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## ANALYTICAL STUDY OF LOW-CONCENTRATION GASES

### II\*. COLLECTION OF ACETALDEHYDE AT LOW CONCENTRATIONS IN AIR IN A SOLID REACTION TUBE AND ITS ANALYSIS USING A FLAME THERMIONIC DETECTOR

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#### SUMMARY

A method for the determination of acetaldehyde at low concentrations in air is discussed. Acetaldehyde was collected using silica gel treated with 2,4-dinitrophenylhydrazine. Recoveries were 98–100% with good analytical precision, the coefficients of variation being less than 5% when 50–100 l of air were sampled. Determination by gas chromatography with a flame thermionic detector gave a detection limit of 0.05–0.25 ppb\*\* and a coefficient of variation of about 4%. The method is precise, simple and rapid. Acetaldehyde concentrations in air determined by this method were 3–4 ppb.

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#### INTRODUCTION

Acetaldehyde (AA), an ill-smelling substance, has been found in air as one of the reaction products of photochemical smog and from automotive exhausts.

There have been many reports on the determination of aldehydes by means of absorption spectrophotometry<sup>2,3</sup>, atomic-absorption spectrophotometry<sup>4</sup>, high-performance liquid chromatography (HPLC)<sup>5,6</sup> and gas chromatography (GC). AA in air has been determined mainly by GC, as free AA or as a derivative<sup>7,8</sup>. The separation of AA from other components in air is often difficult when it is to be analysed as a derivative such as the 2,4-dinitrophenylhydrazone (DNPH)<sup>9</sup>, thiosemicarbazone<sup>10</sup> or imidazolidine<sup>11</sup>. The DNPH method is frequently used as an authorized method<sup>12</sup>.

We determined AA in air according to the authorized method, which was

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\* Fort Part I, see ref. 1.

\*\* Throughout this article, the American billion ( $10^9$ ) is meant.

unsatisfactory for the determination of low concentrations because of the volume of air sampled and the sensitivity of the GC system. All the reported GC methods involve utilization of a hydrogen flame-ionization detector (FID) and hence will probably be incapable of producing greater analytical sensitivity. We used a flame thermionic detector (FTD) to obtain an increased sensitivity. Although it makes organic nitrogen compounds detectable with high selectivity and sensitivity, it has not previously been widely used. There are a few reports on the determination of ammonia and trimethylamine in air using the method of Hanai *et al.*<sup>13</sup>, but no reports on the determination of AA. GC using an FTD will be widely used in future for the determination of atmospheric components, similarly to the determination of sulphur compounds.

In this work we studied methods for collecting AA and analysing it with an FTD. It could be collected on silica gel coated with 2,4-dinitrophenylhydrazine without decomposition of AA-DNPH when 100 l of air were sampled. Combination of the method for collecting air with the FTD method produced a sufficiently useful method for determination of low concentrations of AA in air.

## EXPERIMENTAL

### *Apparatus*

A Shimazu GC-7A (FTD-8) gas chromatograph and a Nippon Denshi JMS-D-300/JMA-200 gas chromatograph-mass spectrometer were used.

### *Reagents*

All reagents were of special grade.

2,4-Dinitrophenylhydrazine was obtained from Wako, acetaldehyde from Merck, N,N-dimethylformamide and carbon tetrachloride from Tokyo Kasei, hydrochloric acid from Katayama and silica gel (60-80 mesh) from Gaschro.

### *Preparation and standard solution of 2,4-DNPH*

One gram of 2,4-dinitrophenylhydrazine (2,4-DNPH), recrystallized from water, was dissolved in a mixture of 2 ml of concentrated sulphuric acid and 15 ml of ethanol and a solution of 0.5 g of AA in 15 ml of ethanol was added. The precipitated AA-DNPH was suction-filtered, washed with distilled water and ethanol, then dried under reduced pressure. The resulting 50.9 mg of AA-DNPH was dissolved in carbon tetrachloride and made up to 100 ml. This stock solution was appropriately diluted with carbon tetrachloride to make a working standard solution.

