

CHROM. 10,654

## Note

---

### Sensitive gas chromatographic determination of lower aliphatic carbonyl compounds as their pentafluorophenylhydrazones

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 August 1st, 1977; revised manuscript received October 11th, 1977)

For the derivatization of carbonyl compounds, the reaction with 2,4-dinitrophenylhydrazine to form the corresponding solid, water-insoluble 2,4-dinitrophenylhydrazones has been widely used. The analysis of 2,4-dinitrophenylhydrazones by gas chromatography (GC) with high column temperatures had been widely reported<sup>1-14</sup>. In addition, the reaction of carbonyl compounds with pentafluorophenylhydrazine has been reported by Attal *et al.*<sup>15</sup> and Mead *et al.*<sup>16</sup>. However, these methods have been applied only to high-molecular-weight carbonyl compounds.

This paper describes the sensitive and selective GC analysis of lower aliphatic carbonyl compounds with column temperatures lower than those used in the GC analysis of 2,4-dinitrophenylhydrazone derivatives. The carbonyl compounds are converted into the corresponding pentafluorophenylhydrazones, which are detected using an electron-capture detector (ECD).

## EXPERIMENTAL

### *Reagents*

The lower aliphatic carbonyl compounds used in this work were as described earlier<sup>14</sup>. Pentafluorophenylhydrazine (purity 97%) was obtained from Aldrich (Milwaukee, Wisc., U.S.A.). Methanol, obtained from Katayama (Osaka, Japan), was fractionally distilled twice over 2,4-dinitrophenylhydrazine (Katayama) (5 g/l added to methanol with the further addition of 10 ml of concentrated hydrochloric acid) in order to remove all traces of the lower carbonyl compounds. All reagents were of laboratory or analytical-reagent grade.

### *Pentafluorophenylhydrazone derivative formation*

The procedure for the preparation the pentafluorophenylhydrazone derivatives was as follows. An amount of  $0.5 \cdot 10^{-3}$  mole of lower aliphatic carbonyl compound was added, with a 100- $\mu$ l Terumo MS-100 microsyringe, to 1 ml of methanol containing  $1.01 \cdot 10^{-3}$  mole of pentafluorophenylhydrazine and the mixture was allowed to react overnight at room temperature. The extent of the reaction was determined from

the carbonyl compounds remaining after the reaction period. A 1- $\mu$ l volume of the sample solution was injected (with a 10- $\mu$ l Hamilton 701-N microsyringe) into Ethofat or SE-30 columns, and a flame-ionization detector (FID) and a thermal conductivity detector (TCD) were used for detection.

#### Gas chromatography

The gas chromatographs used were a Shimadzu Model GC5AP<sub>5</sub>TF equipped with a TCD, an FID and a digital integrator (Shimadzu Model ITG-2A) for the determination of the extent of the pentafluorophenylhydrazone derivative formation reaction, and a Shimadzu Model GC5AIE equipped with an ECD.

The GC conditions were as follows: (A) analytical column, 3 m  $\times$  3 mm I.D.,

TABLE I

## RETENTION TIMES AND EXTENTS OF REACTION FOR 27 PENTAFLUOROPHENYLHYDRAZONE DERIVATIVES

3-m column, 5% SE-30.

