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RECOGNITION AND QUALITATIVE CHARACTERIZATION OF COMMERCIAL PETROLEUM FUELS AND SYNTHETIC FUELS BY A GAS CHROMATOGRAPHIC FINGERPRINTING TECHNIQUE

I. GENERAL CONSIDERATIONS

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SUMMARY

A simple gas chromatographic fingerprinting technique is described for the fast identification, differentiation, source recognition and qualitative characterization of various petroleum and synthetic liquid fuels (motor gasolines, jet fuels, diesel fuels, fuel oils and coal-hydrogenation liquid fuels). All the analyses are carried out on the same chromatograph and on the same column. The advantages of the technique are the relatively short analysis time (up to 30 min), good repeatability, the possibility of obtaining information on the fuels and the prediction of fuel characteristics, all on the basis of one simple analysis. It is possible, by interpretation of the fingerprint chromatograms, to obtain data of use in quality control. The interpretation of chromatograms of unknown samples is facilitated by comparison with appropriate standard chromatograms obtained by the same method.

INTRODUCTION

Information on the quality of petroleum fuels obtained from gas chromatographic (GC) analysis has often defined the fuels better than data obtained from conventional tests. On the basis of such information, it has even been possible to predict the actual performance of the fuels under certain conditions. As a consequence, the application of GC to the characterization of petroleum fuels has increased. Compositional analysis consists of the determination of either all of the individual hydrocarbons (as in the examination of liquid petroleum gases) or of key components, some important types of hydrocarbons, or the distribution of the hydrocarbons. This type of analysis is of particular interest in the estimation of important characteristics of fuels[1–5], and as such may be used in quality control.

　　　　Gas chromatography has also been used for the characterization of complex mixtures of petroleum products in the form of pollutants of the soil, water and air, as well as for their identification and source recognition. Various fingerprinting techniques have been used for this purpose[6–10]. Jeltes[10] feels that the potential of chromatographic fingerprint techniques has not yet been fully exploited.

　　　　Considering that the GC fingerprinting technique is a valuable method that should find wider usage in the testing and the examination of different liquid fuels, we have examined the possibility of extending its applications. A method is being developed for an extremely simple estimation of the characteristics of petroleum products and the properties of some other fuels. The main goal is to obtain an efficient, simple and fast method for the identification, differentiation, source recognition, and qualitative characterization of various liquid fuels which will be of use in controlling the quality of different process streams, as well as in the control of commercial products. Hence, the interpretation of the fingerprint chromatograms in this case is somewhat different from that of the corresponding chromatograms obtained in the analysis of pollutants.

　　　　In spite of the fact that some workers have used completely different GC conditions for the analysis of complex materials by the fingerprinting technique, in this study all of the fuel chromatograms were obtained on the same column. Moreover, the analytical technique was simple, so that all analyses, when necessary, may be made by one skilled operator on the same chromatograph. The interpretation of the chromatograms is facilitated by comparison with chromatograms of a few reference compounds obtained by the same method. The choice of reference depends on the types of the samples examined and on the fuel characteristics under consideration.

　　　　In the future one might require more detailed investigations which would enable better characterization of liquid fuels and better prediction of their performance[11,12]. Nevertheless, GC fingerprint testing as described in this paper may provide quick preliminary data concerning the type and quality of liquid fuels.

EXPERIMENTAL

　　　　Samples of various liquid fuels were chosen for the investigations, including those from motor gasolines, jet fuels, diesel fuels, and fuel oils, and one sample of a synthetic oil obtained by catalytic (cobalt molybdate) hydrogenation of a Yugoslavian brown coal[13]. All of the samples, except the synthetic fuel, had characteristics of Yugoslavian commercial products.

　　　　The instrument used was a Perkin-Elmer Model 880 gas chromatograph, equipped with a flame-ionization detector.

　　　　The operating conditions used for GC were: column, SCOT (7.5 m × 0.5 mm); liquid phase, Apiezon L; carrier gas, nitrogen; flow-rate, 2.4 ml/min (gasolines), 3.5 ml/min (jet fuels), and 3.5–4.0 ml/min (diesel fuels, fuel oils and synthetic oils). The column temperature was programmed at 8°/min from 40 to 200° (gasolines), from 100 to 200° (jet fuels), from 140 to 240° (middle distillates), from 140 to 270° (diesel fuels, D2), from 160 to 280° (synthetic oil) and from 160 to 290° (fuel oils).

