

Note

Determination of dichlorohydrin in process streams by gas-liquid chromatography using mixed stationary phases

SAJID HUSAIN* and P. NAGESWARA SARMA

Analytical Division, Regional Research Laboratory, Hyderabad-500 007 (India)

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Glycerol chlorohydrins are important intermediates in the synthesis of epichlorohydrin and glycerol derivatives. One of the routes to 1,3-dichlorohydrin (DCH) is chlorohydrination of allyl chloride with chlorine in water¹. DCH prepared by this method is obtained up to a maximum of 5% in the process streams in an aqueous acidic solution. Accurate analytical methods for the determination of DCH in the process streams are obviously important for the control of the reaction, but are not available in the literature. A literature survey revealed that gas-liquid chromatography (GLC) has been employed for the determination of DCH and other chlorinated organic products in atmospheric samples only². Other instrumental methods suggested are time consuming and lacking in accuracy³⁻⁵. Chemical methods for the determination of DCH in process streams are likely to give higher values owing to the presence of 1,2-dichlorohydrin. This paper reports a GLC method for the separation and determination of DCH in process streams using mixed stationary phases.

EXPERIMENTAL

A digital processor-based Hewlett-Packard 5840A gas chromatograph equipped with a thermal conductivity detector was used for all the experiments. The columns were conditioned at 200°C with nitrogen at a flow-rate of 40 ml/min. The GLC conditions were as follows: column temperature, 100°C for 1 min, programmed from 100 to 200°C at 10°C/min, held at 200°C for 10 min; injector and detector temperatures, 250°C; and hydrogen carrier gas flow-rate, 40 ml/min.

Preparation of mixed stationary phases

All the mixed stationary phases were prepared by mixing Porapak Q (80-100 mesh) and 10% diethylene glycol adipate (DEGA) coated on Chromosorb W AW (80-100 mesh) in the required proportions and thoroughly mixed in an automatic shaker for 6 h. The mixtures were prepared with proportions only up to 3:7 of Porapak Q and DEGA; the use of more than 30% of Porapak Q in the mixture gave a sticky and non-homogeneous mixed stationary phase. The mixed stationary phase was packed into the columns after the mixture had completely homogenized. All the columns used were 6 ft. × 1/8 in. stainless-steel tubes.

TABLE I
RELATIVE RETENTION TIMES ON MIXED STATIONARY PHASES

Sample No.	Stationary phase (Porapak Q: DEGA)	Average relative retention time			
		Water	Epichloro- hydrin	Dichloro- hydrin	Monochloro- hydrin
1	1:9	0.12	0.27	1	1.53
2	1:4	0.09	0.55	1	1.31
3	2:3	0.07	0.56	1	1.24
4	3:7	0.06	0.59	1	1.22
5	Porapak Q alone	0.06	0.65	1	1.07
6	DEGA alone	0.15	0.28	1	1.65

Preparation of standard mixtures

Standard mixtures of dichlorohydrin and ethylene glycol (internal standard) were prepared containing 0.2–5.0% of DCH in water. Synthetic mixtures were prepared by adding stoichiometric amounts of hydrochloric acid (for each mole of DCH formed, 1 mole of HCl is obtained). GLC analysis of these mixtures was carried out with electronic integration.

Ethylene glycol was obtained from S.D. Fine-Chem (P) (India) and chlorohydrins from Fluka (Switzerland) and E. Merck (F.R.G.). All other chemicals were of analytical-reagent grade. Doubly distilled water was used for all the experiments.

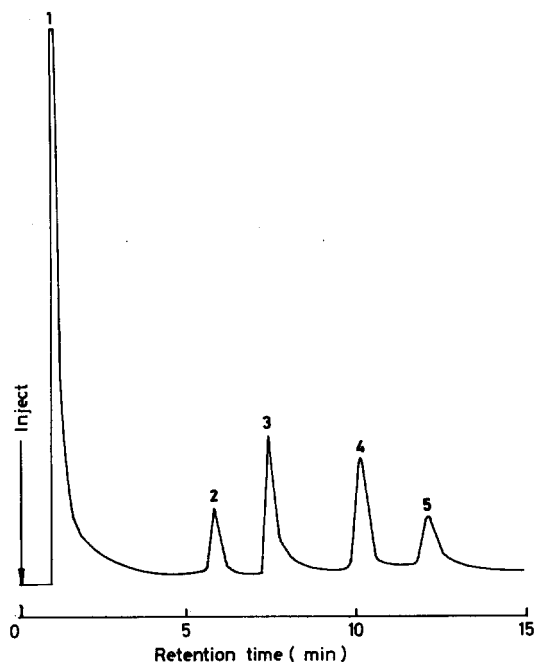


Fig. 1. Separation of water and mono-, di- and epichlorohydrin. Peaks: 1 = water; 2 = epichlorohydrin; 3 = ethylene glycol (internal standard); 4 = dichlorohydrin; 5 = monochlorohydrin.

RESULTS AND DISCUSSION

Porapak Q is a selective stationary phase for the analysis of water, whereas DEGA separates polar compounds effectively. The separation behaviour of mixtures consisting of water and mono-, di- and epichlorohydrins was first studied on these two stationary phases independently. It can be seen from the relative retention times in Table I that the separation between di- and monochlorohydrins is poor on Porapak Q, whereas DEGA does not resolve water and epichlorohydrin properly. This prompted us to study the separation behaviour of these compounds on mixed stationary phases. Porapak Q and DEGA were mixed in different proportions and the separation of the above compounds was studied. A column containing Porapak Q and DEGA (1:4) gave the best results. A typical chromatogram showing the separation of water and mono-, di- and epichlorohydrins is given in Fig. 1.

