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GAS CHROMATOGRAPHIC SEPARATION OF CARBONYL COMPOUNDS AS THEIR 2,4-DINITROPHENYLHYDRAZONES USING GLASS CAPILLARY COLUMNS

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SUMMARY

The gas chromatographic separation of 22 carbonyl compounds as their 2,4-dinitrophenylhydrazones was investigated using glass capillary columns. Complete separation of the 2,4-dinitrophenylhydrazones of ten aliphatic aldehydes, eight aliphatic ketones and four aromatic aldehydes was obtained, except for the derivatives of *n*-valeraldehyde and isobutyl methyl ketone, whose peaks overlapped, and the *o*- and *m*-tolualdehyde derivatives, which were poorly separated.

The optimum conditions were as follows: stationary phase, SF-96; column size, 20 m × 0.25 mm I.D.; column temperature, 200–240°; injection and detector temperatures, 280–290°; carrier gas flow-rate, helium 1.0–1.2 ml/min or nitrogen 1.1–1.2 ml/min.

The method was applied to the analysis of aliphatic carbonyl compounds in car exhaust fumes and cigarette smoke.

INTRODUCTION

The identification and quantitative analysis of carbonyl compounds are problems commonly encountered in organic analyses. For instance, carbonyl compounds are present in very small amounts in foods, tobacco and tobacco smoke, car exhaust gases and odoriferous constituents.

Derivatization to 2,4-dinitrophenylhydrazones has been widely used in carbonyl analyses. The reactions between 2,4-dinitrophenylhydrazine and carbonyl compounds are highly specific, and most aldehydes and ketones yield 2,4-dinitrophenylhydrazones as very insoluble solids. Direct separation of the 2,4-dinitrophenylhydrazones by gas chromatography (GC) with SE-30 [1–5], F-60 [2], SF-96 [6–9], OV-17 [10], OV-101 [11], Dexisil 300 [12] and FFAP[5], and detection with a flame ionization detector (FID)[1,2,4–6,8–10,12], electron capture detector (ECD)[2] and mass spectrometry[11], have been used.

TABLE I

OPERATING CONDITIONS FOR GC ANALYSES

Condition	*I*	*II-1*	*II-2*	*II-3*
Apparatus	Hitachi Model 163	Shimadzu Model GC $5AP_5$	Shimadzu Model GC $5AP_5$	Shimadzu Model GC $5AP_5$
Column	Glass capillary column (Hitachi Chemi-column), 20 m × 0.25 mm I.D.	Glass capillary column (G-SCOT column), 20 m × 0.28 mm I.D.	Glass capillary column (G-SCOT column), 20 m × 0.28 mm I.D.	Glass capillary column (G-SCOT column), 20 m × 0.30 mm I.D.
Stationary phase	SF-96	SF-96	OV-17	OV-101
Column temperature	200–240°	200–240°	180–230°	185–235°
Injector and detector temp.	280–290°	280°	280°	280°
Carrier gas and flow-rate	He, 1.0–1.2 ml/min	N_2, 1.1 ml/min	N_2, 1.2 ml/min	N_2, 1.2 ml/min
Sample volume	1–6 μl	1–6 μl	1–6 μl	1–6 μl
Splitting ratio	1:80–1:150	1:110	1:60	1:60
Detector	FID	FID	FID	FID

The merit of applying GC techniques to the 2,4-dinitrophenylhydrazones is that the complete separation of complex mixtures of their derivatives and the selection of suitable detectors (for example, FID, ECD, AFID) are easy and the analytical precision is high. Further, the time of analysis is relatively short. Unfortunately, when packed columns are employed, the GC separation of mixtures of 2,4-dinitrophenylhydrazones derived from aliphatic carbonyl compounds is poor, except for the derivatives of formaldehyde and acetaldehyde. In particular, peaks of the derivatives of compounds with equal numbers of carbon atoms, such as propionaldehyde, acrolein and acetone, overlap.

In this study, in order to achieve the direct GC separation of the carbonyl compounds as their 2,4-dinitrophenylhydrazones, glass capillary columns of high resolution were used.

