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HYDROCARBON GROUP-TYPE ANALYSES BY ON-LINE MULTI-DIMENSIONAL CHROMATOGRAPHY

II. LIQUID CHROMATOGRAPHY–GAS CHROMATOGRAPHY

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SUMMARY

An on-line multi-dimensional chromatographic system, coupling high-performance liquid chromatography (HPLC) and capillary gas chromatography (GC) is described. The system is controlled by a microprocessor and can be automated. The application of this system to hydrocarbon group-type analysis is demonstrated by using HPLC on silica gel to fractionate petroleum samples into saturates, unsaturates, aromatics and polar compound, followed by the characterization of these groups by capillary GC with flame-ionization detection. Analyses of gasoline and diesel fuel are demonstrated.

INTRODUCTION

In many industrial applications in which petroleum sources are treated either as a raw material or as a product, it is necessary to determine the distribution of the hydrocarbons according to groups, such as saturates, unsaturates, aromatics and polar compounds. There have been several approches to this type of analysis, including fluorescence indicator analysis and high-performance liquid chromatography (HPLC)[2]. In Part I[3] an on-line multi-dimensional chromatographic technique was described, which utilized column switching in HPLC and could provide data on the relative distributions of these groups. Characterization of the hydrocarbon groups by gas chromatography (GC) after their fractionation by HPLC has been reported[4], but these were off-line experiments, requiring the collection and re-injection of the separate fractions. In this paper, a second technique is described, which utilizes an on-line multi-dimensional coupling of HPLC and capillary GC. The use of this instrumentation has been reported for the analysis of pesticides in butter via the coupling of size-exclusion chromatography and packed-column GC. The technique described here is capable of providing information on the distribution not only of the hydrocarbon groups, but also of the compounds within each group.

The separation strategy of the method is as follows. Adsorption HPLC on silica gel with hexane as the mobile phase is used to separate a sample into saturates,

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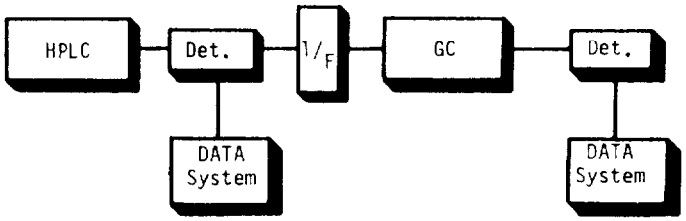


Fig. 1. Diagram of the LC–GC on-line multi-dimensional system. I/F = Interface.

unsaturates and aromatics. A cyanopropyl-bonded silica guard column is used to hold up polar compounds, which would otherwise be irreversibly adsorbed on to the silica gel column. The polar compounds are subsequently backflushed from the guard column. An interface between the LC and the GC systems can selectively sample sections of the LC separation and thus determine distributions within each group. Although the resolution of saturates and unsaturates produced by the silica gel column is less than 1.0, as shown in earlier studies[3], it is sufficient to allow sampling for the GC analysis.

EXPERIMENTAL

Apparatus

A diagram of the apparatus is shown in Fig. 1. A Varian Model 5020 HPLC instrument (Varian, Walnut Creek, CA, U.S.A.) with a refractive index (RI) detector was used. A Varian Model 3700 capillary gas chromatograph with a flame-ionization detector was also used. The conditions for all GC analyses were as follows: 3-μl splitless injections according to Grob and Grob[5,6]; injector, flushed at 30 ml/min for 30 sec after injection; initial column temperature, 40°C, held for 15 min, then programmed at 2°C/min to 220°C; injector temperature, 270°C; detector temperature, 300°C.

Two Varian CDS 111 data systems were used to monitor the GC and HPLC detector outputs. The connection between the liquid chromatograph and the gas chromatograph consisted of a Varian Model 8070 LC–GC interface. The principle of operation of the interface is illustrated in Fig. 2. In the standby position, the effluent from the LC detector enters the flow-through syringe and flows to waste through an air-purged waste receptacle. When an injection is initiated by a time-programmed external event from either the LC microprocessor or the data system, the syringe is lifted from the waste receptacle (which then swings out of the way); the

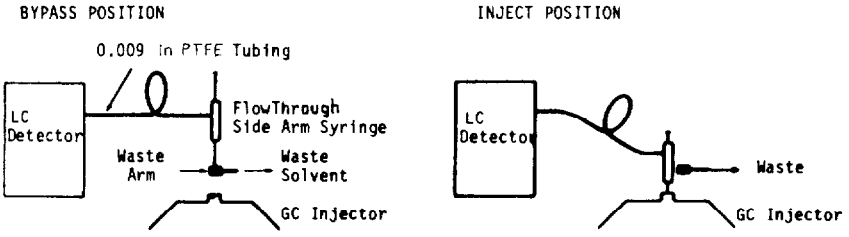


Fig. 2. Operation of the LC–GC interface.

