

New Apparatus and Procedure for the Extraction and Recovery of Asphalt Binder from Pavement Mixtures

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A new apparatus and procedure for the purpose of extracting asphalt binder from hot-mix and pavement samples has been developed. This procedure is the culmination of previous reports on solvents for the extraction of asphalt, the aging of asphalt in solution, and the removal of solvent from asphalt. The apparatus consists of a rotary drum for the purpose of efficient and thorough contacting of the aggregate-binder sample with the solvent, followed by filtration and then solvent removal using a Roto-vap procedure. Intralaboratory tests of the procedure on a variety of samples indicate that the precision associated with one standard deviation is about 6 percent for extracted asphalt viscosities. This compares with interlaboratory precision of about 30 percent for previous methods according to the AASHTO Materials Reference Laboratory proficiency sample program. Additionally, this new procedure provides recovered asphalt that has physical properties, such as viscosity, that are much closer to the "true" physical properties of the binder as it existed in the pavement. This is essential if tests performed on the binder are to have any meaning with respect to pavement performance.

Although properly measuring chemical and physical properties of asphalt in hot mix or pavement samples requires accurate extraction and recovery procedures, currently used methods show poor precision and unknown accuracy. This can be seen in American Association of State Highway and Transportation Officials' (AASHTO) interlaboratory proficiency tests in which various laboratories analyze pavement specimens provided by AASHTO for several properties, including asphalt content and viscosity. Shown in Figure 1 is the scatter in extracted asphalt viscosities of two different but similar asphalt mixtures of unknown origin (samples 27 and 28 in this test) determined by 62 different laboratories. Points inside the box lie within one standard deviation of the mean and the diagonal line represents perfect intralaboratory reproducibility. The standard deviations of viscosities in these tests have ranged from 25 to 42 percent during the years 1986 to 1991. Unfortunately, the extraction methods were not specified and vary considerably between laboratories (1). Nevertheless, it is obvious that even self-consistency is difficult for laboratories to achieve using current methods and that interlaboratory differences can be great. It is likely that the error in extracted asphalt properties stems from the following problems:

1. Asphalt is not completely or consistently extracted from the aggregate;
2. Residual solvent is left in the asphalt after recovery; and
3. Reaction of asphalt while in solution, sometimes called solvent aging, can alter properties during both extraction and recovery.

After studying these error sources for the past three years, we have designed and tested a new asphalt extraction and recovery method for the Strategic Highway Research Program (SHRP) that addresses these problems. Tests to date indicate that the SHRP method is more precise and accurate than any standard method. However, incorporation of certain aspects of our new method can greatly improve the performance of one existing method to the point of being comparable.

To describe briefly the SHRP procedure, the extraction is performed in a rotating drum in which the solvent and pavement sample are thoroughly contacted. The extract is vacuum filtered through a woven polypropylene filter assembly on one end of the drum. The filtrate then goes through a tighter filter to remove most of the aggregate fines before being transferred to a rotary evaporator where the solvent is vacuum distilled. In order to adequately extract strongly adsorbed asphalt, several solvent washes are required. Before final solvent removal, all remaining fines are centrifuged. (Undoubtedly, both absorption and adsorption phenomena are, or may be, important. Throughout this paper we refer to adsorption but recognize that adsorption/absorption is more correct.) Recovery of the asphalt is performed according to the protocol described by Burr et al. (2).

The purpose of this paper is to present in detail the SHRP extraction and recovery method and to compare it with modifications of two commonly used procedures with respect to both precision and accuracy.

HISTORY OF METHODS

Extraction and recovery have been practiced in some form since the turn of the century. In 1903, as discussed by Abson (3), Dow extracted with carbon disulfide (CS₂) and recovered using simple distillation. Bateman and Delp (4) centrifuge-extracted with CS₂ and removed the solvent by vacuum distillation. Soxhlet type reflux extractions using CS₂ were common

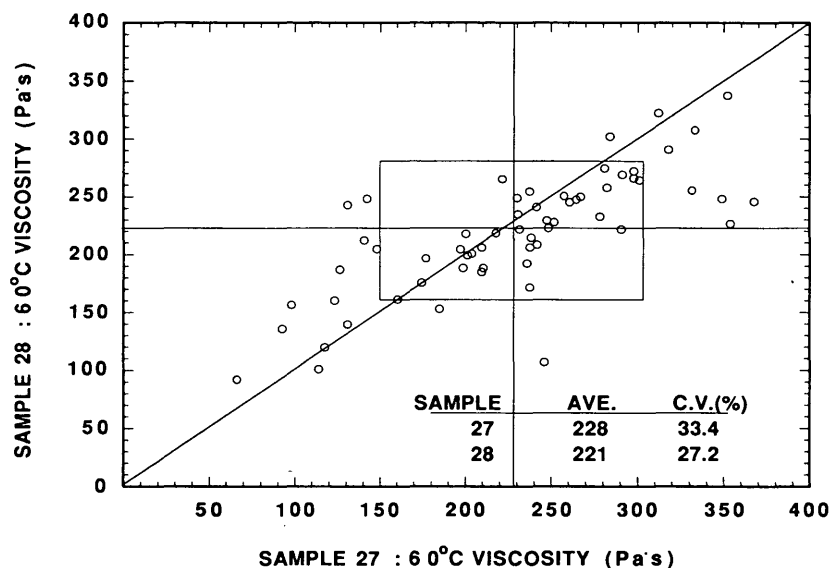


FIGURE 1 Results from the AASHTO Materials Reference Laboratory Proficiency Sample Program. Samples 27 and 28 are replicates.

in this early period. Several other methods were developed through 1930, but none gained lasting acceptance (3,5).

