

range from 1 v.p.m. of carbon dioxide in nitrogen to 100 v.p.m. of carbon dioxide in nitrogen and from 40 to 100 v.p.m. of carbon monoxide in nitrogen. For carbon dioxide, the detector voltage was 260 V and a 1 ml sample loop was used; for carbon monoxide, the detector voltage was 235 V and a 5 ml sample loop was used.

The baseline obtained on the 1 mV recorder was very stable, especially at lower voltages when the sensitivity was extremely high. At voltages above 300 V, the detector not only became noisy but hot as well, which caused the seals, used to obtain leak-proof joints, to melt.

The best performance of the detector was obtained at 235 V when a sensitivity of 1 v.p.m. per 4 scale divisions was obtained for carbon dioxide and a sensitivity of 2 v.p.m. per scale division for carbon monoxide (using 5 ml sample sizes). The responses to oxygen and lower hydrocarbon gases were positive but have not been investigated systematically yet. In fact, with a 0.25 ml sample of air, the oxygen content was high enough to extinguish the discharge unless sustained at 350 V or above.

This preliminary work has confirmed that the direct current discharge type detector provides a sensitive means of determining carbon monoxide and carbon dioxide; the response is linear, and under the conditions of greatest sensitivity, the baseline is most stable.

This work was carried out in the Research and Development Centre, The British Oxygen Company, London, S.W. 19.

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## Gas chromatography of diols

The gas chromatography of the even numbered homologues of  $C_{10}$ - $C_{26}$   $\alpha,\omega$ -diols has been described<sup>1</sup> and some information is available concerning the gas chromatographic separation of lower molecular weight diols<sup>2,3</sup>. This report describes a versatile column packing suitable for the rapid analytical or preparative gas chromatography of homologous and isomeric diols under isothermal conditions.

### *Experimental*

*Preparation of the column packing.* The solid support was silanized by a modification of the method of BOHEMEN *et al.*<sup>4</sup>. Celite (60-80, 250 g) was added to petroleum ether 60-80 (1.2 l) containing hexamethyldisilazane (62.5 ml) and the mixture refluxed with exclusion of atmospheric moisture for 20 h. The solid was washed with petroleum

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ether 60-80 (2 × 500 ml), *n*-propanol (500 ml), again with petroleum ether 60-80 (2 × 500 ml), and finally with petroleum ether 30-40 (2 × 500 ml). The solid was transferred to a 2 l wide necked conical flask and dried on a steam bath for 2 h in an atmosphere of nitrogen. To dry silanized Celite (185 g) was added chloroform (750 ml) then, with vigorous swirling by hand, 27.4 g (15 %) of LAC-2R-446 (diethylene glycol adipate cross-linked with pentaerythritol; Cambridge Industries Co., Inc., 101 Potter St., Cambridge, Massachusetts, U.S.A.) in chloroform (150 ml) and tergitol (0.6 g). Swirling was continued for 5 min and the solvent removed on a rotary evaporator until the solid was free flowing.

*Construction of the columns.* The above packing was used to prepare 20 ft. × 3/8 in. O.D., 25 ft. × 3/16 in. O.D., and 6 ft. × 1/4 in. O.D., columns. In all cases copper tubing was used, the tubing being held vertically and filled slowly under gravity with manual tapping. After winding and before use the columns were conditioned at 170° for 20 h in a stream of nitrogen.

Analytical gas chromatography was performed with an F & M model 720 instrument using the 25 ft. column at 40 ml/min and 175° and the 6 ft. column at 60 ml/

