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## Note

### Capillary gas chromatography of impurities in cyclohexanone

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Gas chromatography (GC) on packed columns has been used for identification and determination of the main constituents of mixtures formed during oxidation of cyclohexane to cyclohexanone<sup>1-7</sup>. The impurities of industrial cyclohexanone<sup>8-19</sup> can include many different classes of compound such as alcohols, aldehydes, esters, ethers, hydrocarbons and ketones. In the majority of analyses described, packed GC columns have been used with polar liquid stationary phases of a polyethylene glycol type.

This paper describes the GC separation of the impurities in cyclohexanone by use of a capillary column. The method allowed the separation and identification of a large number of impurities and was shown to be suitable for studies of the cyclohexanone rectification process.

#### EXPERIMENTAL

For the analyses a Hewlett-Packard Series 5710 A gas chromatograph with a flame-ionization detector was employed. The capillary column (100 × 0.25 mm I.D.) was coated with polypropylene glycol (Ucon LB 550 X) as the polar stationary phase. Separations on this column were performed at both a constant temperature (130°C) and with programming (2 min initial hold at 90°C, then 2°C/min to 150°C and final hold to complete elution). The flow-rate of the carrier gas (argon) was 1 ml/min (splitting ratio *ca.* 1:100). Cumene was used as an internal standard.

For the preparation of the cyclohexanone sample enriched in low-boiling impurities, a distillation apparatus equipped with a spinning-band column (according to Dr. Abegg, W. Büchi, Flawil, Switzerland) was used. The rotating spiral band in the distillation column permits efficient separation of small volumes of lower boiling components from a large test sample. The test sample (80 ml) was placed in the distillation flask and *ca.* 0.5 ml of the distillate was collected. The working temperatures were: 157 (flask), 155 (mantle) and 110°C (head). The condensed distillate was transferred into the collector for 1 sec of each 30-sec period of distillation.

Most of the standard compounds for measurement of retention times were commercial samples and were used without further purification. 2-Methylcyclopentanone was synthesized by Dr. H. Urbańska (Department of Heavy Organic Synthesis, Institute of Industrial Chemistry, Warsaw, Poland). Measurements of adjusted retention times were made with the assistance of Mrs. E. Kurek (Gas Chromatography Section, Institute of Industrial Chemistry, Warsaw, Poland).

TABLE I

ADJUSTED RETENTION TIMES RELATIVE TO CUMENE ON UCON LB-550X CAPILLARY COLUMN

No.	Compound	Constant temperature (130°C)	Programmed temperature
1	Cyclohexane	0.192	0.137
2	Methyl propyl ketone	0.286	0.282
3	Valeraldehyde	0.298	0.299
4	Isobutanol	0.335	0.393
5	Methyl isobutyl ketone	0.366	0.385
6	1-Butanol	0.435	0.517
7	Methyl butyl ketone	0.491	0.543
8	Caproaldehyde	0.509	0.564
9	Cyclopentanone	0.640	0.684
10	Dipropyl ketone	0.714	0.778
11	2-Methylpentanone	0.774	0.816
12	1-Pentanol	0.776	0.876
13	Ethyl butyl ketone	0.789	0.846
14	Methyl pentyl ketone	0.845	0.897
15	Cyclopentanol	0.888	0.957
16	Cumene	1.000	1.000
17	Cyclohexanone	1.199	1.137
18	Butylcyclohexane	1.279	1.192
19	1-Hexanol	1.379	1.286
20	2-Methylcyclohexanone	1.435	1.278
21	Cyclohexyl formate	1.466	1.303
22	3-Methylcyclohexanone	1.528	1.333
23	Cyclohexanol	1.559	1.370
24	4-Methylcyclohexanone	1.590	1.374
25	Dipentyl ether	1.601	1.382
26	2-Cyclohexenone	1.720	1.436
27	2-Cyclohexenol	2.006	1.513
28	Cyclohexyl acetate	2.093	1.590
29	Butyl cyclohexyl ether	2.220	1.690
30	Pentylcyclohexane	2.229	1.692

## RESULTS AND DISCUSSION

The adjusted retention data for a number of compounds usually encountered as impurities in analysed samples of cyclohexanone are listed in Table I. The hold-up volume of the column was measured by injection of methane.