### *Preparation of silica gel coated with 2,4-DNPH*

Collection of aldehydes at low concentrations in air in a solid reaction tube has been reported only by Kato *et al.*<sup>14</sup>, using glass beads, and by Beasley *et al.*<sup>15</sup>. Beasley *et al.* collected formaldehyde on silica gel coated with 2,4-DNPH and determined it by HPLC. We therefore prepared silica gel coated with 2,4-DNPH by the method of Beasley *et al.* in order to apply the method to the collection of AA. A 15-g amount of silica gel was placed in a 200-ml round-bottomed flask, to which 15 ml of 6 N hydrochloric acid were added. To the acidic solution was quickly added a filtrate prepared by dissolving 6 g of 2,4-dinitrophenylhydrazine in 48 ml of di-

methylformamide and the mixture was filtered through a cotton plug. The solution was suction-filtered through a glass filter (G3) to separate the silica gel, which was placed in another round-bottomed flask and thoroughly dried using a rotary evaporator at 55°C under reduced pressure.

### Analytical method

One gram of silica gel obtained by the above method was packed into a sampling tube as shown in Fig. 1. Air (50–100 l) was sampled at a flow-rate of 1 l/min using the apparatus shown in Fig. 2. The silica gel in the sampling tube was placed in a 10-ml test-tube, to which 6 ml of carbon tetrachloride were added. The sampling tube was washed with an additional 2 ml of carbon tetrachloride and the washings were also placed in the test-tube, which was heated for 10 min at 50°C to extract the AA-DNPH. After cooling, the extract was filtered and the filtrate was concentrated to 1–2 ml at 40–50°C and a 1–5- $\mu$ g portion was injected into the gas chromatograph.

### Gas chromatographic conditions

The GC conditions were as follows: glass column (2 m  $\times$  3 mm I.D.), 3% OV-17 on Chromosorb G (60–80 mesh); column temperature, 220°C; injection temperature, 240°C; flow-rate (helium), 50 ml/min; hydrogen, 0.6 kg/cm<sup>2</sup>; air, 0.5 kg/cm<sup>2</sup>; detector: FTD (rubidium silicate).

Determination was based on peak areas calculated as the peak height times the width at half-height. The peak areas given by the sample were compared with those given by a known standard solution. Because no suitable internal standard substance was available, the standard solution was injected into the gas chromato-

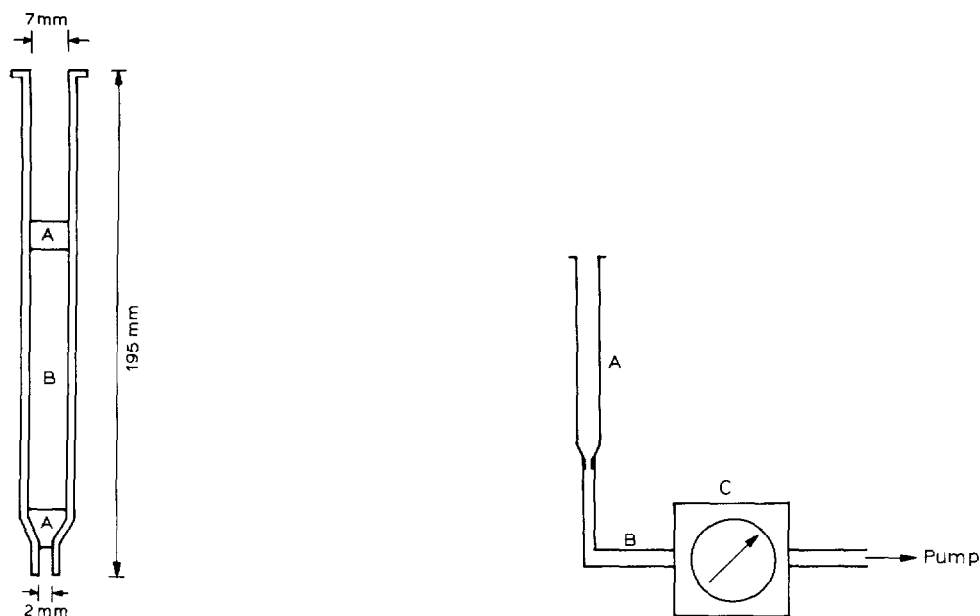


Fig. 1. Sampling tube. A, Glass-wool; B, coated with silica gel.

