

CHROM. 15,431

Note

Gas chromatographic separation of acetylated chlorinated phenols, guaiacols and catechols on an SE-30 quartz capillary column

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(Received October 7th, 1982)

Recently, the gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) of acetylated chlorophenols¹, chloroguaiacols^{2,3} and chlorinated 4-hydroxybenzaldehydes⁴ have been studied in our laboratory. Chlorinated catechols⁵ and guaiacols⁶ have been found to occur in spent bleach liquors of kraft pulp mills, and studies in this area have been reported, *e.g.*, by Finnish⁷⁻⁹, Swedish^{10,11} and Canadian workers¹²⁻¹⁵.

The purpose of this work was to establish the optimum operating conditions for the simultaneous determination of all acetylated phenols, guaiacols and catechols. The GC data given are especially practical as most of the model substances are not commercially available, some of them having been synthesized only in our laboratory¹⁶.

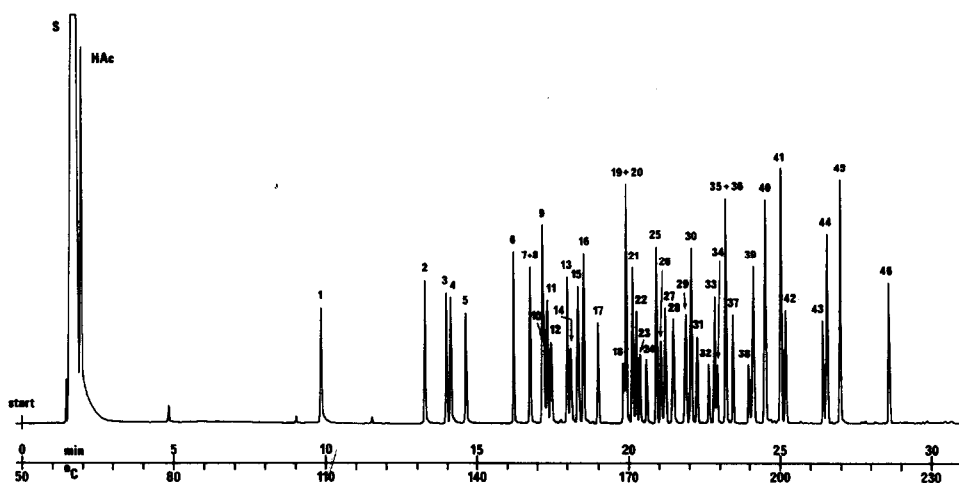
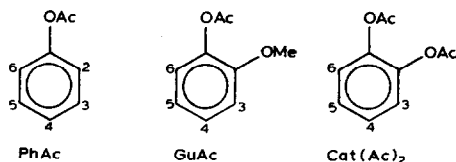


Fig. 1. Chromatogram of a mixture of acetyl derivatives of phenols, guaiacols and catechols on an SE-30 quartz capillary column. Temperature programmed from 50°C at 6°C/min. S = solvent; HAc = acetic acid; peaks identified in Table I.

TABLE I

ABSOLUTE AND RELATIVE RETENTION TIMES OF THE TITLE COMPOUNDS AND THEIR CHLORINATED DERIVATIVES ON AN SE-30 QUARTZ CAPILLARY COLUMN

Column temperature programmed from 50 to 240°C at 6°C/min. Conditions as shown in Fig. 1. Me = Methyl.



Peak No.	Compound*	ART**	RRT***	RRT [†]
1	PhAc	9.84	1.00	0.48
2	PhAc 2	13.23	1.34	0.65
3	PhAc 3	13.93	1.42	0.68
4	PhAc 4	14.07	1.43	0.69
5	GuAc	14.57	1.00	0.72
6	PhAc 2,6	16.18	1.64	0.79
7	PhAc 2,4	16.72	1.70	0.82
8	PhAc 2,5	16.72	1.70	0.82
9	Cat (Ac) ₂	17.13	1.00	0.84
10	PhAc 3,5	17.17	1.74	0.84
11	GuAc 3	17.28	1.19	0.85
12	PhAc 2,3	17.41	1.77	0.85
13	GuAc 6	17.94	1.23	0.88
14	PhAc 3,4	18.05	1.83	0.89
15	GuAc 4	18.29	1.26	0.90
16	GuAc 5	18.47	1.27	0.91
17	PhAc 2,4,6	18.94	1.92	0.93
18	PhAc 2,3,6	19.83	2.02	0.97
19	Cat (Ac) ₂ 3	19.92	1.16	0.98
20	GuAc 3,6	19.94	1.37	0.98
21	PhAc 2,3,5	20.12	2.04	0.99
22	PhAc 2,4,5	20.24	2.06	0.99
23	GuAc 3,5	20.37	1.40	1.00
24	Cat (Ac) ₂ 4	20.60	1.20	1.01
25	GuAc 4,6	20.93	1.44	1.03
26	PhAc 2,3,4	21.10	2.14	1.04
27	GuAc 3,4	21.22	1.46	1.04
28	PhAc 3,4,5	21.49	2.18	1.05
29	GuAc 5,6	21.90	1.50	1.08
30	GuAc 4,5	22.06	1.51	1.08
31	Cat (Ac) ₂ 3,6	22.25	1.30	1.09
32	Cat (Ac) ₂ 3,5	22.65	1.32	1.11
33	PhAc 2,3,5,6	22.84	2.32	1.12
34	PhAc 2,3,4,6	22.92	2.33	1.13
35	GuAc 3,4,6	23.21	1.59	1.14
36	GuAc 3,5,6	23.21	1.59	1.14
37	Cat (Ac) ₂ 3,4	23.45	1.37	1.15
38	Cat (Ac) ₂ 4,5	23.98	1.40	1.18
39	PhAc 2,3,4,5	24.12	2.45	1.18
40	GuAc 3,4,5	24.51	1.68	1.20

