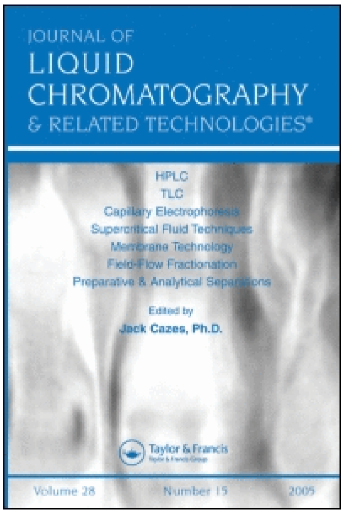

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Characterization of Bituminous Compounds by Gel Permeation Chromatography (GPC)

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CHARACTERIZATION OF BITUMINOUS COMPOUNDS BY GEL PERMEATION CHROMATOGRAPHY (GPC)*

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ABSTRACT

Gel permeation chromatography is applied to the qualitative and quantitative characterization of asphalt, asphaltenes and maltenes. The nature of their molecular size distributions, micellar dimensions, and degree of aromatic polycondensation are described. The resultant data are used to provide insight into the nature of associative processes involving these materials.

INTRODUCTION

One of the aims of research on the chemical or physico-chemical characterization of asphalts is to establish relationships between compositional parameters, their colloidal structure and technological properties.

Much work has been done to separate asphalts into as well-defined fractions as possible, the recombination of these enabling one to assess the relative influence of the various fractions on the rheological behaviour of the binder.

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Research workers have performed more and more complex fractionations based on the fundamental operations of distillation, extraction, chromatography and selective precipitation.

These techniques are open to certain criticisms, especially when the asphalts are subjected either to prolonged heating (in the case of distillation), or to an interphase distribution related to a partition coefficient leading to a fractionation that depends upon the composition of the sample (case of extraction techniques and chromatography).

GPC, to a first approximation, circumvents these criticisms insofar as it gives a fractionation depending only upon molecular size, whereas all the other techniques involve both the functional nature and the molecular weight.

FUNDAMENTAL IDEAS CONCERNING GPC

GPC differs from other types of liquid chromatography:

- separation takes place according to molecular size,
- large molecules are eluted before small ones,
- fractionation takes place with a quantity of solvent which is less than one column volume.

This type of fractionation is obtained by passing the mixture to be analyzed over a porous medium. The large molecules, due to their size, cannot penetrate the pores of the gel and are eluted first, whereas the small molecules do penetrate the gel and are eluted at greater volumes.

Figure 1 displays the magnitudes of the fundamental parameters. These are the exclusion volume, i.e. the elution volume for large molecules which do not penetrate the pores and the internal volume, i.e. the elution volume for a small molecule which penetrates right through the pores. We may imagine that each molecule analyzed shall have access to some fraction of the volume of the pores, a fraction known as K_d, the distribution coefficient. (1). A practical method of calibration consists of establishing a correlation between this dis-

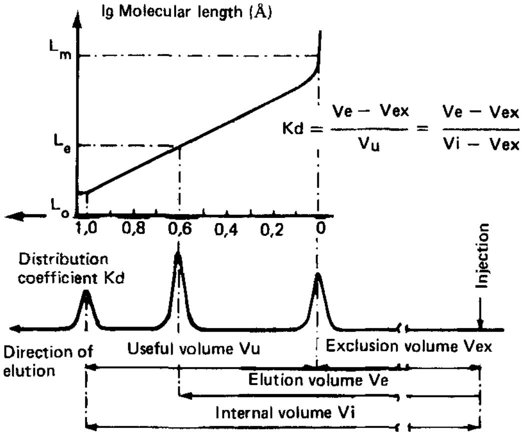

Fig. 1 - Construction of calibration curve.

tribution coefficient, and the logarithm of the molecular size. The relation found is often linear. The advantage of such a calibration lies in the fact that it is almost independent of the flow and of the temperature within practical experimental limits.

We should, however, mention that matters are not always as simple as this, and that the elution volume of a given compound may be shifted:

-either to lower volumes (and therefore to greater molecular sizes), which implies *solute-solvent or solute-solute association*.

-or to higher volumes, in which case the fundamental process of GPC is complicated by superposition of an adsorption phenomenon.

Without going into the detail of the technology of the GPC instrument, we shall briefly mention the supports used. The most common consist of polystyrene gels cross-linked with divinylbenzene. In their "traditional" form, their particle size lies between 37 and 75 micrometers. In view of geometrical dimensions of column, and necessity of having four columns so as to obtain a sufficient number of "theoretical plates", an analysis with a traditional packing requires about four hours and 250 ml of solvent (in general, freshly distilled THF, tetrahydrofuran). It is this packing which was used in the first tests, but we rapidly replaced it with a much more recent material of identical stucture, but with particle size 10 ± 1 micrometer. For an identical performance, this brings the analysis time down to less than ten minutes and the volume of solvent down to less than 30 milliliters per analysis.

QUALITATIVE ANALYSIS WITH A TRADITIONAL PACKING

We first present qualitative results obtained with a traditional packing. Figure 2 shows calibration curves for various systems used. In the case of the traditional support, because of the combination of various porosities used,

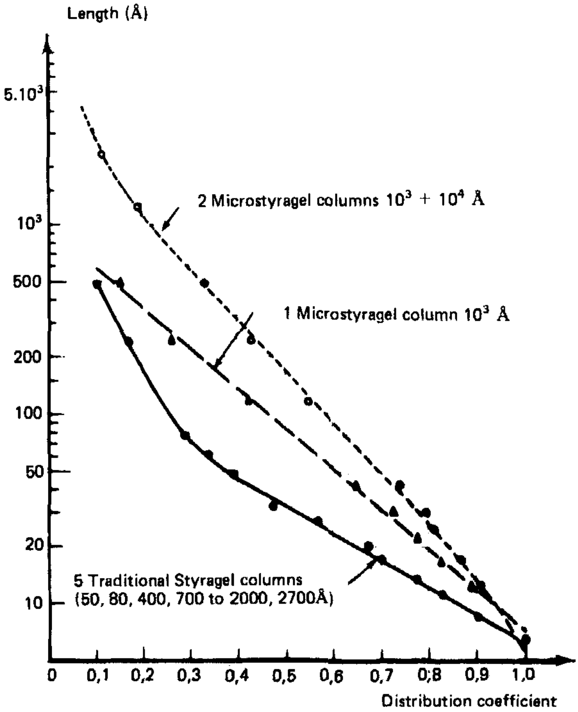

Fig. 2 - Calibration curves

this curve is not linear and the system, which performs best in the range 10 to 50 Å may be operated up to about 500 Å.