Although less convenient for routine analysis, use of the temperature programme proved to be more effective for the separation of 1-pentanol and 2-methylcyclopentanone. However in some cases the separation was not as good as that obtained at constant temperature and changes in the order of emergence of peak pairs were observed.

Fig. 1 shows a chromatogram of a sample of cyclohexanone to which had been added small amounts of standard impurities together with cumene as a reference.

By direct capillary GC, single impurities could be determined in quantities above 5 ppm. Much smaller amounts of components having boiling points lower than

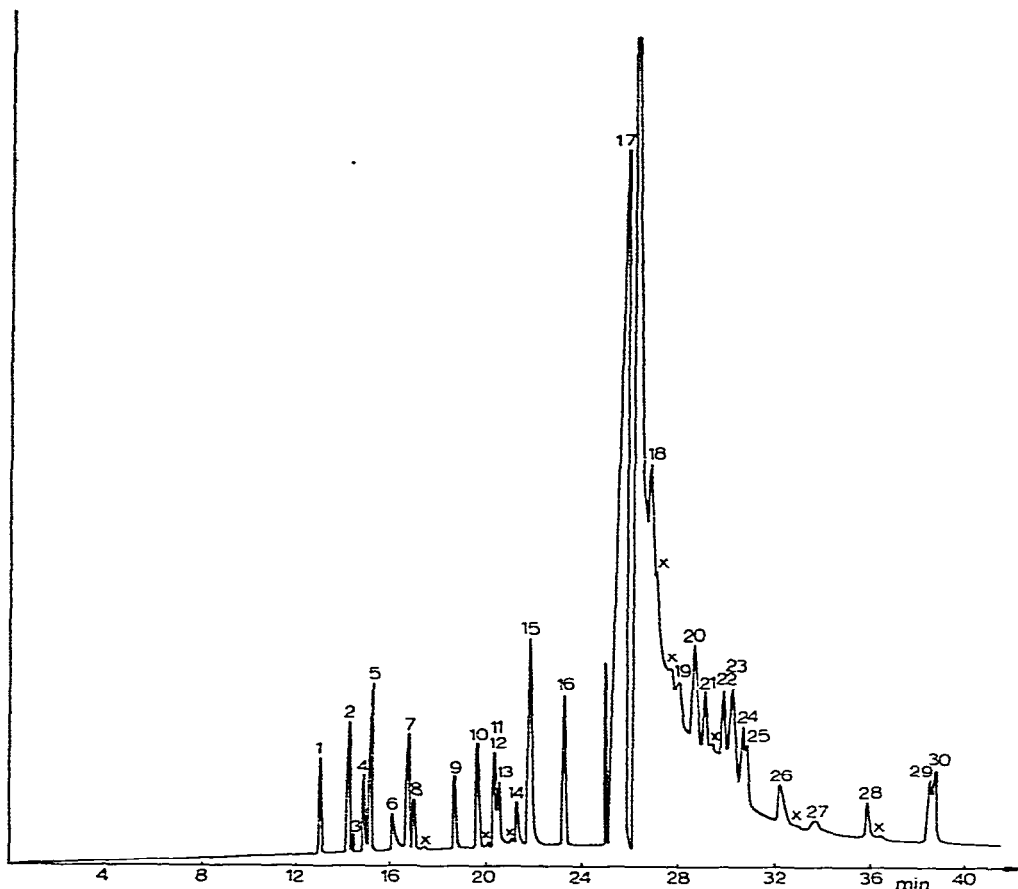


Fig. 1. Gas chromatogram of industrial cyclohexanone sample with added standard impurities. Capillary column at 130°C. Sample: 1  $\mu$ l. Electrometer range 1, attenuation 8 for impurities and 1024 for cyclohexanone. Peaks numbered according to Table I. x = unknown.

cyclohexanone could be detected by analysing samples of distillates enriched with these impurities. The second fraction, after collecting *ca.* 0.5 ml of distillate, gave chromatograms practically devoid of peaks preceding cyclohexanone. Thus it is possible to apply distillation enrichment for quantitative evaluation of low-boiling impurities.

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