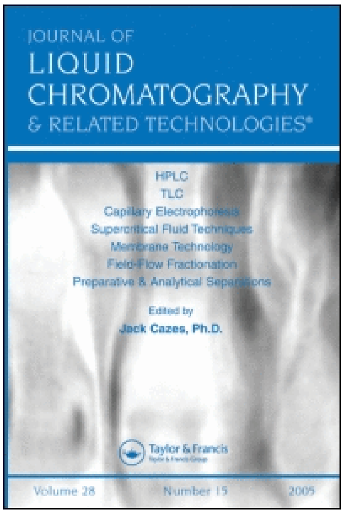

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CHARACTERIZATION OF A ROAD ASPHALT BY CHROMATOGRAPHIC TECHNIQUES (GPC AND HPLC)*

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ABSTRACT

There has long been a need to fractionate asphalt into as well-defined entities as possible. It is known that asphalt consists of a mixture of a very great number of components, too numerous and complex to isolate in the chemically pure state, in appreciable quantities. Consequently, attention has begun to turn towards fractionation of this binder into generic groups, the recombination of which, in varying proportions, should permit experimental evaluation of the influence of a particular fraction on one or another technological property (susceptibility, hardness, etc.) (1). It is also understood that the chemical structures of these generic groups, and their relative proportions, have a fundamental effect on the colloidal structure of asphalt (2,3), a colloidal structure responsible for rheological behavior (4,5). Molecular weight distribution has been shown to be a parameter of prime importance (6).

It is, therefore, of interest to compare two modern fractionatoin techniques - gel permeation chromatography (GPC), and high performance liquid chromatography (HPLC) - and to characterize, by means of the latter, the fractions of bitumen isolated by the former. Only the key experimental results are given in this paper. Their interpretation, aimed at a deeper knowledge of the physico-chemical structure of asphalts in connection with their colloidal structure and their rheological behaviour, will no doubt require further long experiments with other samples of different origin.

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PREPARATION AND CHARACTERIZATION OF FRACTIONS BY GPC

Choice of asphalt and preparative fractionation

A single type of asphalt was used in this experiment, namely a straight-run asphalt with 80/100 penetration, obtained from a Safaniya crude. Preparative fractionation was performed with a Chromatoprep instrument (Waters Associates, Milford, MA, USA) fitted with two columns 120 cm long and 6.5 cm external diameter filled with Styragel (polystyrene gel cross-linked with divinylbenzene) of particle size 37 to 75 μm and porosity 10^3 and 10^4Å. The sample was introduced as 80 ml of a 10% w/w solution in chloroform, and fractionation carried out by recovery of the eluate every 120 ml. Each fraction was then evaporated and dried, under vacuum, to constant weight. Twenty-three fractions were thus isolated, of which a dozen, judged to be the most representative and numbered from 18 to 7, were used for the remainder of this work.

Characterization of fractions by analytical GPC

The distribution of molecular sizes in the fractions was determined by analytical GPC under the following conditions:

Instrument: Waters Model 244, with a Model 6000 pump, U6K injector, R-401 differential refractometer and a UV absorbance detector operated at 350 nm.

Columns: Two micro-Styragel columns (10^3 and 10^4 Å), length 30 cm and external diameter 1 cm.

Solvent: Tetrahydrofuran at 3.5 ml/min flow-rate.

Injection: 15 μl of 2% solution, i.e. 0.3 mg.

The chromatograms, obtained with a differential refractometer detector, of fractions 7 to 18 are reproduced in Figure 1. This enabled us to assess the efficiency of the fractionation, and to appreciate the low dispersity of samples which were to be characterized by HPLC. We also see that fractions of large molecular size (fractions 7, 8 and 9) do not give a single narrow peak in analytical GPC, but instead, a large peak near the high weights (distribution coefficient K_d from 0.3 to 0.4), and a second less intense peak near the low

