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Note

Separation and identification of chloropyridine isomers and quantitative determination of pentachloropyridine in chlorinated pyridine residues by gas chromatography–mass spectrometry

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Chloropyridine compounds are important intermediates in the preparation of pesticides, herbicides, dyes, pharmaceuticals and plastics. Chlorination of pyridine and the reduction of pentachloropyridine (PCP) are widely employed[1–5] to give desired chlorinated pyridine isomers. Giacobbe *et al.*[6] have reported UV data of individual chloropyridine isomers in various solvents. The separation of 2,3,5,6-tetrachloro-, 2,3,6-trichloro- and 2,6-dichloropyridine isomers by column chromatography[4] has been studied. The separation of 2,5-, 2,6-, and 3,5-dichloropyridine isomers by gas chromatography has been reported[7]. Several other methods[8–21] are available for characterization.

The literature survey revealed that no specific method is available for the analysis of chloropyridine isomers in mixtures. Hence, the separation and identification of these chloropyridine isomers in chlorinated pyridine residues by gas chromatography–mass spectrometry (GC–MS) was studied and the results are reported here. Owing to the importance of PCP in industry, a method for its quantitative determination by GC was developed and the results are presented.

EXPERIMENTAL

Instrumentation

A Hewlett-Packard Model 5840 A gas–liquid chromatograph equipped with a flame-ionization detector and an electronic integrator was used for GC studies. A Micromass 70-70H mass spectrometer coupled with a Pye Unicam gas chromatograph was used for GC–MS studies.

The following columns were used: I, 6 ft. × 1/8 in. O.D. stainless-steel column packed with 10% DEGA on Chromosorb P AW (80–100 mesh); II, 12 ft. × 1/8 in. O.D. stainless-steel column packed with 3% DEGA on Chromosorb W AW (80–100 mesh).

GC conditions

Column I was used for GC studies. The temperatures were column 180°C, injector 300°C and flame-ionization detector 300°C. The carrier gas (nitrogen) flow-rate was 32 ml/min.

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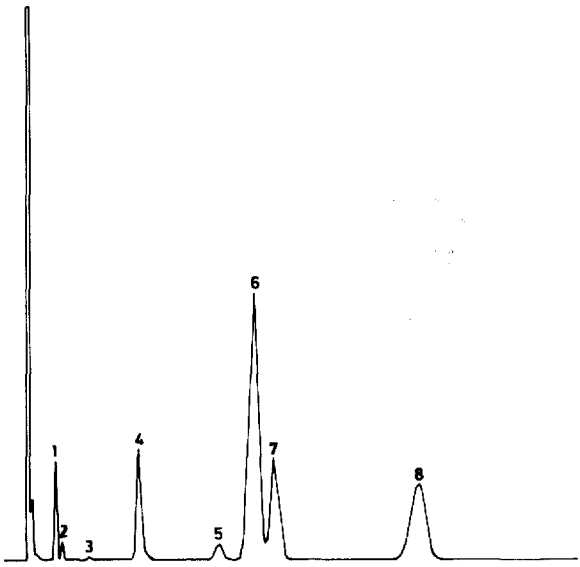

Fig. 1. Separation of chloropyridine isomers by GC. For conditions, see text. Peaks: 4 and 5 = trichloropyridine isomers; 6 and 7 = tetrachloropyridine isomers; 8 = pentachloropyridine.

GC–MS conditions

Column II was used for GC–MS studies. The temperatures were column 130°C, injector 250°C and ion Source 200°C. The helium flow-rate was 30 ml/min and the ionizing voltage was 35 eV. The data were processed by a PDP 8 computer.

RESULTS AND DISCUSSION

The separation of chloropyridine isomers in chlorinated pyridine residues on column I is shown in Fig. 1 and the relative retention times of the various isomers are given in Table I. The peaks were identified as penta-, tetra- and trichloropyridine isomers by means of mass spectra.

