Recovery of Asphalt from Methylene Chloride and Trichloroethylene by the Abson Method

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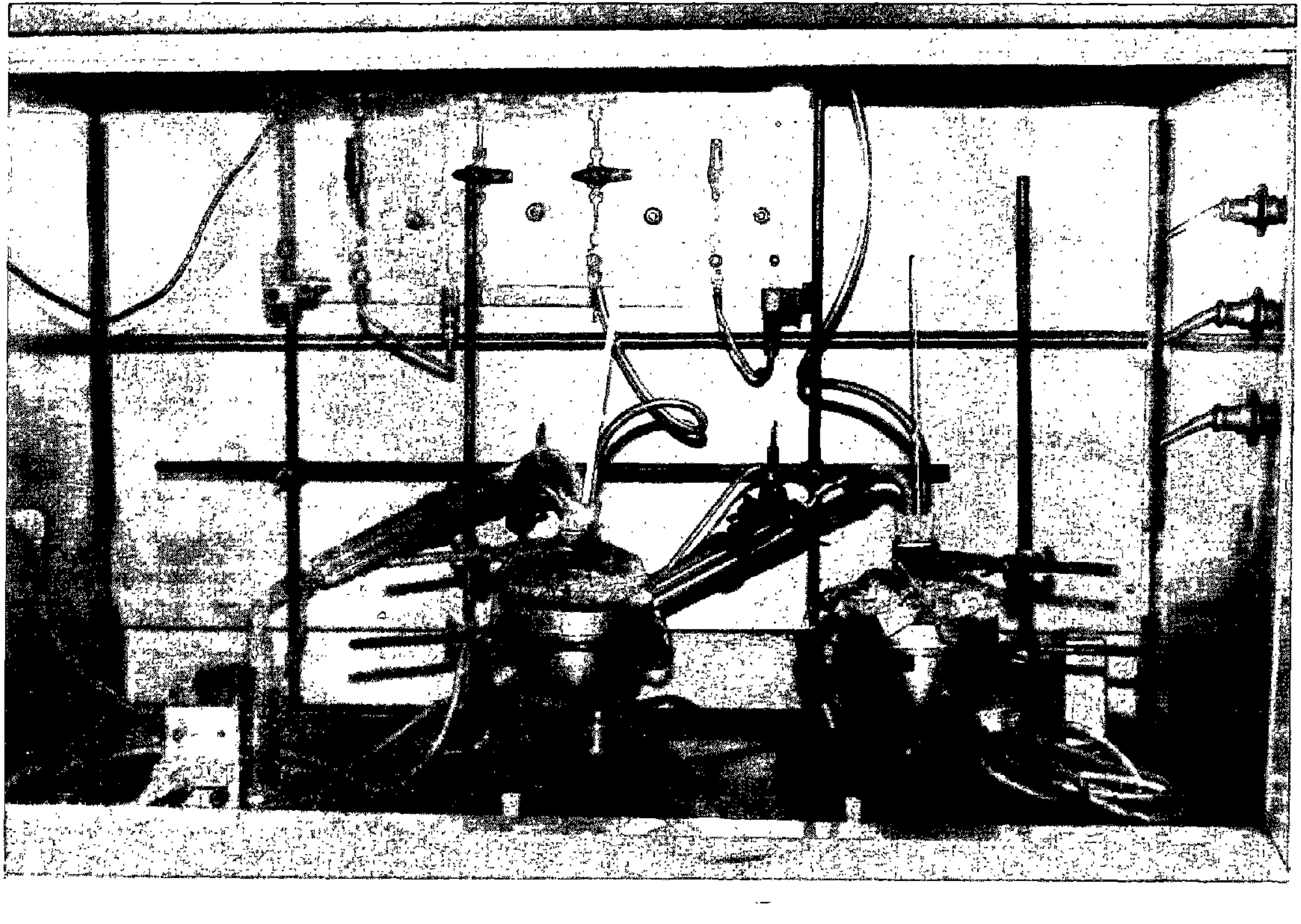

U.S. Department of Transportation
Federal Highway Administration

Research, Development, and Technology
Turner-Fairbank Highway Research Center
6300 Georgetown Pike
McLean, Virginia 22101-2296

FOREWORD

This report presents the findings of a research study to determine if methylene chloride (CH_2Cl_2) can be used to recover asphalts using the Abson Method (AASHTO T 170 and ASTM D 1856), and to compare its effects on recovered binder properties to those of trichloroethylene (C_2HCl_3). This report will be of interest to individuals concerned with quality control testing of hot-mix asphalt concrete.