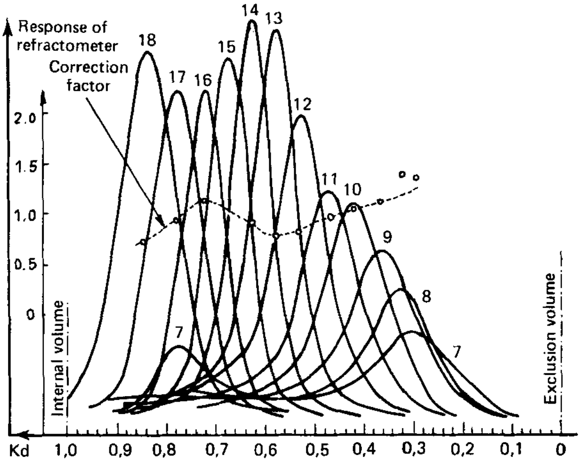

Fig. 1 - Characterization of fractions from preparative GPC by analytical GPC (refractometric detector).

weights. This observation is probably related to the dissociability of heavy fractions already observed in asphalts (7). Actually, the preparative fractionation was carried out at a relatively high concentration (15% on injection and of the order of 0.4% on elution) at which entities are expected to be associated. The concentration of the eluate in analytical GPC is about twenty times lower, which causes partial dissociation of associated aggregates eluted in preparative GPC. Figure 2 shows the chromatograms obtained by UV detection.

Characterization of the asphalt by analytical GPC

With the preceding chromatograms, we can construct correction curves for the two detectors. The corrected chromatograms are given in Figure 3. It is seen that they are very similar to one another (which confirms that the basis for the correction method is sound) except near the large molecular sizes, for which the determination of a correction coefficient becomes hazardous owing to the dissociability of the species involved. We shall therefore assume that the real gel permeation chromatogram for the asphalt (quantity of material a func-

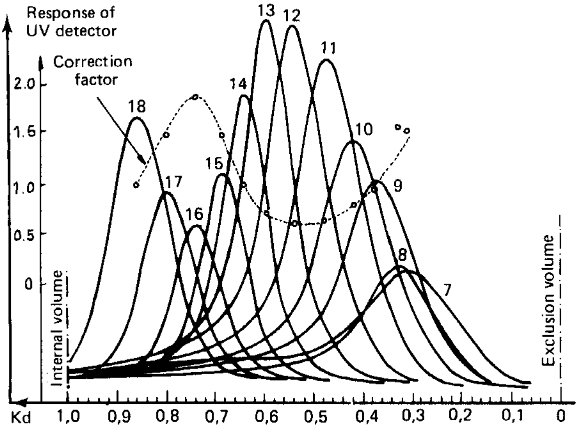

Fig. 2 - Characterization of fractions from preparative GPC by analytical GPC (UV detector at 350 nm).

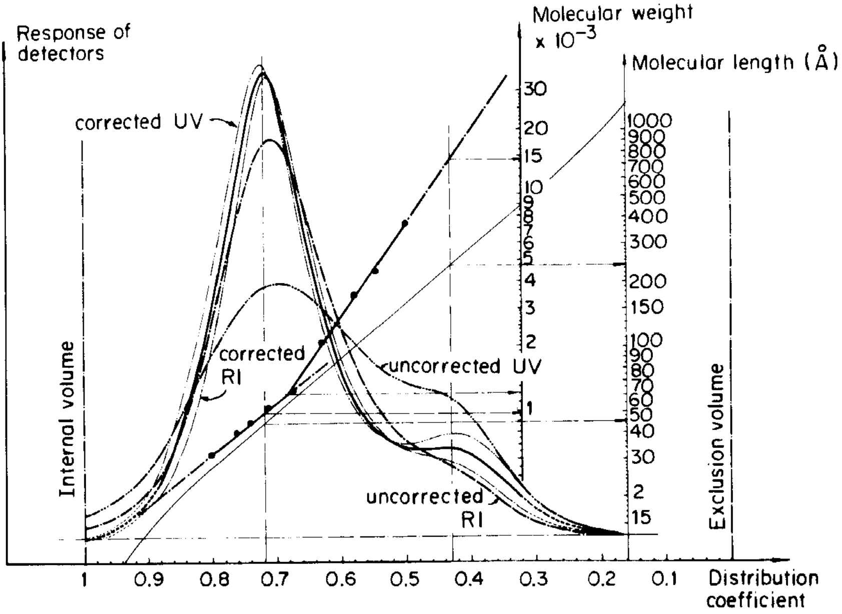

Fig. 3 - Corrected GPC chromatograms of an 80/100 straight-run asphalt and calibration curves.

tion of the elution volume) corresponds to the average of the two corrected curves (solid black line in Figure 3).

