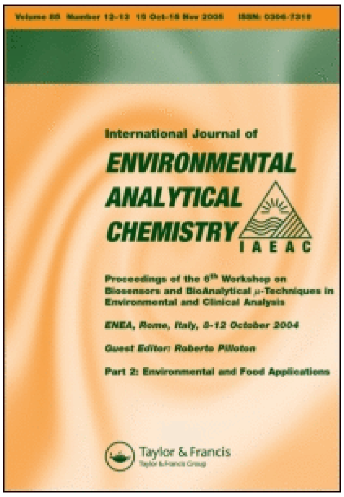

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Alkaline Degradation of Halogenated Pesticides and PCBs on Precolumn and Microreactor by Gas Chromatography

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The use of a precolumn or microreactor with KOH and NaOH packings is described for the degradation of twenty halogenated pesticides and PCBs. In both cases the recoveries and their time degradation development are studied.

It is found that after 48 h of conditioning of the precolumn or the microreactor, the recovery of aldrin and several other organochlorines is quantitative. For those pesticides which give a partial recovery, the microreactor is more convenient to use. For trifluralin, heptachlor, heptachlor epoxide and mirex the recoveries are lower than those obtained with ethanolic KOH.

KEY WORDS: Alkaline degradation, halogenated pesticide analysis, precolumn, microreactor, gas chromatography.

INTRODUCTION

The methods of analysis of halogenated pesticides and polychlorinated biphenyls (PCBs) in environmental samples by GC include several clean-up steps prior to the actual separation and determination. To this end adsorption columns such as Florisil,[1] alumina[2] or silica[3] columns are frequently used. However, these procedures require a considerable amount of time and reagents. In some cases the use of capillary GC can solve the overlapping of pesticide peaks.[4] Alternatively, derivatization[5] or chemical degradation[6] can be used, which present more advantages in routine analysis, offering derivatives which show an improved chromatographic separation.

The results obtained by chemical degradation help to confirm and determine several halogenated pesticides, by either the decrease or disappearance of their chromatographic signal, or the appearance of conversion products.

Ethanolic KOH is the reagent most used in order to carry out the degradation of a large number of pesticides.[7] For the DDTs, the use of ethanolic KOH and the subsequent oxidation into olefines with CrO_3 allows to determine PCBs without their interference.[8] Treatment with KOH, sulphuric acid, Raney nickel and Florisil have been used as clean-up procedures for PCB analysis.[9]

The alkaline treatment can be effected in the same chromatographic system in the gaseous phase, on a precolumn. With this system, and using KOH and NaOH as alkaline packings some pesticides have been studied.[10] This treatment can be carried out also by a microreactor situated before the chromatographic column with MgO[11] or KOH[12] packings for the DDTs and their metabolites.

EXPERIMENTAL

A Perkin-Elmer (Norwalk, CT, USA) Model Sigma 3B Gas Chromatograph with an electron-capture detector was used, as well as a Varian (Walnut Creek, CA, USA) Register-Integrator 4270 SP, 2 meter $\frac{1}{4}''$ o.d. glass columns packed with 1.5% OV-17 and 1.95% QF-1 on 80–100 mesh Chromosorb W-HP, and 25% NaOH on Chromosorb W-HP and 25% on Chromosorb W-HP as alkaline packings. The chromatographic conditions were: injector, 250°C; column, 185°C; detector, 300°C; column flow, 16 ml/min of N_2 for the non-alkaline system and 19 ml/min for precolumn and microreactor systems; make-up flow, 45 ml/min. Standard grade pesticides were used from Chem Service (P.O. Box 3108, West Cester, PA 19381, USA) and Alltech Associates (2051 Waukegan Road, Deerfield, IL 60015, USA). Chlordane was a technical mixture from Xpectrix Analytica (Crta, Cerdanyola 73–75, 08024, Sant Cugat del Vallés, Barcelona, Spain). Standard solutions were prepared in bidistilled benzene.

RESULTS AND DISCUSSION

The behaviour of the halogenated pesticides and PCBs on the precolumn and microreactor systems was studied based on the recoveries of either the original compounds or the conversion products. Injections of the corresponding pesticides were carried out with and without the presence of the alkaline packing. In the case of the precolumn system, it was necessary to use two chromatographic columns; one of them contained the alkaline packing in the head column, similar to the system used by Miller and Wells[10] (Figure 1a). In the microreactor system the alkaline packing was situated in the glass-liner of the injection port (Figure 1b); therefore it was only necessary to change the liner tube for another one without KOH to