Extraction Methods

Today centrifuge and reflux extraction methods (usually in the form of ASTM D-2172, methods *A* and *B* respectively) are used almost exclusively. Vacuum extraction (6) and sonication methods (7,8) also have been used, but infrequently. The centrifuge method was developed in the 1920s (4,5) and eventually adopted by ASTM as D-2172A (6) in 1963. The reflux extraction method was in existence before 1949 and there were reservations about its use in obtaining asphalt for property analysis (5). ASTM warns that the reflux method D-2172B should not be used if asphalt properties are to be measured. Despite the warnings, use of reflux extractions is far more prevalent in the literature than other methods (2). In this paper, Methods *A* and *B* refer specifically to ASTM D-2172 *A* and *B*.

Incomplete extraction and solvent aging are two problems to consider when selecting an extraction method. Reflux methods expose the asphalt to solvent at elevated temperatures for long periods of time. This has been shown to cause considerable hardening caused by reactions that the asphalt undergoes when it is in a dissolved state. The reactions occur at room temperature, but have higher rates at reflux temperatures (9,10). In general, reaction rates increase exponentially with temperature and are constant over time, so it is desirable to minimize these variables to limit any reactions that might occur. Asphalt concentration in solution and type of solvent can be other important variables, but it is not yet clear what effect, if any, these have on this system.

The extraction methods' means of contacting the samples, choice of extraction solvents, and aggregate adsorptivity determine how much of the asphalt is extracted. Method *A* typically leaves 2 to 4 percent of the asphalt on the aggregate

when trichloroethylene (TCE) is the extraction solvent. Method *B*, which seems to have poor solvent contacting, leaves much more asphalt unextracted (11). Modification of Method *A* by adding 15 percent ethanol to the TCE in later washes and mixing thoroughly during each wash removes about half of the strongly adsorbed material that method *A* leaves behind (11).

The choice of extraction solvent is important in determining how much of the asphalt is extracted by a given method. TCE with 15 percent ethanol and pyridine are the most powerful solvents for extracting asphalts. Toluene with 15 percent ethanol, although not as powerful as the other two, is good and has safety advantages that make it more attractive (11).

Solvent Removal Methods

Typically, removal of solvent is performed by the Abson method, ASTM D-1856 (6) or by rotary evaporation (12,13). These two methods share equal popularity (2).

Both methods have been plagued with the problem of incomplete solvent removal because the prescribed distillation times and temperatures do not guarantee complete solvent removal. Even low solvent concentrations in asphalt (about 0.2 percent) are enough to cause significant physical property errors. Gel permeation chromatography (GPC) has been used to detect small amounts of residual TCE and toluene. Both recovery methods were calibrated using this direct TCE detection to determine appropriate recovery conditions for different sample masses and viscosities (2).

EXPERIMENTAL PROCEDURES

The intent of this study is to evaluate the performance of the SHRP extraction and recovery method, and compare it with

current extraction methods, modified to achieve improved recovery. A suitable solvent removal method had been developed earlier (2), and it was used after all extractions in this study with only minor variations in some cases. This was so that all extraction methods could be judged fairly, instead of tainting the results of one method by using an inadequate recovery method.

Extraction Methods

SHRP Method

The SHRP extraction and recovery apparatus is shown in Figure 2. The extractor drum, made of 15.2-cm (6-in.) Sch. 80 aluminum pipe and 1.27-cm (½-in.) aluminum discs, has a filter arrangement consisting of a 10-mesh steel screen followed by about 2.54 cm (1 in.) of glass wool packing, an 8- μ m polypropylene monofilament filter (Filter-All, Inc. #13118, from Magnolia, Texas), and another 10-mesh steel screen for filter support. The drum is also fitted with four baffles to improve mixing. The fine filter is composed of two 33-cm (13-in.) aluminum discs containing about 1.27 cm (½ in.) of liquid space followed by a 1- to 2- μ m polypropylene monofilament filter (Filter-All, Inc. #13107) and a 10-mesh steel screen filter support.

To begin an extraction, 1 kg of pavement sample and 600 mL of toluene (or TCE) are charged to the extractor drum. The drum is attached as shown to the 30 rpm, 49.7 W (⅓ hp) shaded pole gear motor and turned for 5 min. Next, the drum is connected above the first filtrate flask, about 39.9

kPa vacuum is applied (61.3 kPa pressure, absolute), and the extract is filtered. This filtrate is further put through the fine filter to remove as many small aggregate particles as possible. Unfortunately the coarse filter by itself passes too many fines to the recovery step, and a 1 to 2 μ m filter plugs when it is used as the drum filter.