　　　　The selection of SCOT column and of Apiezon L as the liquid phase represented a compromise, because it is well known that, for the analysis of, for example, motor gasolines or fuel oils, other liquid phases are more convenient and more

efficient (*e.g.*, squalane and OV-101, respectively). Furthermore, for the analysis of synthetic oils obtained from coal, having in mind their high content of aromatic hydrocarbons, the suggested column was not the most appropriate. However, a SCOT column that was shorter than usual was used because a packed column would be less efficient and the usage of an open-tubular column or of a longer SCOT column, although enabling high-resolution GC, would not contribute to the main purpose of the investigation.

In order to prevent the contamination of the column inlet system and of the column, a pre-treatment of the fuel oils and of the synthetic oil was necessary. In similar cases, the inlet systems were either adapted by including a pre-column or the main portions of the samples were separated from the insoluble or heavy components, usually by evaporation, vacuum distillation or extraction. In this work the fuel oils and the synthetic oil obtained on liquefaction of coal were extracted with *n*-heptane, and the heptane extract only was injected into the column for analysis. Chromatograms of fuel-oil extracts contained components of up to C_{34}. The synthetic oil extract was somewhat lighter.

RESULTS AND DISCUSSION

Only a limited number of chromatograms will be presented as an illustration of the application of the fingerprinting technique to the examination of liquid fuels. A systematic review of all of the investigations of the individual types of fuels will be given in the succeeding parts of this work.

Motor gasolines

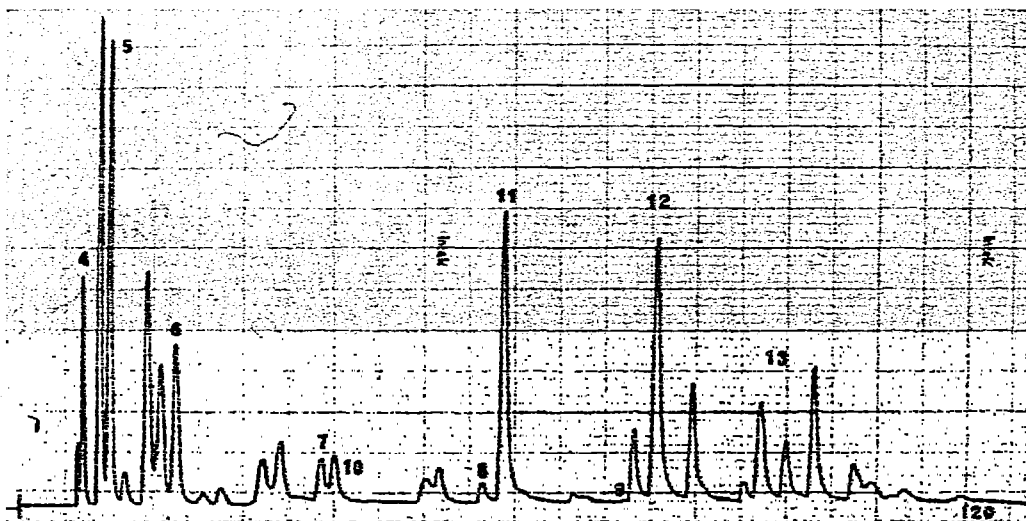Chromatograms of two samples of motor gasolines are shown in Figs. 1 and 2.