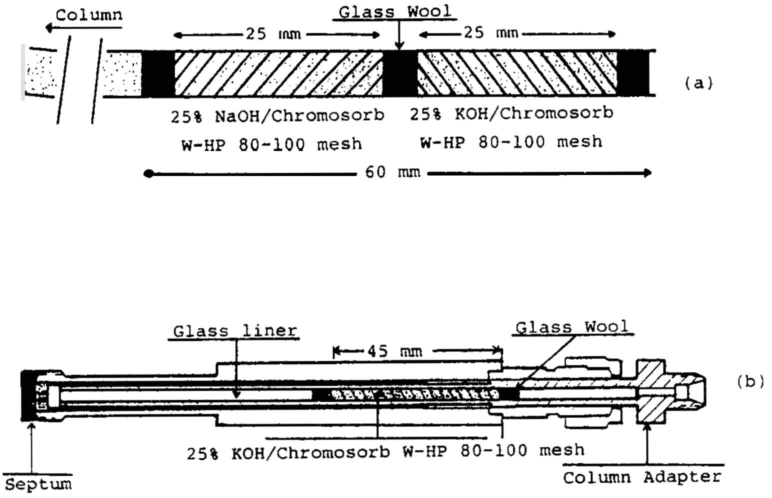

Figure 1 (a) Precolumn scheme. (b) Microreactor scheme.

obtain the corresponding recoveries. Recoveries were calculated by comparing peak areas for each component with and without the alkaline packing.

Precolumn system

In early experiments we observed that the use of a freshly prepared precolumn gave low recoveries for many pesticides and that this percentage increased with the time of use. This made necessary a previous conditioning of the system, also described by Miller and Wells.[10] After preconditioning at 185°C for 72 h we obtained recoveries higher than 90% for aldrin and the DDEs, while dieldrin and endrin gave a 48% recovery and HCB a recovery of only 7%. However, after preconditioning at 250°C for 48 h satisfactory recoveries were obtained for all the test solutes. Therefore, the precolumn system was conditioned at 250°C during 48 h with a nitrogen flow of 40 ml/min.

Replicate injections of aldrin showed an absolute recovery of 97–101%; this compound was therefore used as reference to obtain the recoveries of the other pesticides.

Table I gives retention times relative to aldrin for each pesticide with and without alkaline treatment. This table also shows the mean recovery values relative to aldrin ($n = 6$). After the alkaline treatment the results for unchanged pesticides were practically the same, with recoveries relative to aldrin of 97–102%.

According to their behaviour on the alkaline precolumn, the organochlorines studied were divided in three groups. The first is composed of those which do not suffer any type of degradation and whose recovery is complete: aldrin, dieldrin, endrin, HCB, o,p′-DDE, p,p′-DDE, Aroclor 1254 and Aroclor 1260. The recovery is close to 100% in all cases, and the relative standard deviation is about 3%. The second group comprises the compounds which are completely converted into a new product as a consequence of the alkaline treatment with the degradation products showing up as chromatographic peaks: o,p′-DDD, p,p′-DDD, o,p′-DDT, p,p′-DDT, dichloran, α- and β-endosulfan and methoxychlor; partial breakdown is shown by PCNB. In the third place or organochlorines which are completely (lindane and captan) or partly (trifluralin, heptachlor, heptachlor epoxide and mirex) converted into degradation product(s) without the latter showing up as chromatographic peaks. With

Table I Retention time and recovery relative to aldrin ($RRT_{aldrin} = 6.01$ min) using 1.5% QF-1 and 1.95% OV-17 column

Pesticide	Concentration (ppb)	Retention time relative to aldrin		Mean recovery (rel. to aldrin, %)	Observations
		Without precolumn	With precolumn		
HCB	20	0.459	0.456	109	Unchanged
Trifluralin	46	0.465	0.467	[b]	Partial recovery
Lindane	13	0.669	—	0	Decomposed
PCNB	57	0.679	0.248[a]	[b]	New product of degradation
Dichloran	600	0.761	1.043[a]	0	New product of degradation
Heptachlor	53	0.819	0.817	[b]	Partial recovery
Aldrin	52	1.000	1.000	100	Unchanged
Heptachlor epoxide	52	1.602	1.602	[b]	Partial recovery
o,p′-DDE	100	1.923	1.931	104	Unchanged
α-Endosulfan	60	2.049	0.786[a]	0	Endosulfandiol[c]
β-Endosulfan	26	3.896	0.786[a]	0	Endosulfandiol[c]
p,p′-DDE	100	2.391	2.408	99	Unchanged
Dieldrin	79	2.535	2.547	103	Unchanged
o,p′-DDD	84	2.899	1.551[a]	0	o,p′-DDMU[c]
Endrin	165	3.122	3.115	96	Unchanged
o,p′-DDT	100	3.540	1.935[a]	0	o,p′-DDE[c] (70%)
p,p′-DDD	96	3.887	1.921[a]	0	p,p′-DDMU[c]
p,p′-DDT	80	4.717	2.405[a]	0	p,p′-DDE[c] (95%)
Mirex	80	6.837	6.837	[b]	Partial recovery
Captan	121	9.483	—	0	Decomposed
Methoxychlor	135	9.573	5.435[a]	0	Methoxychlor olefine[c]
Aroclor 1254	646			100	Unchanged
Aroclor 1260	800			97	Unchanged