Fig. 2. Apparatus for sampling. A, Sampling tube; B, silicone-rubber tube; C, gas meter.

graph after every few samples to take account of variations in the sensitivity of the gas chromatograph.

## RESULTS AND DISCUSSION

### *Amount of silica gel packed*

Beasley *et al.*<sup>15</sup> packed about 400 mg of silica gel when collecting aldehydes in air and samples air at a flow-rate of 0.1–0.2 l/min. However, the method is impractical because too long a time is required for sampling owing to the low concentrations and the GC sensitivity when AA in air is to be analysed. We investigated the amounts of silica gel packed in the sampling tube when 50 l of air were sampled with a tentative injection rate of air of 1.0 l/min. The sampling tubes shown in Fig. 1 were packed with 100–1000 mg of silica gel. The standard solution of AA (10  $\mu$ g as AA) was added to the tubes with treatment as described under *Analytical method*. Recoveries were calculated on the basis of the peak areas on the gas chromatograms obtained. The results in Fig. 3 show that the recoveries were 84% and 96% when 400 mg (as suggested by Beasley *et al.*<sup>15</sup>) and 700 mg or more of silica gel were packed into the tubes, respectively. The amount of silica gel was increased to 1000 mg and the following experiment was carried out.

### *Efficiency of collection*

The efficiency of collection of AA was investigated using a sampling tube packed with 1000 mg of silica gel when 50–200 l of air was sampled using the apparatus as shown in Fig. 4 at injection rates of 1.0–1.3 l/min. The results are given in Table I, showing the percentage recovery of AA when 0.4 l/min of AA was collected in a sampling tube into which 1 l of nitrogen gas was passed. As Table I shows, the efficiency of collection was 98% when 100 l of air were sampled at an injection rate of 1.0 l/min, 85% when 200 l of air were sampled and 68% when 50 l of air were sampled at an injection rate of 2.0 l/min. The coefficients of variation were more than 10% when more than 100 l of air were sampled, with lower precision. An injection rate of 3.0 l/min produced a lower efficiency of collection. When 50–100 l of air were

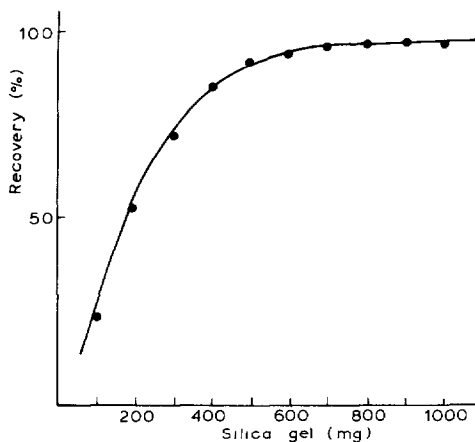


Fig. 3. Variation of efficiency of collection with amount of silica gel.

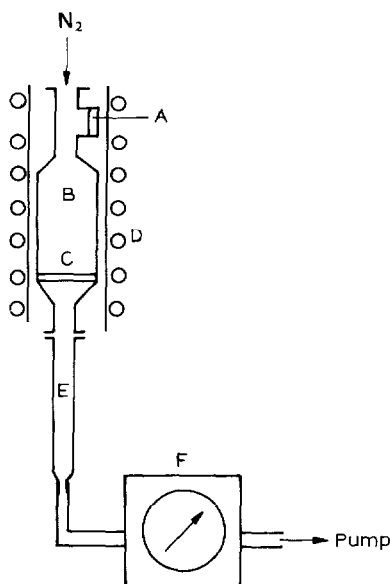


Fig. 4. Apparatus for preparation of the standard gas. A, AA-standard solution inlet; B, preparation of the AA gas; C, glass filter; D, heater; E, sampling tube; F, gas meter.

sampled, the efficiency was 98–100% at a flow-rate of 1.0 l/min with coefficients of variation of less than 5%.