EXPERIMENTAL

2,4-Dinitrophenylhydrazone derivatives of carbonyl compounds

The 2,4-dinitrophenylhydrazones were prepared by a standard method[13]. The precipitates formed were isolated by filtration, washed with 2 *N* HCl, water and cold ethanol and dried over silica gel in a vacuum desiccator. The derivatives were then sufficiently pure for GC analysis.

Gas chromatography

The gas chromatographs used were a Hitachi Model 163 and a Shimadzu Model GC $5AP_5$ instrument, each equipped with on-column injection and a flame ionization detector. Other GC conditions are listed in Table I.

Two types of glass capillary column and three liquid phases were used: a Hitachi Chemi-column[14] with SF-96, 20 m × 0.25 mm I.D., and a G-SCOT column[15] with SF-96, OV-17 and OV-101, 20 m × 0.28 or 0.30 mm I.D. The latter columns were purchased from Gasukuro Kogyo (Tokyo, Japan).

The 2,4-dinitrophenylhydrazones were dissolved in ethanol, acetone or carbon tetrachloride to give 0.01% (w/v) solutions. The volume injected in most instances was 1–6 μl with a splitting ratio of 1:60–1:150.

The Shimadzu GC $5AP_5$ gas chromatograph was also equipped with a digital integrator for the determination of the response factors (F_i) and relative retention times of the 2,4-dinitrophenylhydrazones.

RESULTS AND DISCUSSION

Typical gas chromatograms

Typical gas chromatograms of the 2,4-dinitrophenylhydrazones of 22 carbonyl compounds are shown in Figs. 1–3. These chromatograms were recorded using the GC conditions listed in Table I.

As shown in Fig. 1, complete separation of the 2,4-dinitrophenylhydrazones of ten aliphatic aldehydes was obtained, although the peaks of each component gave rise to obvious double peaks[2,3,7,10], except for the peaks of the derivatives of formaldehyde, acrolein, isobutyraldehyde and crotonaldehyde.

The ratios of the sizes of each peak in the double peaks are listed in Table II.

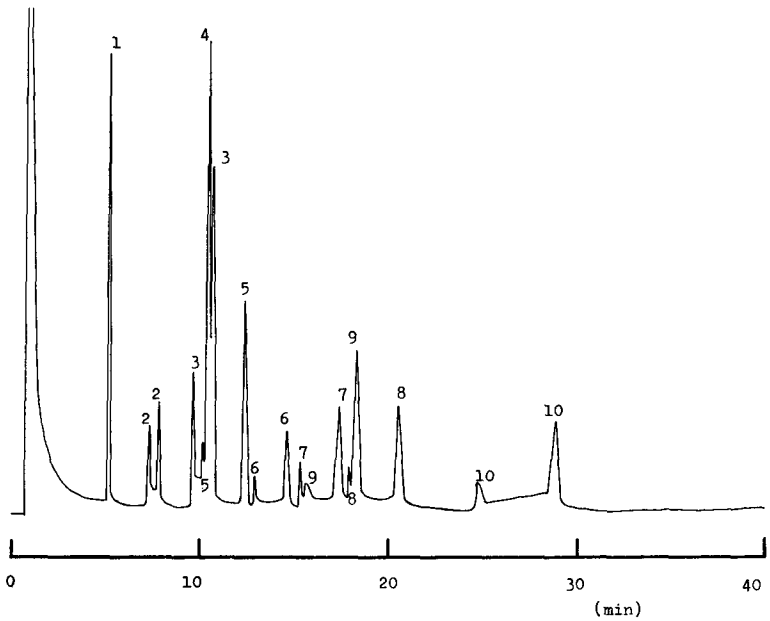

Fig. 1. Typical gas chromatogram of the 2,4-dinitrophenylhydrazones of ten aliphatic aldehydes. GC conditions I in Table I: column 200°, injector and detector 290°, He, 1.0 ml/min, splitting ratio 1:150, sample solution (ethanol) 0.01%, amount injected 3 μl. Peaks of 2,4-dinitrophenylhydrazones: 1, formaldehyde; 2, acetaldehyde; 3, propionaldehyde; 4, acrolein; 5, isobutyraldehyde; 6, *n*-butyraldehyde; 7, isovaleraldehyde; 8, *n*-valeraldehyde; 9, crotonaldehyde; 10, *n*-capronaldehyde.

