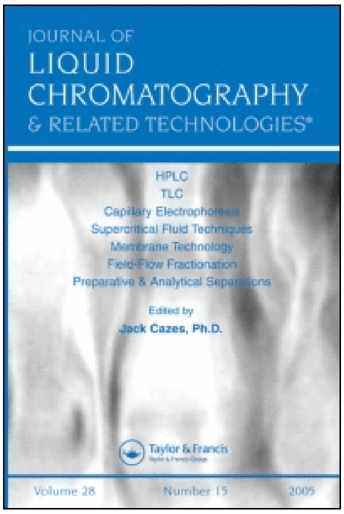

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# THE USE OF TOLUENE AS A CARRIER SOLVENT FOR GEL PERMEATION CHROMATOGRAPHY ANALYSES OF ASPHALT

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## ABSTRACT

Toluene, used as a carrier solvent in GPC analyses provides different elution profiles for asphalt materials than does THF. With proper precautions and technique, chromatogram reproducibility is excellent. GPC analyses of Corbett fractions in both THF and toluene provide insight into the refractive index, solvent power, and column interaction effects which give rise to the different elution profiles in toluene. The differences provide additional information on asphalt composition which may be of use in predicting asphalt performance.

## INTRODUCTION

Gel permeation chromatography from very early in its development has been recognized as a technique with considerable potential for evaluating asphalts. Altgelt (1), based on gel permeation chromatography profiles of asphaltene fractions obtained from asphalts, concluded that molecular weights ranged from 700 to more than 40,000 in this fraction. Richman (2) provides an early study which attempted to relate GPC chromatograms to pavement performance. Later, Bynum and Traxler (3) presented a detailed study of nine asphalts used in hot-mix pavements. They provided both GPC and rheological data as well as vanadium and oxygen analyses of the asphalts both before and after aging. In this landmark study, they observed differences in GPC chromatograms for different asphalt suppliers and furthermore observed changes in the asphalt due to aging. More recently, Jennings has related GPC chromatograms of asphalts to pavement cracking and climate (4). Although far from showing a perfect correlation, his data provide strong evidence that cracking, climate, and the fraction of asphalt which is "large molecular size" are related.

Although GPC measures primarily molecular size, a number of other factors have been recognized as important for asphalt analyses. These are a consequence of the fact that asphaltic materials possess a wide spectrum of chemical functionalities in addition to molecular weights. Snyder (5) pointed out the effects of 1) detector sensitivity to different compounds, 2) aggregation and absorption of the various components of asphalt materials, 3) different solvents on the GPC chromatograms, 4) and sample size effects on the large molecular size region of the chromatograms. He also discussed differences in UV (370 nm) and RI detectors. Such, et al. (6) also discussed differences between UV and RI detectors. In their work, they collected 23 fractions from a GPC column for quantitative weight determinations. Twelve of these fractions were used in further analyses. From these results they were able to determine quantitative corrections of both the UV and RI profiles. Brulé (7), in addition to discussing the UV and RI corrections, discussed the choice of column pore size, mobile phase flow rate, and effects of the carrier solvent on the profile, as well as solution age effects. Brulé studied four solvents of differing structure and dielectric constant: THF, chloroform, benzonitrile, and tetrahydronaphthalene (tetralin). He found that the chromatograms varied widely in the extent of association of the large molecular size region. He concluded that GPC can distinguish between different asphalts and that chromatograms vary with flow rate or quantity injected due to micellar agglomerates. Jennings et al. (8) also discussed UV (254 nm) versus RI detectors, column pore size effects, and solvent choice. They report studies using trichloroethylene (TCE), chloroform, methylene chloride, 10% pyridine in toluene, and 15% pyridine in THF. They found that TCE, chloroform, and methylene chloride all produced rapid column fouling.

## OBJECTIVES

The objective of this work was twofold. First, was to develop a GPC technique for asphalt analyses using a solvent different than the traditional tetrahydrofuran (THF). This solvent should be less polar so as to have decidedly different interactions with the column and with the components of asphalt than does THF, thereby producing markedly different chromatograms. Toluene, a solvent not previously reported for asphalt GPC studies, was selected as the second solvent. Second, was to improve our understanding of the GPC technique for multicomponent/multifunctionality systems through analyses of asphalt Corbett fractions using the two solvents.

