

SIMULATED DISTILLATION AND MOLECULAR WEIGHT DETERMINATION BY SUPERCRITICAL FLUID CHROMATOGRAPHY

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INTRODUCTION

Supercritical fluid chromatography (SFC) has recently become a popular technique for the analysis of crude oils. It has been demonstrated for simulated distillation (1) and for hydrocarbon type separation (2-3). The advantages of SFC over gas chromatography (GC) in simulated distillation are the wider boiling range and lower temperature thus preventing cracking of heavy molecules during analysis. Previous work with GC (4) has shown that average molecular weight can be determined for aromatic fractions using a technique similar to simulated distillation. The present study on retention time behaviour of standard compounds shows how the same approach can be applied to SFC. Correlations between retention times and boiling point, molecular weight and melting point have been studied.

EXPERIMENTAL

A Lee Scientific Model 600 SFC/GC was used. The separations were performed on a 10 m x 100 μ m i.d. DB-5 column (for naphtha range) and two 10 m x 100 μ m DB-5 column (for heavier standards) from J&W Scientific, Inc, using carbon dioxide as the mobile phase. The end of the column was connected to a frit restrictor inserted in a 100 μ m i.d. fused silica sleeve. The restrictor was directly inserted in the FID detector. The following pressure or density ramps were used: for the naphtha range (IBP- 200°C), initial pressure of 80 atm for 5 min, followed by a 1 atm/min ramp to 200 atm; for the middle distillate range (200- 350°C), initial density of 0.1444 g/mL for 7.5 min, followed by a ramp of 0.0092 g/mL/min to 0.5930 g/mL; for the gas oil range (350- 525°C), initial density of 0.3095 g/mL for 5 min, followed by a ramp of 0.006 g/mL/min to 0.7411 g/mL. All runs were isothermal at 100°C. Sample introduction was made via a Rheodyne 7520 valve having a 0.5 μ L injection volume.

RESULTS AND DISCUSSION

1- Boiling point

As would be expected from literature on simulated distillation by SFC (1), there is a very good correlation between retention time and boiling point. However, in the light naphtha range, the calibration is not linear. Thus, the pressure (or density) program must be adjusted to provide a linear relation or a proper calibration procedure must be used in order to accurately determine the initial boiling point of a sample. It should be noted that the inflexion point is at about the operating temperature. From this result, it appears that a temperature program would be useful for an adequate calibration of the lighter portion of the sample (low initial temperature) and of the heavier portion (high final temperature).

2- Molecular weight

A previous study (4) has shown that the molecular weight of aromatic fractions from topped (light fractions removed) crude oils can be evaluated by a technique similar to simulated distillation. In that work, after hydrocarbon type separation by column chromatography the aromatics fraction was separated by GC on a non-polar column. Since the compounds are of the same type, boiling points and molecular weights were both well correlated to retention time. This correlation allowed the determination of the boiling range, the average molecular weight as well as the molecular weight distribution of these fractions. A similar approach with SFC would eventually permit monitoring molecular weight of heavier samples.

As shown in Fig. 2, a poor correlation exists between molecular weight and retention time in the naphtha and middle distillate range, except for straight chain paraffins. However, in the gas oil range, the correlation for non-paraffinic standard compounds is improved. As molecular weight increases, it seems that the influence of the functional group becomes less important compared with molecular weight. This could be due to increased steric hindrance or more electron delocalization over the structure of the molecule which reduces the polarity. Thus, it appears that the molecular weight determination would only be effective for heavy fractions.

3- Melting point

Solubility of solids in liquids is determined by intermolecular forces as well as enthalpy of fusion and melting point of the solute (5). Since a supercritical fluid has densities approaching those of a liquid and since the retention time is related to solubility, we investigated how the melting of the solute would be related to the retention time. As shown in Fig. 3, there is no correlation except for the n-paraffins which was expected since their melting point increases regularly with molecular weight.

Melting point was expected to have an influence when the operating temperature was lower than the melting point. All the results shown in Fig. 3 were obtained at 100°C. Although there is some trend in Fig. 3c, there is too much variation to significantly relate melting point and retention time, and the correlation is very poor even within the same family of compounds.

4- Response factors

All simulated distillation techniques assume that the various components of a crude oil sample have nearly identical response factors. Figure 4 shows that response factors can be significantly different. However, within the same class of compounds, it seems that the response factors do not vary to the same extent. Therefore, boiling range determination could lead to erroneous results if the relative quantity of different compound types varies from sample to sample. On the other hand, for hydrocarbon type separation by SFC, results can be reliable if proper response factors are assigned to each compound class. Since the difference between the response factors of saturates and aromatics is small, samples with low heteroatomic content could lead to satisfactory results.

CONCLUSIONS

The study of retention behaviour showed that, for given SFC conditions, retention time is mainly dependent on the boiling point of the solute. Some correlation was found with the molecular weight and no significant link was found with the melting point. Response factors were found to vary between compound classes but to be quite consistent within the same class.

