [1]. The technical mixtures are gained by chlorination of n-alkane feedstock under forcing conditions; over 200 commercial products with different compositions are available [2]. Thus, for a proper quantification, a suitable standard has to be selected. For these reasons, the analysis of PCA is difficult and only limited information of PCA in environmental samples are available [1].

With reference to their chain lengths, CPs are classified as short (C10-C13), middle (C14-C17) and long (C18-C30) chain chlorinated paraffins (SCCP/MCCP/LCCP). Corresponding to their intended use, the chlorine content varies between 30 and 70% [1]. The application range of CPs is wide: e.g. as fire retardants, plasticizers or additives in paints, sealants or rubber and in a number of other industrial applications [1] Annual global production of CPs is approximately 300 kilotonnes, with a majority having MCCPs. Since 2004, SCCPs may not be used (in concentrations higher than >1 %) in metal-working and for liquoring of leather in the European Union.

The acute toxicity of CPs is low but based on their physicochemical properties, dependent on chain length and chlorine contents, CPs exhibit a more or less great bioaccumulation potential [1].

So far, only few semi-quantitative data on SCCPs in house dust exist [3,4]. In this study the concentration of chlorinated paraffins in several house dust samples were determined with a pursued quantification approach. Standards with defined compositions were created and correlation functions were used to compensate the influence of chlorine content [5].

II. MATERIALS AND METHODS

A. Chemicals and standards

CP mixtures with defined chain lengths and varying chlorine contents synthesized as described elsewhere [6] were used for mixing the correlation-standards. Technical MCCP mixtures (42%, 52%, and 57%) were obtained from Ehrenstorfer (Augsburg, Germany). Solvents for residue analysis were purchased from LGC (Wesel, Germany). Silica gel, sulphuric acid as well as sodium hydroxide supplied by Merck (Darmstadt, Germany).

B. Extraction and clean-up

The contents of dust bags from the household vacuum cleaners were sieved through a 2 mm, and thereafter through a 63 µm sieve. Fractionated dusts (0.5 up to 1 g) were extracted with 50 ml solvent mixture consisting of n-hexane/acetone (1+1) in ultra-sonic-bath (60 °C, 1 h). The extract was filtered and subsequently evaporated to dryness.

The first clean-up step was treatment with sulfuric acid (10 ml, 60 °C, 1 h) followed by an acid/basic silicagel column. Hexachlorobenzene (HCB) was used as an injection standard.

C. Instrumentation

A Shimadzu QP 2010 GC-LRMS system operating in ECNI mode, with methane as reactant gas, was used. Separation was carried out on a 30 m x 0.25 mm x 0.25 µm ZB 5 ms column with helium as carrier gas (0.95 ml/min). Splitless injection (1 µl) at 275 °C was done via an autosampler. The ion source temperature was kept at 150 °C; the interface temperature was set at 280 °C. The temperature program started at 120 °C (1 min) rising with 15 °C/min up to 310 °C and held then for 15 minutes.

Selected ion monitoring (SIM) mode was used for the detection of selected fragment ions listed in Table 1. The ion m/z 284 was used for HCB.

D. Quantification

Since the detector response is dependent on the chain length and chlorine content, this influence was minimized by using correlation functions. Therefore, SCCP standards with different chlorination degrees were mixed, each chain having the equal amount. For MCCPs, only one self-made standard could be realized so further technical mixtures were used to create a correlation function. For both, SCCPs (each chain

length) and MCCPs correlation functions between detector response and chlorine content followed a polynomial trend of second order (Figure 1 and 2). The response factors were gained via the correlation functions using the calculated chlorine contents of the several chains. By means of the response factors for each chain and the corresponding signal areas, the amount of CPs in the sample was determined.