We also see, in this figure, as a thin line, the calibration curve of molecular length as established by means of reference polystyrenes and standard alkanes. This calibration curve makes it possible to assign an order of magnitude to the molecular size at any point on the chromatogram. Of particular note is the fact that there is a distribution of molecular sizes in a 80/100 straight-run road bitumen which is bimodal, the first population being centered on 45 Å and the second at about 240 Å.

Finally, number-average molecular weights ($\bar{M}_n$) were determined by vapour pressure osmometry in benzene for the narrow fractions from preparative GPC; with these data it was possible to construct the calibration curve of molar weight (marked as a thick line). It should be noted that the experimental points lie on two straight segments. In the lower part of the curve, the molecular weights measured are "real" molecular weights because, in this region, the solutions have the properties of ideal solutions (such as may be studied by viscosimetry). On the other hand, for fractions of large size, solute-solute interactions become significant at the concentrations used. The determination thus leads to "apparent" molecular weights which include the effects of a certain degree of association. The transition between these two regions corresponds to a molecular weight of the order of 1,200.

General Comments

The complete GPC analysis of an asphalt thus reveals a very large, narrow distribution population of hydrocarbons centered at about 45 Å, which corresponds to a molecular weight of the order of 1,000. Beyond this value, we may characterize a second series of compounds for which any measurement becomes very tricky because of an association process that depends heavily on the concentration. The values estimated at the peak maximum are 240 Å for the molecular weight. For the heaviest fractions, the apparent molecular weight may be as high as 100,000. Finally, the structural factor (ratio of molecular weight to molecular size) is of the order of 23 in the region where it can be determined; this is in good agreement with the assumed chemical structure for the oil fraction in asphalts.

CHARACTERIZATION OF FRACTIONS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

Characterization by means of liquid chromatography may be carried out with two types of support, i.e. either on packing of very low polarity, generally obtained by grafting aliphatic chains (C_{18}) on to silica, or on highly polar supports such as silica gels.

In the first case, the solute is distributed between the mobile phase and the hydrocarbon that is chemically attached to the support (stationary phase). This could thus be described as liquid-liquid partition chromatography, or reverse-phase chromatography. Although this technique is generally very efficient for analysis of compounds which are not extremely polar, it requres the use of solvents of very high polarity (in order to displace the partition coefficient in the direction of passage of the solute into the stationary phase), such as methanol, ethanol or water which are not, unfortunately, very good solvents for asphalt. The choice of a good solvent (for example, tetrahydrofuran) leads to too weak a retention for the fractionation to be efficient, and to results which are not very reproducible and, thus, difficult to use.

In the case of silica packing, the adsorptive properties of polar substances are used to accomplish a separation. The weaker the polarity of the solvent and the greater that of the solute, the stronger will be the adsorptive effects. For identical solute polarity, adsorption increases with molecular weight. The chromatographic fractionation is thus begun with a solvent such as hexane, which permits elution of non-retained saturated compounds and then of compounds of low polarity such as mono, di and polyaromatics. The more polar solutes are gradually taken off the column by continual modification of the mobile phase properties (gradient elution). This technique is better suited to the characterization of bituminous compounds than reverse-phase chromatography insofar as it permits analysis of a range of solutes which may vary very widely in polarity.

Whereas asphalts consist of mixtures of different molecular sizes and structures, much too complex for liquid chromatography to be able to fractionate all components, we can only hope to separate various groups or classes differing from each other in their chemical structures and functionalities.

Analytical Conditions

A Waters Model 244 liquid chromatograph was used (Waters Assoc., Milford, MA, 01757), equipped with two M6000 pumps, M660 solvent programmer, U6K injector, and M440 UV absorbance detector.

