

## A Combination of Mass Spectrometer and Flame Ionisation Detector for Open Tubular Column Chromatography

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Combined gas chromatography-mass spectrometry (GC-MS) has become of increasing use during the last few years. In particular GC-MS has proved of considerable value in the field of natural product chemistry where a single sample may contain a large number of closely related compounds. Optimum results may be obtained in such cases by the use of open tubular columns and this technique has been successfully demonstrated.<sup>1,2</sup>

The coupling of the gas chromatograph to the mass spectrometer may be either direct or involve an enrichment device. The critical factor in deciding which method will be employed is the flow rate. Only in cases where open tubular columns are used with a flow rate of 1 ml/min or less can direct coupling normally be employed.<sup>3</sup> A number of enrichment devices have been described for operation with higher flow rates but the most common are the molecule separators of Watson-Biemann<sup>4</sup> and Becker-Ryhage.<sup>5,6</sup>

The chromatographic record during GC-MS operation is produced by the total ion current monitor and this leads to interruption of the chromatogram, when the ionisation energy is increased from that below the ionisation potential of helium to the standard 70 eV, during the recording of the mass spectra. This problem has been overcome in the case of packed column gas chromatography by the use of a splitter device described by Leemans and McCloskey<sup>7</sup> which allows part of the gas flow to be led to a flame ionisation detector and a complete chromatographic record is thus obtained.

The present work describes a splitter which may be used for open tubular columns and allows a wide choice of split ratio between mass spectrometer and flame ionisation detector without significant loss in GC resolution.

An LKB 9000 gas chromatograph-mass spectrometer was used throughout the

work. The original gas chromatograph in this instrument was removed and replaced by a Perkin Elmer F 11 instrument, equipped with a single flame ionisation detector and a linear temperature programmer. The separator of the LKB 9000 instrument is a two stage jet of the Becker-Ryhage type and has fixed spacing between the jets.

*Construction of the splitter.* To split the gas stream from the column into two parts, a construction was made as shown in Fig. 1. The column flow is led into a piece of stainless steel tubing connected with a swagelock joint. The end of the column was shaped to a jet to obtain better mixing with the make-up gas which entered the swagelock as shown (Fig. 1 A). A precision needle valve was used to control the flow of the make-up gas. In the case of packed column chromatography the mixing device was replaced by a double 1/8" swagelock joint as no make-up gas was required.

At a distance of 4 cm from the center of the swagelock joint a hole was drilled in the main gas lead and a small bore capillary inserted. The end of the capillary was ground to an angle of 45° and it was positioned centrally facing back towards the swagelock (Fig. 1 B). The external part of the capillary was protected by enclosing it in a larger bore tube and led directly to the flame ionisation detector. All joints were silver soldered.

To obtain a time lag between the flame detector and mass spectrometer signal a 1 meter tube was connected between the first stage of the separator and the splitter; the connection between the tube and the splitter is shown in Fig. 1 C. To retain maximum resolution, this connection-tube was a capillary, and was protected by a larger bore tube, to give increased rigidity. The line was evenly heated by means of a heating tape, the temperature of which was controlled by a variable transformer.

*Procedure.* The test columns used were: A 150 ft. 0.01" ID open tubular column coated with Ucon HB 2000 oil and a 6 ft. 1/8" OD packed column, packed with 6 % Apiezon L on Chromosorb W.

The open tubular column was installed and helium was used as both carrier and make-up gas. The gas flows were adjusted to approximately 2 and 20 ml/min, respectively; the carrier gas flow being estimated on the basis of the retention times of reference substances. The packed column was operated at a flow rate of 20 ml/min. The line to the separator was kept slightly, and the separator well, above column temperature.