## EXPERIMENTAL APPARATUS AND PROCEDURES

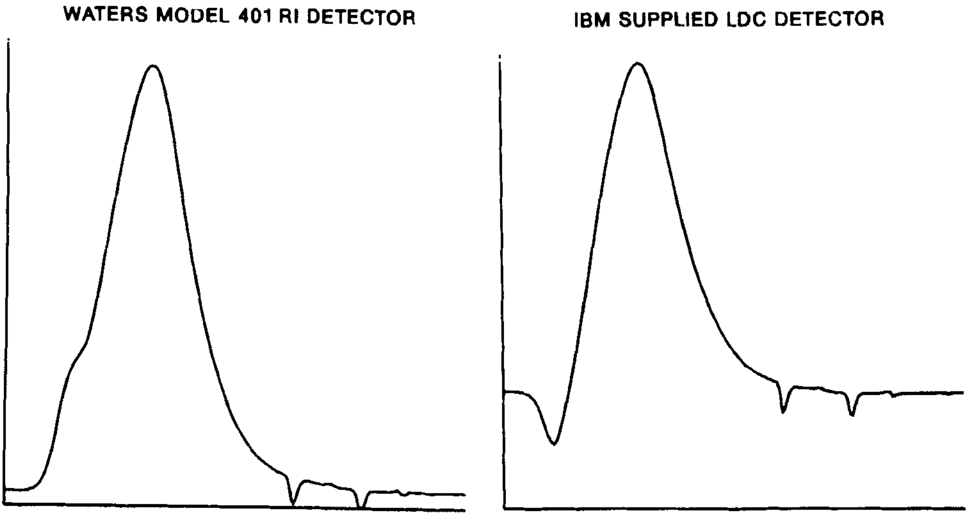
An IBM LC-9533 ternary gradient liquid chromatograph was employed. It used a three-piston pump designed to give a very well controlled flow rate with minimal pressure fluctuation. Solvent flow rate was 1 ml/min ($10^{-6}$ $m^3$/min). The original IBM system was slightly modified by replacing all teflon tubing with stainless steel. Stainless steel tubing required less time for baseline stabilization following a change in solvents. The columns, 60 cm long, were made by Polymer Laboratories and contained 5 $\mu$m, PL Gel Packing. Two refractive index detectors were used in series. The first was a Waters Model 401; the second was a Laboratory Data Control (LDC)

Detector supplied by IBM (IBM Model 9525). Both detectors provided reproducible chromatograms although they did not agree with each other, as discussed below. To aid in processing a large number of samples, an IBM 9505 Autosample Handler was used. A Rheodyne 6-port injection valve was also available for manual injections. An IBM 9002 Bench top computer equipped with 10 megabyte hard disk and dual floppy drives was used to collect and store the data and to control the autosampler and chromatograph. The computer was also used in analysis of data.

The reason for the discrepancy in the GPC analyses using the two RI detectors was studied using a variety of injected samples. Coal liquids and asphalts gave different results in the large molecular size region (Figure 1). For this portion of the chromatogram, the LDC detector produced a negative refractive index response in THF, whereas the Waters detector showed a positive response. This was a consistent result for all asphalts. High polymers, a variety of pure compounds, and a high molecular weight polystyrene motor oil showed no discrepancies between the detectors. Finally, photocopier toner suspended in THF and passed through a blank column also showed differences in the chromatograms for the two detectors.

From these results, we conclude that scattering or absorption of the detector beam by particles causes an anomalous response in the LDC detector. This detector measures the refractive index difference indirectly using Fresnal's Law. Two beams of light are projected through a prism onto the sample and reference cell. The *intensity* of light that is refracted through the solution is measured by a photocell. Thus, light scattering or absorption will affect the response of the detector. The Waters detector measures the *deflection* of the light beam caused by the change in refractive index, a measurement which is unaffected by random light scattering or absorption.

THF was Fischer certified grade and contained 0.025% butylated hydroxytoluene as a preservative. Toluene was Fischer certified ACS grade. Both solvents were further purified to remove peroxides and water by refluxing over sodium metal for 40 to 60 minutes and then distilling to a solvent reservoir for storage under a helium blanket.