Column: 30 cm length, 0.95 cm O.D., filled with 10 micron porous silica.

Solvent Program: Initial solvent was either pure hexane (for fractions 18 to 11) or a hexane/THF mixture (for fractions 10 to 7) depending upon the solubilities of the fractions to be analyzed; final solvent was 100% THF. Flow-rate was 1 ml/min. Initial solvent was maintained for 20 min. after sample injection (5 μl of a 2% solution, i.e., 0.1 mg). Then a linear gradient was run, from initial to final solvent, for 20 minutes. Elution was completed where necessary, with 100% THF.

Experimental Results

Figure 4 shows the position of fractions from preparative GPC relative to the analytical chromatogram of the initial asphalt. These fractions are arbitrarily arranged into three groups. The first group (from 18 to 15) consists of fractions of low molecular size, the second (14 to 11) of fractions situated between the two maxima of the differential curve, and the third (10 to 7) of fractions of large molecular size.

The chromatograms of the fractions in the first group are reproduced in Figure 5. For all these fractions, chromatography leads to elution in two distinct blocks - one for pure hexane until elution of nitrobenzene, used as internal reference, and which corresponds to substances which are not polarized or very slightly polarized (polarity less than nitrobenzene); and the other,

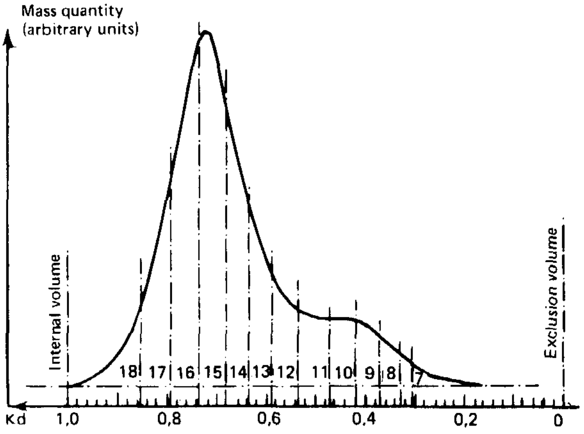

Fig. 4 - Position of fractions relative to the GPC chromatogram of the asphalt.

eluted by the solvent gradient, corresponding to substances for which the polarity is greater than that of the internal reference. In the first block we see, going from fraction 15 to fraction 18 i.e. for decreasing molecular size, a shift of the peak maximum to stronger polarities. This increase of affinity for silica gel with apparent decrease of molecular weight may be due to several structural characteristics, such as:

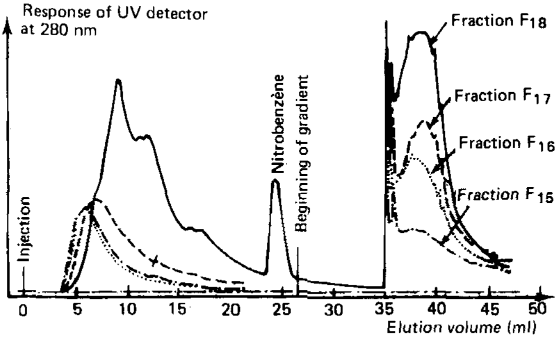

Fig. 5 - HPLC chromatograms of fractions 18 to 15.

-Increase in the number of heteroatoms such as nitrogen, sulphur and oxygen which induce greater polarity,

-increased aromaticity, either by increase of the degree of polycondensation represented by the relative amount of di, tri, and polyaromatic compounds, or by decrease in the amount of substitution by aliphatic chains.

In the second block we observe, in all cases, rapid elution of certain compounds, then an envelope exhibiting shoulders and even some peaks (fraction 16). We also observe a relatively rapid return to the base line at an elution volume of 17 to 18 ml after the beginning of the gradient.