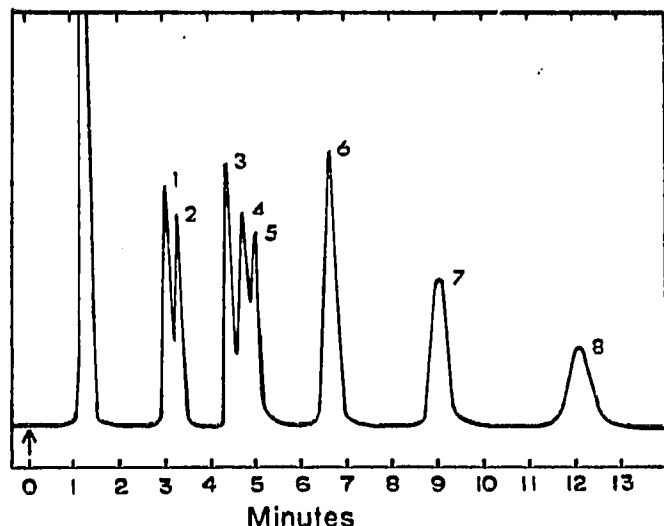


Fig. 1. Diols on a 20 ft. × 3/8 in. 15 % LAC column at 175° and hydrogen carrier gas at 300 ml/min. 1 = Propane-1,2-diol; 2 = ethane-1,2-diol; 3 = butane-1,3-diol; 4 = propane-1,3-diol; 5 = 2,2-dimethyl-propane-1,3-diol; 6 = butane-1,4-diol; 7 = pentane-1,5-diol; 8 = hexane-1,6-diol.

min and 160°. Preparative gas chromatography was carried out with a Wilkens Autoprep A700 using the 20 ft. column at 300 ml/min and 175°. In all cases hydrogen was used as carrier gas at an inlet pressure of 45 p.s.i. The injection port temperature was 200°. For the present study the diols were injected as 50 % solutions in methanol with sample sizes of 1-2 μl for the analytical columns and 50-250 μl for the preparative column.

### Results and discussion

Under the above conditions the 6 ft. analytical column gave similar resolution to the 20 ft. preparative column and the former used as a guide to the elution patterns on the latter. Fig. 1 shows the elution characteristics of a number of homologous diols on the preparative column.

TABLE I

RETENTION TIMES OF DIOLS ON A 20 FT.  $\times$   $\frac{3}{8}$  IN. 15% LAC COLUMN

<i>Diol</i>	<i>Retention time (min)</i>
Ethane-1,2-diol	3.25
Propane-1,2-diol	3.0
Propane-1,3-diol	4.6
Butane-1,3-diol	4.3
2,2-Dimethyl-propane-1,3-diol	4.9
Butane-1,4-diol	6.5
Pentane-1,5-diol	8.8
Hexane-1,6-diol	11.9
Cyclohexane-1,4-diol	12.5
<i>cis</i> -Cyclohexane-1,2-diol	6.0
<i>trans</i> -Cyclohexane-1,2-diol	6.6
<i>cis</i> -Cyclopentane-1,2-diol	4.6
<i>trans</i> -Cyclopentane-1,2-diol	6.2
<i>cis</i> - and <i>trans</i> -Indane-1,2-diol	7.6
<i>cis</i> -2-Hydroxymethyl-cyclopentanol	8.4
<i>trans</i> -2-Hydroxymethyl-cyclopentanol	9.6
<i>cis</i> - and <i>trans</i> -Cyclohexane-1,3-diol	9.3
<i>trans</i> -2-Hydroxymethyl-cyclohexanol	10.8

As a result of the silanization of the solid support the diols were eluted with little tailing. This type of column proved very satisfactory for the separation of a number of isomers of acyclic and alicyclic diols as shown by the retention times given in Table I obtained with the preparative column under the conditions described above. The preparative separation of any particular group of diols could be improved by lowering the temperature of the column. Thus for the *cis*- and *trans*-cyclohexane-1,2-diols the retention times were 8 min and 9 min at 170° and 300 ml/min, and 17 min and 20 min at 140° and 300 ml/min. In all cases where the separation of *cis* and *trans* isomers was achieved the *cis* isomer was eluted before the *trans* isomer. For analytical purposes the 25 ft. column gave high resolution of diols, but retention times were 2-3 times longer than with the 6 ft. column. It was observed that operation of this type of column at temperatures greater than 210° led to a slow loss of liquid phase.

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