#### *Efficiency of extraction of AA-DNPH*

Beasley *et al.*<sup>15</sup> extracted AA-DNPH from silica gel over a period of 24 h using acetonitrile as the solvent. However, it could not be used in this work because an FTD was applied. The solvents recommended for AA-DNPH are carbon tetrachloride for the authorized method<sup>12</sup>, toluene for the Standard Method<sup>18</sup> of Analysis for Hygiene Chemists and methylene chloride for the method of Kido *et al.*<sup>16</sup>. We investigated the efficiency of extraction using carbon tetrachloride. Silica gel on which was collected 1–10  $\mu\text{g}$  of AA was placed in 10-ml test tubes and 6 ml of carbon tetrachloride were added. A mixture of the solvent and washings produced by washing the sampling tube with 2 ml of carbon tetrachloride was extracted at 50°C. The recoveries were calculated by comparing the peak areas with those of standard AA-DNPH. When 1  $\mu\text{g}$  of AA was collected on silica gel, the results were similar to those in Table II. Nearly 100% of AA-DNPH was extracted at 50°C in 10–60 min. Its extraction was found to be possible in a shorter time by heating it even if it had not been allowed to stand. Extraction at 50°C for 10 min was considered to be satisfactory.

#### *Gas chromatogram and reproducibility of AA-DNPH*

Fig. 5 shows the gas chromatograms of standard AA-DNPH, in which two AA-DNPH peaks appear, probably owing to stereoisomerism<sup>17</sup>. When 1–10 ng of AA was injected into the gas chromatograph, the coefficient of variation was 4% ( $n = 6$ ) with good precision and probably sufficient reproducibility (Table III).

TABLE I  
COLLECTION RECOVERIES

Parameter	Aspiration rate (l/min)					
	0.4	1.0	2.0	3.0		
	Amount of air sampled (l)					
	50	100	200	50	100	200
Minimum and maximum recoveries (%)	99-105	96-103	80-87	65-72	62-75	51-62
Average recovery (%) ( $n = 13$ )	101	99.3	84.7	68.3	67.3	55.3
Standard deviation (%)	3.2	3.5	3.1	3.5	6.8	5.9
Coefficient of variation (%)	0.032	0.035	0.031	0.045	0.101	0.106
				0.103	0.132	0.187
				27-33	24-31	19-27
				29.7	26.7	22.3
				3.1	3.5	4.2

TABLE II  
RECOVERY OF AA-DNPH FROM SAMPLING TUBE

Parameter	Extraction time (min)			
	10	30	60	Overnight
Minimum and maximum recoveries (%)	97-104	95-102	94-103	97-103
Average recovery (%) ( $n = 5$ )	100	100	99.5	101
Standard deviation (%)	3.12	2.88	3.36	2.93
Coefficient of variation (%)	0.031	0.029	0.034	0.029

Table IV includes the retention times of aldehyde DNPHs relative to that of AA-DNPH (1.00). The separation of each aldehyde-DNPH from AA-DNPH was satisfactory. Although it is convenient to use an internal standard, the standard solution was injected into the gas chromatograph after every few samples. No remarkable variation in GC sensitivity was observed.

#### Gas chromatography-mass spectrometry (GC-MS) of AA-DNPH

The formation of AA-DNPH in the sampling tube was confirmed by GC-MS under the following conditions: glass column (2 m  $\times$  2 mm I.D.), 3% OV-17 on Chromosorb G (60-80 mesh); column temperature, 220°C; injection temperature, 240°C; flow-rate (helium), 1.5 kg/cm<sup>2</sup>; ionizing current, 100  $\mu$ A; ionizing voltage, 70 eV; ion source temperature, 240°C. Figs. 6 and 7 show the mass spectrum of carbon