Figure 3 displays chromatograms of an 80/100 asphalt, its asphaltenes and its maltenes. Detection was by means of a differential refractometer. The response of this detector (RI) is proportional to the concentration for a given elution volume, although we shall not specify the relation between this response and the quantity of material passing through the detector. We see that the GPC chromatogram of this asphalt is a distribution spectrum of molecular sizes, and that it demonstrates the distributional continuity in the sizes of molecules constituting the binder. The distribution in Figure 3 may be considered as bimodal, the first population being centred at 40 to 50 Å and the second at 200 to 300 Å. It may also be seen from this figure that fractionation into asphaltenes and maltenes cannot be considered to be a separation by weight. In fact, although the average molecular size of the asphaltenes is considerably greater than that of the maltenes, it is still no less true than that practically the whole range of molecular sizes present in asphalt is found in the asphaltenes. This points out the ambiguity of such a fractionation,

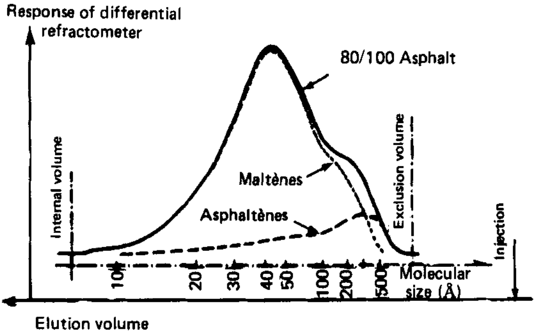

Fig. 3 - GPC chromatograms of an asphalt and its constituents.

which results from differences in both the molar weight and the molecular shape.

Figure 4 gives the chromatograms of two asphalts of the same penetration (80/100), one obtained by air blowing and the other via direct distillation. It gives an idea of the difference in molecular size distribution which results during the production process; blowing leads to a slight increase in the second population centered at 200 to 300 A, and to a slight decrease in the polydispersity of the two populations.

Chromatograms of asphalts of similar origin but different penetrations are given in Figure 5. The decrease in penetration is accomplished by a diminishing of the first population, and a noticeable increase in the second.

QUALITATIVE ANALYSIS ON MICRO-PACKINGS

Characterization of asphalts

The preceding chromatograms are not particularly unique; identical results were previously reported by Altgelt and Snyder (2,3,4) who demonstrated the potential of GPC as an identification technique for bituminous compounds. The development of a micro-packing, which makes it possible to obtain a chromatogram in about ten minutes, led us to reconsider the problem. These new packings, due to their very low response time which minimizes the problems of

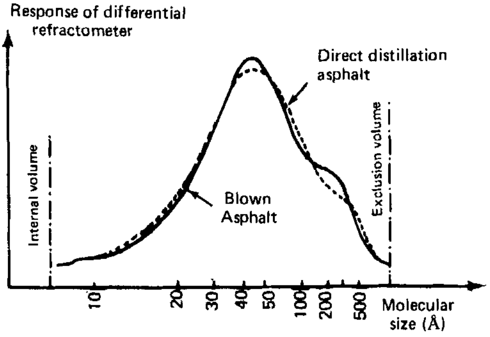

Fig. 4 - GPC chromatograms of two 80/100 asphalts.

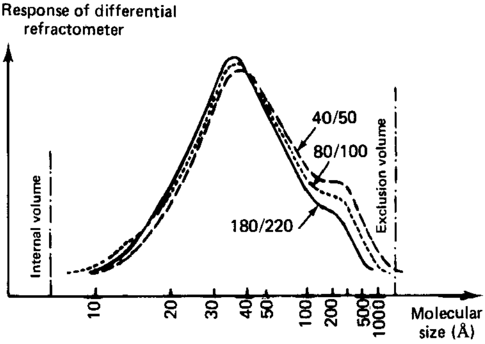

Fig. 5 - GPC chromatograms of three asphalts of similar origin.

drift and background noise, and due to the small quantities of solvent employed which permit injection of much more dilute solutions, make it possible to study, experimentally, the influence of the concentration of the solution injected and, thus, to understand association phenomena. Also, the use of an ultraviolet (UV) detector, continuously recording the optical density of the eluate at 254 or 350 nanometers, enabled us to either use dual detection, or to work exclusively in the UV with extremely dilute solutions, this owing to the very high extinction coefficients of the components of bituminous compounds. The 254 nanometer wavelength may be considered to be relatively specific for all aromatic structures, whereas UV detection at 350 nanometers infers a certain degree of polycondensation.

The first GPC analyses of bituminous compounds on microparticles were carried out with a single column of porosity 10^3Å for which the calibration curve is shown in Figure 2. It may be seen that the useful range of this column is the same as that for the preceding one, i.e. about 10 to 500 Å; but, in contrast to that which is found with traditional columns, this curve is remarkably linear (this linearity is due to homogeneity of distribution of the pores in the packing).

Figure 6 shows chromatograms of the same asphalt injected at various concentrations between 10 and 0.125% (detection being by means of differential refractometer). We see that, in this specific case, concentration does not appreciably alter the shape of the chromatogram except in the small size region where, at low concentrations, a negative signal near 13 Å and and a positive signal near 10 Å appear. These disturbances, which at first caused some concerns, may be interpreted in the following way:

-positive peak at 10 Å appears only with solutions having been exposed to light; it has been identified as the dimer of THF;

-negative peak at 13 Å corresponds to the water retention volume; we believe that this is due to water actually held by the asphalt, and which is not liberated except at high dilution.