The filtrate from the fine filter is transferred to the rotary evaporator's 1000 mL recovery flask, which contains several 3-mm glass boiling beads. The rotary evaporator is a Buchii RE-111, and a common kitchen fryer is used as an oil bath. The bath temperature is held at 100°C and pressure is lowered to 12.0 kPa absolute. The recovery flask is lowered into the oil bath and the solvent is distilled until the condensate rate is down to about one drop every 15 seconds when the flask is raised from the oil bath. The condensate flask is emptied into a container where the solvent is used for subsequent washes.

The oil bath temperature and recovery pressure were chosen to obtain a relatively low distillation temperature without overwhelming the condenser. Having the boiling temperature low limits the rate of solvent aging during the recovery step. The relatively low bath temperature helps reduce unstable boiling in the recovery flask.

While the solvent is distilling, the extractor drum is charged with 400-mL solvent and turned for 15 min. The mixing, filtering, and distilling sequence is repeated for this second wash.

The third wash follows similarly, except that the mixing time is 30 min. After distilling the third wash, the recovery flask is removed and set aside. This flask contains about 90 percent of the asphalt in the sample, and removing it from the recovery conditions helps prevent solvent aging. Another recovery flask is attached to the rotary evaporator for the remaining washes. For the fourth and subsequent washes, toluene (or TCE) with 15 percent ethanol is used. The mix times are 30 min each. When the extract flowing through the transfer tube attains a light brown color, the extraction is completed. This usually takes a total of seven washes, or about 3000 mL of solvent contacting the sample.

Before final recovery, the asphalt in both flasks is mixed into solution and poured into two 250-mL centrifuge jars. The last remaining aggregate fines are centrifuged for 25 min at 3,600 rpm. After centrifuging, the solution is decanted into a 1000-mL recovery flask with boiling beads.

For the final recovery, the bath is heated to 171°C. The recovery flask is attached to the rotary evaporator, pressure is set at 8.0 kPa absolute, the flask is lowered into the bath, and solvent is distilled. When the condensate rate falls to less than one drop every 30 sec, a nitrogen (N_2) purge tube is inserted through the condenser and down to the asphalt surface. The N_2 is bubbled at 1000 mL/min through the asphalt for 30 min to complete the extraction and recovery.

This solvent-removal scheme will be called "the two-flask method." A similar scheme that involves continuously recovering the extracts but uses only one recovery flask will be called "the single-flask method."

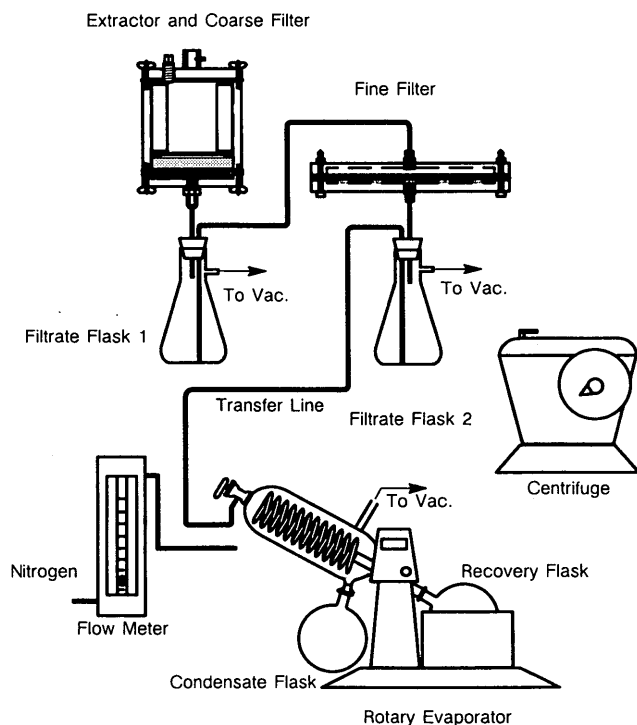


FIGURE 2 Schematic representation of SHRP extraction and recovery apparatus.

Modified Method A

A modified method A procedure also was performed. The instructions in ASTM D-2172A (6) were followed except that

toluene was substituted for TCE in some cases, ethanol (EtOH) was added to the solvent in late washes, and more solvent wash was used than is called for in the standard procedure. After the fourth wash, solvent with 15 percent ethanol was used. The filtrates from all washes were collected in a 4-L bottle until the extraction was completed. The extract was recovered using the rotary evaporator as previously described except that it is not continuous and only one recovery flask was needed. The term "batch method" will be used to describe this type of recovery.

The standard method leaves the number of solvent washes to the user's discretion by stating that the extraction should proceed until the filtrate obtains an arbitrary light straw color. In order to compare Method *A* and the SHRP method on an equal basis, we extracted with 11 washes (about 3000 mL)—considerably more than are used by most experimenters. Consequently, it should be understood that our Modified Method *A* data may not be comparable with those of other laboratories that do not use ethanol addition and employ only six solvent washes, for instance.