[a] Peak due to degradation product. [b] Recovery function of time. [c] Degradation product.

lindane and captan, the degradation peaks are probably obscured by the solvent peak.[7] In Figs. 2 and 3 chromatograms are shown obtained (a) without and (b) with the alkaline precolumn for several standards which belong to the three groups described above.

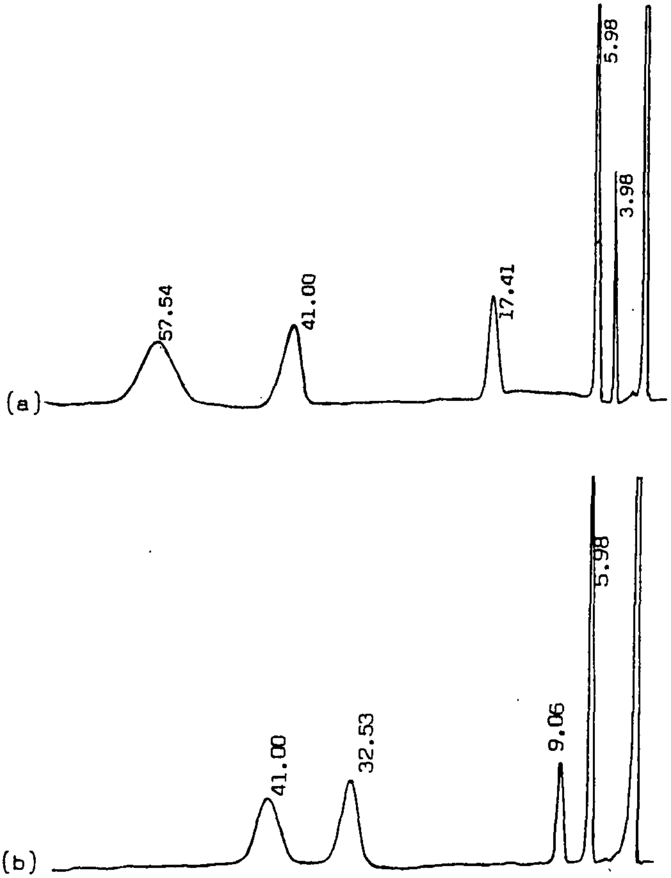

Figure 2 (a) Without precolumn, (b) with precolumn. Lindane (3.98 min), Aldrin (5.98 min), o,p′-DDMU (9.06 min), o,p′-DDD (17.41 min), Methoxychlor olefine (32.53 min), Mirex (41.00 min), Methoxychlor (57.54 min).

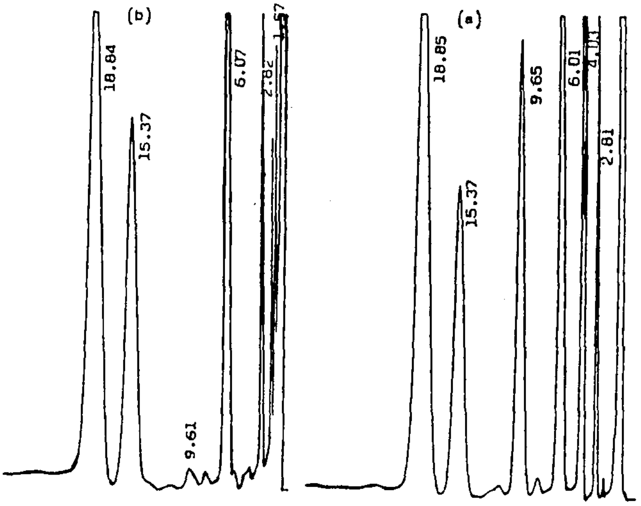

Figure 3 (a) Without precolumn, (b) with precolumn. Degradation product of PCNB (1.57 min), HCB (2.82 min), PCNB (4.03 min), Aldrin (6.01 min), Heptachlor epoxide (9.65 min), Dieldrin (15.37 min), Endrin (18.84 min).