Chromatograms of the same asphalt, shown in Figure 7, still as a function of concentration, were obtained with the UV detector at 254 nanometers (we also reproduce the chromatogram of the 10% solution obtained by refractometry). As this detector is much more sensitive and stable, we were able to go to a concentration as low as 0.015%; here we see the chromatogram change in the re-

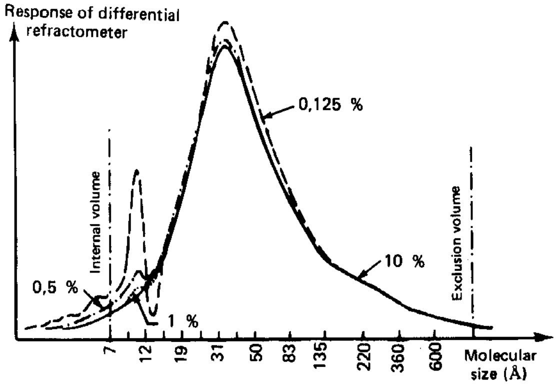

Fig. 6 - GPC chromatograms,obtained by differential refractometer, of a 40/50 asphalt at various concentrations.

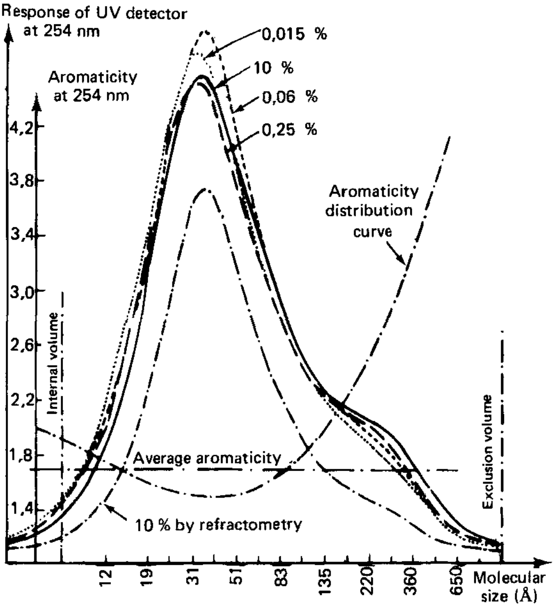

Fig. 7 - GPC chromatograms, obtained by UV detector, of a 40/50 asphalt.

gion of the second population centered at about 200 Å, the latter decreasing with increasing dilution. Further, if we compare the responses of these two detectors for the same injection, and if we assume that the response of the differential refractometer is proportional to the weight of sample, and that the response of the UV detector is proportional to the number of aromatic rings, we may arbitrarily define an overall aromaticity of sample as the ratio of area under the peak given by UV detector to area under the peak given by refractometric detector. Distribution of this aromaticity is then approximated by the ratio, at each point, of height of UV detector signal to height of RI signal. It is seen that aromaticity thus defined describes a curve which is parabolic, and which passes through a minimum for the average molecular size of the first population.

Characterization of asphaltenes

In view of the importance of interaction problems in asphaltenes, it appeared to us of interest to study, as for asphalt, the influence of concentration of the injected solution on the shapes of the chromatograms, this being in the case where these interactions are strongest i.e. the case of asphaltenes from a blown asphalt. The shapes of these chromatograms are shown in Figure 8. First, we see a considerable spread of molecular sizes, ranging from several angstroms to near the exclusion limit of the column used. It is seen that the chromatogram passes through a maximum at a molecular size that is slightly less than the exclusion limit. We do not, therefore, have favourable conditions for a detailed analysis; this would require the use of columns with higher porosities.

Experimentally, the chromatograms of the 3, 4, and 5% solutions may be superimposed. From this value on towards decreasing concentration we observe that, in addition to the appearance of a negative peak due to water, there is a noticeable decrease in the peak due to large molecules. This indicates that they probably undergo dissociation at increased dilution.

As in the case of asphalt, these experiments were also performed with UV detection at 254 nm; principal chromatograms are given in Figure 9. When the dilution increases, we see a decrease in the peak from compounds with large molecules (without being able to specify their dimension with the column used), and this continues until the concentration of the solution injected is of the order of 0.015% without the phenomenon leveling off at all. Also, we see that, while dissociation of asphaltene "agglomerates" enriches the entire distribution spectrum for the lowest molecular sizes, this enrichment is particularly pronounced in the 250 Å region. These observations experimentally confirm a structural model for asphaltenes proposed by Dickie and Yen (5,6), in which asphaltene particles of about 250 Å group together to form agglomerates.