Fig. 1. Chromatogram of motor gasoline A. Peaks: 4–9 = mainly *n*-paraffins of corresponding numbers of carbon atoms; 10 = benzene; 11 = toluene; 12 = C_8 aromatic hydrocarbons; 13 = aromatic hydrocarbons $>C_9$.
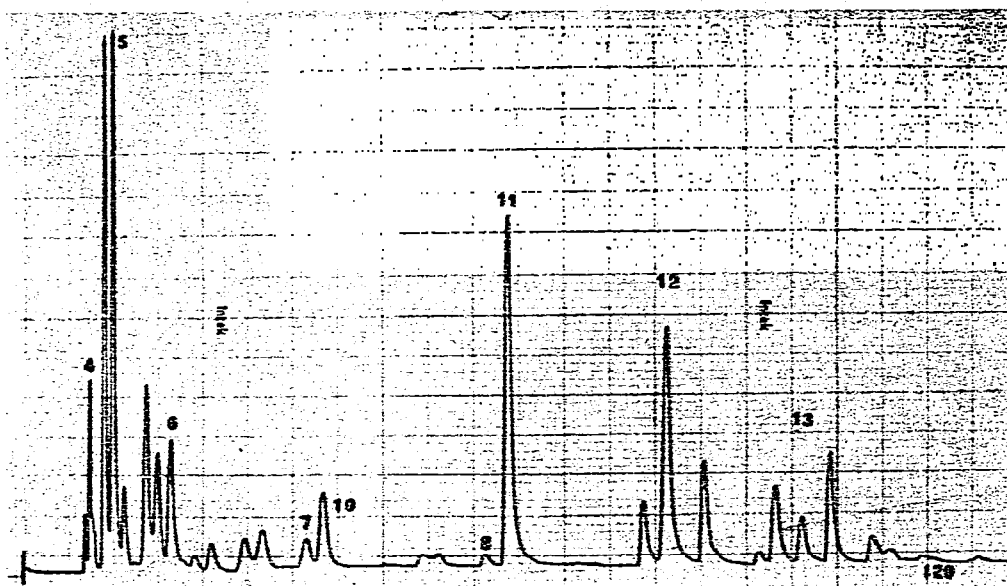
Fig. 2. Chromatogram of motor gasoline B. Peaks 4–8 = n-paraffins; 10–13 = aromatic hydrocarbons.

Both gasolines had RON^* = 98, and a lead content of 0.6 g/l. In spite of the fact that the two chromatograms seem to be very similar, by careful consideration of the chromatograms it is possible to obtain data which form a basis by which these fuels may be differentiated. It is obvious that the two gasolines have approximately the same boiling range. By comparison with a chromatogram of a sample of a reference gasoline, it would be possible to estimate more closely the most important distillation temperatures of the investigated samples.

The chromatograms obtained show that the distribution of hydrocarbons in the two gasolines is not the same. A somewhat lower vapour pressure and a slightly higher 90% ASTM distillation point of sample A (Fig. 1) are indicated. The same 50% ASTM distillation temperature may be expected for both samples. These conclusions were confirmed by conventional analysis of the gasolines. A different distribution of some types of hydrocarbons, which leads to a dissimilar clear octane-number distribution, indicates that the blending of the gasolines was not the same. Their basic blending component was a reformate; other blending components were the light fraction of a straight-run distillate, a butane mixture, and, for gasoline B (Fig. 2), an additional fraction that contained olefins. (This fact is indicated, among others, by the presence of peaks following the peaks of n-butane and n-pentane.) Gasoline A, before addition of lead, thus had a larger ΔR_{100} value**. It is obvious that gasoline A contains less benzene and toluene compared with gasoline B, which shows that benzene and partially toluene were removed from the reformate by extraction

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    * RON = Research octane number.
    ** ΔR_{100} = The difference between the octane number of the gasoline and that of its fraction up to 100°.

prior to blending of the sample A. It also suggests that the two gasolines were derived from two different producers. The olefins which are present in the light fraction of gasoline B may be supposed to originate from a catalytically cracked or steam cracked (light fraction) blending component, or from both.

According to the distribution of the peaks and their ratios, and on the basis of a comparison with chromatograms of reference standards, the presence of isomerizate, alkylate or any significant quantity of catalytically cracked gasoline would not be expected in either of the samples of gasoline. With regard to the clear octane-number distribution in the light fraction, particularly with gasoline A, both samples may contain more tetramethyllead than tetraethyllead. By comparison of fingerprint chromatograms with chromatograms of different reference standards of known clear octane numbers, an estimation of the lead content of the samples may be possible, based on the ratio of several characteristic hydrocarbon peaks in the unknown samples and in the references. This possibility will be discussed in detail in the succeeding parts of this work.

In this study two relatively similar gasolines were purposely chosen for consideration. If the origins and characteristics of the gasolines under investigation had differed to a greater extent, their fingerprints would also have been much more different and easier to interpret. The interpretation of comparable fingerprint chromatograms may become routine with experienced operators.