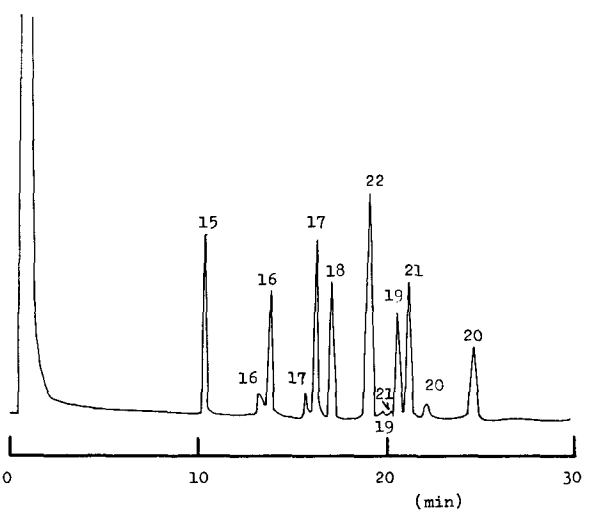

Fig. 2. Typical gas chromatogram of the 2,4-dinitrophenylhydrazones of eight aliphatic ketones. GC conditions I in Table I: column 200°, injector and detector 280°, He, 1.2 ml/min, splitting ratio 1:80, sample solution (acetone) 0.01%, amount injected 3 μl. Peaks of 2,4-dinitrophenylhydrazones: 15, acetone; 16, ethyl methyl ketone; 17, isopropyl methyl ketone; 18, diethyl ketone; 19, isobutyl methyl ketone; 20, *n*-butyl methyl ketone; 21, *sec.*-butyl methyl ketone; 22, *tert.*-butyl methyl ketone.

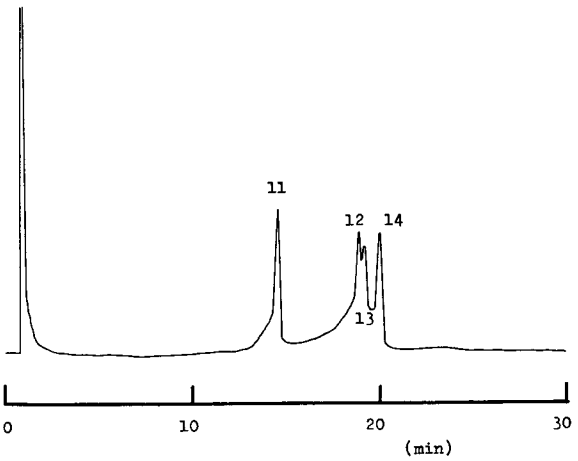

Fig. 3. Typical gas chromatogram of the 2,4-dinitrophenylhydrazones of four aromatic aldehydes. GC conditions I in Table I: column 240°, injector and detector 290°, He, 1.0 ml/min, splitting ratio 1:150, sample solution (carbon tetrachloride) 0.01%, amount injected 6 μl. Peaks of 2,4-dinitrophenylhydrazones: 11, benzaldehyde; 12, *m*-tolualdehyde; 13, *o*-tolualdehyde; 14, *p*-tolualdehyde.

The occurrence of these double peaks and the relative sizes of the two peaks in the double peaks have been observed previously for the 2,4-dinitrophenylhydrazones of furfural by Leonard and Kiefer[3] and Shibasaki and Iwabuchi[7]; however, the same retention time for the red and yellow isomers of furfural 2,4-dinitrophenylhydrazone was obtained.

It has been suggested that these double peaks may be due mainly to the influence of the solvent[2]. However, in this study, no effect on the gas chromatograms of the 2,4-dinitrophenylhydrazones of aliphatic carbonyl compounds was observed when solvents such as ethanol, acetone and carbon tetrachloride were used.