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Director, Office of Engineering
and Highway Operations
Research and Development

NOTICE

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16. Abstract

The objective of ~~this~~ the in-house study was to determine if methylene chloride (CH_2Cl_2) can be used to recover asphalts using the Abson Method (AASHTO T 170 and ASTM D 1856), and to compare its effects on recovered binder properties to those of trichloroethylene (C_2HCl_3). Current nationally standardized test procedures (AASHTO and ASTM) do not allow methylene chloride in the Abson method. Virgin paving grade asphalts and hardened asphalts were used in ~~this~~ the evaluation. Hardened asphalts consisted of paving grade asphalts aged by the thin film oven procedure, paving grade asphalts extracted from aged loose mixtures and cores, and coating grade roofing asphalts. The following tests were performed before and after recovering the asphalts from trichloroethylene or methylene chloride: (1) penetration at 25 °C, (2) viscosity at 60 °C, (3) viscosity at 135 °C, (4) high pressure gel permeation chromatography, and (5) infrared spectral analysis. The data indicated that methylene chloride can be used to recover asphalts from mixtures using the Abson Method. Both solvents had some statistically significant effects on some asphalt properties, but neither solvent could clearly be recommended over the other. The properties which were affected indicated hardening or increased molecular structuring. Methylene chloride may be a slightly better solvent because replicate asphalt samples recovered using this solvent provided more consistent data from sample to sample. For practical purposes, such as quality control testing and evaluating aged pavement properties, both solvents appear suitable for recovering asphalts.

17. Key Words
Methylene Chloride, Trichloroethylene, Recovery, Abson Method, Infrared, Gel Permeation Chromatography, GPC, Rheological, Asphalt Properties

18. Distribution Statement
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SI* (MODERN METRIC) CONVERSION FACTORS

APPROXIMATE CONVERSIONS TO SI UNITS

LENGTH

Symbol	When You Know	Multiply By	To Find	Symbol
in	inches	25.4	millimetres	mm
ft	feet	0.305	metres	m
yd	yards	0.914	metres	m
mi	miles	1.61	kilometres	km

AREA

Symbol	When You Know	Multiply By	To Find	Symbol
in²	square inches	645.2	millimetres squared	mm²
ft²	square feet	0.093	metres squared	m²
yd²	square yards	0.836	metres squared	m²
ac	acres	0.405	hectares	ha
mi²	square miles	2.59	kilometres squared	km²

VOLUME

Symbol	When You Know	Multiply By	To Find	Symbol
fl oz	fluid ounces	29.57	millilitres	mL
gal	gallons	3.785	litres	L
ft³	cubic feet	0.028	metres cubed	m³
yd³	cubic yards	0.765	metres cubed	m³

NOTE. Volumes greater than 1000 L shall be shown in m³.

MASS

Symbol	When You Know	Multiply By	To Find	Symbol
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams	Mg

TEMPERATURE (exact)

Symbol	When You Know	Multiply By	To Find	Symbol
°F	Fahrenheit temperature	5(F-32)/9	Celcius temperature	°C

APPROXIMATE CONVERSIONS FROM SI UNITS

LENGTH

Symbol	When You Know	Multiply By	To Find	Symbol
mm	millimetres	0.039	inches	in
m	metres	3.28	feet	ft
m	metres	1.09	yards	yd
km	kilometres	0.621	miles	mi

AREA

Symbol	When You Know	Multiply By	To Find	Symbol
mm²	millimetres squared	0.0016	square inches	in²
m²	metres squared	10.764	square feet	ft²
ha	hectares	2.47	acres	ac
km²	kilometres squared	0.386	square miles	mi²

VOLUME

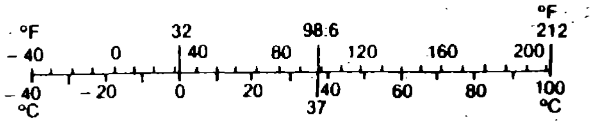
Symbol	When You Know	Multiply By	To Find	Symbol
mL	millilitres	0.034	fluid ounces	fl oz
L	litres	0.264	gallons	gal
m³	metres cubed	35.315	cubic feet	ft³
m³	metres cubed	1.308	cubic yards	yd³