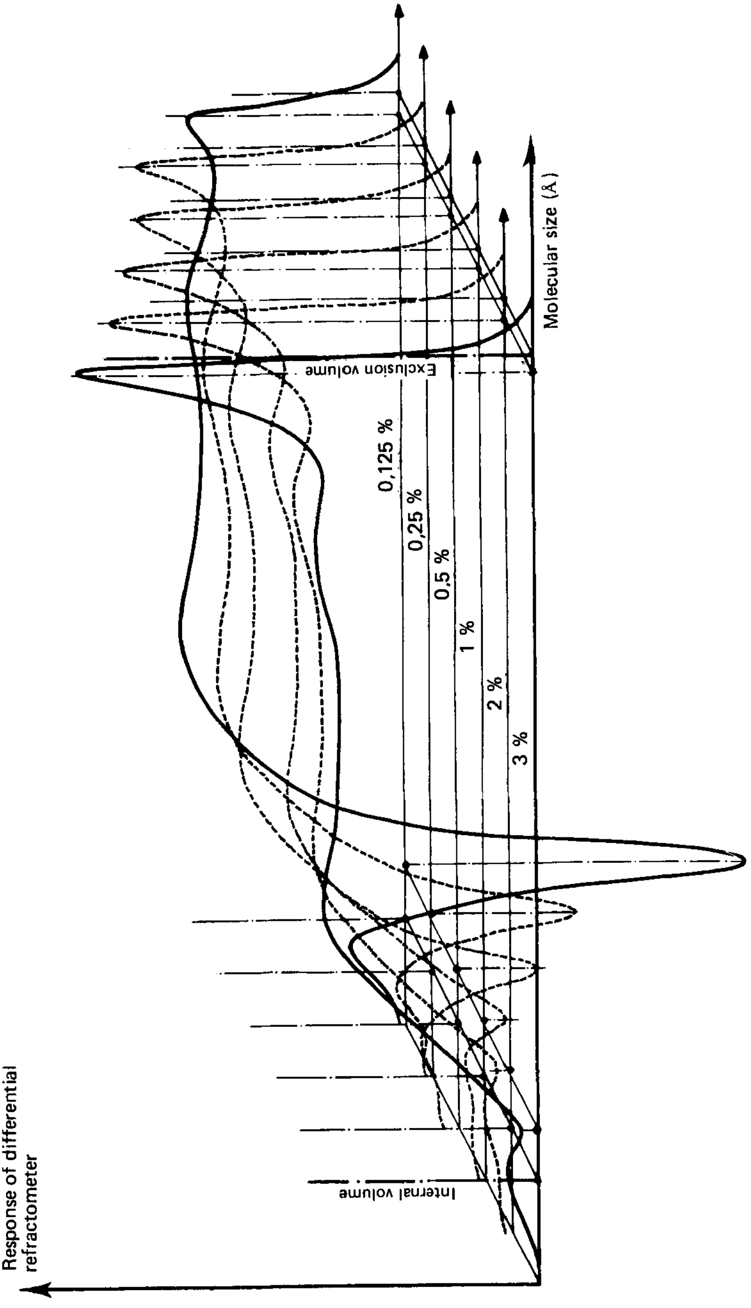

Fig. 8 - GPC chromatograms, obtained by differential refractometer of asphaltenes from a blown asphalt.

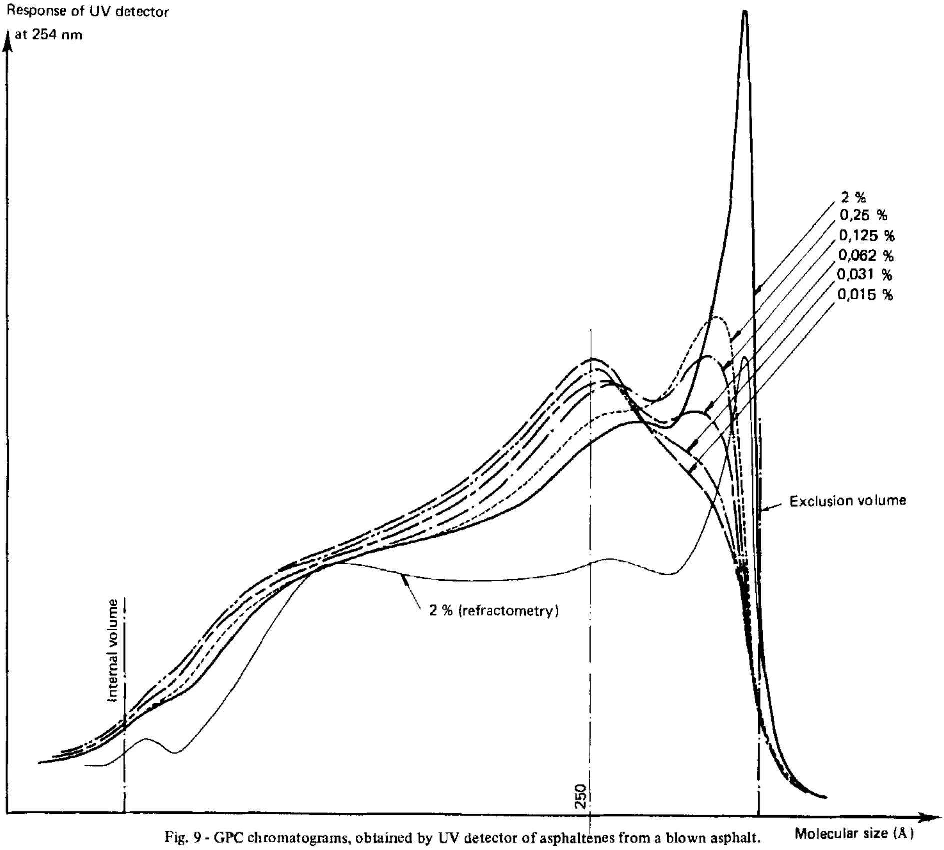

Fig. 9 - GPC chromatograms, obtained by UV detector of asphaltenes from a blown asphalt.

APPLICATIONS

The results described above appeared sufficiently promising for us to look at two specific applications involving asphaltenes. We added a second column of porosity 10^4Å to the column previously used. Figure 2 gives the calibration curve for this new set of columns. The addition of a 10^4Å column extended the region explored to about 3,000 Å.

Most workers are in agreement concerning the fundamental role of asphaltenes in determining the mechanical and rheological properties of asphalts; properties as important as thermal susceptibility or soil-gel transition phenomena depend on their quantity and chemical nature, as the work of Bestougeff, Dron, Morel and Voinovitch (7) has shown. Actually, the characterization of asphaltenes with respect to their effect on rheological properties requires a knowledge of two fundamental characteristics. These are the molecular sizes of the various populations and the nature of the interactions between these various groups of substances.

Characterization of asphaltenes of different origins

In a first set of experiments, we compared the chromatograms for four asphaltenes of different origin. This was done at two concentrations so as to determine, on one hand, the molecular sizes of the various species in the associated state, and on the other, to judge the importance of micellar interaction as a function of origin of samples. The chromatograms in Figure 10 were obtained using refractometric detection, at high concentration, for asphaltenes from a blown asphalt and an unblown one (7), and of "untreated" industrial asphaltenes washed with heptane in a soxhlet extractor.*

The first impression which emerges from examination of this figure is the similarity of distribution for the three samples from blown asphalts. In all cases we have the summation of three populations centered, respectively, on 40,

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*The manufacturing process for this asphaltenes is not revealed, but they would not be obtained by rendering the material insoluble in aliphatic hydrocarbons. Because of the manufacturing technique used, they contain about 30% of products insoluble in heptane.

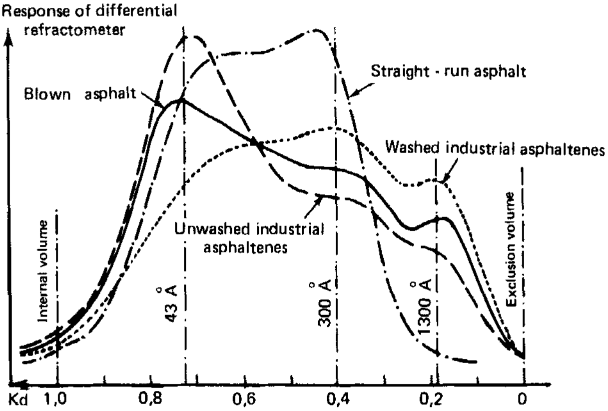

Fig. 10 - GPC chromatograms of asphaltenes.