TABLE I (continued)

Peak No.	Compound*	ART**	RRT***	RRT [†]
41	GuAc 4,5,6	25.02	1.72	1.23
42	Cat (Ac) ₂ 3,4,6	25.17	1.47	1.24
43	Cat (Ac) ₂ 3,4,5	26.40	1.54	1.30
44	PhAc 2,3,4,5,6	26.52	2.70	1.30
45	GuAc 3,4,5,6	26.97	1.85	1.32
46	Cat (Ac) ₂ 3,4,5,6	28.58	1.67	1.40

* PhAc = phenol acetate; GuAc = guaiacol acetate; Cat (Ac)₂ = catechol diacetate; the numbers indicate the chlorinated positions.

** Absolute retention times (min) measured from sample injection (Fig. 1).

*** Relative retention times for the non-chlorinated compounds [PhAc, GuAc, Cat (Ac)₂] taken as 1.00.

[†] Relative retention time for 3,5-dichloroguaiacol acetate (GuAc 3,5) taken as 1.00. (Compound is suitable as an internal standard.)

EXPERIMENTAL

Apparatus

GC analyses were carried out on a Perkin-Elmer Sigma 3 gas chromatograph equipped with a flame-ionization detector and an SE-30 quartz capillary column (25 m × 0.22 mm I.D.), supplied by SGE (North Melbourne, Australia), with a nitrogen flow-rate of 1 ml/min. The column temperature was programmed from 50 to 240°C at 6°C/min. The splitting ratio was 1:20 and the temperatures of the injector and detector were 270°C.

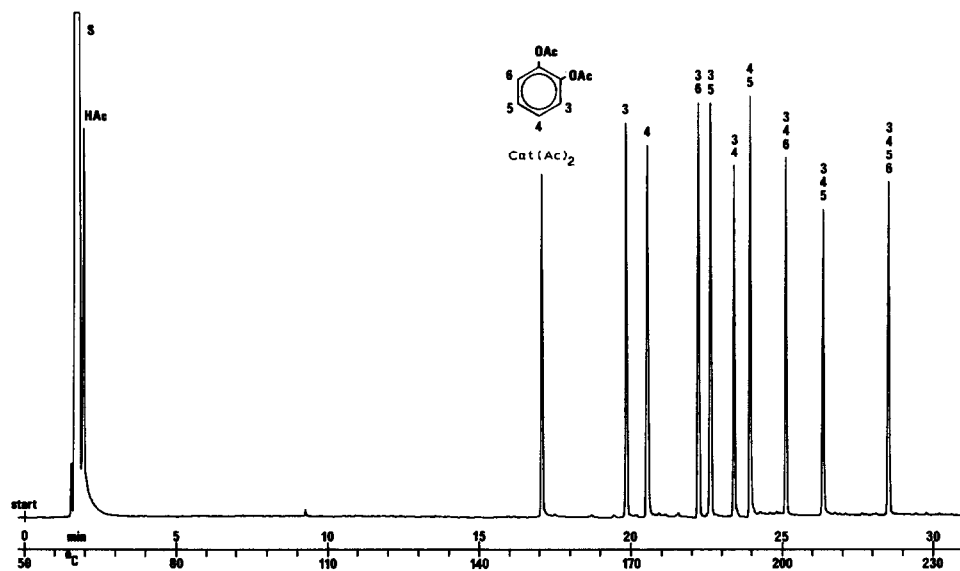


Fig. 2. Chromatogram of catechol diacetate, Cat(Ac)₂, and its chlorinated derivatives. The numbers indicate the chlorinated positions. S = Solvent; HAc = acetic acid.

Samples

Phenol, guaiacol, catechol and chlorinated phenols were commercially available (Fluka, Buchs, Switzerland). The syntheses of chlorinated guaiacols and catechols and the acetylation method used are given in ref. 2. The formation of each derivative was verified by GC-MS.