Method B

The Method *B* extractions followed ASTM D-2172B (6) except that solvent was varied in some of our experiments. The extract was recovered using the batch method. In Method *B*, about 100 g of the asphalt mixture are placed in two cone-shaped filters, one above the other in a cylindrical glass container. About 500 ml of solvent is added to the bottom of the container and heated to boiling on a hot plate. Vapors rise to the top of the container to a condenser. The reflux falls through the sample, extracts asphalt, and flows through the filter and back into the solvent pool. Most of the asphalt is extracted and resides in the pool after several hours of refluxing. It is an inexpensive and labor-saving method and is preferred by most asphalt laboratories. However, it alters the asphalt during extraction caused by solvent aging and its use is discouraged by ASTM if the extracted asphalt is to be studied.

Viscosity Measurements

In this study, some viscosities are measured using Cannon-Manning vacuum capillary viscometers at 60°C according to ASTM D-2171 (6). Some samples were very hard, so it became more practical to use a Carri-Med CSL controlled stress rheometer (CSL) at 60°C and 90°C. The data from the two temperatures were shifted using the principle of time-temperature superposition (14) to provide zero-shear viscosities at 60°C. Though the two methods provide similar information, the data are not comparable and are not combined.

Residual Solvent Analysis

GPC analyses were performed on an IBM Model LC-9533 high-pressure liquid chromatograph (HPLC). A 100- μ L sample of 5-mass percent asphalt in tetrahydrofuran (THF) was injected into the carrier solvent, THF, flowing at 1 mL/min through two Polymer Laboratories (PL) columns containing PL gel of

50 nm (500Å) (Column 1) and 5 nm (50Å) (Column 2) pore sizes. The details of operation are described by Donaldson et al. (15). Solvent detection by GPC requires that the column be able to handle high sample loadings (about 5 mg of asphalt) and have a small pore size (5 nm, 50Å). This is because of problems with peak interference from dissolved water and nitrogen. All extracted asphalts were analyzed by GPC to ensure that solvent was completely removed.

Samples

To properly test the extraction methods, it was necessary to obtain a variety of road pavements containing hard asphalt. This is preferable to generating laboratory cores that do not have enough strongly adsorbed material to properly challenge the methods. Unfortunately, there were no large, uniform quantities of road-aged material of known origin available. Nevertheless, the following samples were obtained:

1. About 23 kg (50 lbm) of pavement found in a pile near the intersection of Texas Highway 21 and US-77 (Tex 21/77) near Giddings, Texas. The pavement had limestone aggregate and asphalt having a 60°C vacuum capillary viscosity of about 2.5 kPa·s (25 kPoise).
2. About 45 kg (100 lbm) of pavement from a pile being readied for recycling at Young Brothers Construction in Bryan, Texas. The aggregate was river gravel but the asphalt's viscosity was about 90 kPa·s (900 kPoise) at 60°C using the CSL.
3. Two hot mixes used in the round robin tests of the SHRP method. The aggregates were limestone and the asphalts were Exxon AC-20 and a polymer modified Coastal AC-10.

Several rolling thin-film oven (RTFO)-aged asphalts were also studied for their susceptibility to solvent aging under various recovery conditions. These asphalts were SHRP-AAK1, -AAD1, -AAF1, Exxon AC-20, and Coastal AC-20.

RESULTS AND DISCUSSION

It is important to recognize that one serious obstacle dictates the way experiments for evaluating extraction methods are designed. This is the fact that one of the goals is to develop a method that does not alter the asphalts' properties. However, there is no way to know the properties of a pavement asphalt before extraction because these properties change when it is mixed with aggregate. Consequently, simulations with tank asphalts under extraction or recovery conditions are often performed. Comparisons of asphalt properties after extraction from pavements subjected to different conditions are also good ways to measure effects of these conditions. However, since the "correct" result is never known, intuitive knowledge of which condition is least damaging is required before a proper analysis can be made.

Optimum Recovery Scheme

Before evaluating the extraction procedure, it was first necessary to determine how much solvent hardening should be

expected in the recovery step. An earlier study indicated that tank asphalts, when dissolved and immediately recovered, hardened from 10 to 40 percent (10). In those tests, the asphalts were mixed to 7 percent by mass in toluene with 15 percent ethanol and recovered in a rotary evaporator.

It was suspected that some of the hardening might be caused by loss of asphalt volatiles during the final recovery step. All pavement samples, though, have been through a hot-mix process that is likely to drive off most volatile material. To get asphalts that had not been solvent aged and lacked volatiles, several tank asphalts were aged in the RTFO according to ASTM D-2872. These imitation pavement asphalts could be used in simulations to measure recovery solvent aging.