WATERS MODEL 401 RI DETECTOR

IBM SUPPLIED LDC DETECTOR

FIGURE 1. Differences in refractive index detector responses (Exxon AC–10 virgin asphalt, 500 Å and 50 Å columns, THF carrier solvent, 100$\mu$l injection of a 7% solution).

Asphalt solutions were prepared to within an accuracy of 0.5%. The sample concentration was closely controlled due to the well-known impact of sample size on the results. To facilitate dissolution, the sample vial was sonicated in a water bath at 40°C for 20 minutes. After dissolution, the sample was filtered through a 0.45 micron filter.

An American Petrofina AC-10 asphalt was selected for use as an asphalt standard and was injected at the beginning and end of each batch of samples being analyzed. This asphalt was chosen because it is typical of the majority of asphalts which we see in Texas and because we have an adequate supply of a single batch. Furthermore, this asphalt has previously been used as a standard for physical tests at the Texas Transportation Institute. Also, a mixture of known pure compounds 2 x $10^6$ molecular weight Polystyrene, 2,350 molecular weight Polystyrene, normal Octacosane and Orthodichlorobenzene (ODCB) were injected. The ODCB peak was used to calculate plate counts to regularly monitor the column condition. Injecting the asphalt standard and known compounds was essential for monitoring performance and obtaining reproducible data.

## RESULTS AND DISCUSSION

A number of operating conditions or parameters may be varied to optimize GPC analyses. These include column pore size, injected sample size, and the carrier solvent. Results of work conducted on choosing each of these parameters for toluene and THF carrier solvents are discussed in the following paragraphs as well as results for a number of asphalts.

### Gel Pore Size

Several column configurations were evaluated and results from two of them for THF carrier solvent show typical pore size effects in Figure 2. Total exclusion, as determined by large molecular weight polystyrene, is represented by an elution time of approximately 10 minutes for a one-column configuration and 20 minutes for a two-column configuration at the 1 ml/min flow rate. The smaller pore size column (100 Å) produced a large, relatively narrow peak in the large molecular size region. The larger pore size column (500 Å) provided greater fractionation or spreading of this large molecular size portion. A 50 Å column was used in series with the 500 Å column to provide some further separation of the smaller molecular size species. The objective of column selection was to obtain more fractionation and therefore more distinctive chromatograms.

### Sample Size

The amount of sample injected has also been found to have a large effect on GPC results in the early eluting materials. This was reported early by Snyder (5) in both THF and 5 vol% methanol–chloroform carrier solvents and later by Brulé (7) with THF. This characteristic is confirmed in the

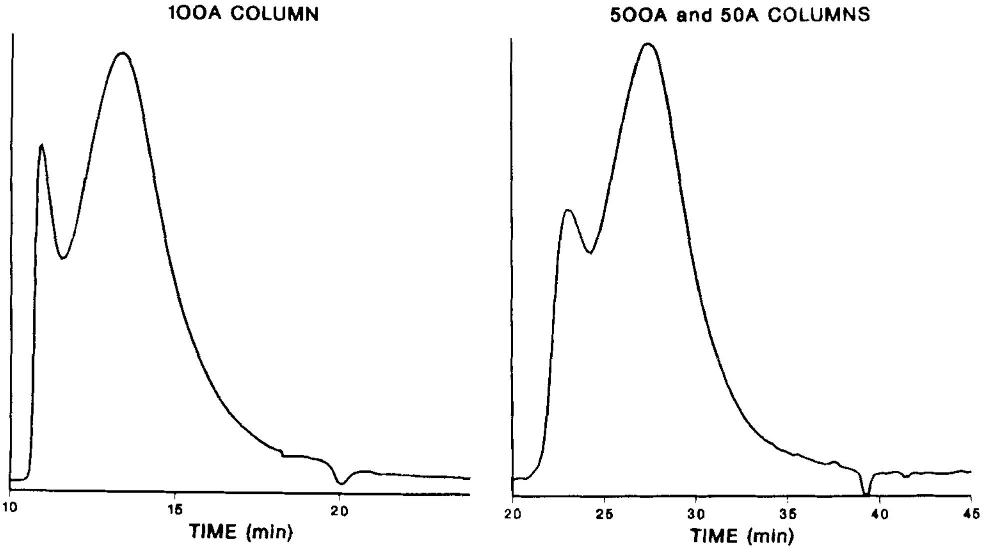


FIGURE 2. Effect of column pore size on chromatographs (Dorchester AC-20 virgin asphalt, THF carrier solvent, 100$\mu$l injection of a 7% solution).