Jet fuels

Chromatograms of two commercial jet fuels, which also were alike, are shown in Figs. 3 and 4 (fuels C and D, respectively). It can be seen that the samples repre-
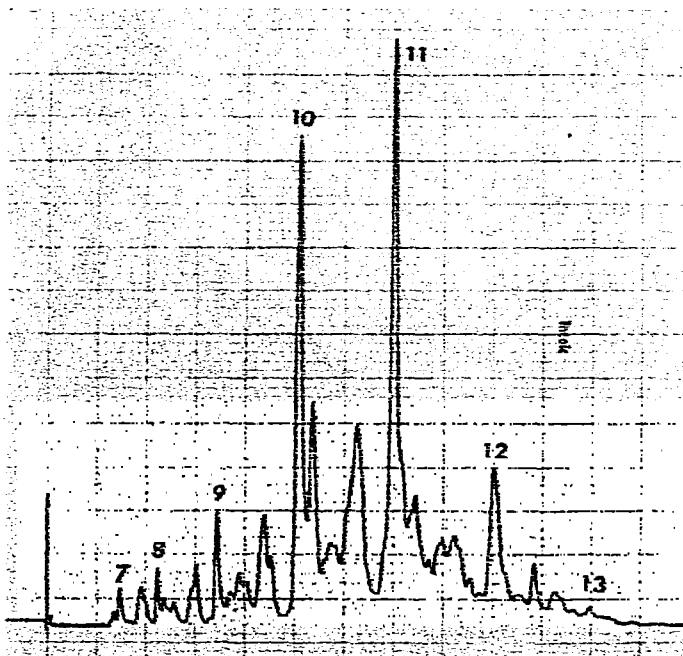

Fig. 3. Chromatogram of jet fuel C. Peaks: 7–13 = C_7–C_{13} n-paraffins, respectively.
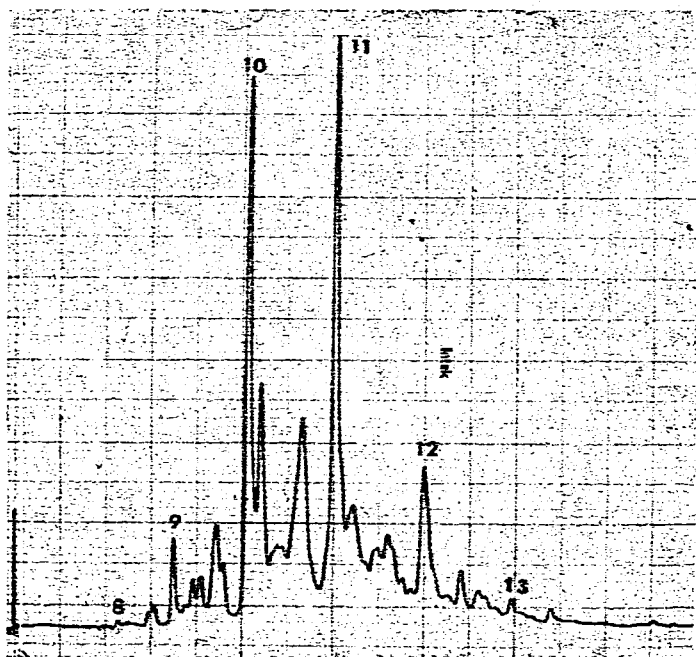
Fig. 4. Chromatogram of jet fuel D. Peaks: 8–13 = C_8–C_{13} n-paraffins, respectively.

sent relatively light jet fuels, fuel C being somewhat lighter than D. On the basis of this fact and a comparison of the boiling ranges, it may be concluded that jet fuel C has a lower flash point than fuel D, and probably has a lower specific gravity as well. By comparison of the fingerprint chromatograms with chromatograms of appropriate references, the values of the flash points could be estimated. Of even greater importance would be the estimation of the freezing points and of some other characteristics of jet fuels, primarily because the usual methods of determination require much more time than the flash-point method.