Three recovery schemes were proposed for the SHRP method. The first was the single flask method in which the extracts are transferred to the recovery flask immediately after filtration and the solvent is removed. Any asphalt extracted before a given wash is exposed to conditions of the recovery of that wash. Because about 90 percent of the asphalt is extracted in the first three washes, most of the asphalt spends a great deal of time in the recovery flask at elevated temperature exposed to some solvent. The two-flask method solves this problem by having the first recovery flask removed after the third wash is recovered and replaced by a new recovery flask. The batch method is essentially the recovery method suggested by ASTM's proposed Roto-vap procedure (12), but applied to the new extraction process. The extracts are stored in a container until all washes are performed. Then the entire quantity of extract is recovered in the rotary evaporator.

To simulate hardening in the two-flask method, 54 g of RTFO-aged tank asphalt were mixed with 450 mL of toluene in the recovery flask. The toluene was distilled at 100°C and 12 kPa absolute. Two more 450 mL aliquots of toluene were added and distilled before the flask was removed and set aside at room temperature. Another flask containing 6 g of the asphalt was attached to the rotary evaporator. Four 450 mL aliquots of toluene with 15 percent ethanol were added and distilled. The asphalts from both flasks were dissolved in toluene with ethanol and the solvent was completely distilled. The viscosity of the asphalt after the simulation was divided by the viscosity of the RTFO-aged asphalt to give a hardening index. The single-flask simulation used the same sequence of asphalt and solvent additions but there was no replacement of the recovery flask with a second one.

The batch method was simulated by adding asphalt to 450 mL toluene aliquots over 30-min intervals and storing them in one 4-L bottle at room temperature. The first aliquot is mixed with 45 g of asphalt, the second with 9 g, and the third with 6 g. Five 500-mL aliquots of toluene with 15 percent (vol/vol) ethanol are added to the bottle in the next 150 min. The solution is then removed using the rotary evaporator.

Hardening indexes for five asphalts subjected to each of the recovery simulations are shown in Table 1. The batch method appears to be the most severe. The two-flask method gave the lowest hardening indexes for all asphalts except for Coastal AC-20. However, several of the asphalts are not susceptible to solvent aging, so method differences, if they exist, are within viscosity measurement error. As expected, SHRP-AAK1 and -AAD1 were quite susceptible to solvent aging. They are both highly sensitive to oven aging and solvent aging (10). Viscosity ratios less than, but near 1, represent viscometer errors rather than solvent "softening" of asphalt.

Differences between the two-flask and single-flask methods are slight. However, it makes sense that the two-flask method is less severe and the data indicate this. The two-flask method is no more time consuming than the single flask method. Therefore, the two-flask method was chosen as the recovery scheme for the SHRP method.

Precision of the SHRP Method

Once a suitable recovery scheme was established, repeatability tests of the SHRP method were performed to obtain precision estimates. Several different pavement samples were extracted. The 60°C viscosities for the extracted asphalts from each pavement are shown in Table 2. GPC chromatograms taken on each of the samples showed that there was no solvent contamination.

In order to combine data from materials of differing viscosities, a normally distributed variable, percent difference (Table 2), was made that represents the percent deviation of the viscosity of the sample from the mean viscosity of that particular material. For example, the average viscosity for Tex 21/77 is 2.57 kPa·s (25,700 poise) and the value of the first trial of that pavement is 2.505 kPa·s (25,050 poise). The

TABLE 1 Comparison of tendencies of different recovery methods to solvent age asphalts

Sample	Method		
	Two Flask	Single Flask	Batch
SHRP-AAK1 (Trial 1)	1.08	1.20	1.30
SHRP-AAK1 (Trial 2)	1.11	1.13	1.13
SHRP-AAF1	.96	1.08	1.07
SHRP-AAD1	1.08	1.15	1.10
Exxon AC-20	.98	.98	1.07
Coastal AC-20	1.02	.99	1.07
Method Average	1.04	1.09	1.12

NOTE: Numbers shown are viscosity ratios.

TABLE 2 Reproducibility of SHRP extraction and recovery method (toluene, toluene/ethanol)

Sample	60°C Viscosity After Extraction (kPa·s)	%Difference
SHRP #1	0.9903	4.27
	0.9092	-4.27
SHRP #2	0.4780	-10.90
	0.5945	10.80
	0.5370	0.10
Tex 21/77	2.505	-2.53
	2.621	1.98
	2.358	-8.25
	2.765	7.59
	2.599	1.13
Young Brothers	95	-4.40
	90	-1.10
	88	-3.30

Coefficient of Variance (C.V.) = 6.1%

Upper 90% Confidence Limit on C.V. = 9.2%

Lower 90% Confidence Limit on C.V. = 4.6%

percent difference for that trial is then

$$\begin{aligned} \text{Percent difference} &= (2.505 - 2.570)/2.570 \times 100 \text{ percent} \\ &= -2.53 \text{ percent} \end{aligned} \quad (1)$$

The percent differences give information about how precise the method is regardless of the sample, as long as there are multiple measurements on that sample. The standard deviation of the percent difference values is an estimate of the coefficient of variance (CV), which is reported in the AASHTO proficiency tests. The estimate of CV for these data is 6.1 percent and there is a 90 percent chance that the true CV lies between 4.6 percent and 9.2 percent. Typical values for CV in recent AASHTO proficiency tests are between 25 and 42 percent. This means that, within our laboratory, the precision in the SHRP method associated with one standard deviation is about 6 percent whereas it is at least 25 percent for several laboratories using the current assortment of extraction and recovery methods. Of course, additional tests, such as the AASHTO proficiency tests, will be required to assess the interlaboratory CV.