300 and 1,300 Å, whereas the sample from an unblown, distillation asphalt is clearly distinct from the preceding ones by absence of the third population and the displacement of the other two.

Figure 11 shows chromatograms from the same samples, obtained with UV detection, for concentrations of injected solution of 5 and 0.2%. For asphaltenes from a blown asphalt, we confirm that dilution of the solution leads to a decrease in the population centered on 1,300 Å with a corresponding increase of the second population centred on 300 Å. The case of asphaltenes from a straight-run asphalt is rather special; dilution does not cause decrease of a given population with an increase in another, but, instead, there is a drift towards small sizes which implies a continual "departure" by molecules of all dimensions.

An interesting observation may be made concerning industrial asphaltenes. Although these, washed with heptane, behave like asphaltenes from a blown asphalt, the effect of dilution on untreated asphaltenes leads to quite a different result. The decrease in the third population no longer takes place with

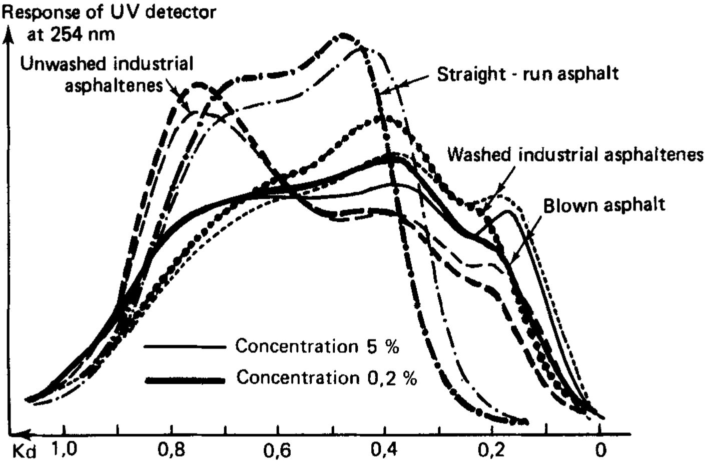

Fig. 11 - Effect of concentration on the UV chromatograms of asphaltenes.

a resultant increase in the second, but rather, there is an incresae in the first. This seems to indicate that, in this case, dissociation of agglomerates leads directly to the constituent molecules, and experimentally demonstrates the asphaltene-maltene adsorption equilibrium.

GPC applied to characterization of asphaltenes therefore experimentally demonstrates:

- that isolated asphaltenes form agglomerates which may be dissociated into micelles by simple dilution, the intensity of the phenomenon characterizing the force of the interactions;
- that the model of Dickie and Yen (5,6) for the structure of asphaltenes, i.e. agglomerates - micelles - unit sheets, is not directly applicable to asphaltenes from a direct straight-run asphalt.
- that the behavior of asphaltenes from a blown asphalt in solution in tetrahydrofuran is profoundly affected by the presence of a certain quantity of maltenes (of the order of 30%) in the presence of which the dissociation of agglomerates leads directly to the unit sheets.

Characterization of asphaltene fractions

In a second series of experiments, we characterized a certain number of asphaltene fractions which were obtained by selective precipitation from the industrial asphaltenes. This characterization, which is essentially qualitative, is approached from the dual viewpoint of molecular size distribution of the various species, and their associating ability.

First, we observed the behaviour of a 5% solution of asphaltenes in benzene on a quasi-analytical basis. Heptane was added, drop by drop, at ambient temperature, to 20 ml of benzene solution until flocculation began to occur. The precipitate was isolated by centrifugation after standing for one hour. This operation was repeated on the supernatant liquid and the final fraction recovered by complete evaporation of the solvent. The operating technique developed above was adapted to treat 20 g of sample in the form of four times 100 ml of 5% solution. Three fractions were thus obtained: F_1 = first precipitation; F_2 = second precipitation and F_3 = residue after elimination of the benzene-heptane mixture, representing respectively 48, 37 and 15% of product treated.

Untreated industrial asphaltenes (A_1), washed with heptane (A_2) and the fractions F_1, F_2, F_3 were characterized by GPC under the following analytical conditions:

Instrument: Waters Associates Model 244, with Model 6000A pump and U6K universal injector.

Columns: Two 30 cm columns, 7.9 mm I.D., packed with μ-Styragel of 10^3 and 10^4 Å, respectively.

Solvent: Freshly distilled tetrahydrofuran, at a flow-rate of 3.5 ml/min.

Detection: Differential refractometer and UV at 350 nm.

Quantity injected: From 0.5 to 0.03 mg.

Figure 12 shows chromatograms for various products at an injected size of 0.5 mg. The chromatograms obtained with the refractometer are marked in thin

