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## SIMPLE AND RAPID GAS-LIQUID-SOLID CHROMATOGRAPHIC ANALYSIS OF TRACE CONCENTRATIONS OF ACETALDEHYDE IN URBAN AIR

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### SUMMARY

A simple and rapid gas-liquid-solid chromatographic method for the analysis of trace concentrations of acetaldehyde in urban air (in the Nagoya area) was developed, with the use of cold trapping with liquid oxygen. In the analytical main column the conditions were: stationary phase, Triton X-100 (0.4%); support, Carbowax B (60-80 mesh); glass column, 1.5 m × 3 mm I.D.; column temperature, 75°; carrier gas (nitrogen) flow-rate, 50-80 ml/min. In the cold trapping pre-column the conditions were: stationary phase, Tris (2-cyanoethoxy) propane (25%); support, Shimalite (AW, DMCS) (60-80 mesh); glass column, 31 cm × 4 mm I.D.; operating temperature for the trapping, -183° (liquid oxygen temperature); operating temperature for injection of the condensed sample into the gas chromatograph, increased from -183° to +100° for 2 min. The acetaldehyde peak was identified by the disappearance method with a 2,4-dinitrophenylhydrazine-orthophosphoric acid-glass beads column.

The ranges and average concentrations of acetaldehyde detected in 13 urban air samples were 1.5-9.6 and 4.7 ppb, respectively.

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### INTRODUCTION

Acetaldehyde and other volatile carbonyl compounds are present in complex mixtures such as tobacco smoke<sup>1-6</sup>, car exhaust gas<sup>6-16</sup>, food flavours and aromas<sup>17-22</sup> and air<sup>23-25</sup>, and have been also reported as important products of photochemical reactions with some organic compounds, SO<sub>x</sub>, NO<sub>x</sub> and ozone<sup>26-28</sup>. Methods for their analysis have involved either prior derivative formation or direct gas chromatography (GC) of gas samples. The formation of derivatives such as 2,4-dinitrophenylhydrazones<sup>7,8,10,11,17-19,29-33</sup>, oximes<sup>34,35</sup>, thiosemicarbazones<sup>36</sup> and Schiff bases<sup>12,37</sup> is time consuming and extractions or special clean-up procedures prior to the GC analysis are often necessary.

Direct injection methods with samples of complex compounds using high-resolution GC columns have also been reported<sup>9,12,38</sup>. Specialized sampling<sup>23</sup> and injection equipment are available for separating large numbers of components, such as in air and cigarette smoke. However, this technique is not suitable for the routine anal-

ysis of large numbers of samples, because in order to complete the separation of the polar components long analysis times are usually necessary.

In this paper, a simple and rapid procedure for the accurate determination of acetaldehyde in urban air (in the Nagoya area) is described. The acetaldehyde is trapped in a pre-column<sup>39-42</sup> that is cooled with liquid oxygen, then the pre-column is heated from liquid oxygen temperature ( $-183^{\circ}$ ) to  $+100^{\circ}$  for 2 min and the sample is then subjected to gas-liquid-solid chromatography (GLSC) with 0.4% Triton X-100 on Carbopack B (60-80 mesh). This column packing is more suitable than Porapak Q and QS and Chromosorb 101 because it gives a better separation of acetaldehyde from other compounds present in urban air, e.g., 1,3-butadiene, *trans*-butene-2 and vinyl chloride. When the Triton X-100 column packing is used, the complete separation of acetaldehyde from mixtures of lower olefins, alcohols, amines, esters, chlorides and other compounds present in urban air is obtained.

## EXPERIMENTAL

### Reagents

Acetaldehyde (99.5%) was obtained from E. Merck (Darmstadt, G.F.R.). Orthophosphoric acid, 2,4-dinitrophenylhydrazine, ethanol and propanol-1 were obtained from Wako Pure Chemical Industries (Osaka, Japan).

### Gas-liquid-solid chromatography

The gas chromatograph used was a Shimadzu Model GC5AP<sub>5</sub>F instrument equipped with on-column injection, a flame-ionization detector (FID) and a digital integrator (Shimadzu Model ITG-2A) for the determination of the relative retention times. The glass analytical column (1.5 m  $\times$  3 mm I.D.) was packed with 0.4% Triton X-100 on Carbopack B (60-80 mesh) (Wako). The chromatographic conditions for the FID were as follows: column temperature,  $75^{\circ}$ ; injection port and detector temperatures,  $150^{\circ}$ ; carrier gas (nitrogen) flow-rate, 50-80 ml/min; hydrogen and air flow-rates, 50 ml/min and 1.0 l/min, respectively.