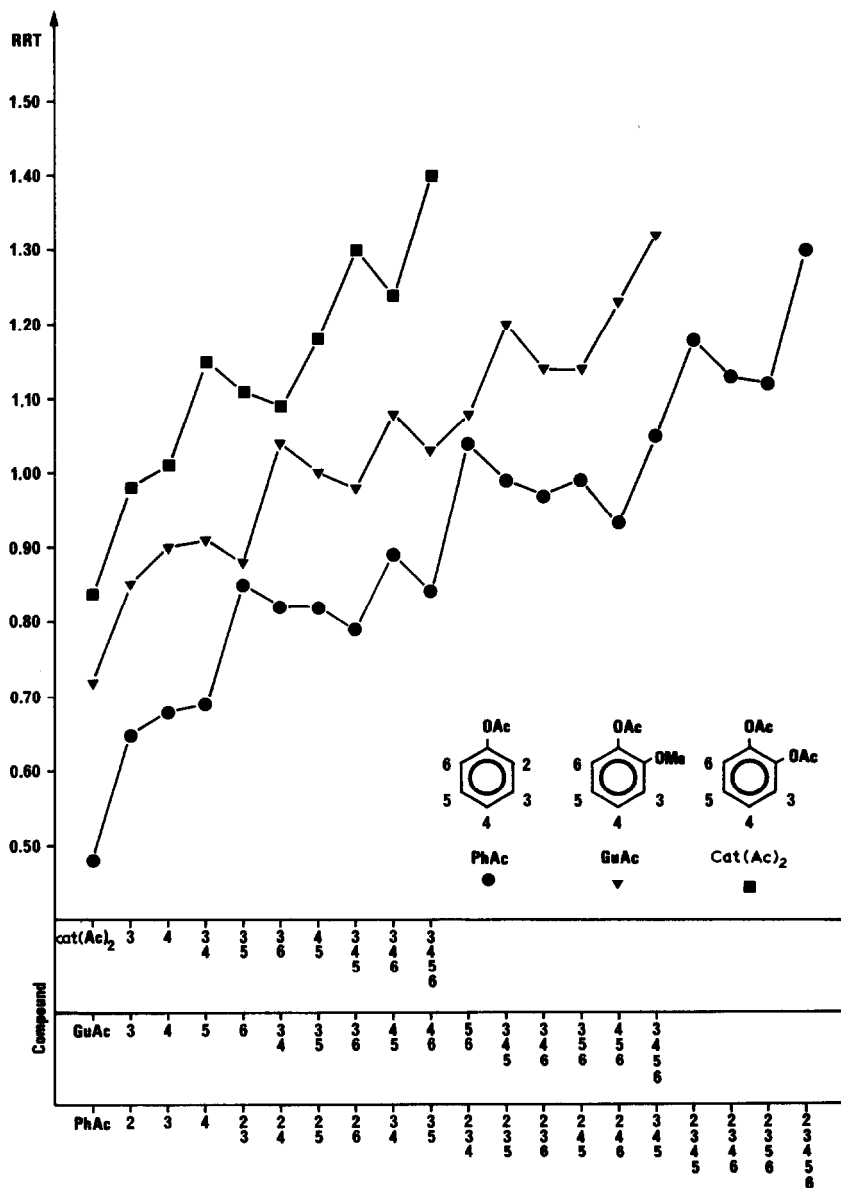


Fig. 3. Relative retention times (RRT) for compounds studied, referred to 3,5-dichloroguaiacol acetate (GuAc 3,5). PhAc = phenol acetate; GuAc = guaiacol acetate; Cat(Ac)₂ = catechol diacetate. The numbers indicate the chlorinated positions.

RESULTS AND DISCUSSION

The best separation of the mixture of the compounds studied occurred with a temperature programme from 50°C at 6°C/min (Fig. 1). The retention data relative to the non-chlorinated compounds and 3,5-dichloroguaiacol acetate (suitable as an internal standard, not found in spent bleach liquors⁶) are given in Table I.

As previously reported¹, the peaks of 2,4- and 2,5-dichlorophenyl acetates overlapped and some partial overlaps of the other isomers were also found. A slightly better separation of the acetylated guaiacols occurred, only 3,4,6- and 3,5,6-trichloro isomers overlapping². On the other hand, the acetylated chlorocatechols were completely separated, as can be seen from Fig. 2.

Fig. 3 shows that the order of elution of the chloro derivatives agrees with that of the corresponding non-chlorinated compounds, *i.e.*, acetylated phenols, guaiacols and catechols. Only two additional overlaps were detected on analysing a mixture of all 46 compounds (Fig. 1). 3,5-Dichlorophenyl acetate was separated as an unresolved shoulder with catechol diacetate and the peaks of 3-chlorocatechol diacetate and 3,6-dichloroguaiacol acetate completely overlapped.

Of special interest is the separation of components formed in the pulp industry. The compounds overlapped (acetates of 2,5-dichlorophenol, 3,5,6-trichloroguaiacol and 2,3,5,6-tetrachlorophenol) have not hitherto been found to occur in the effluents of pulp mills and thus they do not interfere, *e.g.*, in quantitative determinations.

ACKNOWLEDGEMENTS

This work was supported financially by the Foundation for Research on Natural Resources in Finland, the Media Corporation Research Foundation, the Alfred Kordelin Foundation, the Maj and Tor Nessling Foundation and the Academy of Finland.

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