The mass chromatogram of the separation of these isomers on column II is shown in Fig. 2. Table II gives the mass spectral fragmentation data for the isomers separated. It can be seen from Table II that the molecular ions corresponding to peaks 4, 5, 6, 7 and 8 in Fig. 2 represent tri-, tetra- and pentachloropyridine isomers respectively, but could not help in identifying the individual tetra- and trichloro isomers.

The sequences of degradation observed in the mass spectra are regular, corresponding to simple mechanisms with the stepwise elimination of Cl, in analogy with that observed for PCP[11]. There is an indication that monochloropyridine is also present in the mixture, as shown by the mass spectrum and the fact that no dichloropyridine isomers are present.

Peak 1 is due to the solvent. Peaks 2 and 3 are due to some impurities present in the mixture whose concentration is very low and hence can be ignored.

TABLE I

RETENTION DATA OF CHLOROPYRIDINES

GC conditions: 10% DEGA on Chromosorb P AW (80–100 mesh). Temperatures: column, 180°C; injector, 300°C; detector, 300°C. Nitrogen flow-rate, 32 ml/min.

Compound	*Relative retention time*
2,3,5-Trichloropyridine (peak 4)	0.32
2,4,6-Trichloropyridine (peak 5)	0.51
2,3,4,6-Tetrachloropyridine (peak 6)	0.68
2,3,5,6-Tetrachloropyridine (peak 7)	0.65
Pentachloropyridine (PCP) (peak 8)	1.00 (10.69 min)

Chlorination of pyridine by electrophilic substitution is difficult to effect and, if successful, only *meta* derivatives will result[22]. However, vapour-phase chlorination at higher temperatures (above 300°C) gives predominantly substitution in the 2-position of the pyridine ring by a free-radical mechanism[11,23,24]. Taplin[1] carried out chlorination of pyridine at different temperatures (above 280°C) and obtained pentachloro, 2,3,4,6- and 2,3,5,6-tetrachloro, 2,4,6- and 2,3,6-trichloro and 2,6-dichloropyridine isomers of varying composition and amounts. It is highly probable that the chlorinated pyridine residues under study may contain all of the above isomers

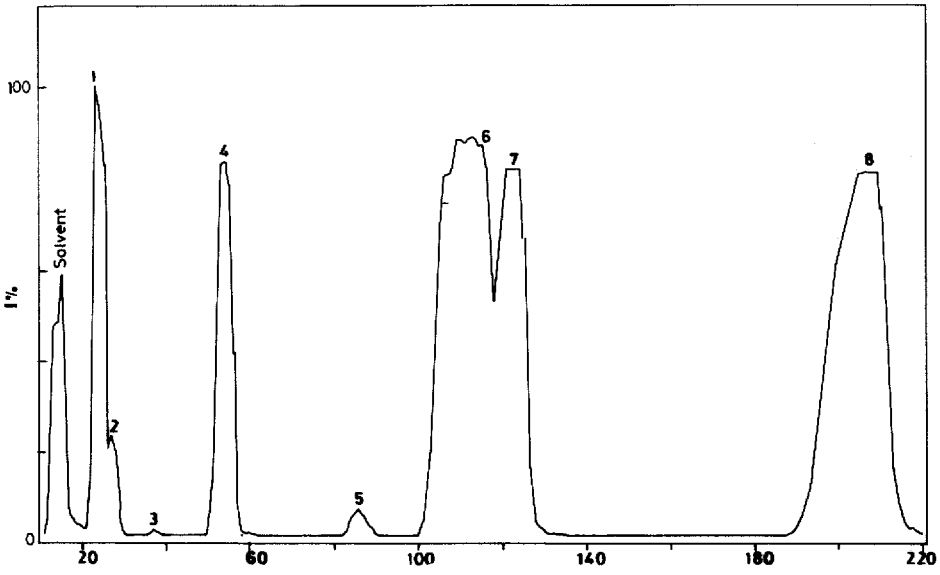

Fig. 2. Mass chromatogram (GC–MS) of chloropyridine isomers. For conditions, see text. Peaks: 4 and 5 = trichloropyridine isomers; 6 and 7 = tetrachloropyridine isomers; 8 = pentachloropyridine.