The chromatograms indicate a natural distribution of hydrocarbons in the jet fuels examined, i.e. the fuels were not obtained by blending. Both fuels may have a ca. 50% ASTM distillation temperature, the distillation temperature of fuel D being slightly higher than that of fuel C. Accordingly, and also because of the higher content of C_{11}–C_{13} n-alkanes in fuel D, it may be concluded that this fuel has a somewhat higher freezing point than fuel C. By using a conventional method, it was found that samples C and D had freezing points of —64.0 and —61.5°, respectively.

By comparison of the chromatograms of the samples C and D with chromatograms of appropriate references of known properties and calculated contents of the individual n-alkanes, it would be possible to predict important characteristics of the burning efficiency such as the smoking point, luminometric number and the content of aromatic compounds. The references would differ in the types of hydrocarbons present.

A skilled operator, even without the references, would conclude that jet fuels C and D meet the standards as far as the above characteristics are concerned: relatively high n-paraffin peaks exclude high contents of aromatic hydrocarbons, and from the

estimated boiling ranges the content of bicyclic aromatic compounds is deduced to be very small.

Diesel fuels

With diesel fuels, as with jet fuels, in addition to the evidence concerning the blending and fractionation, it is possible to obtain data for prediction of important fuel properties such as flash point (on the basis of the content of constituents having low boiling ranges), low-temperature characteristics (on the basis of the content and the distribution of higher n-paraffins) and the cetane index (on the basis of the distribution of some types of hydrocarbons). Comparison with chromatograms of references would enable a better insight to be obtained into the quality of the tested diesel fuels. On the basis of a chromatogram of a commercial diesel fuel, a skilled operator may even discover the presence of depressants* [according to the range and the distribution of n-paraffins compared with the values of the pour point or the cold-filter plugging point (CFPP)].
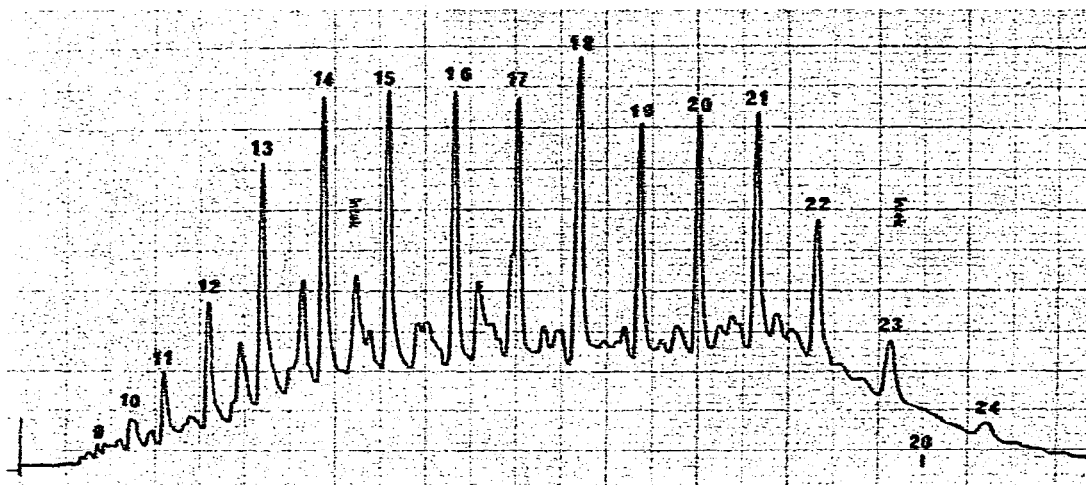

Fig. 5. Chromatogram of a commercial diesel fuel D2, summer grade (CFPP = —1°). Peaks: 9–24 = mainly n-paraffins with corresponding numbers of carbon atoms.

The chromatograms in Figs. 5–7 are shown as an illustration of the possibility of the application of the fingerprint technique to the analysis of various samples or middle distillates: (a) a chromatogram of a typical commercial diesel fuel (summer grade, CFPP = —1°) (Fig. 5); (b) the first part of a chromatogram of a middle distillate having sharp front-end fractionation (Fig. 6); and (c) the final part of a chromatogram of a diesel fuel D2 having an unfavourable distribution of higher n-paraffins, indicating the probable unsatisfactory low-temperature properties of this fuel (Fig. 7).

