

Note

Gas chromatographic and gas chromatographic–mass spectrometric studies of acetate esters of chlorinated phenols

I. O. O. KORHONEN* and J. KNUUTINEN

Department of Chemistry, University of Jyväskylä, Kyllikinkatu 1-3, SF-40100 Jyväskylä 10 (Finland)

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The determination of chlorinated phenolic compounds in waters and other environmental samples is of great importance. Chlorinated phenols cause serious problems with taste and odour in drinking water. Some chlorophenols occur as residues from fungicides, bactericides, herbicides, wood preservatives and as metabolites and degradation products of a number of pesticides. An important source of most chlorophenols is also pulp bleaching. 2,4-Dichlorophenol, 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol, for example have been identified in the effluents from pulp mills¹⁻⁶.

Most of the recent determinations of chlorinated phenols have been based on glass capillary gas chromatography (GC) and glass capillary GC–mass spectrometry (GC–MS). The compounds have in general been determined on non-polar capillary columns as their acetyl^{1,7-9}, ethyloxy^{2,3} or silyl ether derivatives^{4,5}. The sensitivity of an electron capture detector (ECD) to phenol residues has been increased by using a halogen-containing derivatization reagent, *e.g.*, heptafluorobutyric anhydride⁶. To our knowledge, however, a systematic GC study of acetyl derivatives of all possible chlorinated phenols on both polar and non-polar stationary phases has not been made.

Recently, GC and GC–MS studies of a series of chlorinated alkyl acetates¹⁰⁻¹² and acetylated phenolic compounds¹³⁻¹⁶ have been carried out in our laboratory. The aim of this investigation was to study the GC retention behaviour of the acetate esters of chlorophenols on SE-30 and OV-351 quartz capillary columns and to obtain comprehensive GC–MS data for future qualitative and quantitative determinations.

EXPERIMENTAL

Samples

Commercial chlorophenols (Fluka, Buchs, Switzerland) were converted into acetyl derivatives by the method described by Renberg and Lindström¹⁷. The products were identified by glass capillary GC–MS, and the crude reaction mixtures were used for GC analyses.

Gas chromatography

GC analyses were carried out on a Perkin-Elmer Model Sigma 3 instrument under the following running conditions: injector temperature, 260°C; flame-ionization detector temperature, 275°C; nitrogen carrier gas flow-rate, 1 ml/min; splitting