present study for toluene as shown in Figure 3. The profiles in this figure are normalized to the same area for easy comparison. As the concentration of sample is increased, the leading peak clearly grows. The growth of this region probably is attributable to agglomeration of smaller molecules into micelles and aggregates, as was suggested by both Snyder and Brulé (9), which then act as very large, but not necessarily excluded, molecules. These species probably exist as agglomerations in the asphalt binder as well. In the current work, the largest practical sample size was used so as to maximize the differences in the asphalts' profiles, as suggested by Brulé (7). Measuring and understanding this effect likely is important to understanding asphalt performance. For both toluene and THF carrier solvents, the injected sample was 100 $\mu$l of a 7 weight percent solution. This 7 mg sample size compares with 1 mg selected by Brulé (7) to stay within the range of linear UV response, 20 mg by Jennings (10), 2 mg by Jennings (8), and 1, 10, 30, or even 150 mg reported by Snyder (5).

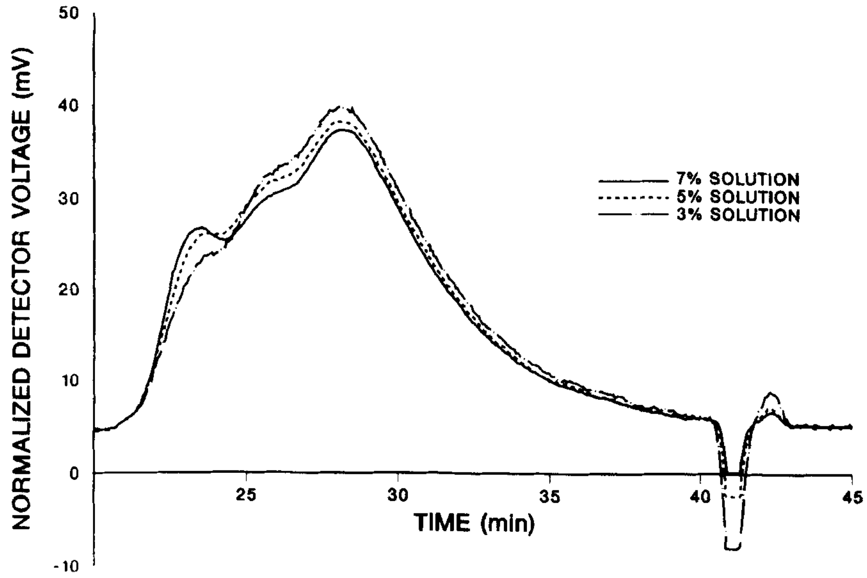


FIGURE 3. Effect of injected sample concentration on chromatographs (500 Å and 50 Å columns, toluene carrier solvent, 100$\mu$l injection).

## Carrier Solvent

The carrier solvent can have a large impact on the GPC results in two ways. First, the refractive index of the carrier is important since RI detectors operate by comparing the refractive index of the sample stream to a reference stream of pure carrier. If the sample has a refractive index similar to that of the carrier it likely will not give a strong response. Thus, since different components of the asphalt will have different refractive indices, the carrier can affect the results given by GPC. Second, solute/solvent and solute/gel interactions play important roles in determining the elution time of components (7). Because asphalts are made up of a wide variety of components, the type of solvent can have a large impact on the time various constituents take to travel through the column. Furthermore, a poor solvent can increase the formation of aggregates of smaller molecules forming apparently larger molecules that elute sooner.

Comparisons of different species retention times in THF and toluene (Philip and Anthony (11), e.g.) suggest the manner in which different solvents can produce different shaped chromatograms for asphalt. The stronger the interactions of the carrier solvent are with a given compound, the sooner the compound will elute from the column. Since THF is strongly polar, it interacts strongly with the polar constituents in asphalts and these molecules would be expected to elute sooner from the column than the less polar ones of equivalent molecular weight and size. Conversely, with a toluene carrier solvent, which is less polar than THF, the polar constituents of asphalt would be held in the column longer than in THF.