There is a difference between our observations and those of several workers[6,7,10] who did not observe double peaks in the chromatograms. This absence may have been due to insufficient resolving power or thermal decomposition on the columns used by other workers. Galetto *et al.*[4] did not find that the 2,4-dinitrophenylhydrazone of isovaleraldehyde decomposes on passage through the column, and Leonard and Kiefer[3] reported that the 2,4-dinitrophenylhydrazone of formaldehyde was not decomposed by heat in preparative gas–liquid chromatography.

As shown in Fig. 2, a complete separation of the 2,4-dinitrophenylhydrazones of eight aliphatic ketones was obtained. The derivatives of acetone, ethyl methyl ketone, *tert.*-butyl methyl ketone and diethyl ketone each gave a single peak, but the derivatives of isopropyl methyl ketone, *n*-butyl methyl ketone, isobutyl methyl ketone and *sec.*-butyl methyl ketone each gave double peaks. These double peaks did not disappear even after each ketone had been purified by distillation. These results suggest that the 2,4-dinitrophenylhydrazones of the latter four ketones exist as isomers.

As shown in Figs. 1 and 2, the separation of the 2,4-dinitrophenylhydrazones of propionaldehyde, acrolein and acetone, which possess equal numbers of carbon atoms, is possible with a glass capillary column, but the peaks of the *n*-valeraldehyde and isobutyl methyl ketone derivatives overlap.

With the packed columns used, it was not possible to separate the members

of other homologous series. In particular, the peaks of the 2,4-dinitrophenylhydrazones of propionaldehyde, acrolein and acetone, with three carbon atoms, usually overlapped.

According to Soukup *et al.*[6], *n*-butyraldehyde, ethyl methyl ketone and isobutyraldehyde, and *n*-valeraldehyde, *n*-propyl methyl ketone and isovaleraldehyde, were resolved, although poorly, on a similar packed column of SF-96.

Fig. 3 shows the separation of the 2,4-dinitrophenylhydrazones of four aromatic aldehydes; the *o*- and *m*-tolualdehyde derivatives were not completely separated.

Relative retention times

The relative retention times of the 2,4-dinitrophenylhydrazones of 22 carbonyl compounds on SF-96, OV-17 and OV-101 columns are given in Table II. The retention

TABLE II

RELATIVE RETENTION TIMES OF THE 2,4-DINITROPHENYLHYDRAZONES OF 22 CARBONYL COMPOUNDS

Compounds		*GC conditions**						
		I, SF-96				*II-1, SF-96*		
Class	*Members*	*Detailed conditions***	*Main peak (A)*	*Secondary peak (B)*	*Ratio, A/B*	*Detailed conditions***	*Main peak (A)*	*Secondary peak (B)*
Aldehydes	HCHO	a	1.00	—	—	d	1.00	—
	CH_3CHO		1.50	1.43	1:0.65		1.47	1.39
	C_2H_5CHO		2.00	1.83	1:0.31		1.97	1.79
	$CH_2=CHCHO$		1.93	1.76	1:0.04		1.92	1.77
	n-C_3H_7CHO		2.70	2.39	1:0.46		2.65	2.36
	iso-C_3H_7CHO		2.31	1.96	1:0.15		2.26	1.94
	$CH_3CH=CHCHO$		3.37	2.93	1:0.15		3.30	2.75
	n-C_4H_9CHO		3.83	3.31	1:0.45		3.72	3.24
	iso-C_4H_9CHO		3.24	2.85	1:0.48		3.15	2.78
	n-$C_5H_{11}CHO$		5.46	4.69	1:0.44		5.19	4.48
	C_6H_5CHO	b	1.00	—	—	e	1.00	—
	o-$C_6H_4(CH_3)CHO$		1.29	—	—		1.27	—
	m-$C_6H_4(CH_3)CHO$		1.26	—	—		1.24	—
	p-$C_6H_4(CH_3)CHO$		1.33	—	—		1.33	—
Ketones	CH_3COCH_3	c	2.02	—	—	d	1.88	—
	$CH_3COC_2H_5$		3.02	2.90	1:0.04		2.52	2.41
	CH_3CO *iso*-C_3H_7		3.17	—	—		2.96	—
	CH_3CO *n*-C_4H_9		4.48	4.00	1:0.24		4.54	4.05
	CH_3CO *iso*-C_4H_9		3.74	3.41	1:0.14		3.79	3.45
	CH_3CO *sec.*-C_4H_9		3.96	3.67	1:0.06		3.87	—
	CH_3CO *tert.*-C_4H_9		3.54	—	—		3.47	—
	$C_2H_5COC_2H_5$		3.20	—	—		3.11	—

* GC conditions are listed in Table I.