Comparison of Extraction Methods

Replicate extractions and recoveries of Tex 21/77 and Young Brothers pavements were performed using the SHRP method, Modified Method A, and Modified Method B. The extractions exactly followed the procedures discussed previously. Toluene was the solvent for the Method B extractions of the Young Brothers pavement and toluene/15 percent EtOH was used to extract the Tex 21/77 samples. Viscosities of the extracted asphalts are listed in Table 3. Aggregates from several of the extractions were collected and soaked in 400 mL of TCE/15 percent EtOH. After four days, the solvent was filtered from the aggregate samples. The asphalt concentrations in the fil-

trates were measured by evaporation. The amount of strongly adsorbed material recovered from each extracted aggregate was determined and the percentage of the total asphalt that this material represents is shown in Table 3. The asphalt content of the Tex 21/77 pavement was found to be 8.3 percent and that for the Young Brothers pavement was 5.1 percent. The viscosities of the recovered asphalt and the total volume of solvent that contacted the aggregate (for the SHRP and Modified Method A tests) are also shown in Table 3. The viscosities are compared in Figures 3 and 4.

The results show that the SHRP method and Modified Method A yield similar average viscosities and have comparable precision. However, the Method B (using TCE) and Modified Method B (using toluene or toluene/ethanol) extractions result in lower viscosities in all cases and generally are less reproducible. This is despite solvent aging, which is more severe in reflux methods and has only hardened asphalts in previous tests. The amount of strongly adsorbed material left on the aggregate after extraction seems to depend heavily on the asphalt-aggregate system. The Tex 21/77 mixture contained limestone aggregate, which is more absorptive than the river gravel aggregate found in the Young Brothers pavement. The amount of strongly adsorbed asphalt varied significantly between methods on the more absorptive Tex 21/77 mixture but was relatively constant on the Young Brothers samples. This suggests that good solvent-aggregate contacting is only important when extracting from absorptive aggregates. The Tex 21/77 samples extracted by Modified Method B yielded very low viscosity asphalts and left large amounts of unextracted material on the aggregate. Modified Method B probably has poor extraction efficiency because the ethanol in the toluene/15 percent EtOH mixture concentrated itself in the vapor phase of the reflux extraction. This caused the condensate, which actually contacts the pavement, to have a higher than optimal ethanol concentration. It is possible that the unextracted material has a very high viscosity. Then its ab-

TABLE 3 Comparison of extraction methods

Sample	Method	Viscosity - 60°C (kPa·s)	Unextracted Asphalt (% of Total)	Total Solvent Used (mL)
Tex 21/77	SHRP: Toluene, Toluene/ETOH	2.51	1.4	2575
		2.62	1.0	3915
		2.36	1.0	2910
		2.77	0.6	3800
		2.60	-	3100
	Average	2.57	1.0	3260
	Modified Method A: Toluene, Toluene/ETOH	2.83	5.2	3085
		3.03	3.8	2985
		2.71	-	3230
	Average	2.86	4.5	3100
	Modified Method B: Toluene/ETOH	0.541	11.4	N/A
		0.655	11.7	N/A
		1.335	-	N/A
		Average	0.844	11.6
	Young Bros. Pavement	SHRP: Toluene, Toluene/ETOH	95.0	1.66
90.3			1.34	3000
88.2			1.26	3000
Average		91.2	1.42	3000
SHRP: TCE, TCE/ETOH		95.4	1.48	3000
		115.0	1.21	3000
		114.0	1.37	3000
Average		108.0	1.35	3000
Modified Method A: Toluene, Toluene/ETOH		93.7	1.60	3000
		90.6	2.04	3000
		91.8	2.00	3000
		Average	92.0	1.88
Modified Method B: Toluene		65.6	1.37	N/A
		62.2	1.16	N/A
	Average	63.9	1.27	N/A
Method B: TCE	67.4	1.75	N/A	
	80.4	1.80	N/A	
	Average	73.9	1.78	N/A

- indicates data not determined

sence would result in low viscosities for the extracted asphalt. However, information presented in the next paragraphs shows that this is probably not an adequate explanation.

There were still differences in viscosities of asphalts extracted using different methods or solvents for the Young Brothers material, even though the amount of asphalt extracted seemed to be constant. The Method *B* and Modified Method *B* extractions of this mixture used TCE or toluene, with no ethanol, and thus no ethanol-rich solvent contacted the aggregate. This, in combination with Young Brother's aggregate being less absorptive, resulted in strongly adsorbed asphalt levels that were comparable with other methods. However, the extracted asphalts had very low viscosities, just as in the Tex 21/77 samples. This indicates that strongly ad-

sorbed material may not be responsible for the low viscosities. Extracted asphalt viscosities varied directly with the power of the contacting solvent, increasing from toluene to toluene/15 percent EtOH to TCE/15 percent EtOH. It appears that, in general, the more rigorous solvent and contacting conditions yield higher viscosity asphalts. The one exception is that Modified Method *A*-extracted Tex 21/77 asphalt has a 10 percent higher viscosity than the SHRP-extracted sample. Possibly, this asphalt is more susceptible to solvent aging and recovery by the batch method would make it slightly harder than the SHRP method's two-flask recovery. Nonetheless, our strongly adsorbed asphalt data do not adequately explain the differences in asphalt viscosities, especially the low viscosities in the Method *B* samples.