Fuel oils

From GC analysis of fuel oils, on the same column, it was also possible to

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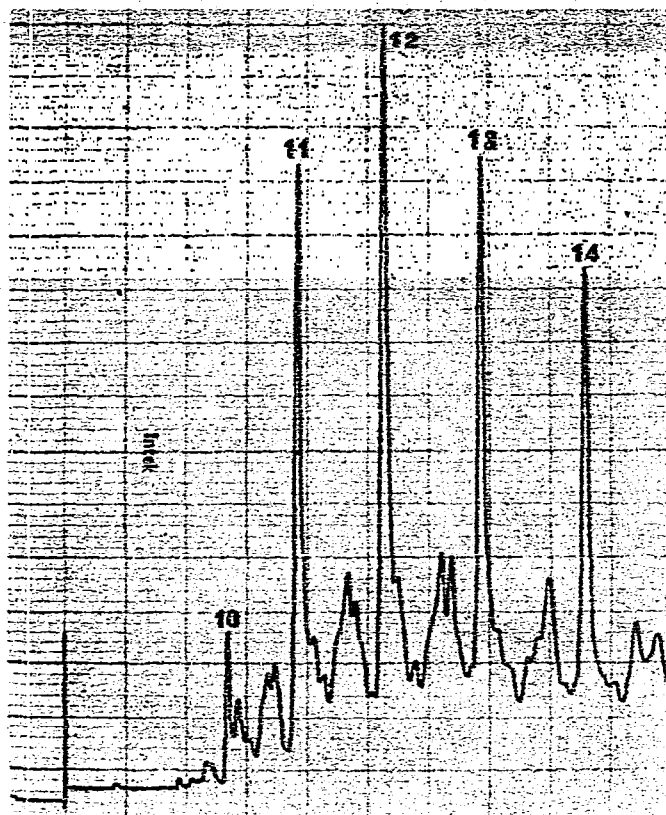* Additives which improve some low temperature characteristics.

Fig. 6. First part of the chromatogram of a middle distillate with sharp front-end fractionation. Peaks: 10–14 = mainly *n*-paraffins with corresponding numbers of carbon atoms.
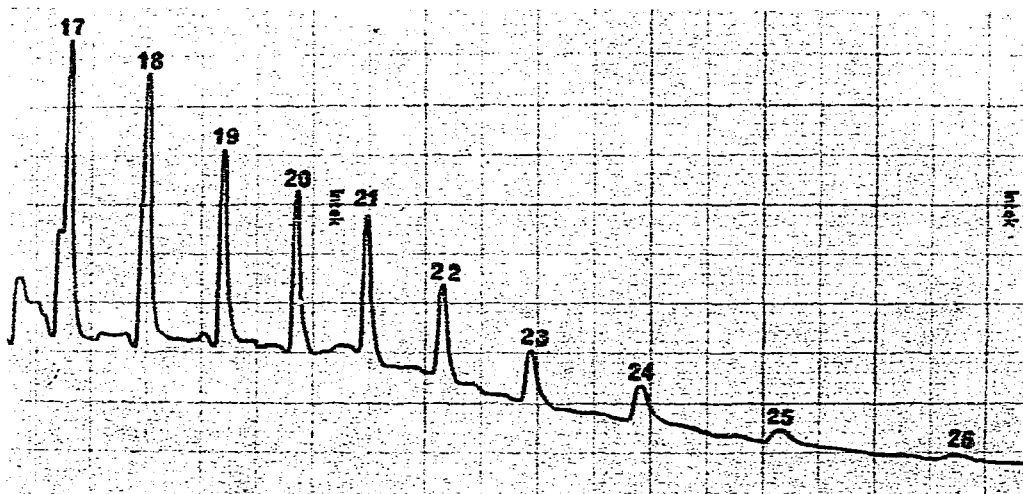

Fig. 7. End part of the chromatogram of a diesel fuel D2. Peaks: 19–25 = mainly *n*-paraffins with corresponding numbers of carbon atoms.

obtain preliminary insight into their quality (flash point, evidence of blending, stability, quantity of sulphur, etc.). Thus, for example, a high content of n-paraffins indicates a better stability of the fuel oil and a smaller quantity of sulphur, the boiling range and the distribution of light and heavy fractions may form a basis for the estimation of the tendency of the fuel components to segregate and a high content of heavy fractions in the fuel may be an indication of possible viscosity problems.