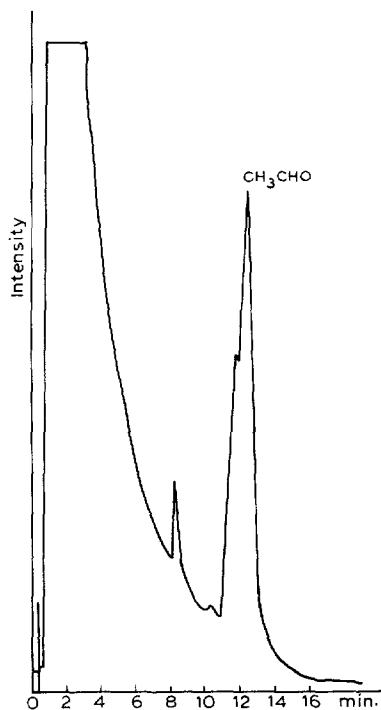


Fig. 5. Gas chromatogram of AA-DNPH.

TABLE III  
PRECISION IN GC DETERMINATION OF AA-DNPH

Parameter	n						Average
	1	2	3	4	5	6	
Recovery (%)	106	98.8	99.7	93.0	102	100	99.9
Standard deviation (%)				4.25			
Coefficient of variation (%)				0.043			

tetrachloride extracted from silica gel and the mass spectrum of the standard solution of AA-DNPH, respectively. The two mass spectra were almost identical and the formation of AA-DNPH in the sampling tubes was confirmed.

#### Detection limit

The detection limit under the GC conditions used was 0.05 nl as AA at 0°C and 1 atm, and the calibration graph was linear between 0.05 and 1.0 nl. The amount of AA required to be sampled into the sampling tube was 5–25 nl when the amount of concentrated carbon tetrachloride extract was 0.5 ml and the amount injected into the gas chromatograph was 1–5  $\mu$ l. In this instance, the detection limit was 0.05–0.25 ppb when 100 l of air were sampled. The GC sensitivity can be decreased up to 10-fold in terms of range and 6-fold in terms of attenuation. The gas chromatogram obtained with a blank contained no peak near the retention time of AA-DNPH.

#### Comparison with authorized method

The results of our method were compared with those of the authorized method (the absorption liquid method) in frequent, general use. Instead of using the sampling tube shown in Fig. 4, AA was introduced into serially connected fritted bubblers specified in the authorized method and determined according to the specified procedure.

TABLE IV  
RETENTION TIMES ( $t_R$ ) OF DNPH DERIVATIVES OF ALDEHYDES, KETONES AND 2,4-DI-NITROANILINE

Compound	$t_R$ (min)	Relative $t_R$
Formaldehyde	8.6	0.68
	11.8	0.94
Acetaldehyde	12.6	1.00
	13.8	1.10
Propionaldehyde	15.2	1.21
<i>n</i> -Butyraldehyde	20.1	1.60
	15.0	1.19
Isobutyraldehyde	16.0	1.27
Acrolein	16.1	1.28
Acetone	14.9	1.18
Methyl ethyl ketone	18.9	1.50
2,4-Dinitroaniline	9.7	0.77



