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GAS–LIQUID–SOLID CHROMATOGRAPHIC DETERMINATION OF PHENOLS IN AIR USING TENAX-GC AND ALKALINE PRECOLUMNS

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SUMMARY

A simple and rapid gas–liquid–solid chromatographic method for the determination of trace concentrations (at ppb* levels) of 11 phenols in air has been developed, using a Tenax-GC precolumn and a Tenax-GC plus alkaline precolumn. The phenols were identified and quantitated from the differences between the chromatogram obtained using the Tenax-GC precolumn and that obtained using the Tenax-GC plus alkaline precolumn. Complete separation was achieved within *ca.* 7 min. No evidence was found for the interference of certain acidic compounds, such as lower fatty acids (C_2–C_7) and mercaptans (C_5–C_7). The method was applied to specimens of ambient air near a phenolic resin factory, and of urban air in the Nagoya area.

INTRODUCTION

Phenols and their derivatives are widely used as antiseptics, disinfectants and pesticides, and in many other chemical applications. Human industrial exposure has been generally limited to accidental contact of phenols with the skin or to inhalation of vapour. Qualitative and quantitative analysis of phenols is a common problem in odour pollution analysis, because these compounds have odour threshold values at ppm or ppb* levels in air[1,2].

Gas chromatography (GC) is widely used for the analysis of mixtures of phenol, cresols and xylenols in automobile exhausts[3,4], cigarette smoke[5–8], waste gas[9], liquid swine manure[10], phenolic resins[11–13] and water[14–17]. However, these analyses were primarily of relatively high concentrations. There have been few reports of the analysis of the lower concentrations of phenols that occur in air.

The complete separation of phenol and *o*-, *m*- and *p*-cresols on GC columns is relatively difficult if packed columns are used. Various types of liquid phase have been proposed for the GC of phenolic isomers[18], but these techniques are not suitable

* Throughout this article, the American billion (10^9) is meant.

for the routine analysis of large numbers of samples, either because long analysis times are necessary to effect complete separation of phenolic isomers, or because the column life is short owing to thermal decomposition.

Recently, DiCorcia[19] reported good separation of phenols using gas–liquid–solid chromatography (GLSC), with a column packed with 0.1–0.5% FFAP on Sterling FT-G (graphitized carbon black). The effectiveness of this packing material is seen from the fact that cresols are separated in an analysis time of only 3 min, and the fractionation of a mixture of more than 20 phenols is achieved by the use of a single column, with an elution time of not more than 45 min.

This paper describes a simple and rapid GLSC method that uses as the column packing material 0.1% SP-1000 on Carbopack C (80–100 mesh). The phenols in air were concentrated on a Tenax-GC precolumn at room temperature, and analysed by GC with a flame ionization detector (FID). The phenols were identified and quantitated from the difference between the chromatogram obtained using the Tenax-GC precolumn and that obtained using the Tenax-GC plus alkaline precolumn. The method was applied to specimens of ambient air near a phenolic resin factory, and of urban air in the Nagoya area.

EXPERIMENTAL

Reagents

Eleven phenols and solvent ethanol were obtained from Wako (Osaka, Japan), or Tokyo Kasei Kogyo (Tokyo, Japan). All reagents were guaranteed- or reagent-grade chemicals. The purity of each phenol was checked by GC. The procedure for the preparation of the standard phenolic solution was as follows: 0.095–0.45 mole of each phenol was dissolved in 10 ml of distilled water or ethanol, and 0.2 ml of each solution were mixed together.

