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## Note

# Separation of chlorophenols and chlorocresols by high-performance liquid chromatographic and gas–liquid chromatographic techniques

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Separation of chlorophenols and chlorocresols using paper chromatographic[1], pH–chromatographic[2], thin-layer chromatographic (TLC)[3,4], gas–liquid chromatographic (GLC)[5] and high-performance liquid chromatographic (HPLC)[6] techniques has been reported. However, none of these methods is satisfactory for the complete analysis of chlorophenols and chlorocresols. Chlorophenols have been recently determined as derivatives in effluent samples by capillary GLC[7]. Separation of chlorophenols and chlorocresols using GLC and HPLC techniques is described here.

## EXPERIMENTAL

Chlorophenols and chlorocresols (99% pure) were obtained from Fluka (Faliric) (Buchs, Switzerland) and Aldrich (Milwaukee, Wisc., U.S.A.) and used as such. Cyclohexane and chloroform were pure and did not show any impurities in the 250–400 nm range.

### *High-performance liquid chromatography*

A Waters Assoc. (Milford, Mass., U.S.A.) Model ALC/GPC/244 high-performance liquid chromatograph equipped with Model 6000 A solvent delivery system, Model U6K septumless injector and Model 440 dual channel absorbance detector at 254 nm was used. The pumps are capable of operation at pressures up to 400 bar. A prepacked column of μPorasil of 10 μm (30 cm × 4 mm I.D.) obtained from Waters Assoc. was used. The operating conditions are given in Figs. 3 and 4. Solutions (0.05%) of chlorophenols and chlorocresols were prepared in chloroform and 2.0-μl samples were injected.

### *Gas–liquid chromatography*

An F & M Model 720 dual column programmed temperature gas chromatograph equipped with a thermal conductivity detector and hydrogen as carrier gas was used. The following stationary phases were employed: silicone elastomer-30 (SE-30), diethylene glycol succinate (DEGS) and Carbowax 20M (CW 20M). The preparation and packing of the stationary phase liquid material were carried out in accordance with methods reported in the literature[8]. The operating conditions are given in Table I.

TABLE I

CONDITIONS FOR GLC SEPARATION OF CHLOROPHENOLS AND CHLOROCRESOLS

| | *SE-30* | *DEGS* | *Carbowax 20M* |
|---|---|---|---|
| Support and content of stationary liquid phase | 5% (w/w) on Chromosorb P, 45–60 mesh | 15% (w/w) on Chromosorb W, 45–60 mesh | 25% (w/w) on Chromosorb P, 45–60 mesh |
| Column length (ft.) | 8 | 8 | 8 |
| Carrier gas | hydrogen | hydrogen | hydrogen |
| Flow rate (l/h) | 7.2 | 3.6 | 7.2 |
| Column temperature (°C) | 200 ± 2 | 200 ± 2 | 200 ± 2 |
| Bridge current (A) | 150 | 150 | 150 |

## RESULTS AND DISCUSSION

The retention times relative to phenol of chlorophenols are given in Table II. These chlorophenols were poorly resolved on SE-30: DEGS gave better results. It can be seen from Table II that all the chlorophenols except 2,4-dichlorophenol and 2,5-dichlorophenol were separated on CW 20M. Further, certain pairs of these compounds (*e.g.*, 2,6-dichlorophenol and *p*-chlorophenol, and 2,4,5-trichlorophenol and 2,4,6-trichlorophenol), which have nearly the same same vapour pressures, are easily separated on CW 20M. Compounds having more *ortho*-substituted chlorine atoms in the benzene nucleus, despite their higher boiling points, emerged earlier than those having lower boiling points but with chlorine atoms in *para*- or *meta*-positions (Table II). The earlier elution of these compounds can be explained in terms of the *ortho*-effect[9]. Typical separation of chlorophenols on CW 20M is shown in Fig. 1. It can be seen that *ortho*-chlorine substituted compounds give sharp peaks whereas broad peaks are obtained for those compounds having chlorine atoms in *meta*- and *para*-positions.