Compound	Temperature (°C)	Retention time (min)	Extent of reaction* (%)
HCHO	130	2.49	100
CH <sub>3</sub> CHO		3.93	80
C <sub>2</sub> H <sub>5</sub> CHO		5.50	100
<i>n</i> -C <sub>3</sub> H <sub>7</sub> CHO		9.30	100
<i>iso</i> -C <sub>3</sub> H <sub>7</sub> CHO		6.88	90
<i>n</i> -C <sub>4</sub> H <sub>9</sub> CHO		23.91	100
<i>iso</i> -C <sub>4</sub> H <sub>9</sub> CHO		11.27	100
<i>n</i> -C <sub>5</sub> H <sub>11</sub> CHO		22.92	100
CH <sub>2</sub> =CHCHO		6.06	100
CH <sub>3</sub> CH=CHCHO		12.04	100
CH <sub>3</sub> COCH <sub>3</sub>		5.44	100
CH <sub>3</sub> COC <sub>2</sub> H <sub>5</sub>		7.99	100
CH <sub>3</sub> CO- <i>iso</i> -C <sub>3</sub> H <sub>7</sub>		10.03	100
CH <sub>3</sub> CO- <i>n</i> -C <sub>4</sub> H <sub>9</sub>		19.45	100
CH <sub>3</sub> CO- <i>iso</i> -C <sub>4</sub> H <sub>9</sub>		14.92	100
CH <sub>3</sub> CO- <i>sec.</i> -C <sub>4</sub> H <sub>9</sub>		14.90	100
CH <sub>3</sub> CO- <i>tert.</i> -C <sub>4</sub> H <sub>9</sub>		12.45	100
C <sub>2</sub> H <sub>5</sub> COC <sub>2</sub> H <sub>5</sub>		11.38	80
C <sub>6</sub> H <sub>5</sub> CHO	170	12.96	100
<i>o</i> -C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> )CHO		19.28	100
<i>m</i> -C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> )CHO		18.75	100
<i>p</i> -C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> )CHO		19.73	100
C <sub>3</sub> H <sub>4</sub> O <sub>2</sub>		7.24	100
C <sub>6</sub> H <sub>10</sub> O		7.80	100
C <sub>6</sub> H <sub>5</sub> COCH <sub>3</sub>		16.76	100
CH <sub>3</sub> COCOCH <sub>3</sub>	130	30	100
CH <sub>3</sub> COCH <sub>2</sub> COCH <sub>3</sub>		5.83	100

\* The extent of the reaction was determined from the carbonyl compounds remaining after the reaction period with an Ethofat column (GC conditions, A, 90°; from formaldehyde to diethyl ketone, and biacetyl and acetyl acetone) and an SE-30 column (GC conditions, B, 130°; from benzaldehyde to acetophenone).

glass; column packing, 20% Ethofat 60/25 on Shimalite F (20–80 mesh); carrier gas (nitrogen) flow-rate, 50 ml/min; air and hydrogen flow-rates, 1.0 l/min and 50 ml/min, respectively; column temperature, 90°; injection port and detector (FID) temperature, 100°; (B) analytical column, 3 m × 3 mm I.D., glass; column packing, 5% SE-30 on Chromosorb W (60–80 mesh), acid washed and silanized; carrier gas (nitrogen) flow-rate, 50 ml/min; air and hydrogen flow-rates, 1.0 l/min and 50 ml/min, respectively; column temperature, 130° or 170°; injection port and detector (FID) temperature, 180°; ECD <sup>63</sup>Ni (10 mCi) carrier gas (nitrogen) flow-rate, 50 ml/min; column temperature, 130°; injection port temperature, 180°; detector temperature, 250°; pulsed voltage, (voltage 48 V, pulse width 8 μsec); (C) analytical column, 30 m × 0.25 mm I.D., glass capillary coated with PEG 20M (obtained from Hitachi, Ibaraki, Japan); carrier gas (helium) flow-rate, 0.8 ml/min; purge gas, (helium) flow-rate, 50 ml/min; air and hydrogen flow-rates, 1.0 l/min and 50 ml/min, respectively; column temperature, 130°; injection port and detector (FID) temperature, 200°; splitting ratio, 1:96.

## RESULTS AND DISCUSSION

The retention times and the extent of the derivatization for 27 pentafluorophenylhydrazone derivatives are given in Table I. All of the carbonyl compounds underwent highly quantitative reactions, except for acetaldehyde and diethyl ketone (80%).