REFERENCES

1. Schwartz, H.E., Brownlee, R.G., Boduszynski, M.W., and Su, F., Anal. Chem., 59, 1393-1401, 1987.
2. Norris, T.A. and Rawdon, M.G., Anal. Chem., 56, 1767-1769, 1984.
3. Campbell, R.M., Djordjevic, N.M., Markides, K.E. and Lee, M.L., Anal. Chem., 60, 356-362, 1988.
4. Coulombe, S. and Sawatzky, H., Fuel, 65, 552-557, 1986.
5. Reid, R.C., Prausnitz, J.M. and Sherwood, T.K., The Properties of Gases and Liquids, 3rd ed., McGraw-Hill, New York, pp.380-384.

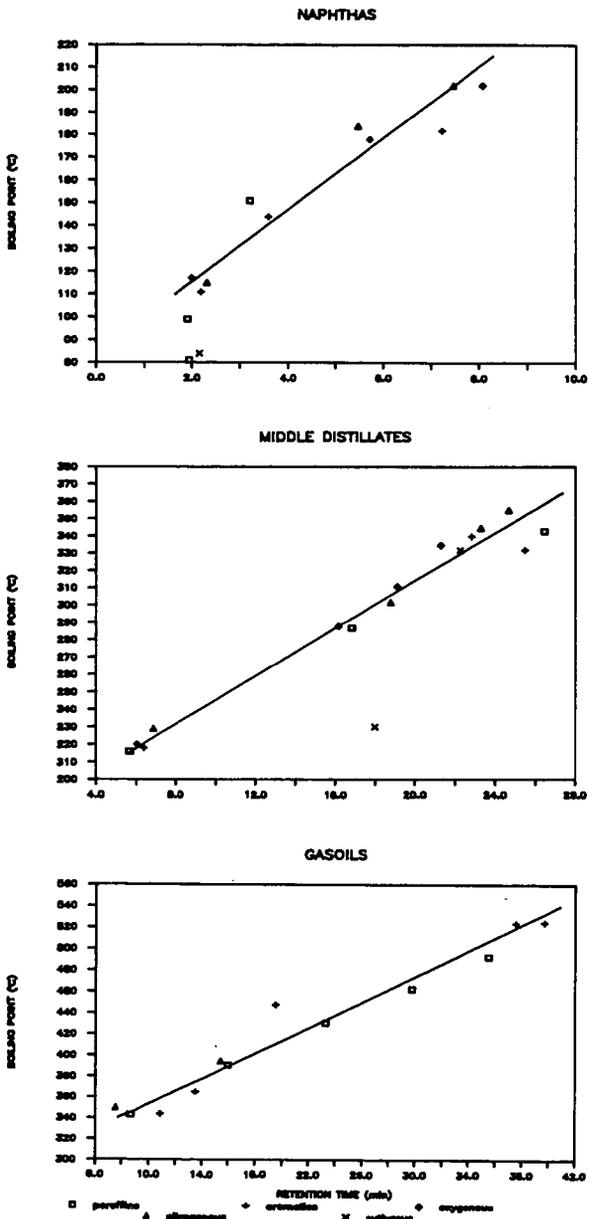


