CARBON SKELETON ANALYSIS OF CHLOROPARAFFINS IN SEDIMENT, MUSSELS AND CRABS

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Introduction

Commercially produced chloroparaffins (CPs) are polychlorinated n-alkanes (PCAs) of the general formula $C_nH_{2n+2-x}Cl_x$ with chain length C_{10} to C_{30} and chlorine content from 15 to 72 %. They are classified into three chain length categories: short-chain (C_{10-13}), medium-chain (C_{14-17}) and long-chain ($C_{>17}$). The physical and chemical characteristics of CPs make them useful as secondary plasticisers in PVC, as additives in sealants, paints and greases as well as in cutting and drawing oils as well as in other products. The present total world production has been estimated to be over 5 000 000 t [1-3].

As a consequence of the manufacturing process, commercial CP products are a mixture of hundreds of congeners, which are impossible to separate satisfactorily by any chromatographic method. At present, there is no accurate analytical procedure [1-3].

Over the last few years, gas chromatography- mass spectrometry (GC-MS) with negative ion chemical ionisation (NCI) has been the usual method for CP analysis [4-9]. The 'carbon skeleton reaction gas chromatography' method existed as an alternative method based on hydrogenation of chloroorganics to their analogous hydrocarbons [10-12] but up to now was not considered suitable for quantitative analysis. From this basis, we optimised and tested the method for quantitative analysis of CPs [13]. Samples from marine sediments, mussels and crabs taken from the area influenced by a CP manufacturer in Yarraville, Australia were examined with the new method.

Material and Methods

Freeze dried sediment samples were extracted with n- hexane using a soxhlet apparatus and sulphur was removed using freshly precipitated copper powder.

Mussel and shrimp meat were rubbed with sodium sulphate and sand, extracted by soxhlet with n-hexane and, using cyclohexane /dichloromethane (8:2), passed over a column of deactivated florisil to separate off the fats. The pre- cleaned extracts, or eluates were then chromatographed over a combined silica gel column (Na_2SO_4/SiO_2-$H_2SO_4/SiO_2/SiO_2$-NaOH) using cyclopentane, followed by cyclopentane/ dichloromethane (1:1). The second fraction was then concentrated and chromatographed over superactive basic aluminium oxide with cyclopentane then cyclopentane/ ethyl formate (3:7). The second fraction was then concentrated to 25 µl and 1µl was injected onto the Pd-catalyser [13] in the injector of the GC-MS (Fisons 8060 GC, Fisons MD800 quadrupole MS). A mixture of hydrogen and helium (1:1) was used as carrier gas, with an inlet pressure of 180 kPa. The separation column (DB 5, f.th. 0,25µm; i.d. 0,25 mm; l. 30 m) was connected via a 1 m length retention gap (deactivated, i.d. 0,32 mm) and a 2 m long restriction capillary (deactivated, i.d. 0,15 mm). Injector temperature was 300 °C, transfer line 280 °C, and ion source 200 °C Good separation was achieved with the temperature programme: 50 °C, 3 min; 10 °C/min, 280 °C, 10 min. Selected Ion Monitoring (SIM) mode was used with mass traces 57, 71, 85 and 99. Identification and quantification were achieved using n-alkane standards from C_{10} to C_{29}.

The total chloroparaffin content w_{Cp} in a sample was calculated from the sum of the alkanes determined ($w_{alk,i}$) and the chlorine content K (e.g. 50 %) according to the formula [13]:

$$w_{Cp} = w_{alk,i} / (1 - 0{,}971[K/100\%])$$
$$w_{Cp} = w_{alk,i} / 0{,}515 .$$

Table. CPs in sediment, mussel and crab samples

	µg/kg d.w.				µg/g fat	
alkane	sed 2a	sed 2b	sed 3a	sed 3b	mussel	crab
C10	18	28	24	46	1.1	15.2
C11	10	9	41	62	0.3	13.0
C12	13	12	49	79	0.5	28.5
C13	20	26	194	259	0.4	8.2
C14	407	385	1035	6434	7.4	10.1
C15	453	428	910	6747	9.5	8.1
C16	191	256	707	2607	4.4	7.9
C17	57	99	456	615	1.9	4.4
C18	51	48	169	268	1.4	4.0
C19	21	47	69	82	0.5	1.3
C20	30	33	66	81	0.9	1.6
C21	24	20	102	48	0.4	0.7
C22	55	42	230	84	0.7	1.0
C23	74	43	342	124	0.4	0.9
C24	91	43	393	136	0.6	0.9
C25	111	59	417	154	0.6	1.3
C26	128	80	377	206	1.2	1.1
C27	159	89	348	222	1.1	0.7
C28	199	138	350	279	0.9	0.5
C29	308	254	329	337	0.6	0.3
Summe	2421	2139	6610	18872	35.0	109.5

Results and discussion

Examination of several commercial chloroparaffins (CP30, CP40, CP52, CP56 and CP70) shows that the short chain commercial CPs consist of C_{10-13}, die medium length mainly of C_{11-19} and CP30 of long chain C_{17-26} n-alkanes (Fig. 1).