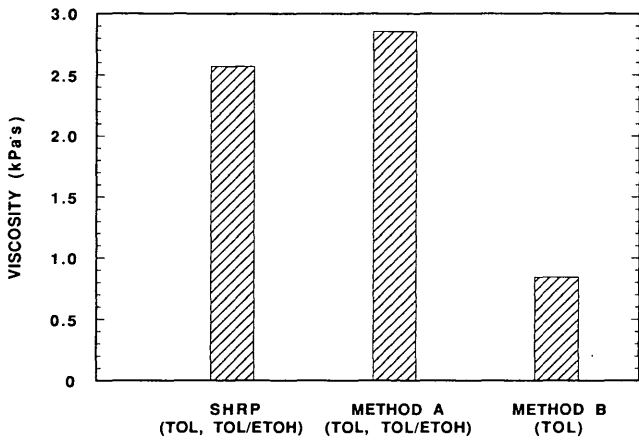


FIGURE 3 Average viscosities of asphalt binder extracted from Tex 21/77 samples using various extraction methods.

Extraction Efficiency of the Methods

Several questions remain concerning the strongly adsorbed material and its effect on the bulk asphalt. It is likely that no practical method will ever remove all of the strongly adsorbed components. Thus it is important to know how many washes are required to attain a certain level of extraction and how much bulk properties might change if the unextracted material were present.

The volume and asphalt concentration in each wash was measured for four SHRP extractions and two Modified Method A extractions of Tex 21/77. The solvents lose their ability to extract additional asphalt as the extraction proceeds (see Figure 5). The first wash always removes a high percentage of the total asphalt, but the extractability drops quickly. The last washes are only extracting small amounts of the total asphalt that was originally on the sample. This indicates that the solvent is not close to being saturated. However, it is still not clear if the strongly adsorbed material has difficulty diffusing

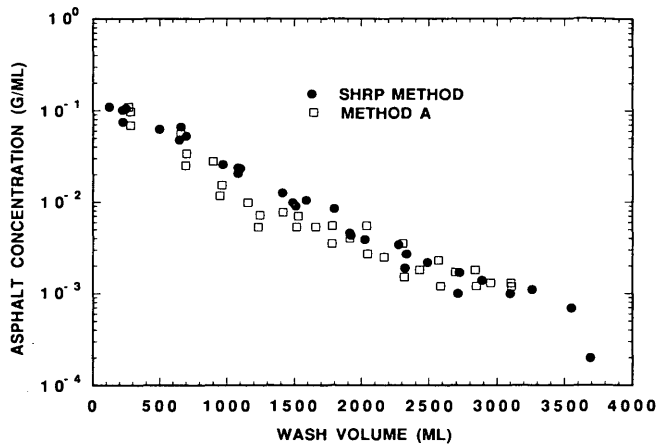


FIGURE 5 Concentration of asphalt in extraction filtrate as a function of cumulative wash volume for SHRP and Modified Method A procedures.

through the aggregate pore structure, or if an adsorption-desorption equilibrium is limiting the amount of asphalt that is extracted. The two methods seem comparable in their asphalt-removal patterns even though, at around 3000 mL, the SHRP Method has removed all but 1 percent of the asphalt and Modified Method A has left about 4.5 percent on the aggregate.

Several SHRP extractions of the Tex 21/77 pavement were extracted using different numbers of washes. Variation of the 60°C viscosity of the extracted asphalt as additional material is extracted is shown in Figure 6. The material extracted in the later washes does not seem to increase greatly the total viscosity of the asphalt. It was originally suspected that the material near the aggregate was very hard because of possible interactions with the aggregate during hot mixing and road aging. This may well be, but the amount of this material is so small that it cannot contribute much to the overall properties of the extracted asphalt. Further studies may involve determining whether it is necessary to achieve complete ex-

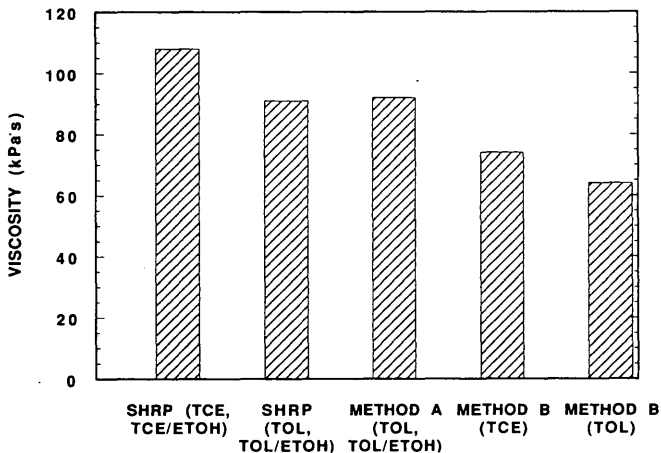


FIGURE 4 Average viscosities of asphalt binder extracted from Young Brothers samples using various extraction methods.