Trifluralin, PCNB, heptachlor, heptachlor epoxide and mirex gave recovery values depending on the time of use of the precolumn as is shown in Table II. For the time studied (24 to 168 h) and continuously operating at 185°C increasing recoveries were obtained for these pesticides. For unchanged or fully degraded compounds the recoveries were constant during the period of 168 h. Operating

Table II Recovery relative to aldrin against the time of use of the precolumn

Pesticide	Continuous development time (hours)					Discontinuous development[a]
	24	72	120	144	168	
Trifluralin	7	31	33	36	38	81
PCNB	1	3	4	6	9	60
Heptachlor	1	1	2	3	4	48
Heptachlor epoxide	4	18	23	26	31	91
o,p′-DDD	0	0	0	0	0	54
o,p′-DDT	0	0	0	0	0	37
Mirex	45	52	59	63	68	93

[a] See text.

discontinuously (deconnecting the precolumn for 48 h after its continuous use for 168 h) gave higher recoveries for all of the compounds and the recovery was almost complete now for heptachlor epoxide and mirex. Besides, under those conditions o,p'-DDT and o,p'-DDD showed less degradation: the original products were partly recovered. This is in contrast with the behaviour of the isomers p,p'-DDT and p,p'-DDD, which are degraded more easily[13] and which did not show up. In contrast, captan and methoxychlor—both when working continuously and discontinuously—disappear completely and instantaneously from our system, as against a slower alkaline degradation in solution.[14,15]

Microreactor system

Early experiments showed low recoveries for most pesticides studied as was also observed on the precolumn and the recoveries increased with the time of its use. If the microreactor was kept at least 48 h at 250°C (injector temperature), the recoveries of the unchanged pesticides were practically quantitative; therefore, the alkaline degradation in this system was carried out between 48 and 168 h.

Aldrin gave a recovery of 98–101% under these conditions. HCB, o,p'-DDE, p,p'-DDE, dieldrin, endrin and the Aroclors 1254 and 1260 were recovered completely (96–103%). Lindane, dichloran, α- and β-endosulfan, o,p'-DDD, p,p'-DDD, o,p'-DDT, p,p'-DDT, captan and methoxychlor were degraded completely as on the precolumn system. The conversion of o,p'-DDT and p,p'-DDT into o,p'-DDE and p,p'-DDE were 69 and 96%, respectively.

In Table III the recovery percentages are shown as a function of

Table III Recovery relative to aldrin against the time of use of the microreactor

Pesticide	Time (hours)				
	48	72	120	144	168
Trifluralin	4	5	12	21	32
PCNB	0.7	1	1	1.2	1
Heptachlor	3	3	3	5	6
Heptachlor epoxide	0.8	1	1	1	1
Mirex	40	41	43	48	52

the time of use of the microreactor for trifluralin, PCNB, heptachlor, heptachlor epoxide and mirex. Values which are lower than those obtained on the precolumn can probably be explained by the higher temperature of the microreactor in comparison with the precolumn system, which causes more degradation, In the case of PCNB and heptachlor epoxide, the recoveries are practically constant with time (about 1%), which contrasts with the increasing recoveries when the precolumn system was used.

CONCLUSIONS

The alkaline packing in the precolumn or microreactor system does not significantly change the retention times relative to aldrin for those compounds which do not suffer any degradation. The recoveries are similar for the unchanged pesticides as well as for those degraded completely. For those which give a partial recovery the microreactor effects more degradation, especially for heptachlor epoxide and PCNB.

The "degradation activity" of both systems decreases with their continuous use: for pesticides which suffer a partial degradation, the recovery increases with time. This fact is less pronounced in the case of the microreactor. Besides, the recoveries obtained with discontinuous operation of the precolumn system indicate a slight loss of degradation activity; even o,p′-DDD and o,p′-DDT are partly recovered.

The precolumn and microreactor treatment yield more degradation than obtained with ethanolic KOH,[7] since those pesticides only partly recovered in our systems such as trifluralin, heptachlor, heptachlor epoxide and mirex, are completely recovered upon treatment with ethanolic KOH. From a practical point of view our precolumn and microreactor systems offer advantages compared with the solution method because they are more rapid and require less sample handling. The microreactor is more convenient to use, since it requires only one column; besides it is easy to replace the degradation element situated in the injector port.

The microreactor system can be used continuously for 40–50 consecutive injections, i.e. for about five days. This was confirmed by analyses carried out with hexane extracts of marine organisms and sediments samples (United Nations Programme for Environment in its Action Plan for Mediterranean Sea, MEDPOL). For the contents of the DDTs, PCBs, HCB, lindane and aldrin found in these samples, no relationship between their concentration and the degradation capacity of the alkaline packing was observed. These concentrations were similar to those of the standard solutions used in this work.

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