Fig. 1(a) shows a typical chromatogram for eight pentafluorophenylhydrazone

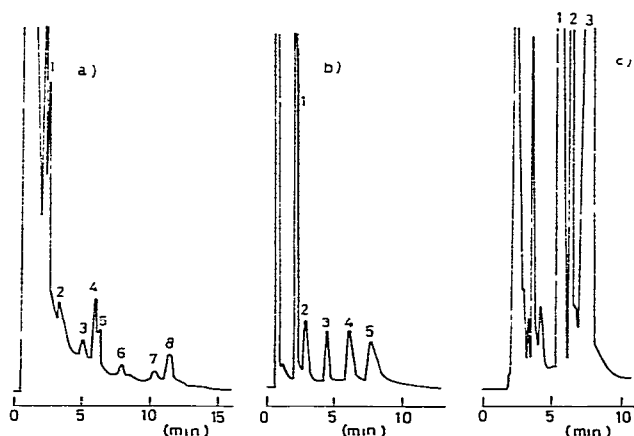


Fig. 1

Fig. 1. (a) Typical chromatogram of eight pentafluorophenylhydrazone derivatives (SE-30, FID). Peaks of pentafluorophenylhydrazones: 1 = formaldehyde (0.53 μg); 2 = acetaldehyde (0.11 μg); 3 = propionaldehyde (0.12 μg); 4 = acrolein (1.2 μg); 5 = isobutyraldehyde (0.13 μg); 6 = *n*-butyraldehyde (0.13 μg); 7 = isovaleraldehyde (0.13 μg); 8 = crotonaldehyde (0.39 μg). (b) Typical chromatogram of five pentafluorophenylhydrazone derivatives (SE-30, ECD). Peaks of pentafluorophenylhydrazones: 1 = formaldehyde (0.11 ng) plus pentafluorophenylhydrazine; 2 = acetaldehyde (0.11 ng); 3 = propionaldehyde (0.12 ng); 4 = isobutyraldehyde (0.13 ng); 5 = *n*-butyraldehyde (0.14 ng). (c) Typical chromatogram of three pentafluorophenylhydrazone derivatives (PEG 20M, glass capillary column, FID). Peaks of pentafluorophenylhydrazones: 1 = acetone ( $5 \cdot 10^{-7}$  mole); 2 = acrolein ( $5 \cdot 10^{-7}$  mole); 3 = propionaldehyde ( $5 \cdot 10^{-7}$  mole).

derivatives using an FID with an SE-30 column (GC conditions B). The separation of the peaks of pentafluorophenylhydrazine and the formaldehyde pentafluorophenylhydrazone derivative was incomplete. Fig. 1(b) shows a typical chromatogram for five pentafluorophenylhydrazone derivatives with highly sensitive electron-capture detection (GC conditions B, 130°). The minimum detectable amount from the chromatogram was about 0.01 ng. However, the peak of the formaldehyde pentafluorophenylhydrazone derivative overlapped that of pentafluorophenylhydrazine. (Fig. 1(c) shows a typical chromatogram for the derivatives of the C<sub>3</sub> compounds propionaldehyde, acrolein and acetone obtained with a 30 m × 0.25 mm I.D. glass capillary column packed with PEG-20M at 130° (GC conditions C). A complete separation was achieved at a lower temperature than that necessary with the 2,4-dinitrophenylhydrazone derivatives<sup>14</sup>.

#### ACKNOWLEDGEMENT

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

#### REFERENCES

- 1 E. Fedeli and M. Cirimele, *J. Chromatogr.*, 15 (1964) 435.
- 2 R. J. Soukup, R. J. Scarpellino and E. Danielczik, *Anal. Chem.*, 36 (1964) 2255.
- 3 R. E. Leonard and J. E. Kiefer, *J. Gas Chromatogr.*, 4 (1966) 142.
- 4 W. G. Galetto, R. E. Kepner and A. D. Webb, *Anal. Chem.*, 38 (1966) 34.
- 5 M. F. Fracchia, F. J. Schuette and P. K. Mueller, *Environ. Sci. Technol.*, 1 (1967) 915.
- 6 K. Shibasaki and S. Iwabuchi, *Nippon Shokuhin Kogyo Gakkai-shi (J. Food Sci. Technol., Tokyo)*, 17 (1970) 193.
- 7 Y. Shimizu, S. Matsuto, Y. Mizunuma and I. Okada, *Nippon Shokuhin Kogyo Gakkai-shi (J. Food Sci. Technol., Tokyo)*, 17 (1970) 385.
- 8 M. M. E. Metwalley, C. H. Amundson and T. Richardson, *J. Amer. Oil Chem. Soc.*, 48 (1971) 149.
- 9 L. J. Papa and L. P. Turner, *J. Chromatogr. Sci.*, 10 (1972) 744.
- 10 H. Kallio, R. R. Linko and J. Kaitaranta, *J. Chromatogr.*, 65 (1972) 355.
- 11 H. Halvarson, *J. Chromatogr.*, 76 (1973) 125.
- 12 R. J. Smythe and F. W. Karasek, *J. Chromatogr.*, 86 (1973) 228.
- 13 M. Deki and M. Yoshimura, *Chem. Pharm. Bull.*, 23 (1975) 1374.
- 14 Y. Hoshika and Y. Takata, *J. Chromatogr.*, 120 (1976) 379.
- 15 J. Attal, S. M. Hendeles and K. B. Eik-Nes, *Anal. Biochem.*, 20 (1967) 394.
- 16 R. A. Mead, G. C. Haltmeyer and K. B. Eik-Nes, *J. Chromatogr. Sci.*, 7 (1969) 554.