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Note

Gas–liquid–solid chromatographic separation of o-, m- and p-tolualdehydes

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The gas chromatographic separation of o-, m- and p-tolualdehydes is difficult, in general, when a packed column is employed, whereas a complete separation of these compounds has been carried out within 8 min by the use of a glass capillary column (PEG-20M, 30 m × 0.25 mm I.D., at 100°)[1]. However, the latter technique has a low sensitivity because a splitter is used for maintaining the resolving power, *i.e.*, the minimum detectable quantity of the technique with a flame-ionization detector (FID) was *ca.* 0.01 µg (10 ng).

In this study, in order to achieve a rapid and complete separation of o-, m- and p-tolualdehydes, SP-1000 was used as stationary phase for the column packing with Carbopack C as support. It was found that 0.1% SP-1000 on Carbopack C (80–100 mesh)[2] in a glass column (1.75 m × 3 mm I.D.) at 210–230° gave the best separation results. The peaks of the three aldehydes were separated completely within 8 min, and the minimum detectable quantity using a FID was *ca.* 0.5 ng.

EXPERIMENTAL

Reagents

Benzaldehyde was obtained from Wako (Osaka, Japan), and o-, m- and p-tolualdehydes were obtained from Tokyo Kasei Kogyo (Tokyo, Japan). All the other reagents used obtained from Wako, Tokyo Kasei, Katayama Chemical Industries (Osaka, Japan) and PolyScience (Niles, Ill., U.S.A.) and were guaranteed or reagent grade chemicals.

Gas–liquid–solid chromatographic (GLSC) conditions

The gas chromatograph used was a Shimadzu Model GC5APₛFFp equipped with a FID and a digital integrator (Shimadzu Model ITG-2A) for the determination of retention times and peak areas (as the counts). The analytical column was made of glass (1.75 m × 3 mm I.D.) packed with 0.1% SP-1000 on Carbopack C (80–100 mesh) (Supelco, Bellefonte, Pa., U.S.A.). The column was preconditioned at the column-oven temperature of 230° for 5 h, and at a constant flow-rate of nitrogen (65 ml/min). The chromatographic conditions for the FID were: carrier gas (nitrogen) flow-rate, 50 ml/min; air and hydrogen flow-rates, 1.0 l/min and 50 ml/min, respectively; column temperature, 210–230°; injection port and detector temperature, 250°.

RESULTS AND DISCUSSION

The retention times data of five aromatic carbonyl compounds are listed in Table I. The retention time of benzaldehyde is defined as unity.

TABLE I

RELATIVE RETENTION TIMES OF FIVE AROMATIC CARBONYL COMPOUNDS (BENZALDEHYDE = 1.00)

Column: 0.1 % SP-1000 on Carbopack C (80–100 mesh), 1.75 m × 3 mm I.D., glass; column temperature, 210°; nitrogen flow-rate, 50 ml/min.

Compound	Relative retention time
Benzaldehyde	1.00 *
Acetophenone	2.37
o-Tolualdehyde	2.72
m-Tolualdehyde	3.09
p-Tolualdehyde	3.63

* The true retention time was 3.55 min.
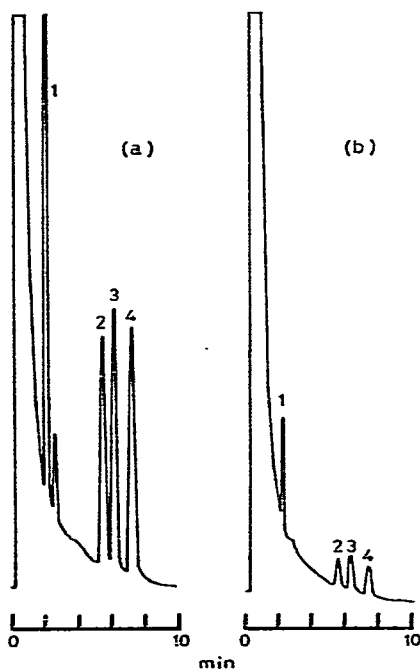

Fig. 1. Typical chromatograms of benzaldehyde, o-, m- and p-tolualdehyde. (a) 100 ng level. Peaks: 1 = benzaldehyde (160 ng); 2 = o-tolualdehyde (158 ng); 3 = m-tolualdehyde (155 ng); 4 = p-tolualdehyde (155 ng). FID: range 16 (×0.01 V); sensitivity, 10^3 (×MΩ). (b) 10 ng level. Peaks: 1 = benzaldehyde (16 ng); 2 = o-tolualdehyde (16 ng); 3 = m-tolualdehyde (15 ng); 4 = p-tolualdehyde (15 ng). Other details as in (a). Conditions: 0.1 % SP-1000 on Carbopack C (80–100 mesh), 1.75 m × 3 mm I.D. glass column; column temperature, 230°; nitrogen flow-rate, 50 ml/min; injected volume of mixed solution of four aldehydes [3.8 μl per 30 ml ethanol for (a), 3.8 μl per 300 ml for (b)], 1.2 μl.

