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Note

Determination of aldehydes in air as dimethone derivatives by gas chromatography with electron-capture detection

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Aldehydes are volatile thermal decomposition products of epoxy oligomers¹ and many other plastics². They are irritative even in low concentrations³, and chromatographic methods are necessary for their evaluation in workplace hygiene.

Carbonyl compounds have been analysed by gas chromatography (GC) as their phenylhydrazones⁴, 2,4-dinitrophenylhydrazones^{5,6} and oximes⁷. Thin-layer chromatography (TLC) and paper chromatography have been applied for 2,4-dinitrophenylhydrazones^{8,9}, oximes¹⁰, semicarbazones¹¹, azines¹² and nitroguanylhydrazones¹³. High-performance liquid chromatography (HPLC) has been used for 2,4-dinitrophenylhydrazones¹⁴.

Dimedone is a specific reagent for aldehydes¹⁵⁻¹⁷, and the derivatives have been determined by TLC¹⁸, GC¹⁹ and fluorometry²⁰. In this paper, we describe a sensitive method for the separation and determination of the dimethone adducts of aldehydes by capillary GC with electron-capture-detection (ECD).

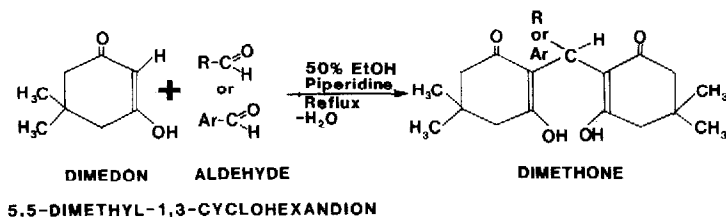


Fig. 1. Reaction of aldehydes with dimedone.

ALDEHYDES	RETENTION TIMES	R or Ar	DIMETHONES
Acetaldehyde	9.52	CH ₃ -	
Propionaldehyde	11.05	CH ₃ CH ₂ -	
Acrylaldehyde	12.20	CH ₂ =CH-	
n-Butyraldehyde	12.39	CH ₃ CH ₂ CH ₂ -	
Crotonaldehyde	12.79	CH ₃ CH=CH-	
n-Valeraldehyde	13.78	CH ₃ (CH ₂) ₃ CH-	
Methacrolein	15.33	CH ₃ =C(CH ₃)-	
Glutaraldehyde	15.38	CHO(CH ₂) ₃ CH-	
Formaldehyde	19.77	H-	
Benzaldehyde	17.69		
o-Tolualdehyde	18.04		
m-Tolualdehyde	18.77		
p-Tolualdehyde	19.27		
Cinnamaldehyde	22.76		

Fig. 2. Prepared aldehyde derivatives and their relative retention times.

EXPERIMENTAL

Preparation of dimethone derivatives

The dimethones were prepared according to the method of Horning and Horning¹⁷ (Fig. 1). The aldehyde (1 mol) and dimeredone (2.5 mol) were dissolved in 50% aqueous ethanol, and two drops of piperidine were added as catalyst. The mixture was refluxed with stirring for 20 min. If the solution remained clear after reflux, water was added dropwise to the cloud point. Crystallisation of the products varied (crystals were formed during reflux in some cases) and sometimes dropwise addition of water was necessary. The methacrolein derivative separated as a yellow oil; the other aldehydes gave solid derivatives.

The dimethones prepared are listed in Fig. 2.

Recovery studies

To test the sampling recovery, a 80 × 6 mm I.D. glass tube with a glasswool plug at the inlet was connected to the bubbler inlet and air was drawn through the system with a personal sampling pump (SKC Model 22-3) at a flow-rate of 0.2

TABLE I

RECOVERY OF ACETALDEHYDE AND *m*-TOLUALDEHYDE

Adsorption to 20% acetone in ethanol.

Compound	Amount added (μ g)	Recovery (%)	Relative standard deviation (%)	Number
Acetaldehyde	0.11	91	6.3	3
	0.57	95	8.3	3
	1.1	73	9.0	3
<i>m</i> -Tolualdehyde	0.11	92	6.1	3
	0.59	90	7.3	3
	1.2	87	7.9	3

l/min²¹. The aldehydes to be tested were injected into the glass tube (10 μ l with an appropriate concentration) and 3 l of air were pumped through the system. During the last few minutes of air flow, hot air (*ca.* 100–150°C) was used to ensure complete volatilisation of the compounds. The recoveries for acetaldehyde and *m*-tolualdehyde are given in Table I.