TABLE II

GC–MS RESULTS FOR CHLOROPYRIDINE ISOMERS

Based on peaks > 10% of the base peak.

Peak	*m/z (relative intensity)*
4	181^+, 183(100%); 185(34.27%); 146(67.12%); 148(42.84%); 110(29.27%); 112(10.00%); 85(10.00%); 75(12.14%)
5	181^+, 183(100%); 185(29.99%); 146(65.69%); 148(40.70%); 110(41.41%); 85 (12.85%); 75(12.14%)
6	217^+, 215(75.08%); 219(50.05%); 221(10.09%); 180(41.52%); 182(41.52%); 184(12.80%); 144(14.36%); 84(12.80%); 75(12.42%)
7	217^+, 215(74.99%); 219(49.78%); 221(10.19%); 180(37.63%); 182(35.28%); 184(10.98%); 144(14.11%); 75(10.19%)
8	251^+, 249(69.70%); 253(72.07%); 255(28.94%); 214(34.85%); 216(36.63%); 218(18.91%); 179(11.22%); 181(11.22%); 109(13.00%); 94(14.77%); 95(14.18%)

as the reaction was carried out at higher temperatures. Possibly 2-chloropyridine was formed in the initial stages and subsequently underwent further substitution to yield higher chlorinated pyridine isomers. Peaks 8, 7 and 6 (Figs. 1 and 2) are pentachloro-, 2,3,5,6-tetrachloro- and 2,3,4,6-tetrachloropyridine respectively, and peaks 5 and 4 may be 2,4,6-trichloro- and 2,3,6-trichloropyridine, respectively. Pentachloro- and 2,3,5,6-tetrachloropyridines were further confirmed with the help of authentic samples. The identity of the trichloropyridine isomers is based on the relative amounts of these isomers present (Fig. 1), as 2,3,6-trichloropyridine may give 2,3,5,6-tetrachloropyridine in lower yield while 2,4,6-trichloropyridine yields 2,3,4,6-tetrachloropyridine. The presence of 2-chloropyridine was also confirmed with a standard sample, but it overlaps with peak 2.

Pentachloropyridine can be determined quantitatively using column I and acenaphthene as an internal standard. Synthetic mixtures with various amounts of PCP were prepared and the PCP contents were determined. The results are given in Table III, and agree with the actual values to within ± 1.75%.

The method was applied successfully to the determination of PCP in chlorinated pyridine residues and the results are given in Table IV.

TABLE III

DETERMINATION OF PCP IN STANDARD MIXTURES

Mixture no.	*PCP (%)*		*Error (%)*
	Taken	*Found**	
1	65.81	66.89	+1.64
2	39.10	39.78	+1.74
3	19.74	19.44	−1.52
4	10.32	10.15	−1.65

* Average of triplicate determinations.

TABLE IV

DETERMINATION OF PCP IN CHLORINATED PYRIDINE RESIDUE

Sample	*Amount of sample (g)*	*Content of PCP**		*Mean (%)*
		Amount (g)	*%*	
Set A	0.6604	0.0493	7.47	7.48 ± 0.05
	0.7056	0.0529	7.50	
	0.6483	0.0488	7.53	
	0.6748	0.0503	7.46	
	0.6516	0.0488	7.44	
Set B	1.1532	0.0863	7.49	7.49 ± 0.04
	1.1481	0.0862	7.51	
	1.1259	0.0838	7.45	
	1.1324	0.0852	7.53	
	1.0763	0.0805	7.48	
Set C	1.5982	0.1195	7.48	7.49 ± 0.03
	1.5263	0.1147	7.52	
	1.5457	0.1153	7.46	
	1.5819	0.1183	7.48	
	1.5776	0.1183	7.50	

* Average of values obtained from duplicate GC runs.

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