** a, Column 200°, injector and detector 290°, He, 1.0 ml/min, splitting ratio 1:150; b, column 240°, other conditions as a; c, column 200°, injector and detector 280°, He, 1.2 ml/min, splitting ratio 1:80; d, column 200°, injector and detector 280°, N_2, 1.1 ml/min, splitting ratio 1:110; e, column 240°, other conditions as d; f, column 180°, injector and detector 280°, N_2, 1.2 ml/min, splitting ratio 1:60; g, column 230°, other conditions as f; h, column 185°, other conditions as f; i, column 235°, other conditions as f.

times of the formaldehyde derivative (for the aliphatic aldehydes and ketones) and the benzaldehyde derivative (for aromatic aldehydes) were defined as unity.

The chromatographic conditions (I) and (II-1) using SF-96 are very similar, but shorter retention times are obtained with the former conditions.

With the OV-17 column, lower column temperatures than with SF-96 could be used, and a better separation of propionaldehyde, acrolein and acetone was obtained than on SF-96.

The shortest retention times were obtained with OV-101, but, as with OV-17, the isomers of tolualdehyde were poorly separated.

Response factors[10,16,17]

The reproducibility and uniformity of the response for various carbonyl com-

	II-2, OV-17				*II-3, OV-101*			
Ratio, A/B	*Detailed conditions***	*Main peak (A)*	*Secondary peak (B)*	*Ratio, A/B*	*Detailed conditions***	*Main peak (A)*	*Secondary peak (B)*	*Ratio, A/B*
—	f	1.00	—	—	h	1.00	—	—
1:0.71		1.56	1.37	1:0.56		1.58	1.64	1:0.59
1:0.25		2.08	1.73	1:0.29		2.20	2.00	1:0.30
1:0.05		1.89	—	—		2.15	—	—
1:0.35		2.77	2.26	1:0.35		3.08	2.68	1:0.31
1:0.07		2.14	1.57	1:0.10		2.56	2.13	1:0.06
1:0.09		3.50	2.66	1:0.05		3.93	3.24	1:0.03
1:0.33		3.96	3.15	1:0.32		4.49	3.82	1:0.27
1:0.41		2.76	2.62	1:0.35		3.70	3.20	1:0.28
1:0.33		5.02	3.93	1:0.36		6.43	5.44	1:0.25
—		1.00	—	—	i	1.00	—	—
—	g	1.25	—	—		1.38	—	—
—		1.25	—	—		1.32	—	—
—		1.32	—	—		1.41	—	—
—	f	1.83	—	—	h	2.07	—	—
1:0.18		2.07	2.21	1:0.15		2.86	2.73	1:0.17
—		2.35	—	—		3.32	—	—
1:0.29		4.32	3.61	1:0.27		5.33	4.68	1:0.40
1:0.31		3.28	2.84	1:0.30		4.35	3.85	1:0.33
—		3.33	2.99	1:0.05		4.45	—	—
—		2.16	—	—		3.79	—	—
—		2.58	—	—		3.50	—	—

pounds were evaluated for the 2,4-dinitrophenylhydrazones of five aliphatic aldehydes, four aliphatic ketones and two aromatic aldehydes.

As seen from Table III, the response factors of these 2,4-dinitrophenylhydrazones with the glass capillary column showed good uniformity and high reproducibility.