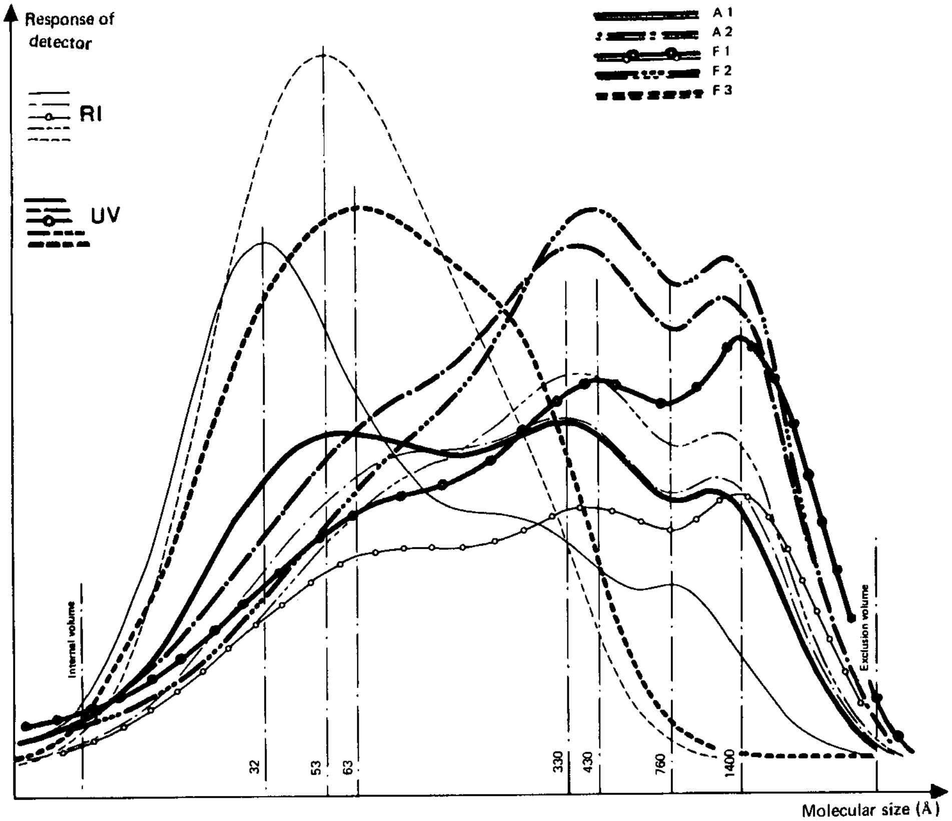

Fig. 12 - UV and Dr chromatograms of products A_1, A_2, F_1, F_2, F_3 for an injected quantity of 0.50 mg.

black lines, whereas those obtained by UV detection are marked in heavy lines. The quantitative interpretation (in abscissae) of this graph makes it possible to assign molecular sizes to the various species. It is seen that all the curves correspond to the summation of three distinct populations. For the first one, we find values ranging from 32 Å (maximum for chromatogram of A_1, refractometric detection) to 63 Å (maximum for UV chromatogram of F_3). For the second, sizes of maxima range from 330 Å to about 430 Å, whereas the third population corresponds to molecular sizes from 760 Å to about 1,400 Å.

We shall assume that the response of the refractometer is related to the quantity of material passing through the detector by a law which, in the case of asphalts and bituminous compounds, is far from simple. The UV detector at 350 nm, on the other hand, registers a certain degree of polycondensation. We may therefore interpret the chromatograms in Figure 12 in terms of distribution of polycondensed compounds, and judge the efficiency of washing industrial asphaltenes with heptane and of the fractionation of A_2 into F_1, F_2 and F_3.

Comparison of the RI and UV chromatograms of A_1 (untreated industrial asphaltenes) reveals an increase in the degree of polycondensation with molecular size, since the ratio of signals RI/UV increases from left to right. On the other hand, if we compare the chromatograms of sample A_2 (asphaltenes washed with heptane) with the chromatograms of untreated asphaltenes (A_1), we see that elimination of maltenes effectively reduces the first population with an increase in the two others. This is accompanied by an increase in the response coefficient of the UV detector and, thus, in the degree of polycondensation.

The chromatograms of samples F_1, F_2, and F_3 display the effect of selective precipitation. Fraction F_1 is very rich in compounds of large molecular size. The second fraction (F_2) is more centered on the second population, and the last one consists essentially of products in the first group. We also find, in the case of F_3, an inversion in the response coefficient of the RI detector relative to the response coefficient of the UV detector, the area of the peak under the latter becoming smaller than the area under the peak from the RI. This experimental observation implies that the level of polycondensed compounds is considerably lower in F_3 than in the other two fractions; this confirms that this type of fractionation incorporates both molecular size and chemical structure.

Figure 13 reproduces the UV chromatograms of various samples for injected quantities of 0.50, 0.125 and 0.03 mg. In all the cases examined, decrease

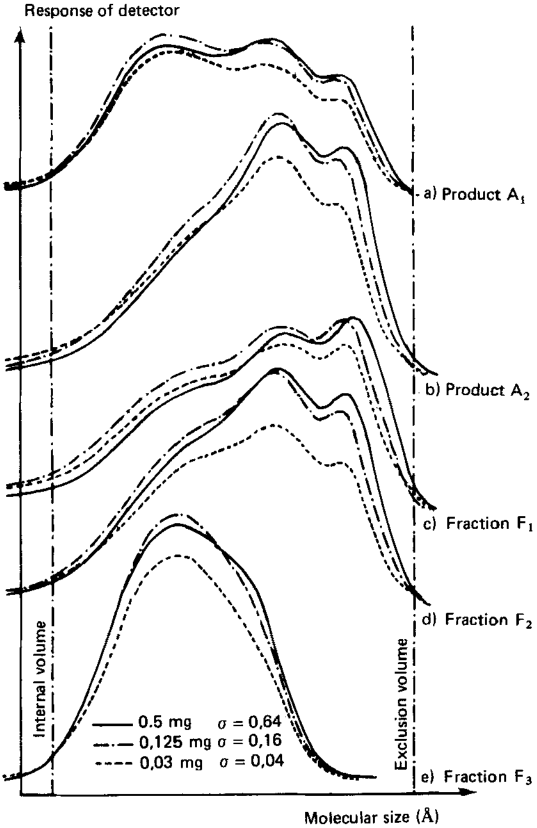

Fig. 13 - UV chromatograms.

of the quantity injected (which corresponds to a decrease in concentration of the solution issuing from the analytical system) causes a relative shift in the various populations towards smaller molecular sizes and thus in the direction of dissociation. Also, the area under the curve corresponding to an injection of 0.125 mg is not much different from the area under the curve corresponding to an injection of 0.5 mg, whereas for the last injection this area becomes very much less. Since the quantities injected are in a ratio of 0.25, the sensitivity of the detector is multiplied by 4 for each new injection. Whereas we verified that the detector was perfectly linear over the whole range of sensitivities, we deduce from this experimental observation that, although the first dilution does not appreciably affect the overall response coefficient of the sample in the UV at 350 nm, the second causes it to decrease. The observation of this dissociation, and this decrease of the UV response coefficient at 350 nm, proves:

-that it is very difficult to observe asphaltenes in the completely dissociated state, as the limit is evidently unattained even for an injected quantity of 0.03 mg, which corresponds, on leaving the columns, to a concentration of the order of 3×10^{-6} g%;

-that the process of association brings two types of interaction into play: one manifested by the differences in the chromatograms for injected quantities of 0.5 and 0.125 mg, and which does not affect the UV extinction coefficient at 350 nm; and another, which causes a decrease in this coefficient and which therefore concerns inter- or intramolecular structural parameters.

