

CHROM. 10,715

Note

Rapid separation of lower aliphatic carbonyl compounds by gas-liquid-solid chromatography

YASUYUKI HOSHIKA

Aichi Environmental Research Centre, 7-6, Tsuji-machi, Kita-ku, Nagoya-shi, Aichi (Japan)

and

GIICHI MUTO

Institute of Industrial Science, University of Tokyo, 7-22-1, Roppongi, Minato-ku, Tokyo (Japan)

(First received September 20th, 1977; revised manuscript received November 8th, 1977)

Acetaldehyde, propionaldehyde, acrolein, *n*- and isobutyraldehyde have unpleasant odours, with low odour threshold values (parts per billion level), and have an irritating effect on the eyes and nose. On the other hand, acetone and ethyl methyl ketone have higher odour threshold values (parts per million level)¹⁻³. The complete separation of lower aliphatic carbonyl compounds is an important problem in organic analysis, odour analysis, hygiene studies and environmental toxicology.

Recently, gas-liquid-solid chromatography with graphitized carbon black as a support for the analysis of lower boiling compounds was reported by DiCorcia *et al.*⁴. This method gave good separations, with no adsorption or tailing of polar compounds, such as lower aliphatic amines, alcohols and fatty acids. Sterling FTG + 0.2% PEG 1500, Graphon + 1% PEG 1500⁴ and 0.4% Triton X-100 on Carbowack A⁵ have been used for the separation of acetaldehyde and other low-boiling polar compounds, such as methanol and ethanol. The gas-liquid-solid chromatography of acetaldehyde at trace concentrations in urban air (in the Nagoya area) using 0.4% Triton X-100 on Carbowack B has also been reported⁶. In this method, acetaldehyde was separated completely from other low-boiling compounds, such as lower aliphatic hydrocarbons, amines, ammonia, chlorides, monoalcohols and esters, which are present in air. However, this column packing was not satisfactory for the separation of propionaldehyde, acrolein and acetone.

In order to achieve a rapid and simple separation of lower aliphatic carbonyl compounds, including acetaldehyde, propionaldehyde, acrolein and acetone, the use of tris(2-cyano)ethoxypropane (TCEP) has been reported⁷. The stationary phase has a strong polarity and was coated to Carbowack B. The use of 5% TCEP on Carbowack B (60-80 mesh), a 1.5 m × 3 mm I.D. glass column and a column temperature of 70° gave a good separation, the peaks of propionaldehyde, acrolein and acetone being separated completely within 5 min.

In this paper, the effect of the percentage of TCEP coated and the use of other stationary phases to obtain good separations of lower aliphatic carbonyl compounds and some other compounds are described.

EXPERIMENTAL

Reagents and materials

Acetaldehyde (99.5%) was obtained from E. Merck (Darmstadt, G.F.R.). Propionaldehyde, acrolein, *n*- and isobutyraldehyde, *n*- and isovaleraldehyde and diethyl ketone were obtained from Tokyo Kasei Kogyo (Tokyo, Japan), acetone from Wako (Osaka, Japan) and ethyl methyl ketone from Katayama (Osaka, Japan). All reagents were guaranteed or reagent-grade chemicals. All column packings were obtained from Wako. A standard solution containing a mixture of lower aliphatic carbonyl compounds was prepared by dissolving each compound in 10 ml of distilled water to give a concentration of about 0.16 mg/ml.

Gas-liquid-solid chromatography

The gas chromatograph was a Shimadzu Model GC5AP₃F equipped with a flame-ionization detector (FID), together with a digital integrator (Shimadzu Model ITG-2A) for the determination of retention times and peak areas. The glass analytical columns were 1.5, 2 and 3 m × 3 mm I.D.; seven column packings were tested (Table I). The TCEP columns were pre-conditioned at a column oven temperature of 145° for 5 h a constant flow-rate of nitrogen (65 ml/min). The Triton X-100 and SP-1000 columns were pre-conditioned at a column temperature of 185° for 5 h and a constant flow-rate of nitrogen (60 ml/min).