TABLE III

RESPONSE FACTORS (F_i)* AND STANDARD DEVIATIONS OF THE 2,4-DINITROPHENYLHYDRAZONES OF 11 CARBONYL COMPOUNDS

*Conditions***	*Compounds*		$F_i \pm$ *standard deviation*
	Class	*Members*	
a	Aldehydes	HCHO	1.12 ± 0.00
		CH_3CHO	1.14 ± 0.01
		C_2H_5CHO	1.02 ± 0.00
		n-C_3H_7CHO	1.05 ± 0.00
		iso-C_3H_7CHO	1.05 ± 0.00
b		C_6H_5CHO	0.99 ± 0.01
		m-$C_6H_4(CH_3)CHO$	1.01 ± 0.01
c	Ketones	CH_3COCH_3	1.13 ± 0.01
		$CH_3COC_2H_5$	1.18 ± 0.03
		CH_3CO-*iso*-C_3H_7	1.13 ± 0.01
		$C_2H_5COC_2H_5$	1.14 ± 0.01

* $F_i = (A_s/W_s)\cdot(W_i/A_i)$ where A_s and W_s = peak area (log) and weight of internal standard (anthracene), respectively, and A_i and W_i = peak area (log) and weight of derivative, respectively.

** GC conditions II-1, SF-96, are listed in Table I. a and c, column 200°, injector and detector 280°, N_2, 1.1 ml/min, splitting ratio 1:110; b, column 240°, other conditions as a. W_s and W_i: a, 0.67 μg; b, 1.0 μg; c, 0.8 μg.

APPLICATIONS

Car exhaust gases

Fig. 4 shows a typical separation of the 2,4-dinitrophenylhydrazones of aliphatic carbonyl compounds isolated from a sample of car exhaust gas, using the glass capillary column. The exhaust gas was produced using a 1973 Mazda Savanna (RE-AP, Rotary Wagon) equipped with a 0.52 L × 2 rotary engine running at normal idling speed.

The procedure for collection the gas sample and preparation of the 2,4-dinitrophenylhydrazones was as follows. The exhaust gas (30 l) was collected and condensed by a direct cold trap with liquid oxygen and dissolved in ethanol (5 ml). The solution obtained was poured into a 0.1% solution of 2,4-dinitrophenylhydrazine in 2 *N* HCl and allowed to crystallize overnight at room temperature. The resulting precipitate was extracted with carbon tetrachloride and then dried under vacuum. The residue was dissolved in acetone (0.5 ml).

Anthracene was used as the internal standard, which was necessary in order to prove the identity of the derivatives and other compounds.

As shown in Fig. 4, at least 13 aliphatic carbonyl compounds were completely

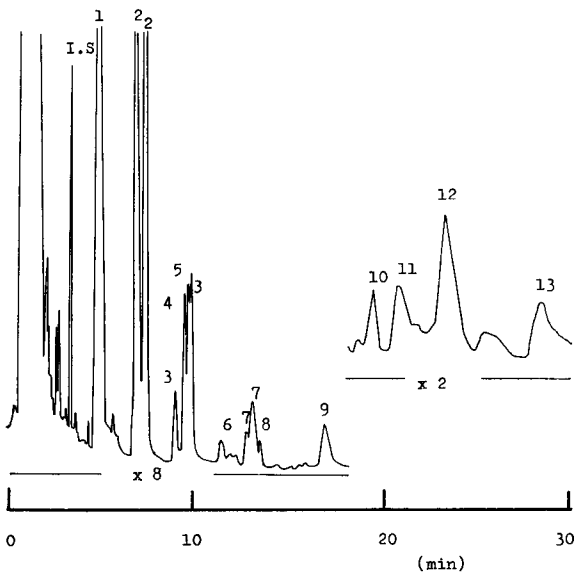

Fig. 4. Typical gas chromatogram of the 2,4-dinitrophenylhydrazones of aliphatic carbonyl compounds isolated from car exhaust gas. GC conditions II-1 in Table I: column 200°, injector and detector 280°, N_2, 1.1 ml/min, splitting ratio 1:110, amount of sample injected 1 μl. Internal standard (I.S.) = anthracene (0.4 μg). Peaks of 2,4-dinitrophenylhydrazones and amounts of parent compounds: 1, formaldehyde (2.3 ppm); 2, acetaldehyde, 1.5 ppm; 3, propionaldehyde, 0.2 ppm; 4, acetone, 0.2 ppm; 5, acrolein, 0.2 ppm; 6, isobutyraldehyde; 7, *n*-butyraldehyde; 8, isopropyl methyl ketone; 9, crotonaldehyde; 10, *n*-valeraldehyde and isobutyl methyl ketone; 11, sec.-butyl methyl ketone; 12, *n*-butyl methyl ketone; 13, *n*-capronaldehyde.

separated and identified, and included high concentrations of formaldehyde and acetaldehyde.