*Cold trapping method.* The sample gas, including acetaldehyde, was collected directly in a glass pre-column (31 cm  $\times$  4 mm I.D.) packed with 25% TCEP (Tris(2-cyanoethoxy)propane) on Shimalite (AW, DMCS) (60-80 mesh) by cold trapping with liquid oxygen, then the pre-column was connected to the carrier-gas line of the gas chromatograph, cooled with liquid oxygen. After about 5 min, the time necessary for a constant flow of carrier gas to be achieved, the pre-column was heated from  $-183^{\circ}$  to  $+100^{\circ}$  (for 2 min) for the injection of the condensed sample into the gas chromatograph.

*2,4-Dinitrophenylhydrazine-orthophosphoric acid-glass beads column.* A 5-g amount of glass beads (30-60 mesh; Wako), 0.05 g of 2,4-dinitrophenylhydrazine and 0.1 ml of orthophosphoric acid were mixed and the mixture obtained was immediately packed into a glass column (12 cm  $\times$  8 mm I.D.). This column was used for the identification of the acetaldehyde peak by means of the disappearance method.

## RESULTS AND DISCUSSION

### *Relative retention times on a Triton X-100 column by the direct injection method*

The relative retention times of 35 compounds on a Triton X-100 column

determined by the direct injection method at a column temperature of 75° are given in Table I. The retention time of acetaldehyde was defined as unity.

Table I shows that acetaldehyde was separated completely from other compounds, such as lower aliphatic hydrocarbons, lower aliphatic amines, ammonia, chlorides, lower aliphatic monoalcohols and esters, present in the air. In particular, the analytical conditions were suitable for separating acetaldehyde from methanol, ethanol, vinyl chloride, butadiene-1,3 and *trans*-butene-2, but when packed columns of Porapak Q, QS and Chromosorb 101 were employed, the GC separation of such mixtures was poor.

TABLE I

RELATIVE RETENTION TIMES OF 35 COMPOUNDS ON A TRITON X-100 COLUMN (ACETALDEHYDE = 1.00)

Column, 1.5 m; carrier gas (nitrogen) flow-rate, 50 ml/min; column temperature, 75°.

<i>Compound</i>	<i>Relative retention time</i>	<i>Compound</i>	<i>Relative retention time</i>
Ammonia	0.34	Isobutane	3.00
Methane	0.36	Dichloromethane	3.07
Acetylene	0.44	Butene-1	3.36
Ethylene	0.49	Isobutene	3.88
Ethane	0.54	Acetone	4.10
Methylamine	0.63	<i>n</i> -Butane	4.20
Methyl chloride	0.73	<i>cis</i> -Butene-2	4.24
Methanol	0.81	Isopropylamine	4.27
Acetaldehyde	1.00	Butadiene-1,3	4.74
Propylene	1.21	Trimethylamine	4.76
Propane	1.32	<i>trans</i> -Butene-2	5.06
Vinyl chloride	1.52	1,2-Dichloroethylene	5.93
Ethylamine	1.57	Ethyl formate	6.05
Dimethylamine	1.67	Vinyl acetate	6.13
Methyl formate	1.72	Methyl acetate	6.36
Ethyl chloride	1.85	1,2-Dichloroethane	7.63
Ethanol	2.05	Diethyl ether	9.41
		Chloroform	10.28

#### *Typical chromatogram of acetaldehyde in urban air*

Fig. 1 (1) shows a typical chromatogram of acetaldehyde in urban air (in the Nagoya area). The volume trapped was 0.5 l, the trapping method of urban air was carried out in the pre-column by the direct cold trapping method with liquid oxygen. Acetaldehyde was identified at a concentration of 8.5 ppb.

Fig. 1 (2) shows a typical chromatogram of urban air trapped by the pre-column in liquid oxygen, but passed through the 2,4-dinitrophenylhydrazine-ortho-phosphoric acid-glass beads column. In this chromatogram, the peak of acetaldehyde has disappeared completely.

#### *Calibration graph*

The FID response produced a straight-line relationship in the range 3–7000 ng

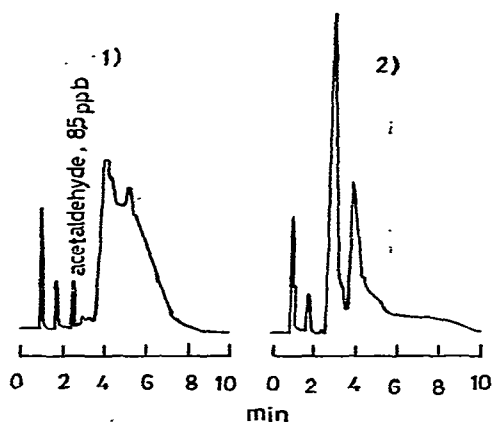


Fig. 1. Typical chromatograms of acetaldehyde in urban air (in the Nagoya area) using the cold trapping method with liquid oxygen. Sample taken on December 15th, 1976. (1) Direct cold trapping volume (0.5 l); (2) cold trapping volume (0.5 l) of sample gas passed through 2,4-dinitrophenylhydrazine-orthophosphoric acid-glass beads column. 0.4% Triton X-100 on Carbowax B (60-80 mesh), 1.5 m  $\times$  3 mm I.D.; 75°; N<sub>2</sub> flow-rate, 80 ml/min; FID; range 4 ( $\times$  0.01 V); sensitivity,  $10^2$  ( $\times$  M.O).

of acetaldehyde (Fig. 2), and the minimum detectable amount at twice the noise level was about 1 ng. Therefore, when the concentration volume is 1.0 l, the minimum detectable concentration is as low as 0.5 ppb. This value is less than that of methods involving specialized sampling injection equipment<sup>23</sup>.