RESULTS AND DISCUSSION

The relative retention times of ten lower aliphatic carbonyl compounds obtained with seven column packings at 70° are given in Table I. The retention time of pro-

TABLE I

RELATIVE RETENTION TIMES OF TEN LOWER ALIPHATIC CARBONYL COMPOUNDS WITH SEVEN COLUMN PACKINGS

Retention time of propionaldehyde = 1.00. Column temperature 70° and carrier gas (nitrogen) flow-rate 55 ml/min in each instance.

Compound	Column packing*						
	A	B	C	D	E	F	G
Acetaldehyde	0.32	0.27	0.34	0.32	0.33	0.48	0.67
Propionaldehyde	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Acrolein	1.13	1.06	1.22	1.28	1.25	1.15	1.30
<i>n</i> -Butyraldehyde	3.95	3.93	3.83	3.95	3.51	2.32	1.50
Isobutyraldehyde	2.79	2.84	2.68	2.73	2.45	1.75	1.04
<i>n</i> -Valeraldehyde	—	—	—	—	—	5.98	—
IsoValeraldehyde	—	—	—	—	—	4.60	1.84
Acetone	1.15	0.94	1.26	1.30	1.26	1.39	1.43
Ethyl methyl ketone	4.42	4.41	4.43	4.45	3.94	2.91	2.07
Diethyl ketone	—	—	—	—	—	5.59	2.95

* A: 0.4% Triton X-100 on Carbowack B (60-80 mesh), 1.5 m × 3 mm I.D. B: 0.2% SP 1000 on Carbowack B (60-80 mesh), 2 m × 3 mm I.D. C: 0.4% TCEP on Carbowack B (60-80 mesh), 1.5 m × 3 mm I.D. D: 1% TCEP on Carbowack B (60-80 mesh), 1.5 m × 3 mm I.D. E: 2% TCEP on Carbowack B (60-80 mesh), 1.5 m × 3 mm I.D. F: 5% TCEP on Carbowack B (60-80 mesh), 1.5 m × 3 mm I.D. G: 25% TCEP on Shimalite (AW DMCS) (60-80 mesh), 3 m × 3 mm I.D.