Another way in which a less polar solvent (say toluene) might create different chromatograms from the strongly polar THF is by causing aggregation of asphalt molecules which are difficult to hold in solution. Asphaltenes, being, on average, the largest molecular weight species in asphalt and also the highest in polarity, are the most difficult to maintain in solution. Evidence suggests that they can associate or agglomerate in solution, especially in toluene, to form still larger species. For these molecules, a less polar solvent, rather than leading to a longer elution time through effects discussed in the preceding paragraph, may actually produce a shorter time, relative to the strongly polar THF.

## GPC Studies of Asphalts Using Toluene

With literature reports showing clear differences in THF and toluene as GPC solvents as well as the previous work of Snyder (5), Brulé (7), and Jennings (8) on solvents for GPC analysis of asphalts, a study of the use of toluene for asphalt analysis was begun. This study addressed the reproducibility of asphalt chromatograms using toluene and the solvent's effects on profile shapes.

Extensive effort was required to achieve an acceptable level of reproducibility in the method when using toluene for asphalt analyses. It was found that the asphalt fouled the column when toluene was employed as the carrier, drastically reducing the separation efficiency of the column. This problem seemed to affect the smaller pore size (100 Å, 50 Å) columns most, leading to the use of the 500 Å column. Fortunately, the fouling process was found to be reversible by using appropriate time intervals between injections. As a result, approximately three column volumes of toluene were allowed to pass through the column between asphalt injections. An ODCB injection before each asphalt injection was used to assure adequate plate counts for the column. Typical reproducibility that was obtained when these procedures were followed is as good as with THF and is shown in Figure 4. Degradation of column performance due to asphalts has not been observed in THF.

Comparisons of THF and toluene analyses for several asphalts are shown in Figure 5. All analyses were made by injecting 100$\mu$l of a 7% solution. Properties characterizing these virgin asphalts, as well as the aged core asphalt in Figure 6, MacMillan AC–20, are given in Table 1. These asphalts were used in test sections placed at three locations in Texas in 1981–82 (12,13). Generally, the toluene profiles have more peaks or shoulders than do those with THF.

GPC analyses of the Corbett fractions (14) for one asphalt provide insight as to why these differences can occur, in the context of the effects discussed above (Figure 6). (For these analyses, solutions of the fractions were made which would put them at the same level as they were in the 7% whole asphalt solution so as to avoid artifacts resulting from detector nonlinearity. For example, a Corbett fraction which accounted for 40% of the asphalt was made to a 2.8% solution. Then 100$\mu$l of this solution was injected.) First, for this asphalt, we see some shifts in the elution times of the Corbett fractions, relative to each other. In toluene, the saturates peak center elutes before both the polar aromatics and naphthene aromatics fraction peaks whereas in THF it elutes after. Second, significant refractive index effects exist and are most obvious for the saturates which have a lower refractive index than toluene (and hence give a negative peak in toluene) but a larger refractive index than THF (and hence give a positive peak in THF). Also, the naphthene aromatics fraction for this asphalt appears much larger relative to the polar aromatics