Synthetic oil

A chromatogram of the n-heptane extract of a synthetic oil, obtained by catalytic hydrogenation of a Yugoslavian brown coal using a cobalt molybdate catalyst[13], is shown in Fig. 8. The n-heptane was evaporated prior to chromatographic analysis. The distribution of hydrocarbons in the synthetic oil was completely different from that in the petroleum fuel oils. Hence, from the chromatogram, it is easy to recognize the different origin of the synthetic oil. For a more complete characterization of a synthetic oil on the basis of fingerprinting GC, a greater number of similar samples would have to be examined. The composition, and hence the chromatograms, of this type of product will depend essentially on the degree of hydrogenation of the coal.
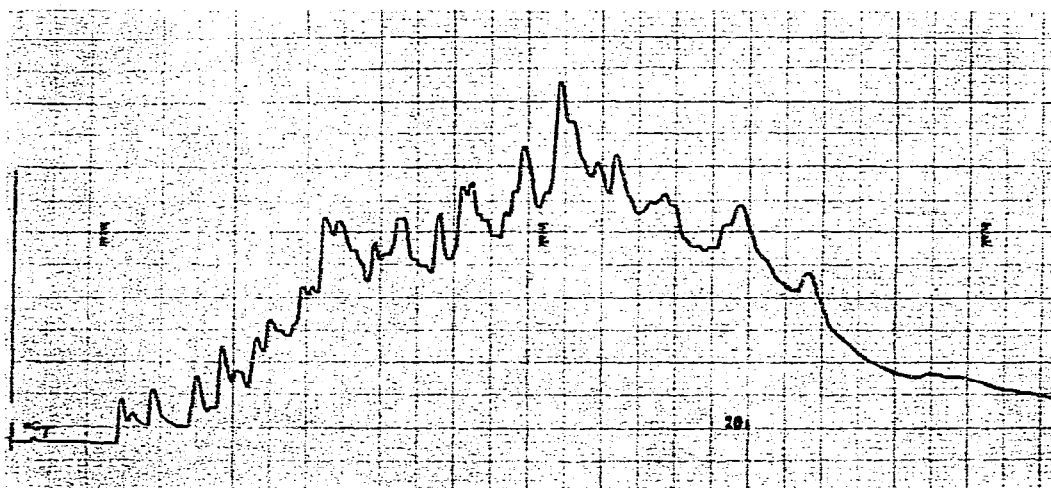

Fig. 8. Chromatogram of the n-heptane extract of a synthetic oil obtained by catalytic hydrogenation of a Yugoslavian brown coal.

CONCLUSIONS

On the basis of a simple GC fingerprint analysis, carried out on one instrument and with the same column and liquid phase, it is suggested that a skilled and experienced analyst may obtain relatively easily data of use for a quick identification and qualitation of completely different kinds of petroleum and synthetic liquid fuels. The interpretation of fingerprints of unknown samples may be facilitated by comparison with chromatograms of appropriate references obtained by the same method. The proposed technique offers several advantages such as a relatively fast analysis

of diverse liquid fuels (up to 30 min), a good repeatability and a minimum loss, due to evaporation, of light fractions.

    As far as the identification and the characterization of the samples is concerned, from this type of analysis one might expect: (1) evidence of the fractionation and blending of the components; (2) evidence of the distribution of some types of hydrocarbons in different liquid fuels; (3) an indication of the process which has been used for the manufacture of the product; (4) evidence of the presence, and possibly of the type, of additives in the fuels; (5) differentiation of various commercial petroleum fuels from each other; (6) differentiation of synthetic liquid fuels from petroleum fuels, recognition of the source of coal-liquefaction products and an indication of the degree of hydrogenation of the coal; (7) identification of the producer of any particular petroleum fuel and a fast and approximate characterization of this fuel; (8) a quick preliminary prediction of some important properties of gasoline and middle distillates, such as vapour pressure, distribution of octane number, distillation temperature, flash point, combustion characteristics, low-temperature properties, etc., and (9) a rapid preliminary prediction of some characteristics of fuel oil such as flash point, viscosity, tendency to segregation, stability and sulphur content. All of these data would be very useful in the quality control and in the examination of different commercial fuels.

ACKNOWLEDGEMENT

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