Sampling of air and preparation of samples

Epicote resin powder paint Oxyplast-8 (from Teknos, Finland) was degraded in a J-shaped glass tube (diameter 4 mm, wall thickness 1 mm, total length 300 mm) inserted into a laboratory oven through a hole. The shorter arm of the tube was completely inside the oven at a temperature of 370°C. An air pump (DuPont P 2500) was used to conduct the air through the degradation tube at a flow-rate of 0.6 l/min for 30 min. The aldehydes in the air were collected into 25 ml of 20% acetone in ethanol with a fritted glass bubbler.

The collection efficiencies of 100% ethanol, 50% aqueous ethanol and 20% acetone in ethanol were tested; two bubblers were used in series and the contents were analysed separately. The mixture of ethanol and acetone appeared to be most efficient: the efficiency varied for individual aldehydes, and was 60% for acetaldehyde (4 μ g/ml) and 90% for the others (0.5–5 μ g/ml) at a flow-rate of 0.6 l/min.

Dimedone (3 mg) was dissolved in 10 ml of 50% aqueous ethanol, and the sample and two drops of piperidine were added. The impinger was washed with 20 ml of water, which was pooled with the sample. The mixture was refluxed for 20 min. After cooling, 60 ml of water was added, and the solution was neutralised with 2 *N* hydrochloric acid. The derivatives were extracted with three 15-ml portions of diethyl ether, and the combined extracts washed three times with 15 ml of water. The ether

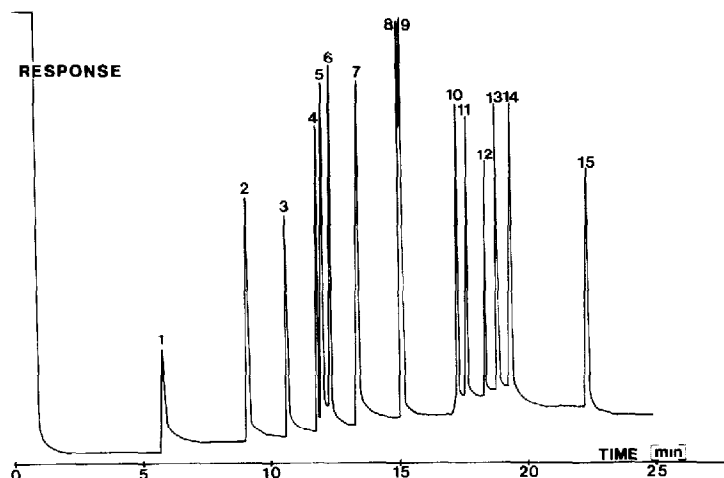


Fig. 3. Typical gas chromatogram of dimedone of aldehydes. GC conditions: column, OV-101 (12.5 m \times 0.2 mm I.D.); carrier gas, helium at 1 ml/min; splitless injection; make-up gas, argon-methane at 80 ml/min; injector temperature, 250°C; detector temperature, 320°C; temperature programme, from 70°C (5 min) at the rate of 10°C/min to 200°C (10 min). Peaks: 1 = dimedone reagent; 2 = acetaldehyde; 3 = propionaldehyde; 4 = acrolein; 5 = *n*-butyraldehyde; 6 = crotonaldehyde; 7 = *n*-valeraldehyde; 8 = methacrolein; 9 = glutaraldehyde; 10 = benzaldehyde; 11 = *o*-tolualdehyde; 12 = *m*-tolualdehyde; 13 = *p*-tolualdehyde; 14 = formaldehyde; 15 = cinnamaldehyde.