GLSC conditions

The gas chromatograph used was a Shimadzu Model GC $5AP_5F$, equipped with a FID and a digital integrator (Shimadzu Model ITG-2A) for the determination of the relative retention times and the calibration curves. The latter were plotted as peak height or peak area (as the counts of the digital integrator) against quantity (ng) of the phenols. The glass analytical column (1.75 m × 3 mm I.D.) was packed with 0.1% SP-1000 on Carbopack C (80–100 mesh), obtained from Gasukuro Kogyo, Tokyo, Japan. The optimum chromatographic conditions for FID were as follows: column temperature; 205–220°; injection port and detector temperature, 250°; carrier gas (nitrogen) flow-rate, 37–55 ml/min; hydrogen and air flow-rates, 50 ml/min and 1.0 l/min, respectively. The glass precolumn[20] (18 cm × 4 mm I.D.) was packed with Tenax-GC (60–80 mesh). Air samples were preconditioned at 250° for 10 h with a constant flow-rate of nitrogen (50 ml/min), and then concentrated at room temperature before being injected into the chromatograph at a temperature of 250° for 35 sec. The concentration velocity of specimen air samples was 0.22–0.33 l/min. The Tenax-GC plus alkaline precolumn contained 2% KOH on glass beads (30–60 mesh; 7 cm × 4 mm I.D.). With the latter precolumn the peaks of phenols disappeared completely in the chromatograms, enabling the phenols to be identified by comparison with the chromatograms from the ordinary Tenax-GC precolumn.

TABLE I

RELATIVE RETENTION TIMES OF 11 PHENOLS AND 10 LOWER FATTY ACIDS USING THE DIRECT INJECTION METHOD (PHENOL = 1.00)

0.1% SP-1000 on Carbopack C (80–100 mesh), 1.75 m, 205°, N_2 55 ml/min.

Compound	*RtRd*	*Compound*	*RtRd*
Phenol	1.00	Acetic acid	0.21
o-Cresol	2.31	Propionic acid	0.31
m-Cresol	2.70	*iso*-Butyric acid	0.37
p-Cresol	2.90	*n*-Butyric acid	0.41
p-Ethylphenol	3.90	*iso*-Valeric acid	0.61
o-Ethylphenol	5.06	*n*-Valeric acid	0.71
2,6-Xylenol	5.85	*iso*-Caproic acid	1.20
2,5-Xylenol	7.38	*n*-Caproic acid	1.43
3,5-Xylenol	8.00	*n*-Heptanoic acid	3.20
2,3-Xylenol	8.04	*n*-Octanoic acid	7.49
3,4-Xylenol	9.47		

RESULTS AND DISCUSSION

Table I shows the relative retention times (*RtRd*) of 11 phenols, and of 10 lower fatty acids (C_2–C_8) that are occasionally found with the phenols in polluted air, as determined by the direct injection method on the SP-1000 column at a column temperature of 205°. The retention time of phenol was defined as unity.

Table II shows the relative retention times (*RtRp*) of 11 phenols as determined by the Tenax-GC precolumn injection method on the SP-1000 column at a column temperature of 220°. The retention time of phenol was again defined as unity.

Fig. 1 shows a plot of *RtRp* against *RtRd* for the 11 phenols. The plot is linear, and thus it is possible to estimate qualitatively *RtRp* values from *RtRd* values. The data in Table I confirm that the analysis of the phenols under these conditions is not interfered with by the fatty acids, because there is no overlap between phenol peaks and fatty acid peaks.

TABLE II

RELATIVE RETENTION TIMES OF 11 PHENOLS USING THE TENAX-GC PRECOLUMN INJECTION METHOD (PHENOL = 1.00)

0.1% SP-1000 on Carbopack C (80–100 mesh), 1.75 m, 220°, N_2 37 ml/min.

Compound	*RtRp*
Phenol	1.00
o-Cresol	1.82
m-Cresol	2.03
p-Cresol	2.14
p-Ethylphenol	2.74
o-Ethylphenol	3.37
2,6-Xylenol	3.92
2,5-Xylenol	4.71
3,5-Xylenol	5.05
2,3-Xylenol	5.03
3,4-Xylenol	5.86