Finally, comparison of the various chromatograms in Figure 13 reveals, apart from differences in the molecular size distribution for the various samples, the modifications in behaviour which occur on dilution. Thus, although, in the case of sample A_1 (Fig. 13a), dissociation of the third population occurs, above all, to the enhancement of the first, the phenomenon is less well-defined in the case of washed asphaltenes (A_2, Fig. 13b). Here again, we find the problem, already mentioned, of the asphaltene-maltene equilibrium, and of the different behaviour of asphaltenes isolated from their original medium. In the case of fraction F_2 (Fig. 13d), dissociation of the third population takes place with enhancement of the second, whereas in the case of fraction F_3 (Fig. 13e) the dissociation, which is very feeble, leads to the disappearance of the second population and an increase in the first. The behaviour of fraction F_1

(Fig. 13c) seems more unusual insofar as the first dilution causes a complete shift of the chromatogram towards the small molecular sizes.

These fractions shall later be characterized with regards to their effect on the physico-mechanical properties of synthetic binders formulated with tetralin (8). It is impossible to forsee the results which will be obtained in this study, but they will shed some light on the importance of molecular size distributions of asphaltenes in the face of such phenomena such as, for example, the soil-gel transition.

QUANTITATIVE CHARACTERIZATION

GPC, applied to the characterization of bituminous compounds, undeniably constitutes a rapid and efficient test which makes possible comparison and identification up to the point of aromaticity distribution. The extraction, from these chromatograms, of the quantitative characteristics of number-average molecular weight and weight-average molecular weight as well as polydispersity, which constitutes the essential aim of GPC applied to the characterization of polymers, poses serious problems which were quite clearly defined by Snyder in 1969 (4).

A fundamental hypothesis in the quantitative treatment of GPC chromatograms of true polymers, involves an assumption that the refractive index increment, $n-n_o$, is linearly related to the concentration, and independent of the molar weight and, thus, of the elution volume. This makes it possible to postulate that, at any point on the chromatogram, the height of the signal from the detector (H_i) is directly proportional to the product of the number of molecules (n_i) by their molecular weight (M_i), i.e.

$$H_i = n_i M_i \qquad (9)$$

M_i may be deduced from the calibration curve by a structural factor Q characteristic of the homopolymer, viz:

$$M_i = QL_i$$

where L_i is the extended chain length of the polymer molecules at M_i. We may thus calculate $\bar{M}_n$ and $\bar{M}_w$, as well as the polydispersity (p) by means of the expressions:

$$\bar{M}_n = \frac{\Sigma M_i n_i}{\Sigma n_i} = \frac{H_i}{\Sigma (H_i/M_i)}$$

$$\bar{M}_n = \frac{\Sigma M_i n_i}{\Sigma n_i} = \frac{\Sigma H_i}{\Sigma (H_i/M_i)}$$

and $$p = \frac{\bar{M}_w}{\bar{M}_n}$$

In the case of asphalts, the index increment is not linearly proportional to the concentration, and is not independent of the elution volume for at least three reasons:

-presence of low molecular weight compounds leads, even in a homologous series, to the dependence of the index increment on the molar weight;

-the structural heterogeneity leads to an average value of the index increment that is dependent upon the composition, and this latter varies throughout the size distribution spectrum;

-because of the nature of differential refractometry, the color of the eluate causes absorption of a certain amount of light energy normally required to determine the refractive index, and this leads to the latter being under-estimated.

Also, while it is possible to assign, to a homopolymer, a structural factor which is characteristic and which represents the molar weight per unit of chain length, this factor cannot be considered as independent of the molar weight, and, thus, of the elution volume, in the case of asphalt.

Finally, if up to now we have been considering GPC from the viewpoint of a fundamental process of fractionation as a function of molecular size, it is still no less true that this process may be obscured by the preferential retention of certain constituents, and the quasi-irreversible adsorption of particular compounds on active sites of the polystyrene gel. We therefore see that the quantitative interpretation of a GPC chromatogram of a bituminous product cannot be made without experimentally constructing two fundamental calibration curves. These are:

-the variation curve of the response coefficient of the detector,

-the variation curve of the structural factor (or the variation curve of molar weight as a function of the elution volume (or of the distribution coefficient).

Such curves can only be obtained by analysis of narrow fractions isolated by preparative GPC. At the present time, we have only been able to begin work on the variation curve of the response coefficient of the detector as a function of elution volume.

Preparative chromatography was performed with samples of 0.50 g to 1 g, and the solvent used was either THF or a 95/5 mixture of chloroform and methanol. Figure 14 is a schematic representation of all the manipulations and calculations. We see at the bottom on the right, the step-like appearance of the flow chart of the preparative fractionation. Each fraction was diluted with a given quantity of THF and analyzed by analytical GPC, with resultant chromatograms shown on the left. These chromatograms make it possible to calculate the distribution coefficient of each fraction, which is entered as abscissa on the central graph. The ordinate, on the central graph, corresponds to the coefficient by which the response of the detector must be multiplied to obtain a value effectively proportional to the quantity of material. For this, an individual response coefficient (k_i) was calculated for each fraction, which is defined as the ratio of the quantity injected (M_i) to the area under the elution peak (A_i).