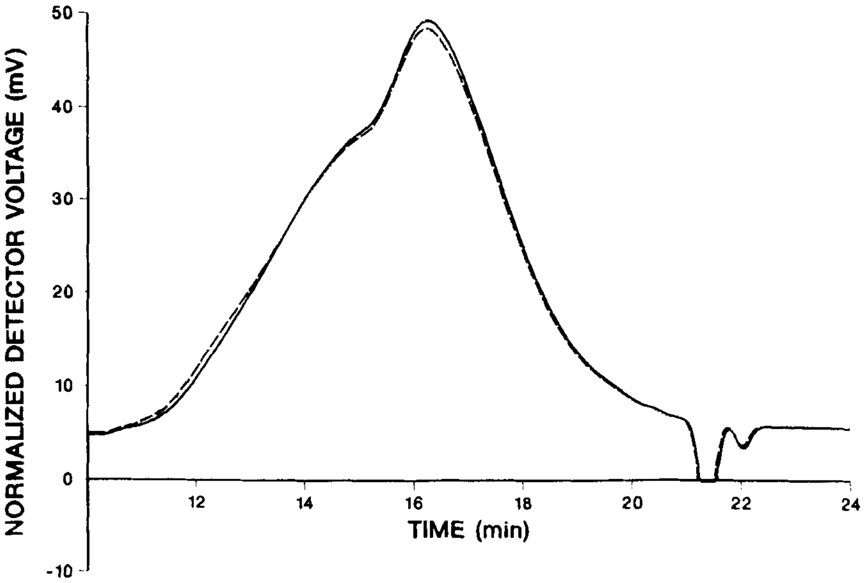


FIGURE 4. Typical reproducibility of asphalt standard chromatograms in toluene (500 Å column, 100$\mu$l injection of a 7% solution).

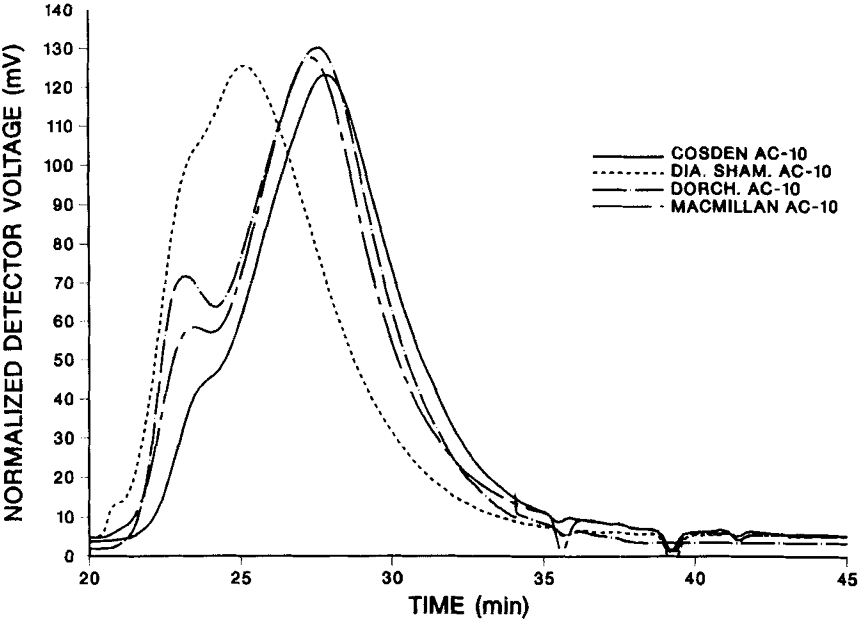


FIGURE 5a. GPC chromatograms for four virgin asphalts using THF carrier solvent (500 Å and 50 Å columns, 100$\mu$l injection of a 7% solution).

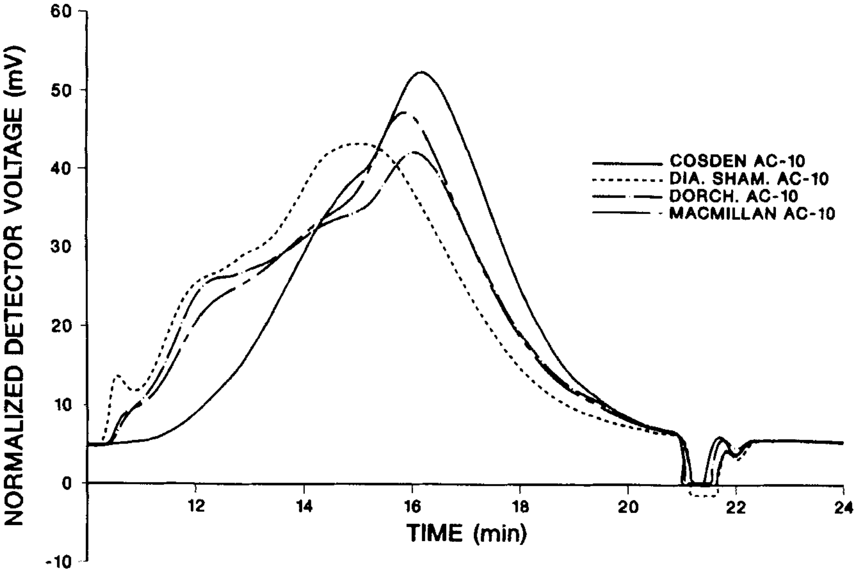


FIGURE 5b. GPC chromatograms for four virgin asphalts using toluene carrier solvent (500 Å column, 100$\mu$l injection of a 7% solution).