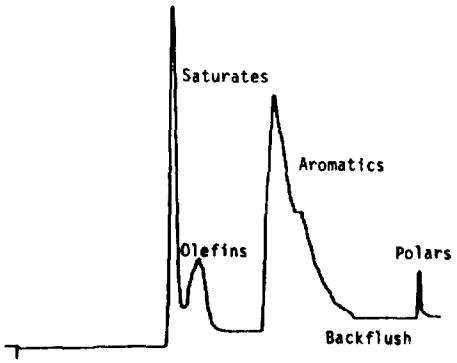


Fig. 3. HPLC fractionation of Texaco unleaded gasoline. Conditions: column, 32 × 4.4 cm I.D., 5-μm silica; mobile phase, hexane, 0.5 ml/min; refractive index detection at × 32 attenuation; sample, 10 μl.

syringe is lowered rapidly until the needle pierces the GC septum; the syringe plunger is depressed to make the injection; the assembly then returns to the standby position. The connection between the LC detector and the LC–GC interface is via 0.009 in. I.D. PTFE tubing. The delay, between the time at which a peak enters the detector and the time it enters the syringe can be calculated by the equation

$$t_d = \frac{f\pi d^2 l}{4} \tag{1}$$

where f is the flow-rate, d the tubing inner diameter and l the tubing length. This time must be taken into account in determining injection times.

Columns. For HPLC a 30 cm × 4.0 mm I.D. silica (5 μm) column was used (Varian Micropak Si-5). The guard column was 8 cm × 4.6 mm I.D., hand-packed with Pelliguard LC-8, a 40-μm pellicular cyanopropyl-bonded silica (Supelco, Bellefonte, PA, U.S.A.). No special procedures were used to activate the silica column.

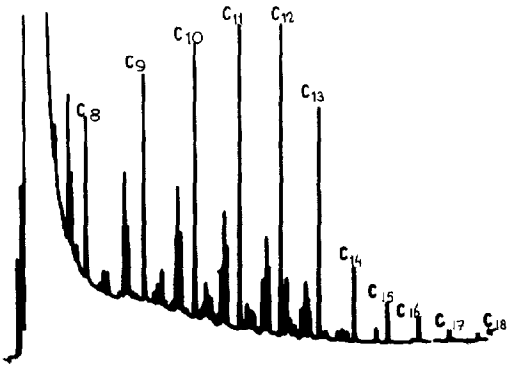


Fig. 4. LC–GC analysis of saturates in Texaco unleaded gasoline. LC conditions as in Fig. 3. GC conditions: column, 33 m × 0.25 mm I.D. WCOT SP-2100; carrier gas, helium at 2 ml/min; temperature programme, 40°C for 15 min, 2°C/min to 220°C; flame ionization detection, $8 \cdot 10^{-11}$ A f.s.; 2-μl splitless injection; sample diluted 1:10 in hexane; LC sampled at 6.81 min.

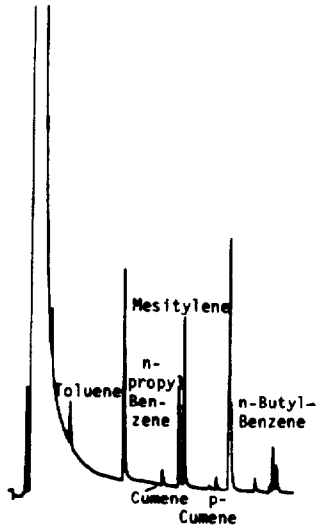


Fig. 5. LC–GC analysis of olefins in Texaco unleaded gasoline. LC sampled at 9.05.

Fig. 6. LC–GC analysis of aromatics in Texaco unleaded gasoline. LC sampled at 12.95 min.

For capillary GC a 33 m × 0.25 mm I.D. wall-coated open tubular SP-2100 column (Supelco) was used. Helium was the carrier gas at 2 ml/min.

Reagents and solvents

Distilled-in-glass hexane (Burdick and Jackson, Muskegon, MI, U.S.A.) was the HPLC mobile phase. Samples of Texaco leaded gasoline and Texaco diesel fuel were purchased locally.