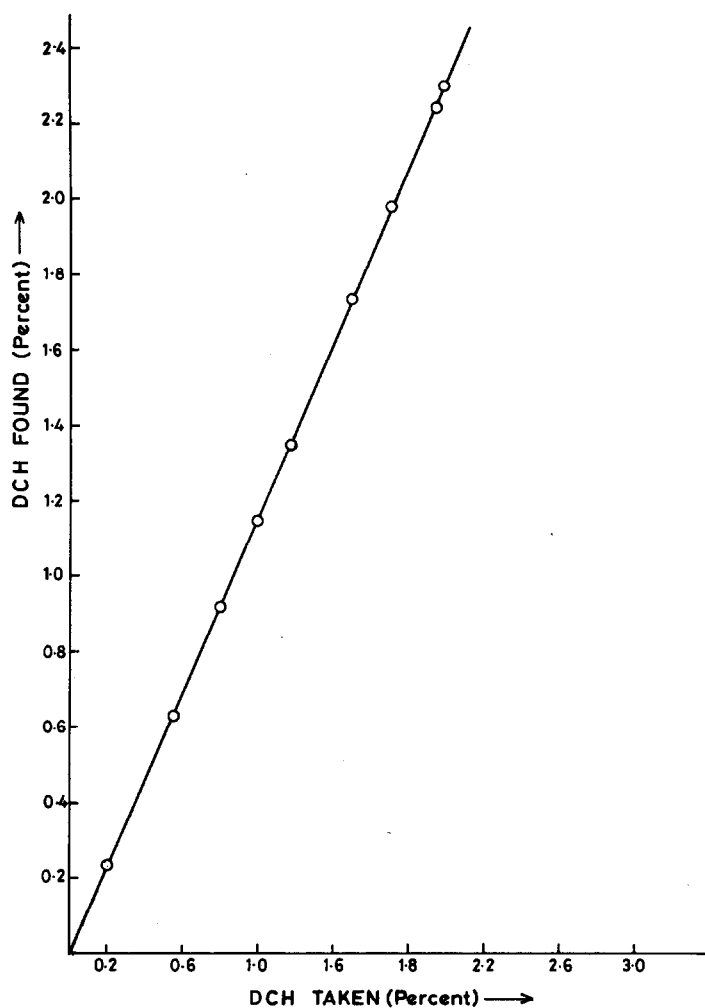


Fig. 2. Calibration graph for the determination of DCH.

TABLE II
GLC OF SYNTHETIC MIXTURES CONTAINING DCH

Sample No.	DCH taken (%)	DCH found (%)	Relative error (%)
1	0.34	0.33	2.94
2	0.66	0.67	1.52
3	0.97	0.95	2.06
4	1.15	1.13	1.74
5	1.31	1.28	2.29
6	1.49	1.51	1.34
7	1.64	1.61	1.83
8	1.86	1.82	2.15

Table I shows that the relative retention times of water and monochlorohydrin decrease with increase in the amount of Porapak Q in the mixed stationary phase. The solubility of the compound in the polymer is an important factor in determining the order of elution⁶. A lower solubility of these compounds in the porous polymer may contribute to this behaviour. With epichlorohydrin, it was observed that with an increase in the proportion of Porapak Q in the mixed stationary phase, there was an increase in the retention time. This may be due to the higher solubility of epichlorohydrin than the other compounds in Porapak Q.

Standard mixtures of DCH in water were prepared, together with ethylene glycol (internal standard), in an acidic medium and the mixtures were subjected to GLC. The percentage of DCH obtained and that taken were plotted against each other (Fig. 2). The graph obtained was linear up to 2% of DCH, but deviated from linearity at higher DCH concentrations (not shown). The results of the analysis of synthetic mixtures prepared with hydrochloric acid and analysed using the above graph are given in Table II.

TABLE III
GLC OF PILOT PLANT STREAMS CONTAINING DCH

Sample series	Amount of sample taken (g)	Content of DCH by GLC (%)	Standard deviation (%)	Content of DCH by chemical method (%)
A	1.2054	0.85	0.0108	0.90
	1.0176	0.83		
	1.0112	0.86		
	0.9968	0.85		
B	1.0182	2.17	0.0229	2.28
	0.9966	2.18		
	1.0237	2.15		
	1.0019	2.12		
C	1.1054	3.86	0.0452	4.05
	1.0375	3.86		
	1.0303	3.87		
	1.0229	3.80		

Epichlorohydrin pilot plant streams containing DCH were diluted to the range 0–2% if necessary. The samples were analysed under the same conditions as those for standard mixtures. The results of the analysis of plant samples are given in Table III.

A chemical method for the determination of DCH in process streams gave higher values than the GLC method. Process streams may contain 1,2-dichlorohydrin in addition to DCH, and the former will interfere in the determination of the latter. During the analysis of process stream samples by GLC, one unidentified peak immediately after the DCH peak was obtained; this may be 1,2-dichlorohydrin.

It is concluded that the GLC method developed for the determination of DCH is accurate up to $\pm 3\%$. It is rapid and process stream samples can be analysed directly. It is specific for DCH present in the process streams.

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