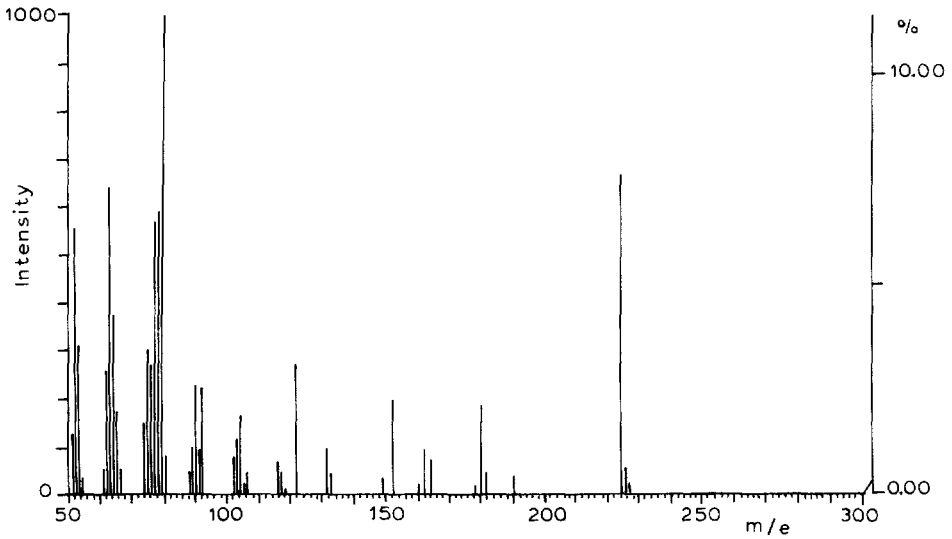


Fig. 6. Mass spectrum of extract from coated silica gel.

A 1- $\mu$ l volume of AA standard (1.57  $\mu$ g/ml as AA) was collected in the sampling tube in Fig. 3 and the receiver. The injection rate and the amount sampled were 1.0 l/min and 50 l, respectively. The results are given in Table V and show that the value obtained by our method is nearly identical with that obtained by the authorized method.

It was found that our method also produced satisfactory values for AA in air.

### Examples

AA in ambient air and air near and in a refuse reclamation area were deter-

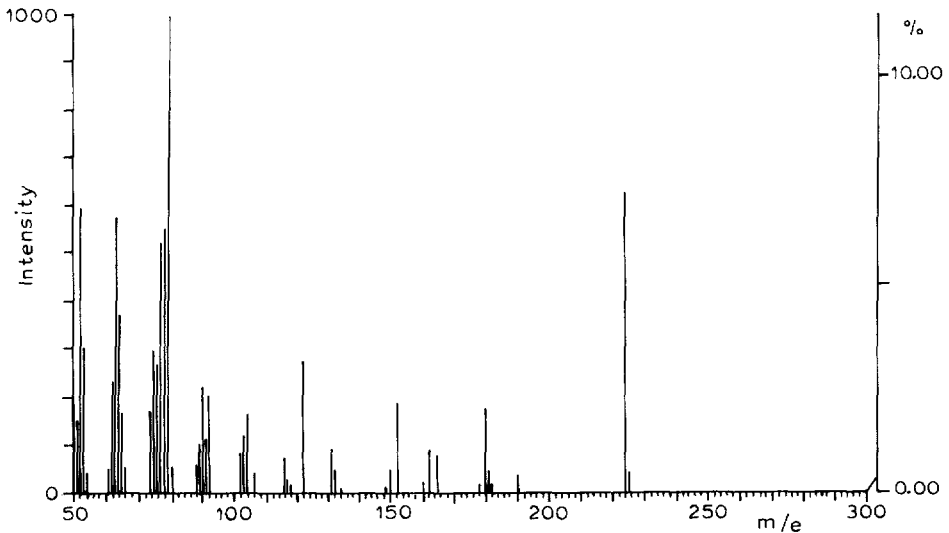


Fig. 7. Mass spectrum of AA-DNPH.

TABLE V  
COMPARISON WITH THE AUTHORIZED METHOD

In the authorized method, 1  $\mu$ l of AA standard solution (1.57  $\mu$ g/ml) was injected into the GC system.

<i>n</i>	<i>Coated solvent (ng)</i>	<i>Authorized method (ng)</i>
1	1.66	1.55
2	1.39	1.48
3	1.68	1.65
4	1.46	1.57
Average	1.55	1.56

TABLE VI  
EXAMPLES OF APPLICATION OF THE METHOD

<i>Sample</i>	<i>Amount of air sampled (l)</i>	<i>Concentration of AA (ppb)</i>
Atmospheric air No. 1	100	3.0
Atmospheric air No. 2	98	4.0
Air near refuse reclamation land	64	7.6