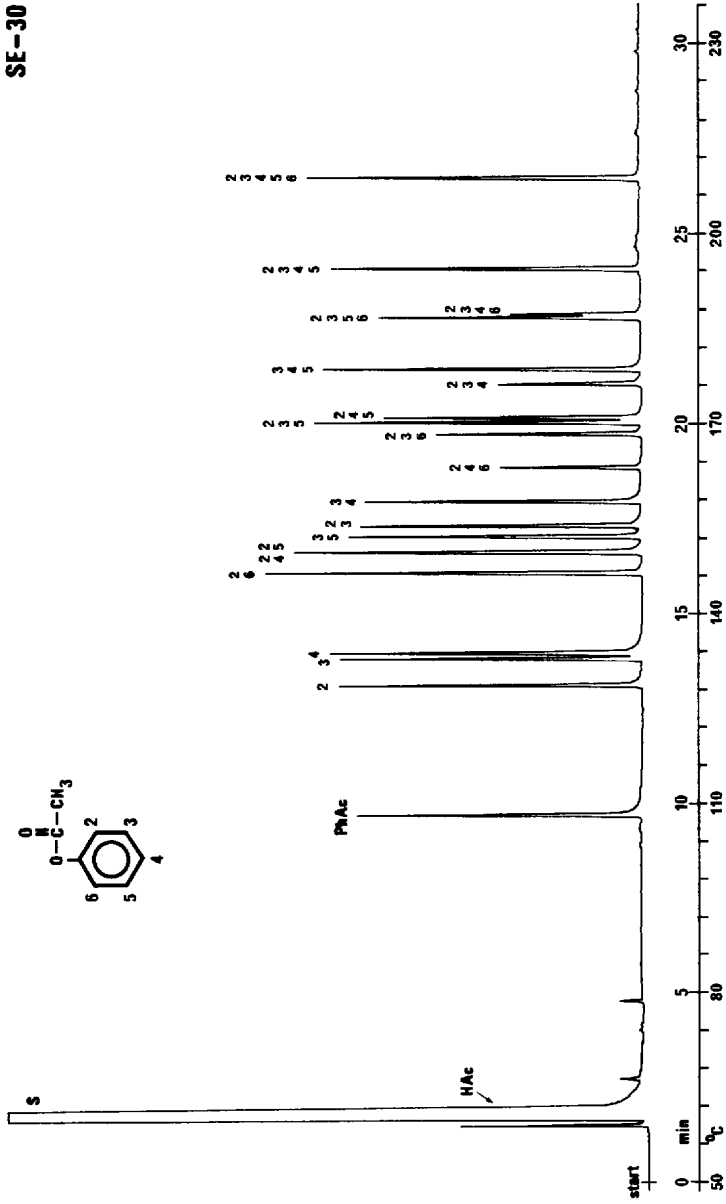


Fig. 1. Chromatogram of a mixture of acetate esters of phenol (PhAc) and chlorophenols (the numbers indicate the chlorinated positions) on an SE-30 quartz capillary column. S = solvent; HAc = acetic acid (formed in the derivatization). Temperature programmed from 50 to 240°C at 6°C/min.

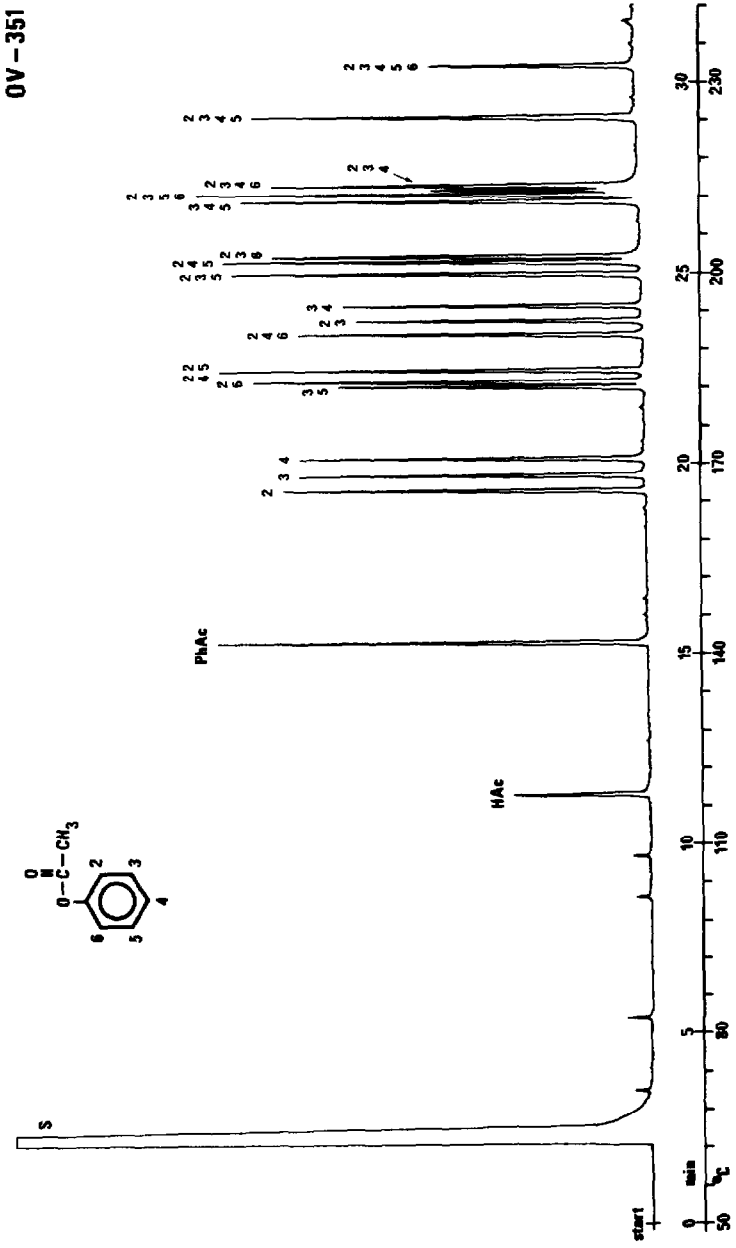


Fig. 2. Chromatogram of a mixture of acetate esters of phenol (PhAc) and chlorophenols (the numbers indicate the chlorinated positions) on an OV-351 quartz capillary column. S = solvent; HAc = acetic acid (formed in the derivatization). Temperature programmed from 50 to 240°C at 6°C/min.