TABLE II

RELATIVE RETENTION TIMES OF CHLOROPHENOLS IN GLC

| *Peak No. (Figs. 1 and 3)* | *Compound* | *Boiling point (°C)* | *Relative retention time (relative to phenol)* | | |
|---|---|---|---|---|---|
| | | | *SE-30* | *DEGS* | *CW 20M* |
| 1 | *o*-Chlorophenol | 175 | 1.00 | 0.84 | 0.60 |
| 2 | Phenol | 180 | 1.00 | 1.00 | 1.00 |
| 3 | 2,6-Dichlorophenol | 219 | 2.50 | 2.12 | 1.43 |
| 4 | 2,4-Dichlorophenol | 210 | 1.87 | 2.08 | 1.65 |
| 5 | 2,5-Dichlorophenol | 211 | 1.87 | 2.08 | 1.65 |
| 6 | 2,4,6-Trichlorophenol | 246 | 2.67 | 3.73 | 2.82 |
| 7 | *p*-Chlorophenol | 219 | 3.12 | 3.45 | 3.73 |
| 8 | 2,4,5-Trichlorophenol | 244 | 3.00 | — | 5.04 |
| 9 | 2,3,4,5-Tetrachlorophenol | — | 5.00 | — | 7.17 |
| 10 | 3,5-Dichlorophenol | 233 | 4.00 | — | 10.69 |

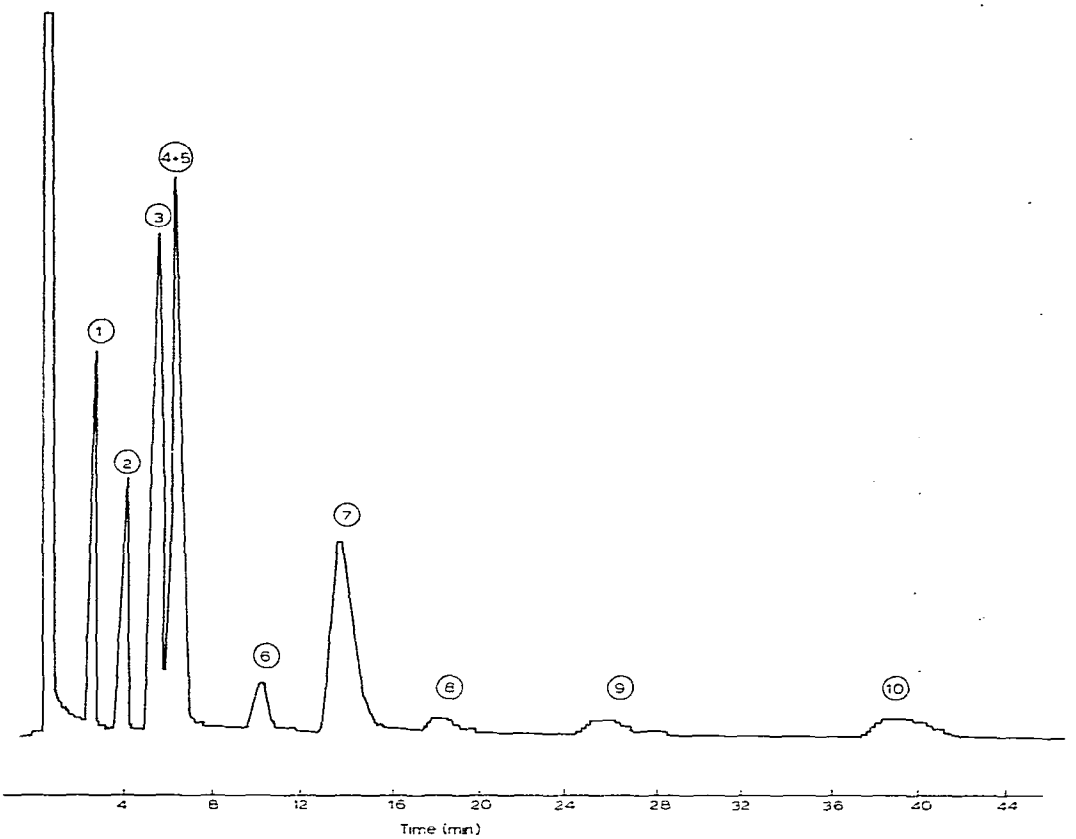


Fig. 1. Separation of isomeric chlorophenols by GLC. For conditions see Table I; for identification of peaks see Table II.

TABLE III
RELATIVE RETENTION TIMES OF CHLOROCRESOLS IN GLC

| *Peak No. (Figs. 2 and 4)* | *Compound* | *Boiling point (°C)* | *Relative retention time (relative to o-cresol)* | | |
|---|---|---|---|---|---|
| | | | *SE-30* | *DEGS* | *CW 20M* |
| 1 | 6-Chloro-*o*-cresol | 188 | 0.62 | 0.87 | 0.63 |
| 2 | *o*-Cresol | 191 | 1.00 | 1.00 | 1.00 |
| 3 | *m*-Cresol | 202 | 2.00 | 1.56 | 1.18 |
| 4 | *p*-Cresol | 202 | 2.00 | 1.56 | 1.18 |
| 5 | 6-Chloro-*m*-cresol | 197 | 2.16 | — | 1.50 |
| 6 | 2,4-Dichloro-*m*-cresol | 235 | 3.00 | — | 2.40 |
| 7 | 4-Chloro-*o*-cresol | 220 | 3.00 | 3.45 | 3.90 |
| 8 | 4-Chloro-*m*-cresol | 235 | 3.00 | — | 4.06 |

Table III gives the relative retention times (relative to *o*-cresol) of chlorocresols. The general trend for the order of elution of these chlorocresols (Table III) and chlorophenols (Table II) was found to be similar on all the liquid stationary

phases used. Almost all the chlorocresols except *m*- and *p*-cresol were separated on CW 20M. A typical chromatogram showing the separation of a mixture of chlorocresols on CW 20M is shown in Fig. 2.