MASS

Symbol	When You Know	Multiply By	To Find	Symbol
g	grams	0.035	ounces	oz
kg	kilograms	2.205	pounds	lb
Mg	megagrams	1.102	short tons (2000 lb)	T

TEMPERATURE (exact)

Symbol	When You Know	Multiply By	To Find	Symbol
°C	Celcius temperature	1.8C + 32	Fahrenheit temperature	°F



(Revised April 1989)

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* SI is the symbol for the International System of Measurement

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INTRODUCTION

1. Recovery Testing

To determine the material composition of an asphalt paving mixture, solvents which can extract and allow the asphalt to be recovered are needed. In the early 1900's, carbon disulfide was used as a solvent for extracting and recovering asphalts and tars. Because of its extremely hazardous, flammable nature, it was an unsatisfactory solvent for routine laboratory use, and safer solvents of approximately the same solvent power were sought.

During the development of the Abson Method for recovering asphalts, many solvents were evaluated, and benzene was chosen as the standard solvent.(1) This solvent, although highly toxic and flammable, was the only suitable one found. Therefore, if an asphalt was to be recovered, benzene had to be used in the extraction procedure. Carbon tetrachloride was the only chlorinated solvent originally evaluated during the development of the Abson Method. It is nonflammable, but was found to harden asphalts, and thus could not be used.

A solvent less flammable than benzene was later sought, and trichloroethylene was found to be suitable for both extracting and recovering asphalts.(1) It is nonflammable and also less toxic than benzene, and thus the use of benzene has been eliminated from extraction and recovery testing. The American Association of State Highway and Transportation Officials (AASHTO) and American Society for Testing and Materials (ASTM) procedures for the recovery of asphalts by the Abson Method (AASHTO T 170-84 and ASTM D 1856-79) only allow trichloroethylene.(2,3)

Note: ASTM D 1856-79 currently includes benzene, but this solvent is to be removed from the method in 1990 because it has been found to be highly carcinogenic. It is currently not allowed in extraction testing.

2. Extraction Testing

Many solvents are capable of extracting asphalts and aggregates if the binder properties are not needed, but the most toxic ones have been excluded from the test procedures. AASHTO and ASTM procedures for extraction testing (AASHTO T 164-86 and ASTM D 2172-88) allow the use of trichloroethylene, methylene chloride, and 1,1,1-trichloroethane.

By current standards, trichloroethylene and methylene chloride are more toxic than 1,1,1-trichloroethane; however, all three require equal safety precautions against skin contact, eye contact, and inhalation. Maximum allowable vapor concentrations are given in table 1. Current Federal regulations on these solvents and their effects on health are reported elsewhere.(4)

Any of the three solvents can be used in four out of the five extraction methods listed under the test procedures. In the fifth method, which uses the vacuum extractor, ASTM only allows methylene chloride, and a small amount of denatured ethyl alcohol must be added to the initial mixture soaking process. The amount of alcohol added is less than 10 percent of the total solvent used in the procedure. AASHTO allows all three solvents in the vacuum extraction method, and the use of denatured ethyl alcohol is optional. With the vacuum extraction procedure, methylene chloride may extract the aggregates faster than the other two solvents, and less solvent may be necessary.

As previously stated, only trichloroethylene can be used in the recovery of asphalts. 1,1,1-trichloroethane cannot be used because, like carbon tetrachloride, it was found to harden asphalts.(1) Methylene chloride is not allowed in the Abson Method, but whether it is a suitable solvent for recovering asphalts is unknown as it has not been evaluated.

Table 1. Maximum allowable vapor concentrations.

Solvent	Time-Weighted Average Concentration for 8-hour Exposure for 5-day week, ppm	
	A	B
Benzene	1	10
Trichloroethylene	50	100
Methylene Chloride	50	500*
1,1,1-Trichloroethane	350	350

A - Committee of the American Conference of Governmental Hygienists, 1988.
B - Code of Federal Regulations, Title 24-Labor, 1987.

* This was to be reduced, but a new level was not available when this table was developed.

Table 2. Virgin asphalts used in Phase I.