Fig. 1 shows typical chromatograms of benzaldehyde, *o*-, *m*- and *p*-tolualdehyde at the 100 and 10 ng levels. As shown, *o*-, *m*- and *p*-tolualdehydes were separated completely within 8 min. The resolution value[3] of the peaks of *o*- and *m*-tolualdehydes was 1.8 (at 210°). Hoshika and Takata[1] reported the separation of the three tolualdehydes using a 30-m glass capillary column coated with PEG-20 M at 100°, under which conditions the resolution value was 1.3.

Fig. 2 shows the retention time data for several compounds involving the three tolualdehydes at 210°. Under these chromatographic conditions, the benzaldehyde peak is overlapped by those of isopropylbenzene and 1-heptanol, and *m*-tolualdehyde is overlapped by 2,6-xylenol.
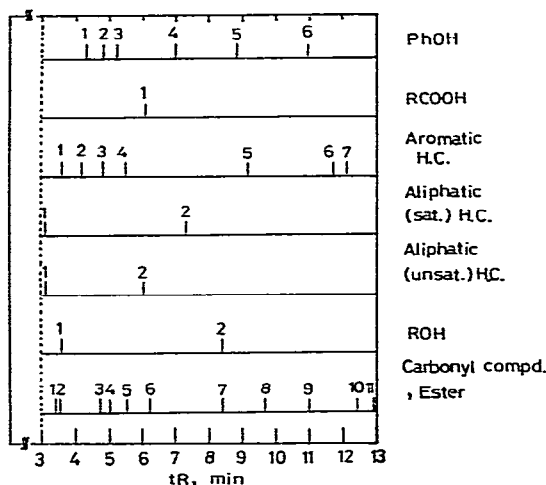

Fig. 2. Retention time data. PhOH: 1 = *o*-cresol; 2 = *m*-cresol; 3 = *p*-cresol; 4 = *p*-ethylphenol; 5 = *o*-ethylphenol; 6 = 2,6-xylenol. RCOOH :1= *n*-heptanoic acid. Aromatic hydrocarbons (H.C.): 1 = isopropylbenzene; 2 = styrene; 3 = *o*-, *m*- and *p*-xylene; 4 = *n*-propylbenzene; 5 = *p*-cymene; 6 = *n*-butylbenzene; 7 = mesitylene. Aliphatic saturated H.C.: 1 = *n*-octane; 2 = *n*-nonane. Aliphatic unsaturated H.C.: 1 = 2-octene; 2 = 1- and 4-nonene. ROH: 1 = 1-heptanol; 2 = 1-octanol. Carbonyl compounds and esters: 1 = *n*-hexyl formate; 2 = benzaldehyde; 3 = isopentyl propionate; 4 = isooctyl acetate; 5 = 2-octanone; 6 = *n*-hexyl acetate; 7 = acetophenone; 8 = *o*-tolualdehyde; 9 = *m*-tolualdehyde; 10 = 2-nonanone + *n*-octyl acetate; 11 = *p*-tolualdehyde. Column temperature, 210°; other column conditions as in Fig. 1.

The FID response produced a linear relation in the range 4–4000 ng of benzaldehyde, *o*-, *m*- and *p*-tolualdehydes, and the minimum detectable quantity at twice the noise level was *ca.* 0.5 ng. This value is 20 times less than that obtainable with a glass capillary-column technique[1].

The repeatability and uniformity of the retention times and peak areas of *o*-, *m*- and *p*-tolualdehydes were evaluated. As can be seen from Table II, they showed good uniformity and high repeatability.

CONCLUSION

The GLSC separation of *o*-, *m*- and *p*-tolualdehydes has been attained using 0.1% SP-1000 on Carbopack C .The peaks of the three tolualdehydes were separated

TABLE II

REPEATABILITY OF RETENTION TIMES AND PEAK AREAS OF o-, m- AND p-TOLUALDEHYDES ($n = 6$)

Retention times were determined by means of a digital integrator. FID: range 16 ($\times 0.01$ V); sensitivity 10^3 ($\times$ MΩ); count ($\times 10^2$). Column temperature, 230°. Other GC conditions as in Table I.

Compound	Amount (ng)	Retention time (min)	Peak area (counts)
o-Tolualdehyde	16	5.79 ± 0.01	79 ± 4.0
m-Tolualdehyde	15	6.50 ± 0.01	114 ± 5.0
p-Tolualdehyde	15	7.58 ± 0.02	108 ± 5.6

completely within 8 min, and the resolution value of the peaks of o- and m-tolualdehydes was 1.8.

ACKNOWLEDGEMENT

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