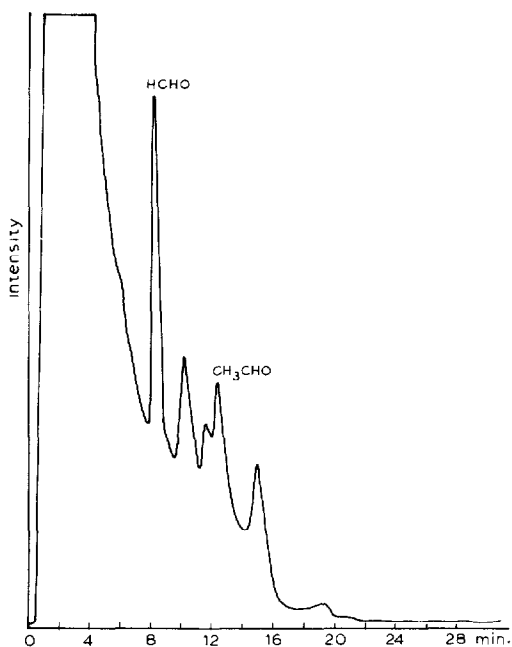


Fig. 8. Gas chromatogram of air sample.

mined by the sampling tube method. The results and the gas chromatogram are shown in Table VI and Fig. 8, respectively.

## CONCLUSION

The method described for determining low concentrations of AA in air gave the following results:

(1) Collection of AA by the method was possible with air sampling volumes up to 100 l. The maximum volume in this method is twice that in the authorized method (50 l).

(2) The use of an FTD resulted in increased GC sensitivity compared with the use of conventional FID methods, and permitted the determination of low concentrations of AA in air.

(3) Although phosphoric acid is usually used as a catalyst in reactions between aldehydes and DNPH, AA-DNPH was produced without using a catalyst in this method. No detailed reason is available, although Beasley *et al.*<sup>15</sup> reported that there are differences in the efficiency of collection of AA when silica gel treated with hydrochloric acid followed by coating with DNPH is used and when no hydrochloric acid treatment is applied. Further study on this aspect is necessary, although hydrochloric acid may be responsible for the reaction in some manner.

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## REFERENCES

- 1 T. Aoyama, *Eisei Kagaku*, 23 (1977) 95.
- 2 G. R. Lyles, F. B. Lowling and V. J. Blanchard, *J. Air Pollut. Contr. Ass.*, 15 (1965) 106.
- 3 H. Mimura, M. Kaneko, N. Nishiyama, S. Fukui and S. Kanno, *Eisei Kagaku*, 22 (1976) 39.
- 4 T. Mitsui and T. Kojima, *Bunseki Kagaku (Jap. Anal.)*, 26 (1977) 182.
- 5 L. P. Pana and L. P. Turner, *J. Chromatogr. Sci.*, 10 (1972) 747.
- 6 S. Selim, *J. Chromatogr.*, 136 (1977) 271.
- 7 I. H. Williams, *Anal. Chem.*, 37 (1965) 1723.
- 8 Y. Hoshiya, *J. Odor Control*, 8 (1979) 17.
- 9 H. Kallio, R. R. Linko and J. Kaitaranta, *J. Chromatogr.*, 65 (1972) 355.
- 10 Y. Baba, *Bull. Chem. Soc. Jap.*, 48 (1975) 270.
- 11 K. Oono and T. Hayakawa, *Taiki Osen Gakkaishi (J. Air Pollut. Soc.)*, 14 (1979) 479.
- 12 Notification No. 47, Japanese Environmental Protection Agency, 1979 (*Kogai-to Taisaku* 16 (1980) 1037).
- 13 Y. Hanai and Kato *Bull. Inst. Environ. Sci. Technol. Yokohama Natl. Univ.*, 7 (1981) 29.
- 14 T. Kato and Y. Iwamatsu, *Bull. Inst. Environ. Sci. Technol. Yokohama Natl. Univ.*, 1 (1974) 12.
- 15 R. K. Beasley, *Anal. Chem.*, 52 (1980) 1110.
- 16 K. Kido and T. Sakuma, *Eisei Kagaku*, 25 (1979) 39.
- 17 S. Takahashi, T. Murata, S. Yasui and M. Sakata, *22nd Annual Meeting of Japanese Analytical Chemistry Association, 1973*, Abstracts, p. 185.
- 18 Pharmaceutical Society of Japan, *Eisei Kagaku*, 164 (1977) 23.