The impurities, of course, decreased in amount with each fraction through fraction 6 and were not present starting with fraction 7. The chromatogram for fraction 20, Fig. 1, is representative of those obtained for each of the fractions 7 through 63. These fractions represent the pure PMH obtained by the fractional distillation of the crude material. Starting with fraction 64, a small peak was present immediately after the PMH peak, even though there was no apparent change in the boiling point or refractive index. This showed that the higher boiling impurity, 2,2,4,4,6-pentamethylheptane, was present, and the amount increased with each succeeding fraction. The chromatogram for fraction 65 is representative of the chromatograms for these fractions, with the higher boiling impurity increasing with each fraction. The utilization of gas chromatography in this particular case provided the necessary information as to which fractions were pure PMH, and, therefore, a maximum amount of pure PMH was obtained.

Gas chromatography offers a valuable analytical tool in following the course of the fractional distillation of multi-component systems. In those cases where differences in boiling points are small and differences in refractive indices are non-existent, gas chromatography is virtually indispensable.

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Use of 2-methylpiperazine diformamide in gas chromatography

In the course of a research project being carried out in this laboratory, an experimental quantity of 2-methylpiperazine diformamide was prepared from 2-methylpiperazine and formic acid. This compound proved to be very polar and showed good thermal stability. It distilled at 200° at about 5 mm pressure without decomposition and melted at about 36°.

Because of its high polarity, low melting point, and thermal stability, this compound appeared to be a logical choice as a stationary phase in gas chromatography as a substitute for dimethylformamide or dimethylsulfolane, especially under

conditions in which these materials would have an undesirably high vapor pressure. Dimethylformamide has a vapor pressure of about 1 mm at 0°, so that its use is limited by a short column life, even at this temperature. Dimethylsulfolane is recommended for use only at 40° and below, again because of a relatively high vapor pressure. Since the methylpiperazine diformamide has a vapor pressure of only about 5 mm at 200°, it should be usable as a stationary phase at least to 100°.

A comparison was made between 2-methylpiperazine diformamide and sulfolane, a highly polar compound known to give large deviations from perfect solution behavior for the various classes of hydrocarbons. This comparison is given in Table I.

TABLE I

RETENTION VOLUMES

	2-Methylpiperazine diformamide ml	*Sulfolane* ml
2,2,4-Trimethylhexane	38	42
Methylcyclohexane	35	36
n-Decane	192	202
Octene	65	74
Toluene	339	386

In each case, the stationary phase was 15 % by weight on 35–80 mesh firebrick, and the column was 1 m long by 0.2 in. diameter. The temperature was 68.5° in both cases. Helium was used as the carrier gas.

The octene (practical grade) was partially resolved into 3 components by the diformamide, and was resolved less well by the sulfolane.

A comparison of the separation factors for close-boiling pairs of different types is given in Table II.

TABLE II

SEPARATION FACTORS

	2-Methylpiperazine diformamide	*Sulfolane*
Octene/trimethylhexane	1.69	1.74
Toluene/methylcyclohexane	9.8	10.8

It is seen that the separation factors for the two stationary phases are quite similar, with sulfolane giving slightly better results. However, since the vapor pressure of the diformamide is much lower than that of sulfolane, the use of 2-methylpiperazine diformamide would be preferable.

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