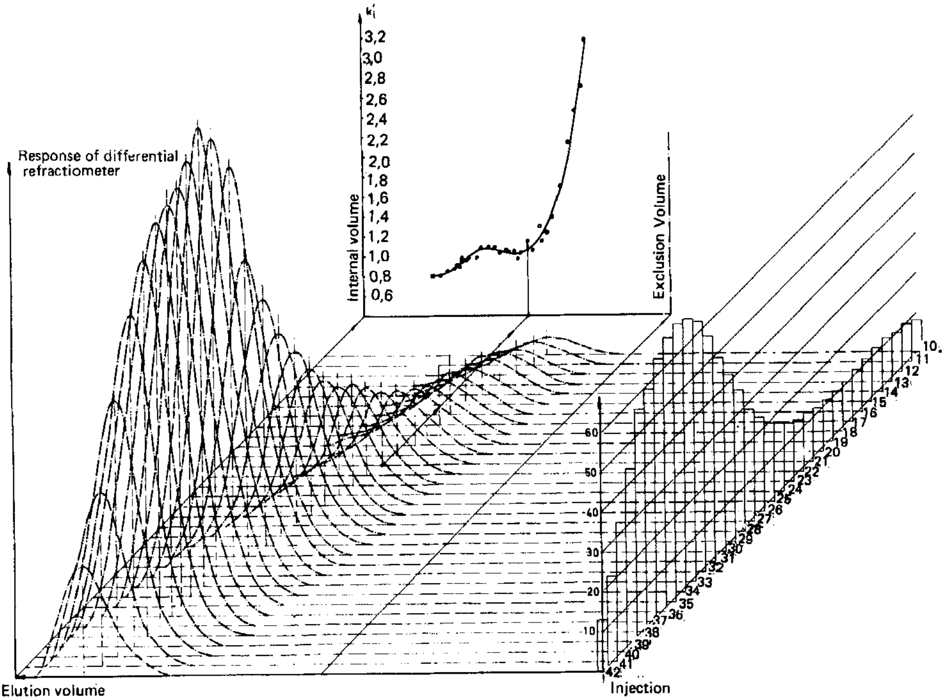

Fig. 14 - Construction of the response coefficient curve.

An average response coefficient was also calculated for the whole sample,

$$K = \frac{\Sigma M_i}{\Sigma A_i}$$

and each individual coefficient was reduced to the average coefficient by

$$k'_i = k_i/K$$

The curve passing closest to these experimental points gives the variation curve of the response coefficient as a function of the distribution coefficient:

$$k' = f\ (K_d).$$

The response coefficient curves for three asphalts are given in Figure 15. The essential characteristic common to these curves is a very noticeable rise

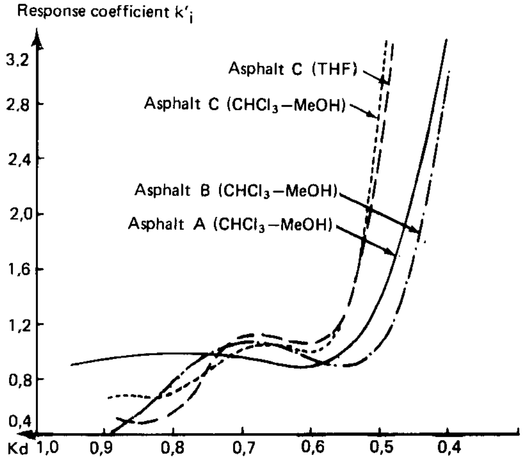

Fig. 15 - Response coefficient curves of various 180/220 asphalts.

of the response coefficient in the region of large molecular sizes. Among the parameters which might explain this rise of the curve for the large molar weights we should mention the influence of colour, the irreversible adsorption of certain large molecules, and the dissociation equilibrium. A knowledge of the variation curve of the response coefficient makes it possible to correct the chromatogram as it is obtained in differential refractometry, and Figure 16 provides an example of such a correction. The effect of this correction is relatively small for the small molecules, but becomes very noticeable at the other end of the distribution spectrum, and has the effect of considerably emphasizing the bimodality of the distribution. This correction is all the more important as it is the high molecular weight components which affect the computed results as to $\bar{M}_w$ and polydispersity.

CONCLUSION

Gel permeation chromatography, applied to the characterization of bituminous compounds, constitutes a powerful and attractive analytical tool. It

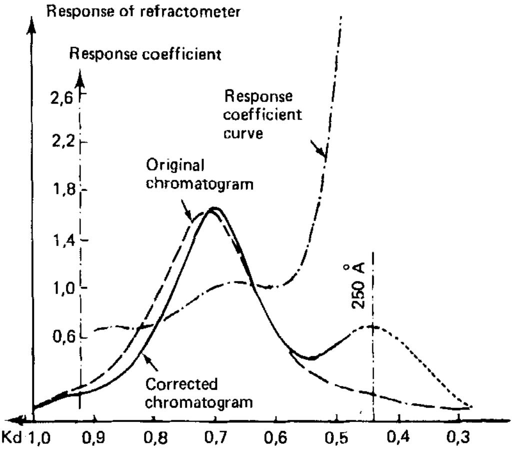

Fig. 16 - Correction of GPC chromatogram of an 180/220 asphalt.

treats the whole sample (after cold dilution in an appropriate solvent) by the particular criterion of molecular size, without subjecting it to the hazards associated with the other methods of fractionation - and it does so within a time span of the order of ten minutes. Qualitatively, this analytical technique is extremely useful for comparison and, quite often, identification, and permits determination of certain molecular and micellar dimensions.

In the case of asphalts, we established that the molecular size distribution was bimodal. It was also shown that modifications, either of penetration or in the manufacturing process, were accompanied by noticeable modifications in the shapes of the chromatograms. The study of asphaltenes led to equally interesting results, as a fundamental difference was observed between asphaltenes from a blown asphalt and those from a straight-run asphalt. In fact, the molecular size distribution in the first case is trimodal, whereas that for asphaltenes from a straight-run asphalt is bimodal. Also, the experimental observation of a fundamental difference in behaviour of these two types of asphaltenes on dilution (study of chromatograms as a function of concentration of the solution injected), proves the difference in the nature of the micellar interactions.

The use of dual detection (differential refractometry and UV detection at 350 nm) makes it possible to show, in the case of industrial asphaltenes, the increase of polycondensed character with molecular size. This characteristic persists throughout the various fractions. Further, study of the shape of the chromatograms as a function of the quantity injected (and therefore of the concentration of the solution at the detector) leads us to formulate the hypothesis whereby the process of association brings two different types of interaction into play. One of these does not appreciably modify the UV response coefficient at 350 nm whereas the other, which appears at greater dilutions, is accompanied by a decrease of the overall extinction coefficient of the product at this wavelength. While the first dissociation may be due to interactions of the type, induced dipole - induced dipole, the second must be attributed to stronger interactions (stacking of polyaromatic sheets by delocalisation of π electrons, hydrogen bonds, etc.), related to the actual structure of the polycondensed products.

The quantitative applications (interpretation of chromatograms in terms of average molecular weights and polydispersity) have only been touched upon. The determination of the response coefficient curves of the detector shall later be refined, and followed by a study of the variation curves of molar weight (determined by osmometry) as a function of distribution coefficients.

It would therefore appear that GPC constitutes a unique analytical tool, of which the application to characterization of bituminous binders should facilitate acquisition of the knowledge necessary for a good understanding of their physico-mechanical behaviour.

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