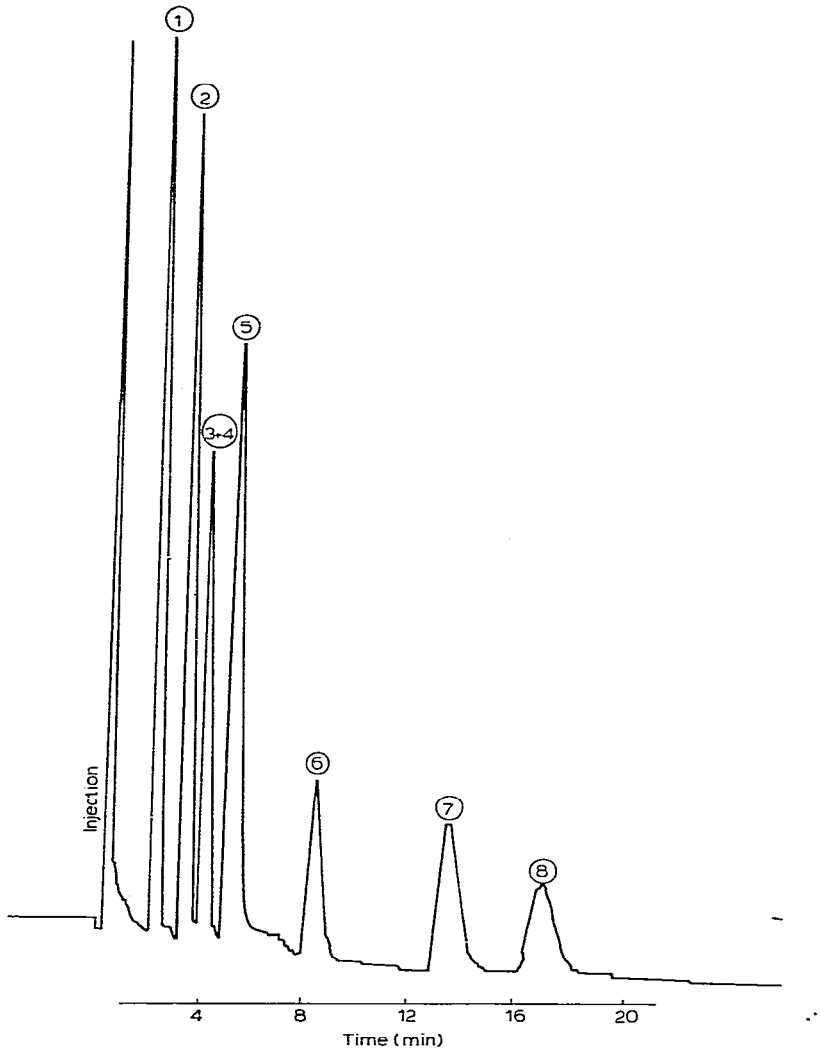


Fig. 2. Separation of isomeric chlorocresols by GLC. For conditions see Table I; for identification of peaks see Table III.

Separation of chlorophenols by HPLC is shown in Fig. 3. Almost all the chlorophenols were separated by HPLC. However, the separation of 2,3,4,5-tetrachlorophenol was not satisfactory as it appeared only as a shoulder of *o*-chlorophenol. Certain compounds such as 2,4-dichlorophenol and 2,5-dichlorophenol which could not be separated by GLC (Fig. 2) were separated by HPLC.