RESULTS AND DISCUSSION

Chromatograms of gasoline obtained by capillary GC have been published numerous times. Over 300 peaks are resolved; however, the identification of specific compounds or even specific hydrocarbon group distributions is still impossible. This problem is handled well by the on-line multi-dimensional system. Fig. 3 shows the

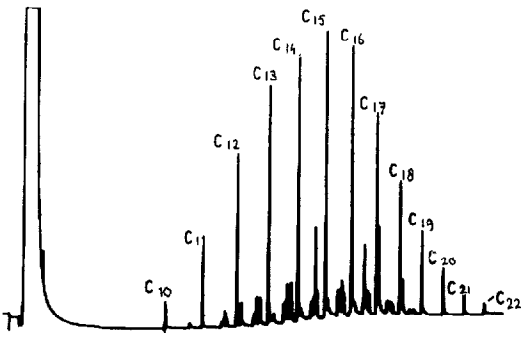
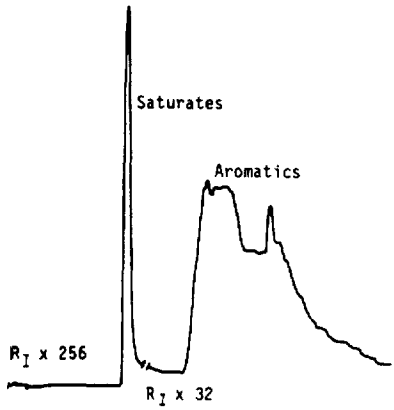


Fig. 7. LC–GC analysis of aromatics in Texaco unleaded gasoline. LC sampled at 14.95 min.

LC separation of a 10-μl sample of undiluted leaded gasoline. The column was back-flushed after 17 min to clean it for the next sample. By sampling the maxima of the peaks of saturates and unsaturates the chromatograms shown in Figs. 4 and 5 were generated. By sampling at the two aromatic maxima, at 12.95 and 14.95 min, respectively, the chromatograms shown in Figs. 6 and 7 were generated. In Fig. 4, the saturates are separated into *n*-alkanes and two groups of alkyl isomers by carbon number. Note that for gasoline the alkanes are distributed around a maximum of C_{11}. In Fig. 5, the unsaturates are separated into groups of isomers by carbon number. In Figs. 6 and 7, two different distributions of aromatics are shown. As the sampling sections in the LC separation are well separated in time, the distributions in the two GC analyses are not identical. It would be impossible to take one sample for GC analysis that is representative of this LC fraction. Toluene is present in both chromatograms and the sample at 12.95 min appears to have been on the leading edge of the toluene peak, whereas the sample at 14.95 min appears to be closer to the maximum of the toluene peak in the LC separation. All identifications of the aromatic peaks in the gas chromatograms were based on the comparison of retention times with standards.

Similar results were obtained in the analysis of diesel fuel. Fig. 8 shows the LC fractionation of a 10-μl sample of diesel fuel. Note that the initial RI attenuation was $\times 128$; for the gasoline it was $\times 32$. In the diesel fuel analysis the attenuation was changed during analysis to $\times 32$. In the diesel fuel, obviously, the saturates are more concentrated than in the gasoline sample, whereas the aromatics are of similar concentration. In the diesel fuel there appears to be a relatively low concentration of unsaturates. Note that the flow-rate in the LC analysis of diesel fuel was 1 ml/min, compared with 0.5 ml/min for the gasoline sample.

The diesel saturates peak was sampled at 3.99 min for GC analysis, with the results shown in Fig. 9. Again, the *n*-alkanes and two groups of alkyl isomers are separated by carbon number. In the diesel fuel the distribution is around a maximum



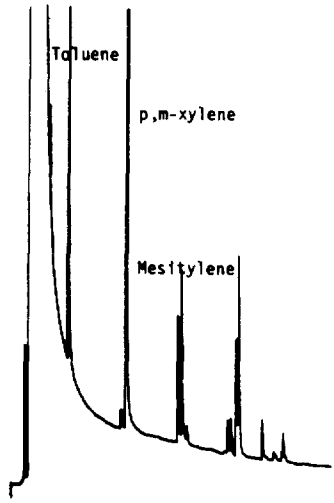


Fig. 8. HPLC fractionation of diesel fuel. Conditions as in Fig. 3, except flow-rate, 1 ml/min.

Fig. 9. LC–GC analysis of saturates in diesel fuel. LC sampled at 3.99 min.

of C_{15}. The aromatics fraction of the diesel fuel separation by LC was sampled at 1-min intervals. As in the gasoline example, the efficiency of the LC column was sufficient to produce many aromatics peaks narrower than 1 min and, therefore, the resulting chromatograms represent four different aromatic distributions. It would be better if the LC column did not separate the aromatic fraction.

CONCLUSION

In summary, the method described allows the rapid automatable analysis of hydrocarbon group types and of the distributions of compounds within the individual groups. It offers a number of advantages over simple LC analysis: (1) it provides valuable information concerning the carbon number distribution within each group; (2) by taking advantage of the two sets of retention data thus produced, qualitative identification should be improved; and (3) quantitation is simplified by the use of a flame-ionization detector that responds to all organics. In contrast to the multi-dimensional HPLC method described in Part I[3], the LC–GC technique provides complete separation of saturates and unsaturates but, in some complex samples, there may be overlap of these groups in the GC analysis.

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