The chromatograms of fractions 14 to 11 are given in Figure 6. They were obtained under the same operating conditions as for fractions 18 to 15. In this group, we observe a very clear decrease of the area under the first block, an area which tends practically to zero in the case of fraction 11. As for the area under the second block, this increases regularly with molecular size. An increasingly pronounced shoulder is to be seen near 12 to 13 ml after the beginning of the gradient. This shoulder makes it possible, for this second, block, to define three groups of products as a function of elution volume. The

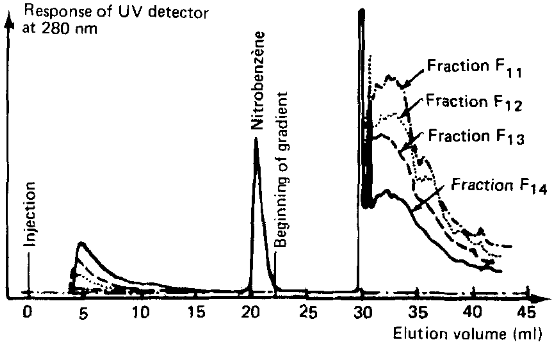

Fig. 6 - HPLC chromatograms of fractions 14 to 11.

first is eluted for a volume less than 35 ml, the second for a volume between 35 and 40 ml and the last for a volume greater than 40 ml.

The chromatograms for fractions in the third group (10 to 7) are obtained by beginning elution with a hexane-THF mixture. They are given in Figure 7 (fraction 11 was reinjected under these new conditions). We again observe a decrease in the area under the first block, with the number of the fraction which, to a first approximation, implies a decrease in the amount of compounds that are sufficiently non-polar to be eluted under these conditions. Fraction 7 apparently falls outside of this trend; in fact, its behaviour confirms the phenomenon of dissociation already observed in analytical GPC. As for the second block, it becomes much more complex than in the preceding cases. We also see, without being able to explain it at the present time, that the shape of this block varies depending upon the fraction injected.

Comments

The presence, in certain chromatograms, of preferential peaks (notably for the fractions of high molecular weight) leads us to enquire into the technical reasons for their appearance. It is a case of the chromatography of specific

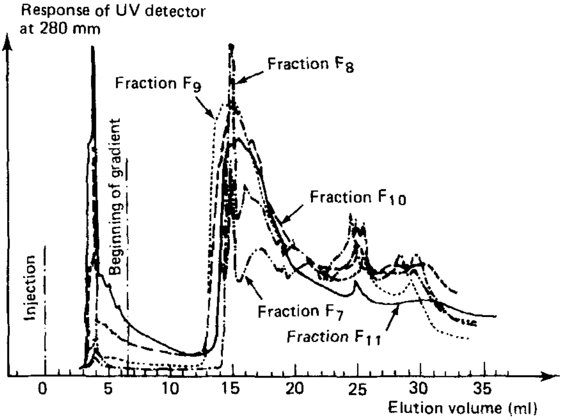

Fig. 7 - HPLC chromatograms of fractions 11 to 7.

isomolecular compounds having a definite chemical structure, or of a secondary phenomenon related to the composition of the products subjected to analysis and to the technological conditions under which this characterization is carried out.

Let us note, first of all, that the width of these peaks is of the same order of magnitude as that of a non-retained compound. It would therefore appear that the only contribution to their broadening is that of the instrument (dead volume of the colume and tubing), which does not completely exclude the hypothesis of chromatographic elution of a particular entity, but strongly reduces the probability of it (insofar as the process of chromatography makes its contribution to broadening of the signal).

The second explanation, which seems to us the most plausible, is based on the hypothesis of introduction into the system not of individual molecules in an ideal solution, but of a complex solution containing a certain number of associated forms. These agglomerates would behave like individual molecules and would be fractionated chromatographically as such, as long as the dielectric constant of the solvent remains below a limiting value corresponding to that which is required to support their dissociation. From this value on, and for this exact value, there would be dissociation of the aggregates and quasi-punctual liberation of "molecules" not retained on the gel. This hypothesis is not in contradiction with the fact that these peaks appear at constant retention volumes (and thus for a well-defined polarity) from one fraction to another.