TABLE I

RELATIVE RETENTION TIMES (RRT) FOR CHLORINATED PHENYL ACETATES ON SE-30 AND OV-351 QUARTZ CAPILLARY COLUMNS WITH TEMPERATURE-PROGRAMMING FROM 50 TO 240°C

For formula, see inserts in Figs. 1 and 2.

Compound*	Relative retention time**									
	2°C/min		4°C/min		6°C/min		8°C/min		10°C/min	
	SE-30	OV-351	SE-30	OV-351	SE-30	OV-351	SE-30	OV-351	SE-30	OV-351
PhAc	1.00 (15.74)	1.00 (30.69)	1.00 (11.70)	1.00 (20.08)	1.00 (9.67)	1.00 (15.31)	1.00 (8.42)	1.00 (12.80)	1.00 (7.56)	1.00 (11.17)
2	1.55	1.38	1.41	1.28	1.35	1.26	1.31	1.24	1.28	1.23
3	1.68	1.42	1.50	1.31	1.43	1.29	1.37	1.26	1.34	1.25
4	1.70	1.46	1.52	1.35	1.44	1.32	1.38	1.29	1.35	1.27
23	2.30	1.76	1.95	1.60	1.79	1.55	1.69	1.51	1.63	1.47
24 + 25	2.18	1.65	1.86	1.51	1.72	1.46	1.63	1.43	1.57	1.40
26	2.07	1.62	1.79	1.48	1.66	1.45	1.56	1.41	1.53	1.38
34	2.42	1.80	2.03	1.63	1.86	1.58	1.75	1.53	1.68	1.49
35	2.26	1.61	1.91	1.48	1.76	1.44	1.67	1.40	1.60	1.38
234	2.96	2.07	2.41	1.85	2.17	1.78	2.03	1.71	1.94	1.67
235	2.80	1.87	2.29	1.69	2.07	1.63	1.94	1.58	1.85	1.54
236	2.74	1.91	2.25	1.72	2.04	1.66	1.92	1.61	1.83	1.57
245	2.81	1.90	2.30	1.71	2.08	1.65	1.95	1.60	1.86	1.56
246	2.58	1.73	2.14	1.57	1.95	1.53	1.83	1.48	1.76	1.45
345	3.04	2.04	2.46	1.83	2.22	1.76	2.07	1.69	1.97	1.65
2345	3.50	2.24	2.79	1.98	2.49	1.90	2.31	1.83	2.18	1.76
2346	3.28	2.08	2.64	1.85	2.36	1.78	2.20	1.72	2.09	1.67
2356	3.27	2.06	2.63	1.84	2.36	1.77	2.19	1.71	2.08	1.66
23456	3.92	2.35	3.09	2.08	2.74	1.99	2.53	1.91	2.38	1.87

* PhAc = phenyl acetate; the numbers indicate the chlorinated positions.

** Relative retention time for phenyl acetate (PhAc) taken as 1.00; the absolute retention time of PhAc is given in parentheses.

ratio, 1:25; and chart speed, 10 mm/min. The columns used were a vitreous silica SE-30 wall-coated open-tubular (WCOT) column (25 m × 0.22 mm I.D.), supplied by Scientific Glass (North Melbourne, Australia) and a fused-silica OV-351 WCOT column (25 m × 0.32 mm I.D.), supplied by Orion Analytica (Espoo, Finland). The column temperatures used are given in Table I.

Gas chromatography-mass spectrometry

GC-MS data were recorded on a Varian MAT-212 mass spectrometer connected with a Varian Model 3700 gas chromatograph, equipped with a 50 m × 0.30 mm I.D. vitreous silica SE-30 WCOT column (Scientific Glass). The helium flow-rate was 1 ml/min and the column temperature was programmed from 50 to 240°C at 6°C/min. The electron ionizing energy was 70 eV and the ion source temperature *ca.* 230°C. Data were acquired and processed on a Spectro System MAT-188. Mass numbers from *m/z* 50 to 320 were recorded. The most characteristic fragment ions of the compounds studied are given in Table II.