The results from the sediment, mussel and crab samples are presented in the table as well as in Figs 2 to 4. Bioaccumulation is clearly evident, the mussel meat containing around double and crab meat around six times the amount of chloroparaffins found in the most contaminated sediment sample (Fig 2).

Figure 1: Distribution of n-alkanes in 5 commercial CPs

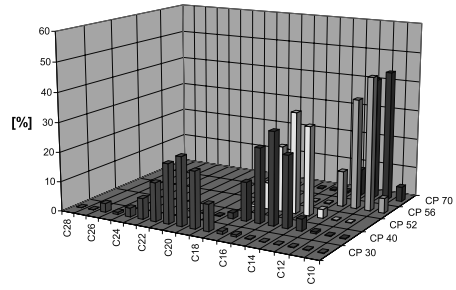


Figure 2

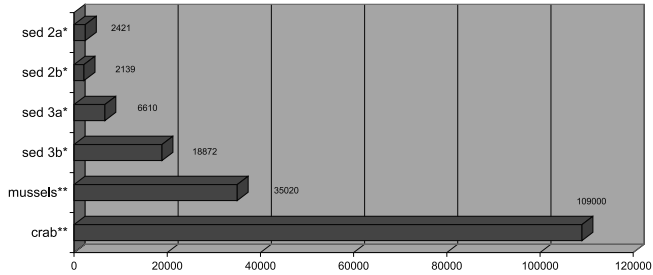
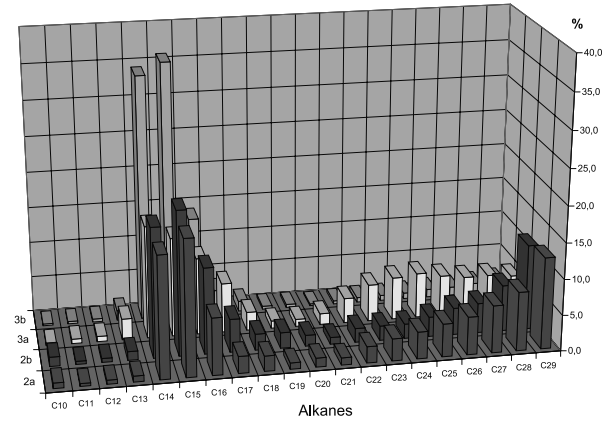
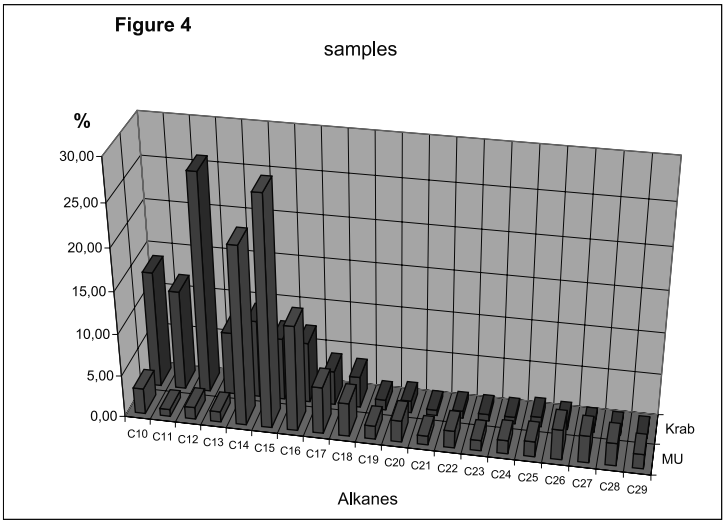


Figure 3: Alkane distribution of CPs in sediment samples





The n-alkane fingerprint for the sediment samples (Fig 3) shows the typical medium chain length chloroparaffin pattern. The samples additionally contain an increased proportion of longer chain paraffin waxes, which are indicative of either long chain paraffins with a low degree of chlorination (chlorine content 20 - 40 %) or chloroparaffin resins (chlorine content to 71 %) (see Fig. 1).

Figure 4 shows the percentile chloroparaffin content of mussel and crab meat. The alkane distribution, including longer chain paraffins, in mussel meat is similar to that of the sediment samples. Additional short chain alkanes (C_{10} to C_{13}) are found in crab meat, these are typical of short chain paraffins with a medium to high degree of chlorination (56 to 70 %).

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