CHARACTERIZATION BY HPLC OF MALTENE FRACTIONS ISOLATED BY ADSORPTION LIQUID CHROMATOGRAPHY

Although the characterization of bituminous compounds by HPLC is relatively recent, much work has been carried out on the fractionation of asphalt by adsorption chromatography either on silica gel or alumina. But this separation is only very rarely applied to untreated asphalt, and one generally begins by removing from the latter the fractionation insoluble in heptane, asphaltenes, preparative chromatography then being applied to the soluble fraction, known as maltenes. The classical chromatographic processes for fractionating maltenes generally lead to three fractions of increasing polarity, these being known as saturated oils, aromatic oils and resins.

It seemed of interest to us to examine, by HPLC, the chromatograms of these various fractions and to compare the results with those obtained in the characterization of the fractions from preparative GPC. Following separation of the asphaltenes, the maltenes were fractionated on alumina under operating conditions derived from the Hubbard and Stanfield method (8). This involves filtration of the heptane solution and evaporation to give the aliphatic and naphthenic saturated oils (fraction F_1), then desorption of the aromatic oils with benzene (fraction F_2) and finally of the resins (fraction F_3) by a benzene-methanol mixture containing 20% methanol.

Before their characterization by HPLC, the fractions F_1, F_2, F_3 and the asphaltenes were analysed by analytical GPC under the usual conditions using dual detection; their chromatograms are reproduced in Figure 8. It is interesting to note, on one hand, that the saturated oils contain practically no aromatic constituents, as the response from the UV detector is nil for this fraction; and on the other, that the resins do not occupy a specific narrow region of the chromatogram but consist of a mixture of molecules of all sizes. Finally, the aromaticity, such as it may be estimated by assessment of the area under the peak from the UV detector, also increases with polarity.

We have also marked in the GPC chromatograms, obtained by differential refractometry, the various fractions from preparative GPC. Comparison of all these chromatograms shows:

- That the aliphatic oils are mainly present in fractions 17, 16, 15, and 14, with a maximum in fraction 16;
- that the aromatic oils are present, to all intents, only in fractions 18 to 12, these also having a maximum in fraction 16 - in this case, the dispersity is higher and covers that of the preceding fraction;

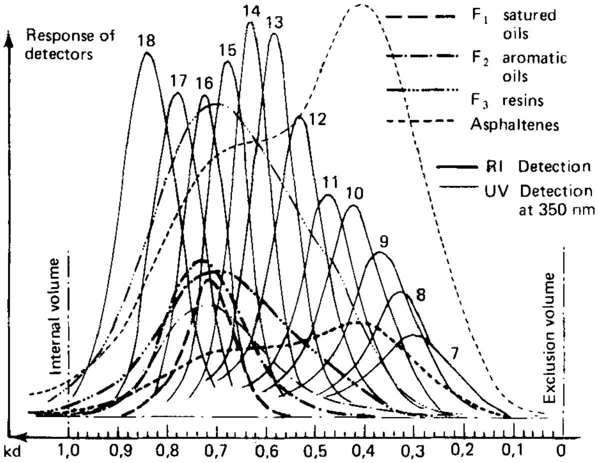

Fig. 8 - Chromatograms of asphalt fractions.

-that the resins are distributed in fractions 18 to 9 with a maximum in fraction 15. This result seems to us important insofar as it shows that, although the average value of molecular weight is shifted towards the highest values (relative to the preceding two fractions), the range of distribution is very broad, in particular towards the low molecular weight end;

-finally, that asphaltenes may be found in practically all the fractions, excepting 18, and that fractions 8 and 7 contain practically nothing but asphaltenes.

These three fractions, F_1, F_2 and F_3, were injected, for HPLC, under the same conditions as the lightest fractions from asphalt; the chromatograms are given in Figure 9. This confirms the observation, already made by GPC, of the saturated nature of fraction F_1, as the latter gives only a very small signal in the UV at 280 nm in the region of unretained products. The aromatic oils give rise to a relatively intense first band and to a very weak second band; whereas the resins lead to the inverse result, but with a complete desorption