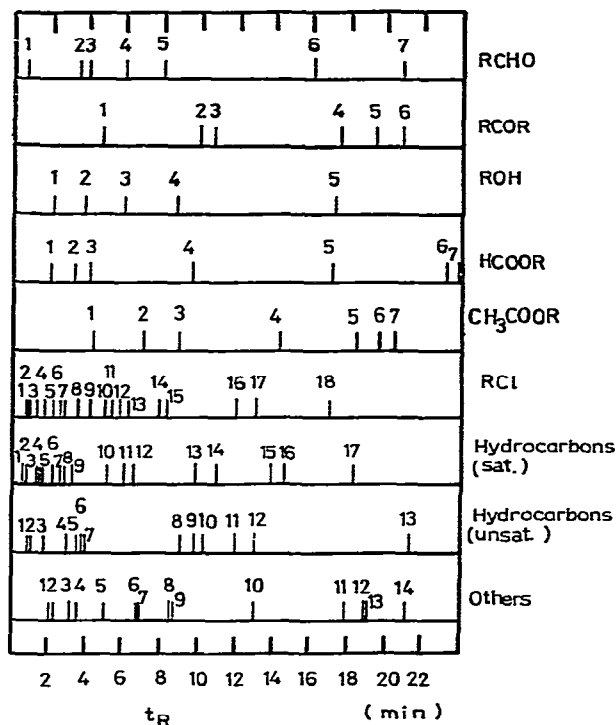


Fig. 1. Retention times of 107 compounds. Analytical column, 5% TCEP on Carbowack B (60-80 mesh), 1.5 m \times 3 mm I.D., glass; column temperature, 70°; injection port and detector (FID) temperatures, 150°; carrier gas (nitrogen) flow-rate, 55 ml/min. RCHO: 1 = acetaldehyde; 2 = propionaldehyde; 3 = acrolein; 4 = isobutyraldehyde; 5 = *n*-butyraldehyde; 6 = isovaleraldehyde; 7 = *n*-valeraldehyde. RCOR: 1 = acetone; 2 = ethyl methyl ketone; 3 = biacetyl; 4 = isopropyl methyl ketone; 5 = diethyl ketone; 6 = *n*-propyl methyl ketone. ROH: 1 = methanol; 2 = ethanol; 3 = 2-propanol; 4 = 1-propanol + 2-methyl-2-propanol; 5 = 2-methyl-1-propanol. HCOOR: 1 = methyl formate; 2 = vinyl formate; 3 = ethyl formate; 4 = *n*-propyl formate; 5 = allyl formate; 6 = isobutyl formate; 7 = *n*-butyl formate. CH₃COOR: 1 = methyl acetate; 2 = vinyl acetate; 3 = ethyl acetate; 4 = isopropyl acetate; 5 = *tert*-butyl acetate; 6 = *n*-propyl acetate; 7 = allyl acetate. RCl: 1 = methyl chloride; 2 = vinyl chloride; 3 = ethyl chloride; 4 = 1,2-dichloroethylene; 5 = isopropyl chloride; 6 = *n*-propyl chloride; 7 = dichloromethane; 8 = *tert*-butyl chloride; 9 = ethylidene chloride; 10 = isobutyl chloride + *sec*-butyl chloride + 3-chloro-1-butene; 11 = 1,1,1-trichloroethane; 12 = chloroform; 13 = *n*-butyl chloride; 14 = trichloroethylene + *trans*-1-chloro-2-butene; 15 = 1,2-dichloroethane; 16 = 1,2-dichloropropane; 17 = isoamyl chloride; 18 = *n*-amyl chloride. Hydrocarbons (saturated): 1 = *n*-propane; 2 = *n*-butane; 3 = isobutane; 4 = isopentane; 5 = *n*-pentane; 6 = 2,2-dimethylbutane; 7 = 2,3-dimethylbutane; 8 = 3-methylpentane; 9 = *n*-hexane; 10 = 2,4-dimethylpentane; 11 = 2,3-dimethylpentane; 12 = 3-methylhexane; 13 = *n*-heptane; 14 = 2,2,4-trimethylpentane; 15 = 2,4- and 2,5-dimethylhexane; 16 = 2,3,4-trimethylpentane; 17 = 3-methylheptane. Hydrocarbons (unsaturated): 1 = butene-1 + isobutylene + *trans*-butene-2 + *cis*-butene-2; 2 = 1,3-butadiene; 3 = 2-methylbutene-1; 4 = 4-methylpentene-1 + 4-methylpentene-2 (*cis* and *trans*); 5 = 3-methylpentene-1 + 2-ethylbutene-1; 6 = hexene-1; 7 = hexene-2; 8 = heptene-3; 9 = heptene-1; 10 = heptene-2 (*cis* and *trans*); 11 = 2,4,4-trimethylpentene-2; 12 = 2,4,4-trimethylpentene-1; 13 = 2-ethylhexene-1. Others: 1 = furan; 2 = diethyl ether; 3 = cyclohexane; 4 = trimethylene oxide; 5 = 2-methylfuran; 6 = acetonitrile; 7 = methylcyclohexane + acrylonitrile + benzene; 8 = methyl propionate; 9 = methyl acrylate; 10 = methyl isobutyrate; 11 = ethyl propionate; 12 = methyl methacrylate + ethyl acrylate; 13 = methyl *n*-butyrate; 14 = toluene.

pionaldehyde was defined as unity. The peaks of acrolein and acetone overlapped on the Triton X-100 column, and the peaks of propionaldehyde, acrolein and acetone overlapped on the SP-1000 column. These poor separations may be due to the polarity of Triton X-100 and SP-1000. Although the peaks of acrolein and acetone overlapped on the 0.4–2% TCEP columns, with a 5% TCEP coating the peaks separated completely within 5 min. Using a column packed with 25% TCEP on Shimalite (AW, DMCS), 60–80 mesh, the peaks of propionaldehyde and isobutyraldehyde were poorly separated, but the peak of acrolein was separated completely from the peaks of other lower aliphatic carbonyl compounds.

Fig. 1 shows the retention times of 107 compounds. This tabular presentation is useful because it indicates immediately the separability of the lower aliphatic carbonyl compounds and other compounds, As shown in Fig. 1, overlapping occurs with many compounds. Of the 107 compounds tested, only the peak of isovaleraldehyde does not interfere with those of other compounds. Hence the identification of lower aliphatic carbonyl compounds in an unknown sample is an important problem.

