

Fig. 1. 25-ft. acetylacetone column; 0° C.; flow gas, hydrogen, 30 ml./min.

small and large samples have to be analysed, it is an advantage to use gas-liquid chromatography, and a single column of dimethylsulpholane on firebrick may be used⁴. Two-stage columns have also been used successfully to carry out this separation⁴; further, a commercial column is manufactured with which this analysis can be carried out⁵.

In this laboratory this mixture has been analysed repeatedly on a single column, packed with acetylacetone on firebrick (a copper coil, 25 ft. \times $\frac{1}{4}$ in.) operated at 0° C. This column not only resolves the hydrocarbons mentioned, but also resolves nearly all the possible isomers of the C₂ to C₅ hydrocarbons, including many cyclic isomers, in a total running time of 1 hr. The column may be used to carry out the difficult analysis of *isobutylene* and *but-1-ene* in the presence of the other hydrocarbons. Fig. 1 shows the resolution obtained with this column and a mixture of *isobutene* and *but-1-ene*.

This column does not resolve 1,1-dimethylcyclopropane and 3-methyl but-1-ene, two compounds which have closely similar boiling points. However, these compounds are easily separated using a solution of silver nitrate in ethylene glycol on fireclay. No difficulty has been experienced in using a short glass column (3 ft. \times $\frac{1}{4}$ in.) packed with this material and attached to the end of the acetylacetone-packed column. Such a double column allows this difficult separation to be carried out and still allows the other

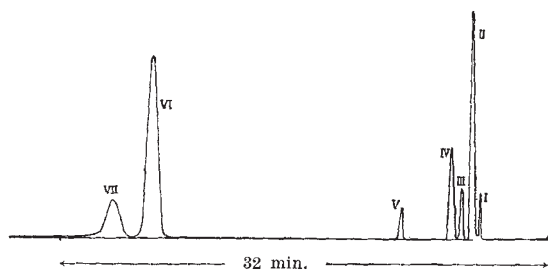


Fig. 2. Double column; 0° C.; flow gas, hydrogen, 30 ml. per min. I, Ethane; II, ethylene; III, propane; IV, propylene; V, *n*-butane; VI, 1,1-dimethylcyclopropane; VII, 3-methylbut-1-ene. Ethylene peak has been attenuated by a factor of 10

C₂ to C₅ hydrocarbons to be separated (see Fig. 2). A mixed column of these two packings has been used successfully, but was found to have a relatively short 'life' when compared with the double column.

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Jan. 28.

¹ Barnard, J. A., and Hughes, H. W. D., *Nature*, **183**, 250 (1959).

² Frey, H. M., and Kistiakowsky, G. B., *J. Amer. Chem. Soc.*, **79**, 6373 (1957).

³ Drew, C. M., and McNesby, J. R., "Vapour Phase Chromatography", edit. by Desty, D. H., 213 (Butterworths, 1957).

⁴ Fredericks, E. M., and Brooks, F. R., *Anal. Chem.*, **28**, 297 (1956).

⁵ Hausdorff, H. H., ref. 3, p. 377.

DR. FREY'S letter is of considerable interest. We were, of course, aware of several methods reported in the literature for the separation of the C₂ and C₃ hydrocarbons. However, the purpose of our original communication was to direct attention to a *simple* method of separating the lower hydrocarbons, not involving any of the complexities of very long coiled columns, temperature programming or the necessity of maintaining temperatures below the ambient.

Our experiences with series columns had not been particularly successful, but the experiments with the *mixed* columns, using the same preparations of packing materials and identical packing procedures, were so fruitful that we thought it worth while directing attention to what was, to us at least, a new technique.

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Structure of 'Cystine Disulphoxide'

ALTHOUGH the reactions of aromatic 'disulphoxides' have been studied by Smiles and his co-workers¹ and by Vinkler and Klivenyi² among others, the structures of these compounds remained uncertain until their infra-red spectra were examined by Cymerman and Willis³. The latter work confirmed earlier evidence that the compounds hitherto known as disulphoxides should be assigned the thiolsulphonate structure (I) rather than the disulphoxide structure (II).



Grushko and Guryanova⁴ have recently made a study of some aliphatic analogues and conclude that they also have structures of type (I). The best-known aliphatic 'disulphoxide' appears to be that from cystine and this compound was assigned a structure of type (II) on chemical evidence⁵, a structure which is still current in recent biochemical literature⁶. In connexion with other work we have obtained the infra-red spectrum of this compound and find it to have the characteristics of a thiolsulphonate rather than a disulphoxide. The strong bands at 1,110 cm.⁻¹ and 1,300 cm.⁻¹ agree well with those given by aromatic thiolsulphonates^{3,7} and the spectrum showed no strong band near 1,050 cm.⁻¹ as exhibited by sulphoxides.

Using structure (II) Toennies and Lavine⁸ found it necessary to introduce a series of intermediates to explain the reactions of 'cystine disulphoxide', but it is evident that these reactions can be more readily explained on the basis of structure (I). For example,