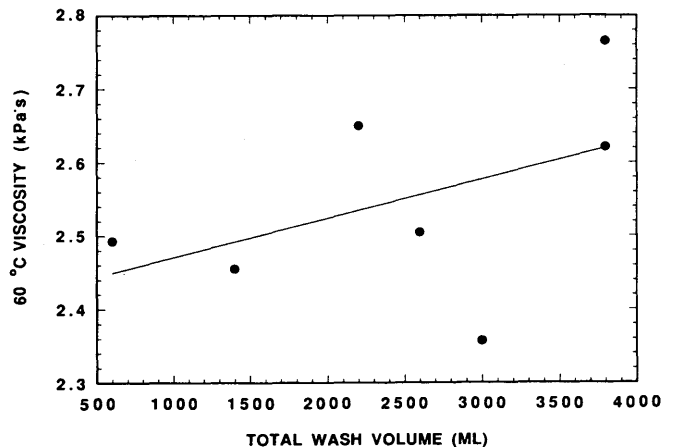


FIGURE 6 Viscosity of the recovered asphalt binder as affected by total wash volume of solvent used in extraction process for SHRP Method (Tex 21/77 pavement).

traction if representative asphalt can be obtained in the early washes.

While working to remove the last traces of asphalt from the aggregate, it is worth considering that material that is so strongly adsorbed or associated with the aggregate may not be contributing to asphalt "binder" properties. If this material is caught in aggregate pores, or is adsorbed, it cannot be performing any of the mechanical functions of a binder. It may be important in adhesion or water-stripping phenomena, but those effects could not be measured if the strongly adsorbed material were mixed with the bulk asphalt.

SUMMARY

An integrated asphalt extraction and recovery procedure, the SHRP method, has been developed and tested. It improves on previous methods by accomplishing complete solvent removal, limiting solvent aging, and extracting more of the strongly adsorbed material from the aggregate. Reproducibility tests indicate that the method is precise to about 7 percent for one standard deviation for a single operator. Additional tests are required to determine interlaboratory precision. Tests for solvent aging in the recovery method show that little hardening occurs during recovery for the SHRP method.

ASTM Methods *A* and *B*, modified using toluene and toluene/15 percent EtOH as solvents, were also tested for comparison. Extracted asphalt viscosities for Modified Method *A* were about 10 percent higher than those for the SHRP method on the Tex 21/77 pavement and were similar on the Young Brothers' samples. Modified Method *A* also left about 5 percent of the total asphalt on the aggregate after extraction of the Tex 21/77 samples, whereas the SHRP method removed all but the last 1 percent. The differences in the viscosities of the methods may be caused by differences in extraction efficiency, or solvent hardening in Modified Method *A* because it employs a more severe recovery scheme. However, differences between the SHRP method and Method *A*, with the modifications we have described, are negligible.

Method *B* and Modified Method *B* consistently yielded lower viscosities than the other methods and were less precise. From past experience, one might expect Method *B*-extracted asphalts to have higher viscosities because of solvent aging and lower viscosities caused by incomplete extraction of asphalt. Neither one of these phenomena adequately describes the behavior of the Method *B*-extracted samples. However, Method *B* does have an inherent problem in that it maintains the asphalt in a dissolved state for several hours at high temperature. This is likely to promote reactions that can distort properties. Also, ethanol additions to the extraction solvent in Modified Method *B* extractions are not advised because it is difficult to control the ethanol content in the reflux that contacts the aggregate.

Comparisons of viscosities of asphalts extracted using different methods showed that viscosities varied directly with solvent strength, contacting efficiency, and volume of solvent used in the extraction. The viscosities were not, however, related to the amount of strongly adsorbed material that we could recover from the aggregate after extraction.

Because the real properties of a pavement asphalt are indeterminate and a method that removes all of the asphalt from the aggregate would be impractical, the specification of proper extraction methods and operating conditions will be somewhat arbitrary. Both the SHRP and Method *A* (with modifications in procedure) equipment are suitable for such extraction methods. The adoption of the Roto-vap method using the proper recovery conditions would guarantee complete solvent removal and improve the accuracy and precision of extraction methods. Also, periodic checks of residual solvent contamination in recovered asphalts by using GPC analysis is advised.

At the moment, the SHRP and Modified Method *A* procedures will provide researchers with better asphalt samples that are free of contaminants, represent all of the asphalt in the mixture, and have properties that are nearly unaltered during extraction. Still, there are problems with the methods because they require considerable operator attention and too much laboratory space. Further work addressing these problems is needed before the methods will be appreciated by a large portion of the practitioners.

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