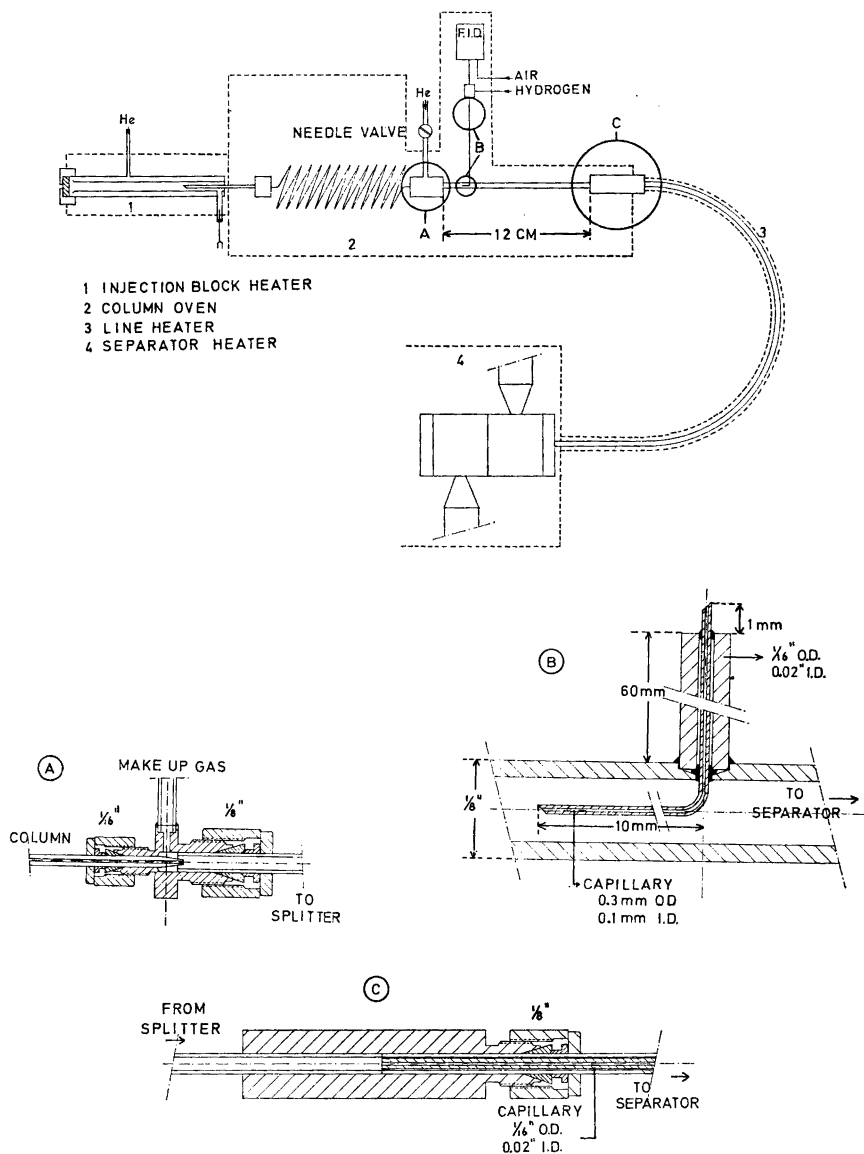


Fig. 1.

*Results and discussion.* The addition of make-up gas improves the separator efficiency as the Becker-Ryhage separator used works best at flow rates of about 20–40

ml/min; improved sensitivity through reduced loss of material by addition of make-up gas in the Becker-Ryhage separator when used in conjunction with capillary

columns has been demonstrated previously.<sup>8</sup> A further advantage of the system is that there is a slight delay between the total ion current and the signal from the flame ionisation detector.<sup>7</sup> This delay (about 2 sec) permits the chromatogram to be previewed and facilitates the mass scan of partially resolved components. The GC resolution is comparable to that obtained on a corresponding F 11 instrument.

The split ratio between the mass spectrometer and the flame ionisation detector can be varied by adjusting the make-up gas flow. When the amount of make-up gas is decreased more component will pass into the separator because of the difference in pressure between separator and flame ionisation detector. A small make-up gas flow should always be maintained otherwise the hydrogen may flow into the mass spectrometer and the flame be extinguished. Since changes in the make-up gas flow alter the column flow the latter has to be re-estimated with the aid of the retention time of a known compound. In practice a constant preset split ratio is preferable.

Under normal operating conditions about 90 % of the eluate passes into the mass spectrometer, as estimated from the increase in the total ion current observed on almost closing the make-up gas valve; this eliminates the flame ionisation detector signal. The 9:1 split ratio gives about the same response on the total ion current monitor as on the flame ionisation detector.

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Received August 9, 1968.

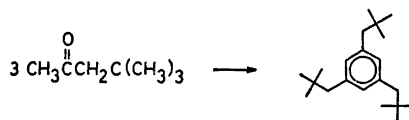
## 1,3,5-Trineopentylbenzene

### II. Synthesis by Base-Catalysed Trimerization of Methyl Neopentyl Ketone

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In Part I<sup>1</sup> the multi-step synthesis of 1,3,5-trineopentylbenzene from pinacolone *via* 1,3,5-tripivaloylbenzene is described. As an alternative synthetic method we have investigated the trimerization of methyl neopentyl ketone to 1,3,5-trineopentylbenzene.



The formation of mesitylene from acetone under acidic conditions has long been well-known.<sup>2</sup> However, ethyl methyl ketone, the simplest member in the extended series of aliphatic methyl ketones, has been reported to give not a trialkylbenzene, but only products of condensation at the methylene carbon.<sup>3,4</sup> In condensations of ketones of the type  $\text{CH}_3\text{COCHR}'$  ( $\text{R}' = \text{alkyl or H}$ ;  $\text{R} = \text{alkyl}$ ) acid catalysts favour condensation at the more substituted carbon except when steric factors prevent it.<sup>5</sup> In a study of the acid-catalysed deuteration of some methyl ketones Rappe and Sachs reported that the bulky *t*-butyl group in methyl neopentyl ketone increased the rate of methyl relative to methylene deuteration.<sup>6</sup> It was expected that this diminished reactivity of the methylene group of methyl neopentyl ketone might possibly aid in the sulphuric acid-catalysed trimerization to 1,3,5-trineopentylbenzene, but all efforts were unsuccessful.

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