RESULTS AND DISCUSSION

Chromatograms of a mixture of acetate esters of phenol and chlorinated phenols on SE-30 and OV-351 quartz capillary columns obtained under the optimum

operating conditions are illustrated in Figs. 1 and 2. The retention data are given in Table I.

Fig. 1 shows that the compounds are eluted on a non-polar column in order of their degree of chlorination (*i.e.*, all dichloro isomers before trichloro isomers and the latter before tetrachloro isomers). Our results for the elution order of compounds on the SE-30 quartz capillary column are, with one exception, the same as those obtained on SE-30 glass capillary columns by other workers^{7,8}; however, 3,4- and 3,5-dichloro isomers were eluted in the reverse order. Owing to the latter diverging results, we repeated the derivatization of pure commercial phenols but the same reversed elution order was observed. The pure 3,4- and 3,5-dichlorophenols were eluted on the SE-30 column used in the same order as their acetylated derivatives, the 3,5-dichloro isomer being eluted first.

Fig. 2 shows that a different elution order on a polar column is observed, 2,4,6-trichlorophenyl acetate (246) being eluted between dichloro isomers (24 + 25 and 23) and the 2,3,4-trichloro derivative (234) between tetrachloro isomers (2356 and 2346).

Comparison of the results obtained on OV-351 and SE-30 indicates that electron-withdrawing chlorine substituent(s) at the carbon atom(s) adjacent to the acyl group (*i.e.*, in the *ortho*-position) have stronger polar and steric effects than substituents further away, as in halogenated alkyl acetates^{11,12}. Vicinal chloro substituents give rise to strong steric hindrance, which seems to exceed the polar effects. This can be seen from the relatively long retention times of 23, 34, 234, 236, 345 and 2345 on OV-351. With symmetrical 35 and 246 compounds the chloro substituents are at a considerable distance from each other, giving rise to relatively short retention times and reversed elution orders on a polar phase compared with the other isomers (Fig. 2).

Of special interest is the retention behaviour of the compounds that may be formed in the pulp industry and occur in nature as residues from some other sources. For example, 2,4-dichlorophenol has been analysed as its acetyl derivative on a non-polar column¹. However, the present study shows that this compound has the same retention behaviour as the 2,5-dichloro derivative on both a polar and a non-polar stationary phase. In addition, some partial overlapping has been observed. Unfortunately, 2346, which has been found in pulp bleach liquors^{1,5}, was overlapped with 2356 on SE-30 and with 234 on OV-351. However, those compounds are unlikely reaction products of chlorine and lignin and thus do not occur in effluents. Nevertheless, the most important 246 isomer clearly has different retention times to the other chlorinated phenyl acetates on both columns.

CONCLUSIONS

The present GC and GC-MS data are useful for the analysis of chlorinated phenols and related compounds. The best separation of the compounds studied was observed on an SE-30 quartz capillary column. However, a polar column is suitable for the separation of some structural isomers. Hence, the simultaneous use of columns with polar and non-polar stationary phases is recommended.

The electron-impact mass spectral fragmentations of structural isomers were very similar (Table II). However, the relative intensities of the epoxide ion and also some other fragments can be used for identification purposes, by plotting mass chromatograms to increase the sensitivity of the method. However, the use of commercially available model substances and GC-MS studies gives the best structural verification of unknown isomers in multi-component samples.

TABLE II
70 eV ELECTRON-IMPACT MS DATA FOR PHENYL ACETATE AND CHLORINATED PHENYL ACETATES

Ions containing ^{37}Cl are not shown. For formula, see inserts in Figs. 1 and 2.