Fig. 2 shows the retention times of phenols, lower fatty acids, aromatic hydrocarbons, aliphatic hydrocarbons (saturated) and aliphatic hydrocarbons (unsaturated), alcohols, mercaptans, halides and other compounds as determined by the direct injection method on a SP-1000 column at a column temperature of 210° and nitrogen carrier flow-rate of 50 ml/min. Phenol overlaps with 2,3,4-trimethylpentane and hexachloroethane; *o*-cresol overlaps with styrene; *m*-cresol overlaps with *o*-, *m*- and *p*-xylene, and *iso*-amyl propionate; 2,6-xylenol overlaps with *m*-tolualdehyde; 2,3- and

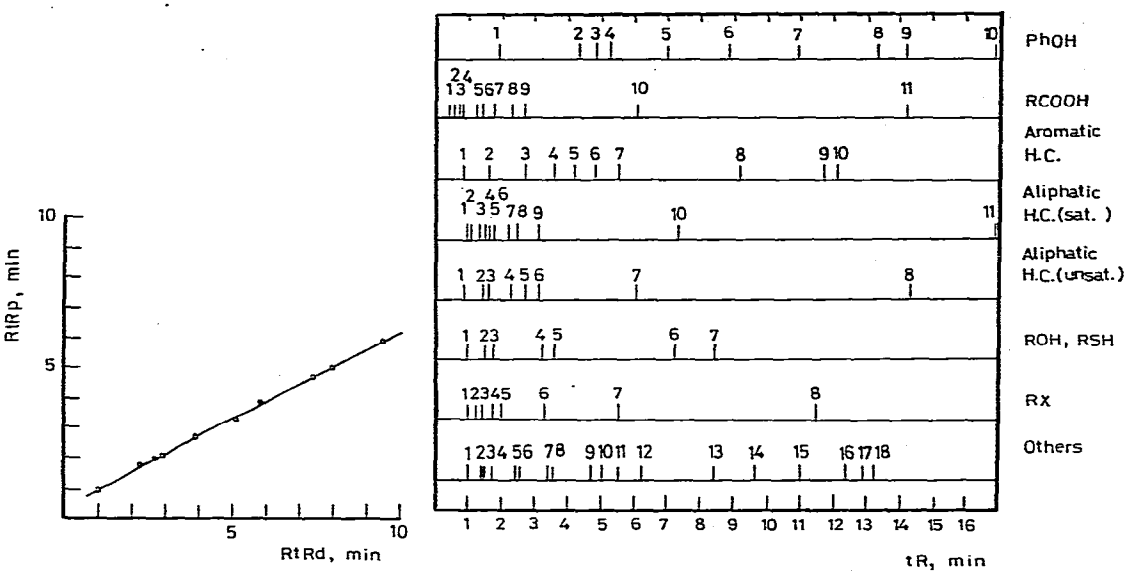

Fig. 1. A plot of *RtRp* against *RtRd* for 11 phenols.