Figure 1 - Correlation between boiling point and retention time

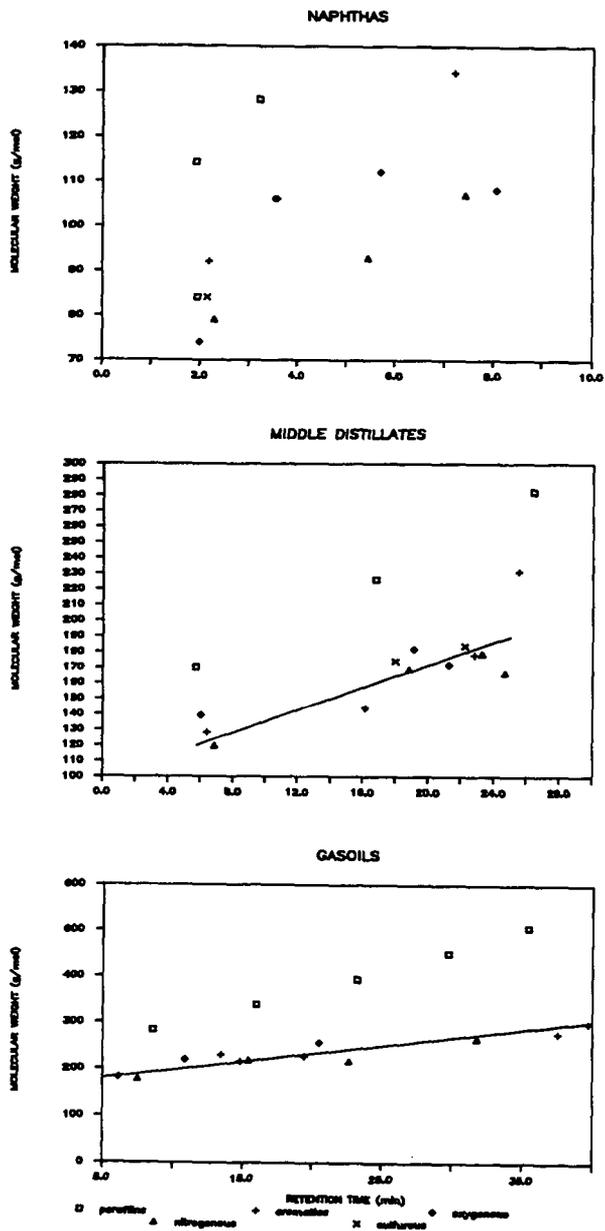


Figure 2 - Correlation between molecular weight and retention time

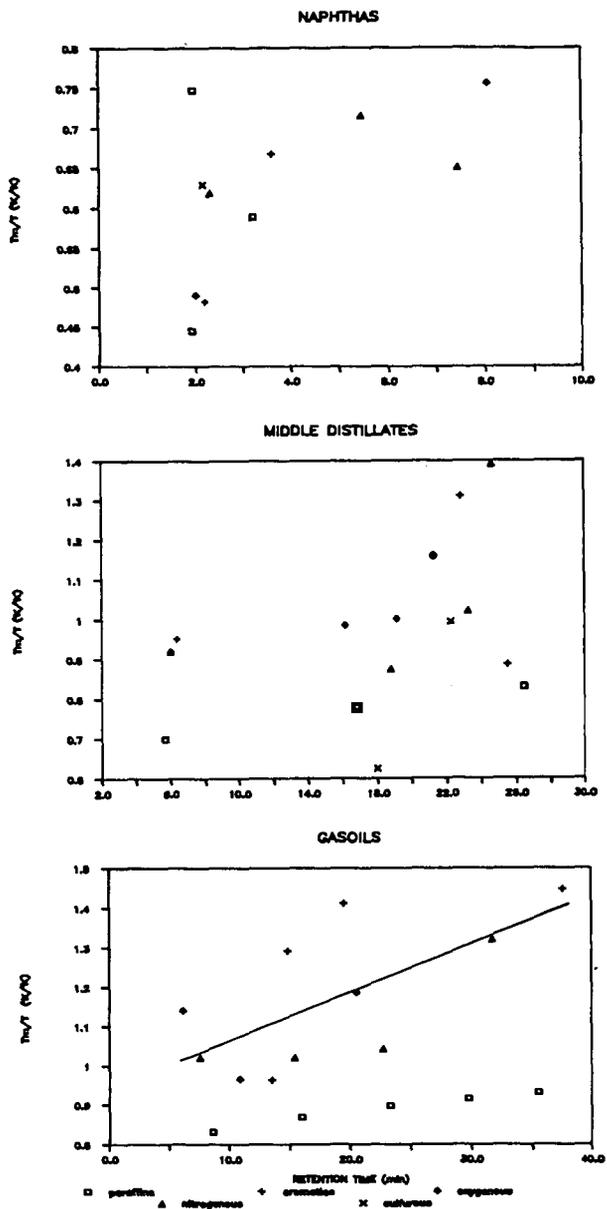


Figure 3 - Correlation between melting point and retention time (T_m : melting point; T : operating temperature)

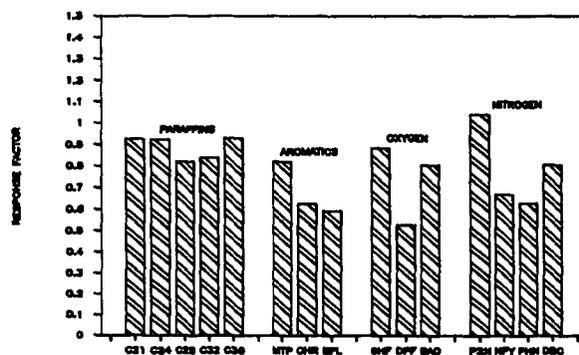
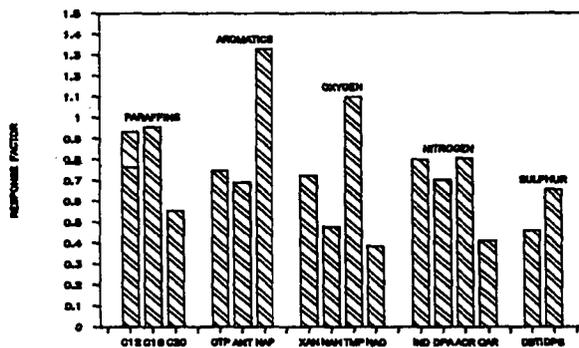
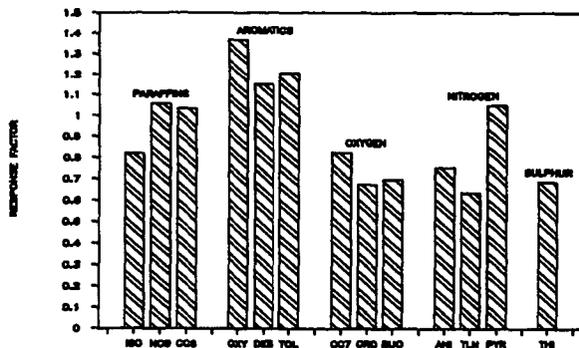


Figure 4 - Response factors (SFC with FID)