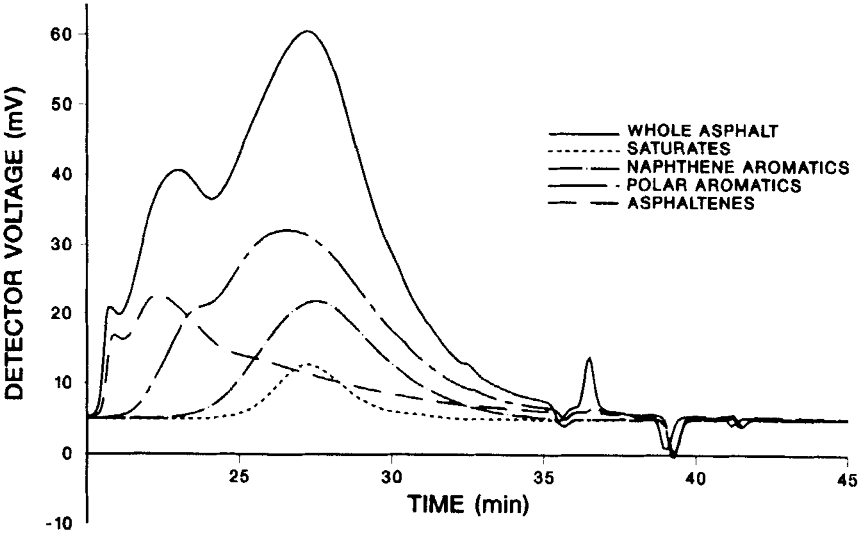


FIGURE 6a. Chromatograms of Corbett fractions and whole asphalt in THF (MacMillan AC–20, Dickens 1984 core, 500 Å and 50 Å columns).

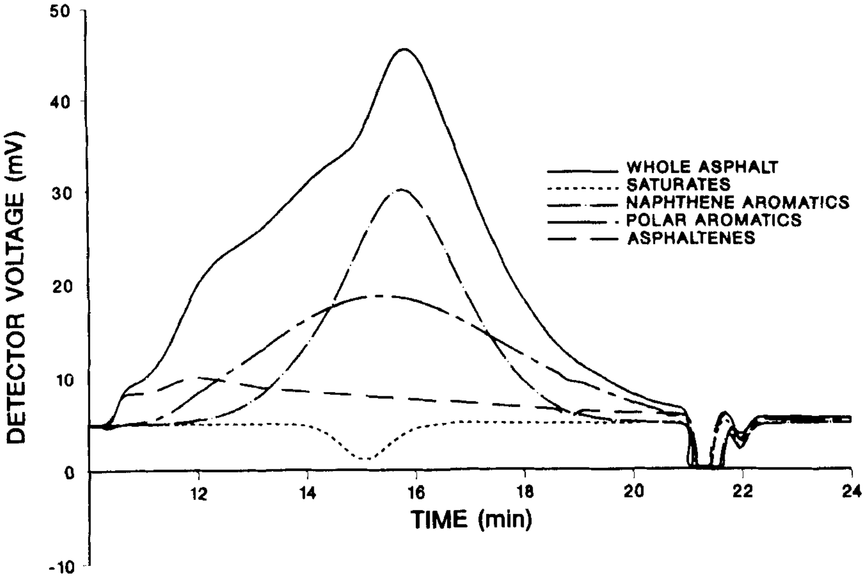


FIGURE 6b. Chromatograms of Corbett fractions and whole asphalt in toluene (MacMillan AC-20, Dickens 1984 core, 500 Å column).

or asphaltene fractions in toluene, probably again due to refractive index differences. Third, there is some alteration of the peak shapes in that the polar aromatics profile in toluene does not have the leading peak observed in THF but is instead a smooth, nearly symmetric, single peak. The combination of these effects produces the significantly different profiles.

The data of Figure 6 are for a single asphalt and may not be entirely representative of all asphalts and their Corbett fractions. However, they are representative of the limited number of asphalts which we have so far analyzed.