Fig. 2. Retention times data. *PhOH*: 1 = phenol; 2 = *o*-cresol; 3 = *m*-cresol; 4 = *p*-cresol; 5 = *p*-ethylphenol; 6 = *o*-ethylphenol; 7 = 2,6-xylenol; 8 = 2,5-xylenol; 9 = 2,3- + 3,5-xylenols; 10 = 3,4-xylenol. *RCOOH*: 1 = acetic acid; 2 = propionic acid; 3 = *iso*-butyric acid; 4 = *n*-butyric acid; 5 = *iso*-valeric acid; 6 = *n*-valeric acid; 7 = diethylacetic acid; 8 = *iso*-caproic acid; 9 = *n*-caproic acid; 10 = *n*-heptanoic acid; 11 = *n*-octanoic acid. *Aromatic hydrocarbons:* 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = *iso*-propylbenzene; 5 = styrene; 6 = *o*-, *m*- and *p*-xylene; 7 = *n*-propylbenzene; 8 = *p*-cymene; 9 = *n*-butylbenzene; 10 = mesitylene. *Aliphatic hydrocarbons (saturated):* 1 = *n*-hexane; 2 = methylcyclohexane; 3 = 3-methylhexane; 4 = 2,2,4-trimethylpentane; 5 = *n*-heptane; 6 = 2,3,4-trimethylpentane; 7 = 2,4- + 2,5-dimethylhexane; 8 = 3-methylheptane; 9 = *n*-octane; 10 = *n*-nonane; 11 = *n*-decane. *Aliphatic hydrocarbons (unsaturated):* 1 = hex-1-ene; 2 = hept-1-ene + hept-2-ene (*cis*, *trans*) + hept-3-ene + 2,4,4-trimethylpent-2-ene; 3 = 2,4,4-trimethylpent-1-ene; 4 = 2-ethylhex-1-ene; 5 = oct-1-ene; 6 = oct-2-ene; 7 = non-1-ene + non-4-ene; 8 = dec-1-ene. *ROH, RSH*: 1 = pentan-1-ol; 2 = *n*-amyl mercaptan; 3 = hexan-1-ol; 4 = *n*-hexyl mercaptan; 5 = heptan-1-ol; 6 = *n*-heptyl mercaptan; 7 = octan-1-ol. *RX*: 1 = *iso*-amyl chloride; 2 = *n*-amyl chloride; 3 = 1,1,2,2-tetra-chloroethane + tetrachloroethylene; 4 = *p*-dibromobenzene; 5 = hexachloroethane; 6 = benzyl chloride; 7 = *o*-dichlorobenzene; 8 = *n*-octyl chloride. *Others*: 1 = cyclohexanone; 2 = *n*-capronaldehyde + hexan-2-one; 3 = *n*-butyl acetate + *iso*-amyl formate; 4 = *n*-amyl formate; 5 = *iso*-amylacetate + *n*-butyl propionate; 6 = heptan-2-one; 7 = *n*-hexyl formate; 8 = benzaldehyde; 9 = *iso*-amyl propionate; 10 = *iso*-octyl acetate; 11 = octan-2-one; 12 = *n*-hexyl acetate; 13 = acetophenone; 14 = *o*-tolualdehyde; 15 = *m*-tolualdehyde; 16 = nonan-2-one + *n*-octyl acetate; 17 = *p*-tolualdehyde; 18 = n-hexyl propionate. Conditions: 0.1% SP-1000 on Carbopack C (80–100 mesh), 1.75 m, 210°, N_2 50 ml/min, direct injection method.

3,5-xylenol overlap with *n*-octanic acid and dec-1-ene; and 3,4-xylenol overlaps with *n*-decane. These compounds, except for *n*-octanoic acid, passed through the alkaline precolumn, but phenols were completely trapped. Therefore, the phenols in the sample air can be identified and quantitated from the differences between the chromatograms obtained using the Tenax-GC precolumn and that obtained using the Tenax-GC plus alkaline precolumn.

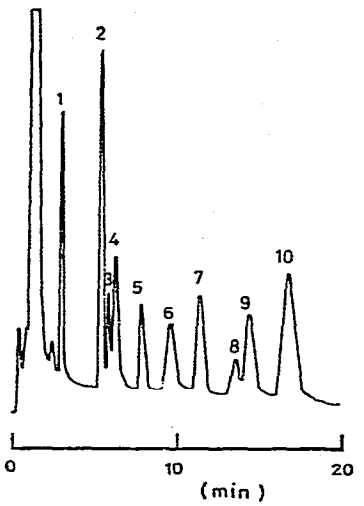

Fig. 3. Typical chromatogram of 11 phenols obtained with Tenax-GC precolumn. Peaks: 1 = phenol 68 ng; 2 = *o*-cresol 180 ng; 3 = *m*-cresol 38 ng; 4 = *p*-cresol 64 ng; 5 = *p*-ethylphenol 52 ng; 6 = *o*-ethylphenol 56 ng; 7 = 2,6-xylenol 96 ng; 8 = 2,5-xylenol 36 ng; 9 = 2,3- + 3,5-xylenol (36 + 64 ng); 10 = 3,4-xylenol 180 ng. Conditions: 0.1% SP-1000 on Carbopack C (80–100 mesh), 1.75 m × 3 mm I.D., 220°, N_2 37 ml/min; FID: range 2 (× 0.01 V), sensitivity 10^2 (× MΩ).