As a method for the identification of the lower aliphatic carbonyl compounds, the reaction with 2,4-dinitrophenylhydrazine to form the corresponding 2,4-dinitrophenylhydrazones is useful, as it is easy to carry out and is selective towards the lower aliphatic carbonyl compounds. Fig. 2 shows the chromatogram of the lower aliphatic carbonyl compounds obtained with a 1.5-m column packed with 5% TCEP on Carbo-pack B. It can be seen that ten lower aliphatic carbonyl compounds separated completely within about 20 min, except for *n*-valeraldehyde and diethyl ketone, the peaks of which overlapped. Propionaldehyde, acrolein and acetone, each of which contain

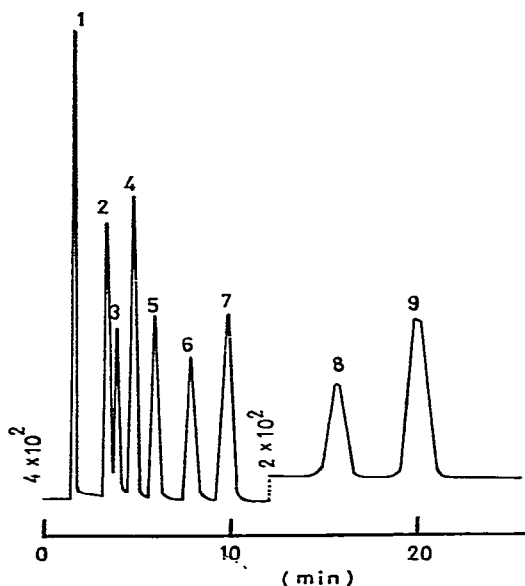


Fig. 2. Typical chromatogram of ten lower aliphatic carbonyl compounds. Standard solution of ten lower aliphatic carbonyl compounds ($2 \mu\text{l}$) injected. Conditions as in Fig. 1. Peaks: 1 = acetaldehyde (312 ng); 2 = propionaldehyde (324 ng); 3 = acrolein (235 ng); 4 = acetone (316 ng); 5 = isobutyraldehyde (320 ng); 6 = *n*-butyraldehyde (328 ng); 7 = ethyl methyl ketone (324 ng); 8 = isovaleraldehyde (312 ng); 9 = *n*-valeraldehyde (312 ng) + diethyl ketone (312 ng).

three carbon atoms, and isobutyraldehyde separated completely within about 6 min.

Grob⁸ reported the separation of the volatile compounds of cigarette smoke using a 25–50 m glass capillary column. However, the separation of the peaks of acetone and isobutyraldehyde was not satisfactory. In addition, in this analysis a low column temperature (0°) is necessary for good separations. However, this temperature cannot be controlled easily in common gas chromatographs and the method gives poor sensitivity, because a stream splitter is used in order to maintain a high resolving power.

In other gas-liquid chromatographic procedures, generally the complete separation of lower aliphatic carbonyl compounds, such as propionaldehyde, acrolein, isobutyraldehyde and acetone, requires long times, *e.g.*, more than 10 min.

ACKNOWLEDGEMENT

The authors thank K. Yoshimoto, Aichi Environmental Research Centre, for useful suggestions.

REFERENCES

- 1 F. A. Patty (Editor), *Industrial Hygiene and Toxicology, Vol. II, Toxicology*, Interscience, New York, 2nd ed., 1962, pp. 1719 and 1959.
- 2 G. Leonardos, D. Kendall and N. Barnard, *J. Air Pollut. Control Assoc.*, 19 (1969) 91.
- 3 T. M. Hellman and F. H. Small, *J. Air Pollut. Control Assoc.*, 24 (1974) 979.
- 4 A. DiCorcia, A. Liberti and R. Samperi, *Anal. Chem.*, 45 (1973) 1228.
- 5 *Carbopack*, Bulletin No. 738, Supelco, Bellefonte, Pa., 1974.
- 6 Y. Hoshika, *J. Chromatogr.*, 137 (1977) 455.
- 7 Y. Hoshika and G. Muto, *J. Chromatogr.*, 150 (1978) 254.
- 8 K. Grob, *Chem. Ind. (London)*, 17 (1973) 248.