Compound*	Ion, m/z (> 50), relative intensity (%)	M^+	$ M-\text{CH}_2\text{CO} ^{++}$	$ M-\text{CH}_2\text{CO}-\text{CO} ^{++}$	$ M-\text{CH}_2\text{CO}-\text{CHO} ^{++}$	$ M-\text{CH}_2\text{CO}-\text{HC} ^{++}$	$ M-\text{CH}_2\text{CO}-\text{CO}-\text{Cl} ^+$	$ M-\text{CH}_2\text{CO}-\text{CHO}-\text{Cl} ^{++}$	$ M-\text{CH}_2\text{CO}-\text{CO}-\text{HC} ^{++}$	$ M-\text{CH}_2\text{CO}-\text{CHO}-\text{HC} ^+$	Remaining peaks, m/z (rel. intensity $\geq 10\%$)
PhAc	136 (6)	94 (100)	66 (20)	65 (11)	—	—	—	64 (20)	—	63 (16)	73 (10).
2	170 (5)	128 (100)	100 (7)	99 (7)	92 (10)	—	65 (8)	64 (13)	—	63 (16)	73 (11).
3	170 (6)	128 (100)	100 (13)	99 (9)	92 (4)	—	65 (24)	64 (8)	—	63 (13)	73 (12).
4	170 (5)	128 (100)	100 (13)	99 (8)	92 (2)	—	65 (21)	98 (18)	—	97 (4)	73 (11), 63 (39).
23	204 (6)	162 (100)	134 (1)	133 (10)	126 (30)	—	99 (8)	—	—	—	62 (11).
24	204 (3)	162 (100)	134 (1)	133 (11)	126 (11)	—	99 (10)	98 (25)	—	97 (3)	73 (21), 63 (44), 62 (13)
25	204 (6)	162 (100)	134 (3)	133 (8)	126 (5)	—	99 (13)	98 (13)	—	97 (3)	73 (15), 63 (30).
26	204 (4)	162 (100)	134 (1)	133 (10)	126 (13)	—	99 (10)	98 (19)	—	97 (5)	73 (27), 63 (59), 62 (19).
34	204 (4)	162 (100)	134 (8)	133 (8)	126 (4)	—	99 (26)	98 (10)	—	97 (4)	73 (16), 63 (29), 62 (11).
35	204 (9)	162 (100)	134 (5)	133 (9)	126 (4)	—	99 (27)	98 (11)	—	97 (4)	73 (19), 63 (38), 62 (15).
234	238 (1)	196 (100)	168 (—)	167 (9)	160 (23)	—	133 (4)	132 (19)	—	131 (5)	107 (17), 97 (70), 96 (18), 83 (16), 73 (22), 71 (24), 62 (39), 61 (35).
235	238 (7)	196 (100)	168 (1)	167 (10)	160 (25)	—	133 (10)	132 (14)	—	131 (3)	107 (17), 97 (57), 96 (10), 73 (16), 62 (36), 61 (25).

236	238	(6)	196 (100)	168 (-)	167 (13)	160 (17)	133 (8)	132 (19)	131 (2)	107 (18), 97 (67), 96 (13), 83 (13), 73 (20), 67 (15), 62 (33), 61 (28), 107 (19), 97 (58), 96 (11), 83 (10), 73 (24), 62 (47), 61 (32).
245	238	(4)	196 (100)	168 (1)	167 (12)	160 (5)	133 (14)	132 (22)	131 (3)	
246	238	(2)	196 (100)	168 (-)	167 (9)	160 (11)	133 (5)	132 (22)	131 (4)	107 (20), 97 (39), 83 (12), 73 (10), 62 (27), 61 (26), 107 (11), 97 (41), 83 (11), 73 (16), 62 (43), 61 (25).
345	238	(5)	196 (100)	168 (1)	167 (10)	160 (8)	133 (24)	132 (11)	131 (1)	141 (11), 131 (64), 107 (24), 96 (59), 95 (16), 83 (23), 71 (16), 61 (75).
2345	272	(2)	230 (87)	202 (-)	201 (9)	194 (14)	167 (10)	166 (12)	165 (1)	
2346	272	(3)	230 (88)	202 (-)	201 (10)	194 (15)	167 (6)	166 (16)	165 (-)	141 (11), 131 (69), 107 (19), 97 (36), 96 (59), 83 (36), 73 (18), 65 (17), 61 (72).
2356	272	(7)	230 (86)	202 (-)	201 (14)	194 (12)	167 (4)	166 (13)	165 (-)	131 (55), 107 (25), 97 (21), 96 (50), 83 (22), 71 (14), 65 (14), 61 (48).
23456	306	(2)	264 (63)	236 (-)	235 (11)	228 (7)	201 (2)	200 (9)	199 (-)	165 (42), 141 (19), 130 (49), 117 (18), 95 (57), 71 (24), 66 (15), 65 (20).

* PhAc = phenyl acetate; the numbers indicate the chlorinated positions.

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