Fig. 3 shows a typical chromatogram of the 11 phenols obtained using the Tenax-GC precolumn injection method. Complete separation occurred within 18 min with no tailing, except for 2,3- and 3,5-xylenols, the peaks of which overlapped. It is particularly noteworthy that *o*-, *m*- and *p*-cresols were completely separated within *ca.* 7 min, with no tailing.

Under these GC conditions, the mixture of 11 phenols gives 10 peaks, and the components present in lower concentrations can be detected by normal FID. This GC column has a separating power better than that of some glass capillary columns. Because capillary columns are necessary, in general the splitter holding for a high resolving power which is low produced the lower sensitivity to lower concentration compounds[18].

Table III shows that the values of the retention times and the peak areas of nine phenols determined by the Tenax-GC precolumn injection method show good uniformity and reproducibility.

The FID response produced a linear relationship in the range 2–3000 ng for four representative phenols (phenol and *o*-, *m*- and *p*-cresols), and the minimum detectable amount at twice the noise level was *ca.* 1 ng for all four phenols, using the

TABLE III

REPRODUCIBILITY OF RETENTION TIMES AND PEAK AREAS OF NINE PHENOLS USING THE TENAX-GC PRECOLUMN INJECTION METHOD

$n = 6$; C.V. = coefficient of variation. For chromatographic conditions see Experimental. N_2 55 ml/min; column temperature 205°; FID range 4 (× 0.01 V), sensitivity 10^2 (× MΩ); Tenax-GC precolumn 18 cm × 4 mm I.D. (60–80 mesh).

Compound	*Amount (ng)*	*Retention time (min)*	*C.V. (%)*	*Peak area**	*C.V. (%)*
Phenol	170	2.70 ± 0.026	0.96	267 ± 18.3	6.85
o-Cresol	450	5.17 ± 0.035	0.68	545 ± 28.2	5.17
m-Cresol	94	5.86 ± 0.035	0.60	144 ± 8.52	5.92
p-Cresol	160	6.22 ± 0.039	0.63	224 ± 23.1	10.31
p-Ethylphenol	130	8.05 ± 0.046	0.57	200 ± 8.89	4.45
o-Ethylphenol	140	10.15 ± 0.052	0.51	158 ± 11.6	7.34
2,6-Xylenol	240	11.75 ± 0.055	0.47	328 ± 18.5	5.64
2,5-Xylenol	91	15.65 ± 0.067	0.43	280 ± 19.1	6.82
3,4-Xylenol	450	18.47 ± 0.085	0.46	667 ± 39.9	5.98

* Expressed as the counts of a digital integrator.

Tenax-GC precolumn injection method. Fig. 4 shows the typical calibration curves for phenol and *o*-, *m*- and *p*-cresols.

Fig. 5(a) shows a typical chromatogram of phenol (peak 1) and *o*-cresol (peak 2) in the ambient air of a phenolic resin factory. The volume collected was 0.3 l, and the sample was trapped directly into the Tenax-GC precolumn. Fig. 5(b) shows a typical chromatogram of the air collected on the Tenax-GC precolumn, but passed through the alkaline precolumn. In this chromatogram the phenol peak has completely disappeared, but the *o*-cresol peak is still present, confirming the identification of