TABLE 1: SELECTED FRAGMENT IONS FOR SCCPS AND MCCPS

m/z							
313	327	332	339	347	348	355	360
361	368	375	381	382	389	395	396
403	409	415	417	419	423	429	430
431	437	445	449	451	459	463	465
467	473	479	487	493	501	493	501

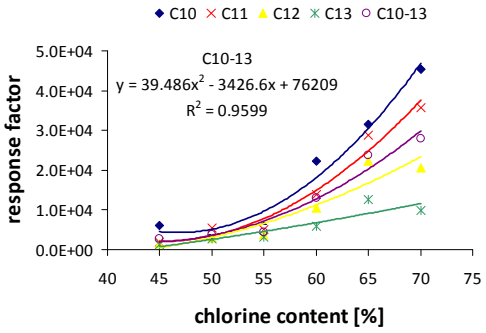

Figure 1. Correlation functions for SCCPs

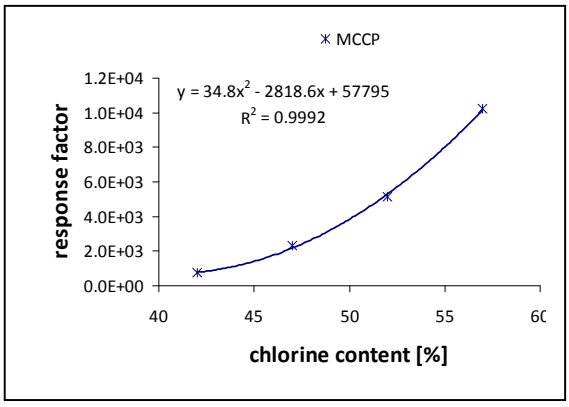

Figure 2. Correlation functions for MCCPs

E. Quality control

Since no CPs free dust samples were available, CPs were removed via solvent extraction and examined for CPs before it was used as blank. This blank material (0.75 g) was spiked with 5 µg of a technical SCCPs mixture with 63.5% chlorine content, and 25 µg of a technical MCCP mixture with 52% chlorine content. A further blank material without spiking was worked up as described above. The intra-day reproducibility of 6 determinations was good as the relative standard deviations were 12.2% for SCCPs and 12.6% for MCCPs. The recovery rates for SCCPs were between 87% and 120% respectively and 70% and 96% respectively for MCCPs.

The detection limits (LODs) were roughly estimated via standard solutions. The LODd varied depending on the chlorine content and chain length. For SCCPs, the LODs ranged from 1 ng/µl to 5 ng/µl for 45% chlorine content, and from 0.2 ng/µl to 1 ng/µl for 60% chlorination degree. Furthermore, the LODs for MCCPs were estimated at 50% chlorine content; the values were in the range of 5 ng/µl for a polychlorinated tetradecane mixture to 10 ng/µl for a polychlorinated hexadecane mixture.

III. RESULTS AND DISCUSSION

In Table 2, the determined CP amounts of the dust samples were displayed, with the values originating from duplicate estimations with relative standard deviations < 20%.

TABLE 2: CONCENTRATIONS OF SCCPS AND MCCPS IN THE INVESTIGATED HOUSE DUST SAMPLES

Sample	SCCP		MCCP		$\frac{MCCP}{SCCP}$
	conc. µg/g	chlorine content %	conc. µg/g	chlorine content %	
1	4.84	56.8	84.91	52.7	18
2	n.d.		187.65	52.6	
3	1.31	62.3	4.12	54.7	3
4	7.14	61.9	42.45	52.9	6
5	1.90	58.8	237.54	56.9	125
6	1.91	63.4	68.53	55.0	36
7	0.79	61.8	53.45	53.1	68
8	2.08	60.8	12.55	53.6	6
9	0.76	57.1	35.80	53.1	47
10	n.d.		4.38	54.7	
11	0.96	61.8	46.45	54.4	48
average	2.41	60.5	70.71	54.0	29

n.d. = not detected (< LOD; see quality control)

MCCPs were detected in all examined samples, with the concentrations ranging from 4.12 µg/g to 237.54 µg/g with an averaged value of 70.71 µg/g. In nine out of the eleven investigated samples, SCCPs were detected. The highest determined SCCP concentration was 7.14 µg/g, with an average value of 2.41 µg/g being calculated. These findings fit well to the reported SCCP values from dust samples of Belgian and UK with average values of 2.08 µg/g and 4.34

µg/g, respectively. In both cases, the highest value was about 13 µg/g [3,4].

The amount of MCCPs in each sample clearly predominate the SCCPs concentrations. Similar findings were referred to sediment and sludge samples from Czech Republic [7] and some air samples from the United Kingdom [8].

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