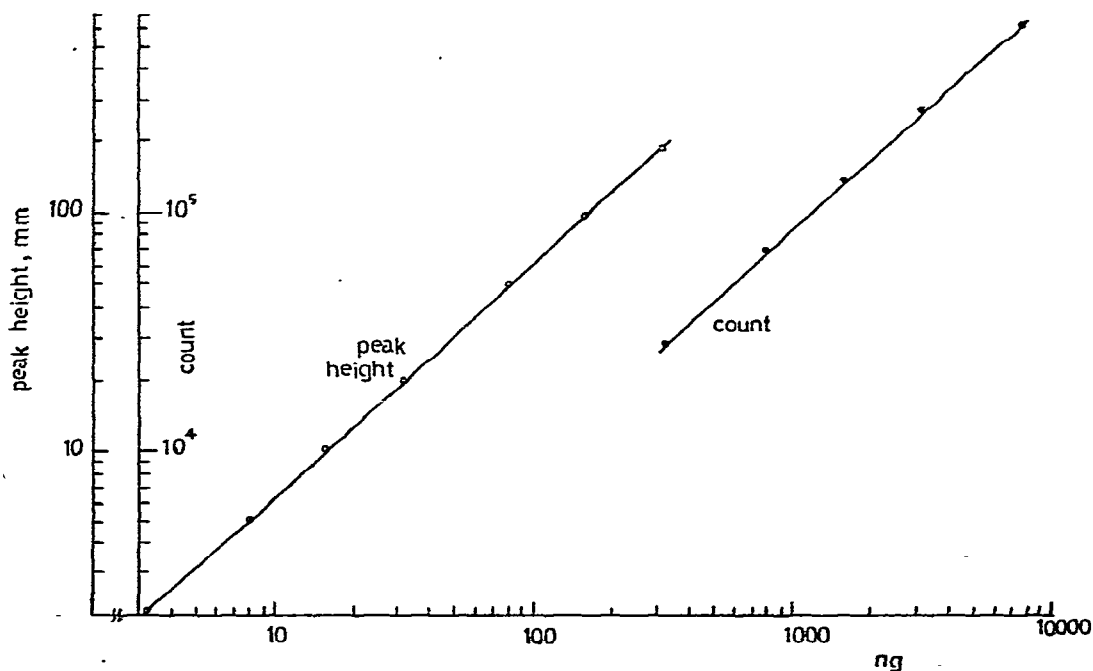


Fig. 2. Calibration graphs for acetaldehyde using the cold trapping method with liquid oxygen.

*Repeatability of the cold trapping method*

The repeatability and uniformity of the retention time and peak height of acetaldehyde were evaluated by the cold trapping method with liquid oxygen. As can be seen from Table II, they showed good uniformity and high repeatability.

TABLE II

REPEATABILITY OF RETENTION TIME AND PEAK HEIGHT OF ACETALDEHYDE USING COLD TRAPPING METHOD ( $n = 6$ )

Amount (ng)	Retention time (min) *	Peak height (mm) **
7.8	$2.80 \pm 0.043$	$5.7 \pm 0.5$
78	$2.78 \pm 0.037$	$48 \pm 1.4$
780	$2.76 \pm 0.024$	$511 \pm 24.1$

\* By means of a digital integrator.

\*\* For chromatographic conditions see Experimental. Nitrogen flow-rate, 80 ml/min; FID; range 4 ( $\times 0.01$  V); sensitivity,  $10^2$  ( $\times$  M $\Omega$ ).

*Quantitative data*

The ranges and average concentrations of acetaldehyde detected in 13 urban air samples were 1.5–9.6 ppb, and 4.7 ppb, respectively. The results were in reasonable agreement with a literature value<sup>23</sup>.

The time required for the whole procedure, including the concentration and GC analysis of one sample, was about 12 min. There was no interference from lower aliphatic and aromatic hydrocarbons and other compounds in the analysis of acetaldehyde.

## CONCLUSION

The direct GLSC analysis of trace concentrations of acetaldehyde in urban air using Triton X-100 on a Carboxpack B column and the cold trapping concentration method with liquid oxygen has been demonstrated. The identification of acetaldehyde was confirmed by the peak disappearance method with a 2,4-dinitrophenylhydrazine-orthophosphoric acid-glass beads column.

It is possible that the proposed method may be able to give complete separations of acetaldehyde in car and diesel engine exhaust gases, cigarette smoke, alcoholic beverages, etc.

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