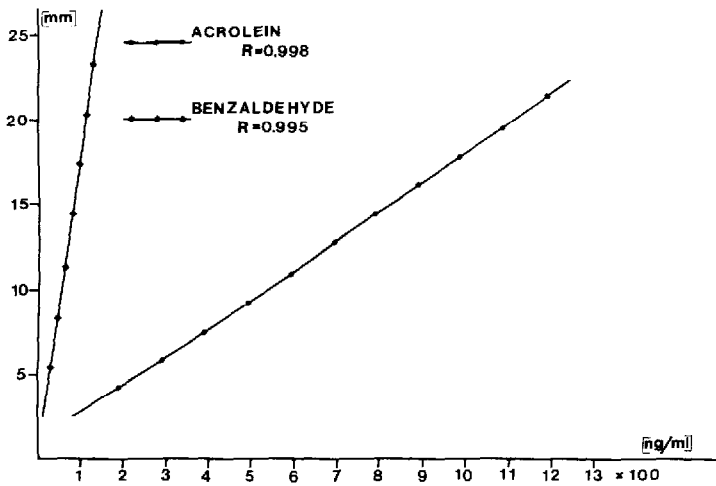


Fig. 4. Standard curves for dimethone derivatives of acrolein and benzaldehyde: the detection limits were 80 pg and 17 pg per injection, respectively.

was evaporated after overnight drying on anhydrous calcium chloride, and the residue was dissolved in 1 ml of acetone.

Apparatus

The gas chromatograph was a Hewlett-Packard 5790-A with splitless injection and an electron-capture detector (^{63}Ni). The column was 12.5 m \times 0.2 mm I.D. OV-101 (cross-linked dimethyl silicone); the carrier gas was helium at a flow-rate of 1 ml/min; the make-up gas was argon-methane (95:5) at a flow-rate of 80 ml/min; the injector temperature was 250°C, the detector temperature 320°C, and a temperature programme from 70°C (5 min) at the rate of 10°C/min to 200°C (10 min) was used. The injected volume was 1 μl .

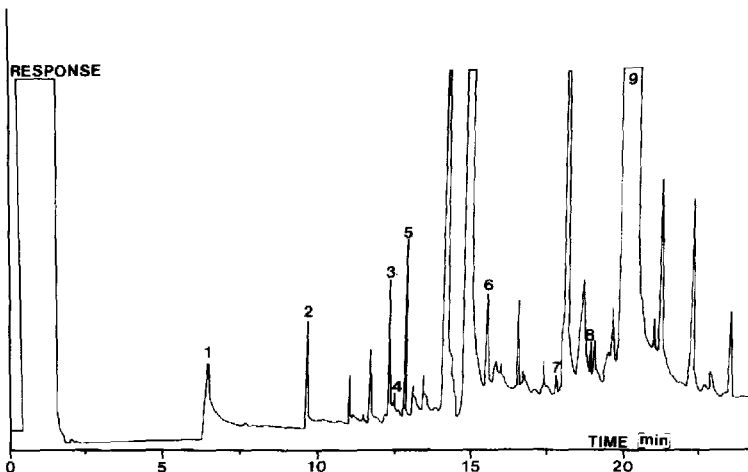


Fig. 5. Gas chromatogram of thermally degraded epoxy paint. Peaks: 1 = dimedone reagent; 2 = acetaldehyde; 3 = acrolein; 4 = butyraldehyde; 5 = crotonaldehyde; 6 = methacrolein; 7 = benzaldehyde; 8 = *m*-tolualdehyde; 9 = formaldehyde.

The chromatograms were registered with a Hewlett-Packard 3390-A integrator, and the heights of the peaks were used for standard curves.

RESULTS AND DISCUSSION

A typical gas chromatogram of fourteen dimethone derivatives is shown in Fig. 3, and the standard curves of acrolein and benzaldehyde derivatives are shown in Fig. 4. The correlation coefficient of acrolein was 0.998 ($n=6$) and of benzaldehyde 0.995 ($n=5$). The detection limits of these aldehyde derivatives were 80 pg and 17 pg per injection, respectively.

The chromatogram of air sample from the thermal degraded epoxy plastic is shown in Fig. 5. Eight aldehydes were detected. Formaldehyde was the major component.

The method described is suitable for foodstuffs^{6,18} and for biological samples¹⁹. We developed the method further for determining the air samples.

The method is superior to the GC 2,4-dinitrophenylhydrazone method⁴ for separating *o*-, *m*- and *p*-tolualdehyde. It also separates well acetone, acrolein and propionaldehyde, which are poorly separated with HPLC.

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