Papa and Turner[10] reported a typical separation of a mixture of 2,4-dinitrophenylhydrazones of formaldehyde, acetaldehyde, *n*-butyraldehyde and other compounds, isolated from car exhaust gas, with a chromatographic analysis time of 25 min. However, the separation of the 2,4-dinitrophenylhydrazones of propionaldehyde, acrolein and acetone, and of isovaleraldehyde and crotonaldehyde, was poor.

The concentrations of representative carbonyl compounds detected were: formaldehyde 2.3, acetaldehyde 1.5, and propionaldehyde, acrolein and acetone 0.2 ppm. The results were in reasonable agreement with literature values[9,18].

Cigarette smoke

Fig. 5 shows a typical separation of 2,4-dinitrophenylhydrazones of aliphatic carbonyl compounds in the smoke obtained from a Japanese cigarette. The pretreatment procedures were the same as for the car exhaust gas.

At least eight aliphatic carbonyl compounds were separated and identified, mainly acetaldehyde and acetone. The concentrations of representative carbonyl compounds detected were: acetaldehyde 8, acetone 5.3 and propionaldehyde 0.4 mg/g. These results agree closely with several earlier reports[19–22].

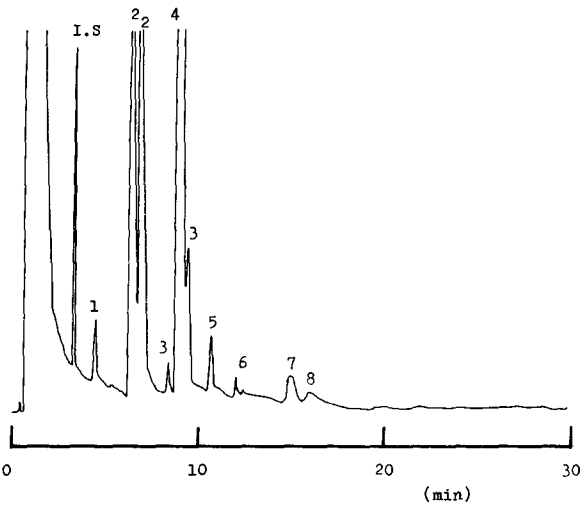

Fig. 5. Typical gas chromatogram of the 2,4-dinitrophenylhydrazones of aliphatic carbonyl compounds isolated from the smoke of a Japanese cigarette. GC conditions II-1 in Table I: column 200°; injector and detector 280°, N_2, 1.1 ml/min, splitting ratio 1:110. The sample of a cigarette smoke was collected in liquid oxygen, dissolved in 5 ml of ethanol, then the solution was poured into a 0.1% solution of 2,4-dinitrophenylhydrazine in 2 *N* HCl and allowed to crystallize overnight. The precipitate produced was extracted with carbon tetrachloride and dried under vacuum. The residue was then dissolved in 2 ml of acetone and the amount injected was 5 μl. Internal standard (I.S.) = anthracene (0.4 μg). Peaks of 2,4-dinitrophenylhydrazones and amounts of parent compounds: 1, formaldehyde; 2, acetaldehyde, 8 mg/g; 3, propionaldehyde, 0.4 mg/g; 4, acetone, 5.3 mg/g; 5, isobutyraldehyde; 6, ethyl methyl ketone; 7, isovaleraldehyde; 8, *tert.*-butyl methyl ketone.

CONCLUSION

The direct gas chromatographic separation of 22 carbonyl compounds as their 2,4-dinitrophenylhydrazones using glass capillary columns has been demonstrated. The separation of the derivatives of ten aliphatic aldehydes, eight aliphatic ketones and four aromatic aldehydes was good, except for the derivatives of *n*-valeraldehyde and isobutyl methyl ketone, whose peaks overlapped, and *o*- and *m*-tolualdehyde, which were poorly separated.

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