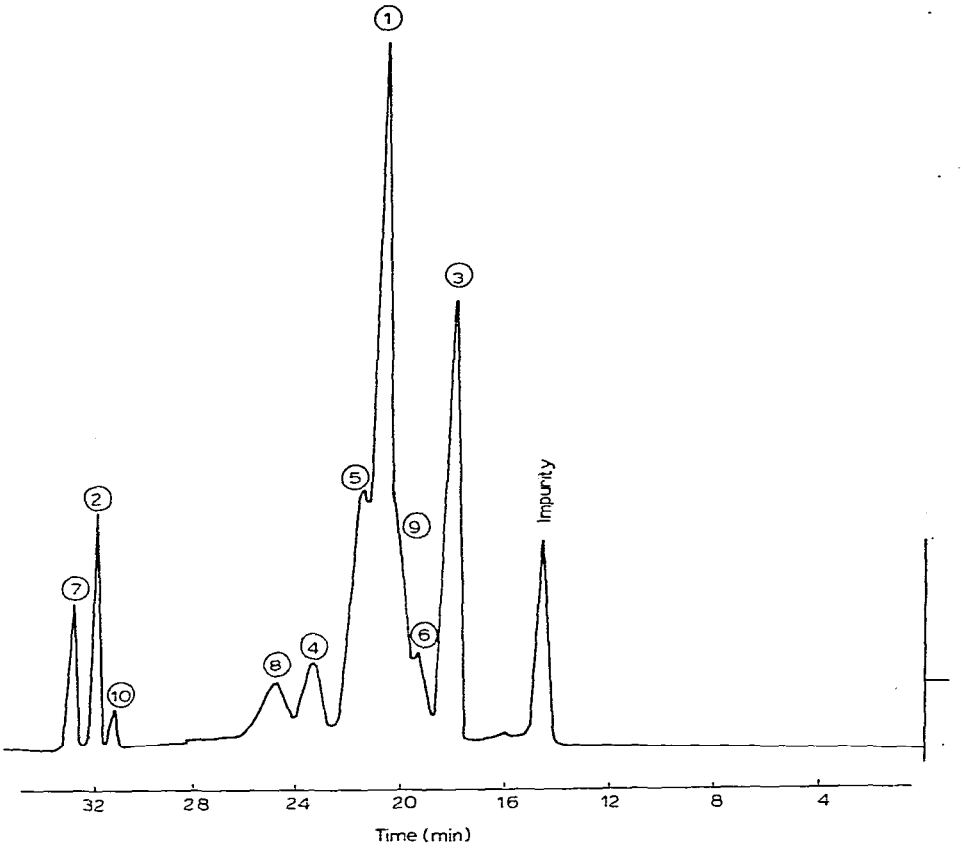


Fig. 3. Separation of chlorophenols by HPLC. For identification of peaks see Table II. Conditions: 300 × 4 mm I.D. column of μPorasil; pressure, 250 p.s.i.; eluent, chloroform–cyclohexane (7:3); flow-rate, 0.3 ml/min.

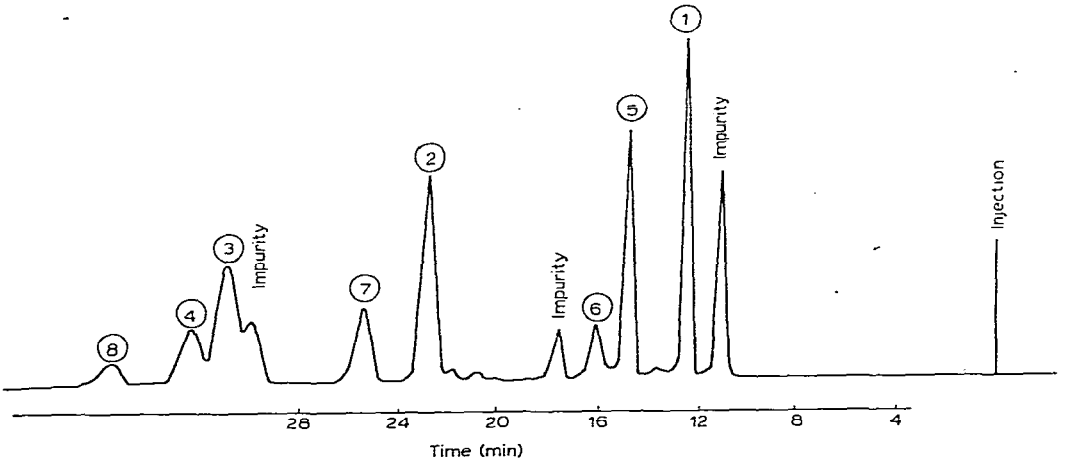


Fig. 4. Separation of chlorocresols by HPLC. For identification of peaks see Table III. Conditions: 300 × 4 mm I.D. column of μPorasil; pressure, 285 p.s.i.; eluent, chloroform–cyclohexane (7:3); flow-rate, 0.4 ml/min.

Separation of chlorocresols by HPLC is shown in Fig. 4. It is evident that all the chlorocresols can be separated by HPLC. *m*-Cresol and *p*-cresol were separated by HPLC (Fig. 4) but not by GLC (Table III, Fig. 2).

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