The shifts in the fractions' elution times and the broadening of profiles in toluene are consistent with the effects of solvent and gel interactions with the asphalt components. The more polar and hydrogen bonding fractions (naphthene aromatics and polar aromatics) tend to adsorb onto the column

## TABLE 1

Properties of the Asphalts Reported in Figures 5 and 6.

| Property | Cosden AC-10 (Fig. 5) | Diamond Shamrock AC-10 (Fig. 5) | Dorchester AC-10 (Fig. 5) | MacMillan AC-10 (Fig. 5) | MacMillan AC-20 (Fig. 6) |
|---|---|---|---|---|---|
| Viscosity (poise) at: | | | | | |
| 77°F | 0.97 x $10^6$ | 0.56 x $10^6$ | 0.53 x $10^6$ | 0.36 x $10^6$ | 21.0 x $10^6$ |
| 140°F | 1,038 | 958 | 1,030 | 961 | 9,790 |
| 275°F | 2.48 | 4.65 | 3.21 | 3.63 | 5.67 |
| Penetration at: | | | | | |
| 39.2°F | 16 | 16 | 30 | 39 | 3 |
| 77°F | 71 | 104 | 105 | 133 | 17 |
| Corbett Fractions (wt. %): | | | | | |
| Asphaltenes | 9.8 | 0.8 | 14.7 | 11.0 | 19.9 |
| Polar Arom | 37.3 | 42.0 | 30.5 | 28.0 | 42.4 |
| Naph Arom | 40.9 | 55.1 | 44.6 | 52.0 | 25.8 |
| Saturates | 12.0 | 2.2 | 10.2 | 9.1 | 12.0 |

gel to a greater extent in the presence of a less polar solvent (toluene) than they do in a more polar one (THF). Consequently, these fractions are delayed in their elution relative to the non-polar saturates fraction. Also, the greater tailing of the asphaltenes fraction in toluene is consistent with greater adsorptive effects.

The net effect of these results is that the THF and toluene chromatograms are, to some extent, seeing different parts of the asphalt cements. Analyses using THF reflect, to a large degree, the asphaltene and polar aromatic fractions. By contrast, analyses in toluene are more strongly influenced by the naphthene aromatics.

Most likely, both analyses will be of value in evaluating asphalts for performance, in the manner suggested previously, e.g. (4). Characteristics or properties which depend primarily on asphaltene and polar aromatic content will be better evaluated using THF. On the other hand, characteristics or properties related to the naphthene aromatics may be better evaluated with toluene as the carrier solvent.

## CONCLUSIONS

Concerning the GPC technique using toluene as a solvent for asphalt analyses, considerable precautions must be taken to ensure reproducibility. Asphalts tend to degrade column performance which can be reversed with a sufficient throughput of clear solvent. Frequent monitoring of column performance by measuring plate counts and by analyzing an asphalt for which the profile is known are essential precautions.

Concerning comparisons of THF and toluene as solvents for GPC: 1) solvent/solute effects can cause relative shifts in retention volume for different species, 2) the different refractive indices of THF and toluene provide different relative strengths of detection for different compounds, and 3) in asphaltic materials, the more polar or more hydrogen bonding species may tend to agglomerate or complex together in a less polar solvent (toluene versus THF, e.g.) to form effectively larger size species, thereby causing differences in elution times in the two solvents.

All of these effects produce certain results which have implications on asphalt analyses: 1) profiles in toluene may look distinctively different from profiles in THF. The chromatograms in toluene frequently tend to be more dispersed and tend to have a larger number of distinctive peaks or shoulders, 2) GPC analyses of the Corbett fractions of an asphalt show that the relative sizes of the fractions detected in THF or toluene can be significantly different due to refractive index differences and that relative shifts in the fractions' elution times can occur, apparently due to the solvent interaction and species agglomeration effects. Because of these differences, measurements in the two solvents tend to emphasize different parts of the asphalt to a different extent. Finally, multiple analyses of asphalts using different solvents may be of particular benefit because these different components are detected with different sensitivity in different solvents.

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The contents of this report reflect the views of the authors who are responsible for the facts and the accuracy of the data presented herein. The contents do not necessarily reflect the official views or policies of the Federal Highway Administration or the State Department of Highways and Public Transportation. This report does not constitute a standard, specification, or regulation.

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