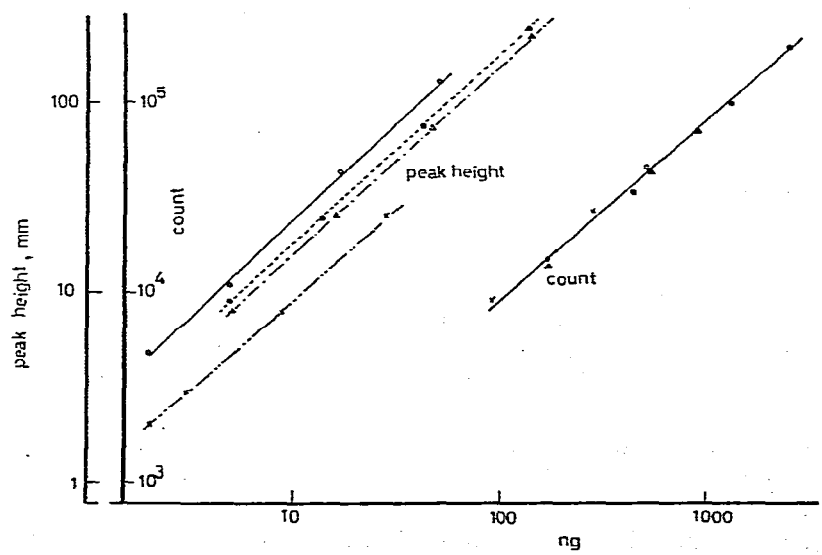

Fig. 4. Typical calibration curves for phenol (○), *o*-cresol (●), *m*-cresol (×) and *p*-cresol (△) using Tenax-GC precolumn. FID: range 1 (× 0.01 V), sensitivity 10^2 (× MΩ).

phenol and *o*-cresol made from the chromatogram in Fig. 5(a). Fig. 5(c) shows a typical chromatogram of small amounts of the standard 11 phenols. The concentrations of phenol and *o*-cresol detected were calculated to be 50 and 40 ppb, respectively.

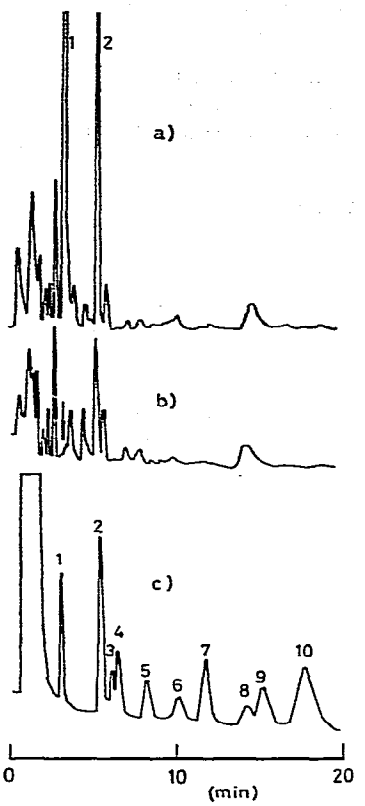

Fig. 5. Typical chromatograms of phenols in the ambient air near a phenolic resin factory, using (a) Tenax-GC precolumn only, (b) Tenax-GC plus alkaline precolumn, and (c) the standard 11 phenols with Tenax-GC precolumn injection. (a) Collected volume added to the Tenax-GC precolumn: 0.3 litre. Peaks: 1 = phenol (50 ppb); 2 = *o*-cresol (40 ppb). (b) Collected volume added to the Tenax-GC plus alkaline precolumn: 0.3 l. (c) Standard 11 phenols with Tenax-GC precolumn injection. Peaks: 1 = phenol 17 ng; 2 = *o*-cresol 45 ng; 3 = *m*-cresol 9 ng; 4 = *p*-cresol 16 ng; 5 = *p*-ethylphenol 13 ng; 6 = *o*-ethylphenol 14 ng; 7 = 2,6-xylenol 24 ng; 8 = 2,5-xylenol 9 ng; 9 = 2,3- + 3,5-xylenols (9 + 16 ng); 10 = 3,4-xylenol 45 ng. The GC conditions are as given in the caption to Fig. 3.

The method was also applied to the determination of phenol in samples of urban air from the Nagoya area. The volume concentrated was 5 l. The range and average concentration of phenols detected in 39 such samples, collected between August 3rd and 20th, 1977, were 0.05–2.3 ppb and 0.44 ppb, respectively.

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