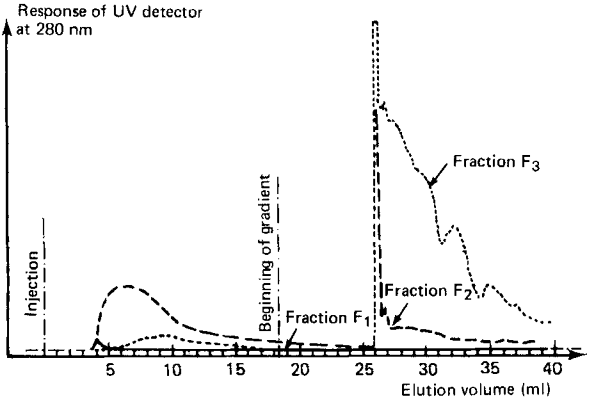

Fig. 9 - HPLC chromatograms of fractions isolated by adsorption chromatography on alumina.

of the second band which is relatively rapid compared to that which had been observed for the heavy fractions (9, 8 and 7) from preparative GPC.

The analysis of fractions isolated by adsorption chromatography therefore makes it possible to assign, to each large region of the HPLC chromatogram of asphalt fractions, a label derived from much more traditional methods of characterization by decomposition into generic groups:

- The first block is indicative of the oil part of the mixture if the initial solvent is pure hexane. It should be noted that, because of the specificity of UV detection, this signal only takes account of the level of aromatic oils, as saturated derivatives are not detected. If the solubility properties of the fraction to be analysed require isocratic elution by a hexane-THF mixture, it will also correspond to elution of part of the resins;
- in all cases the second block, eluted by the solvent gradient, must be attributed mainly to resins for the lowest elution volumes, and then to asphaltenes, the division between the two groups being rather ill-defined.

CONCLUSION

The simultaneous use of gel permeation chromatography (preparative and analytical) and high performance liquid chromatography, makes it possible to elucidate an important number of compositional characteristics of bituminous binders; this can be done with a degree of precision and reproducibility which could never before be attained with traditional fractionation techniques. Moreover, one of the major advantages of these modern analytical methods is in their low response time.

Analysis, by analytical GPC, of narrow fractions isolated by preparative GPC shows, for fractions of large molecular size, a bimodal distribution which indicates the dissociability of these species. This experimental result proves that the constituents of the heavy fractions in asphalt still exhibit strong interactions at concentrations usually considered low enough to destroy all solute-solute associations. This non-ideal behaviour in solutions of fractions of large molecular size explains the discontinuity of the molecular weight calibration curve - below the transition region (corresponding to a number-average molecular weight of the order of 1,200), the values measured by vapour pressure osmometry are true molecular weights, whereas above, they are apparent weights which take into account a rather ill-defined degree of association.

Still on the subject of analytical GPC, the experimental determination of the correction curves for the response of the detectors shows how delicate their interpretation may be, in terms of unit mass concentration, (hence the necessity for their correction), and this is true even in the case of the differential refractometer which is generally considered to be a universal detector.

As for HPLC, this reveals a quasi-continuity in the distribution of chemical funtionality as a function of molecular weight. It should be noted that this distribution may be compared to much more traditional ideas, which attempted to characterize the binder by fractionation into generic groups such as saturated oils, aromatic oils, resins and asphaltenes. It is relatively easy to assign to each block the HPLC chromatogram, a label employing this terminology, and thus facilitate the transition between traditional fractionation techniques of a preparative nature and high performance analytical chromatography. However, it should be noted that the latter goes much further, as each generic group is itself characterized by a detailed chromatogram which enables one to specify, even within this fraction defined as such by traditional methods, the distribution of functionality of its constituents. The results, moreover, cast doubt on certain a priori assumptions concerning the molecular weights of the generic groups. In fact, although it has been verified that the average molecular weights increase from oils to asphaltenes via the resins, it has been shown to be no less true that the constituents of lower molecular weight in asphalts do not belong to the oils, but to the resins.

It is certain that this study is only a first step in the application of HPLC with a view to obtaining a deeper knowledge of molecular weight-functionality relationships in constituents of asphalt. Much work remains to be done, especially in the area of characterization of saturated compounds and of the relationships to be established, as in GPC, between the response of the detector and the quantity of material passing through it. But there is every indication that the information to be obtained will contribute, at least in part, to clarify the difficult problem of the structure of asphalt, its colloidal nature and its stability.

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