FHWA ID	Grade	Supplier
B5603	AC-10	Amoco, Baltimore, MD
B5851	AC-20	Southland, Laurel, MS
B5856	AC-30	Amoco, Lithonia, GA
B5891	AC-10	Cenex, UT
B5901	AC-5	Chevron, Mobile, AL
B5928	AC-20	Arco, Dumfries, VA
B5941	AC-20	Exxon, Bayway, NJ
B5947	60/70 Pen	Amoco, Whiting, IN
C8658	AC-40	Amoco, Savannah, GA
C8724	AC-40	Exxon, Charleston, SC

Table 3. Infrared (IR) spectral regions.

Region	Wave Numbers, cm^{-1}	Functional Group
1	1775 to 1670	C=O (Carbonyl Stretch)
2	1670 to 1532	Unsaturated C=O, C=C (Olefinic Stretch)
3	1180 to 1113	Secondary & Tertiary C-O, S=O
4	1113 to 983	Primary C-O, S=O
5	917 to 843	Polysubstituted Aromatic
6	843 to 785	Aromatic
7	785 to 687	Monosubstituted Aromatic C-H
8	1325 to 1281	Aromatic Amine C-N or Oxidized Nitrogen N-O

OBJECTIVE

The objective of this study is to determine if methylene chloride (CH_2Cl_2) can be used to recover asphalts by the Abson Method, and to compare its effects on recovered binder properties to those of trichloroethylene (C_2HCl_3; abbreviated TCE in this report to avoid confusion). Several State highway agencies use methylene chloride in the vacuum extraction method, and thus including this solvent in the Abson Method would be beneficial. However, there is no published data concerning the suitability of this solvent for recovering asphalts. ASTM proposes to include methylene chloride in the Abson Method in 1990.

PHASE I - VIRGIN ASPHALTS

1. Materials and Test Procedures

The 10 virgin paving grade asphalts identified in table 2 were selected and the following tests were performed before and after recovering the asphalts from solution in either trichloroethylene or methylene chloride:

- Penetration at 77 °F (25 °C), (100 g, 5 s), (AASHTO T 49 and ASTM D 5).(2,3)
- Absolute Viscosity at 140 °F (60 °C), (AASHTO T 202 and ASTM D 2171).(2,3)
- Kinematic Viscosity at 275 °F (135 °C), (AASHTO T 201 and ASTM D 2170).(2,3)
- High Pressure Gel Permeation Chromatography (HP-GPC).(5,6)
- Infrared (IR) Spectral Analysis.(6)

Five samples of each asphalt were poured into 3-fluid ounce tin containers, each sample being approximately 75 g in weight. The difference in penetration between the highest and lowest values for any of the five replicates was 1 dmm. One sample was used to determine the properties before recovery; another sample was dissolved and recovered using Fisher Scientific reagent grade methylene chloride, and another using Fisher Scientific reagent grade trichloroethylene. The remaining two samples were reserves.

The Abson Method for recovering asphalts (AASHTO T 170 and ASTM D 1856) was performed according to the standardized procedure with no deviations. Each neat asphalt sample to be recovered was first dissolved and hand stirred in 500 ml of solvent at room temperature. This was performed over a 2-hour period, which is usually the maximum amount of time an asphalt may be in the solvent during and after extraction. The primary distillation operation, which is used to concentrate the solution to about 200 ml, was included in the procedure. The asphalt properties previously listed were compared before and after recovery to determine whether there were any changes in chemical or physical properties. Most Abson recoveries did not need more than the 15-minute minimum time period required by the method while the flow of carbon dioxide is 900 ml/min.

Rheological properties were measured by standardized penetration and viscosity tests.(2,3)

The HP-GPC technique was used to obtain the percentages of large molecular size (LMS), medium molecular size (MMS), and small molecular size (SMS) contents at 113 °F (45 °C).(5,6) A Waters Associates 600E system controller, 990 Photodiode Array Detector, and three columns connected in series (Waters Associates, Ultrastyragel columns 1000 °A, 500 °A, and 100 °A) were used to obtain these size contents. Tests were performed in duplicate and the data averaged.

An IR spectral analysis was used to detect the amount of infrared absorbance in eight spectral regions, defined by the ranges in wave numbers in table 3.(6) All organic materials absorb infrared radiation at various infrared wave numbers, or energies, according to their molecular structure or functional group composition. The spectrum for each asphalt was obtained at 77 °F (25 °C) using a Nicolet 390 FTIR Spectrometer and by plotting the fraction of infrared absorbance versus the wave number (number of waves per centimeter; cm^{-1}). Ten scans of a sample were taken and the data averaged. An example of a spectrum is shown in figure 1.

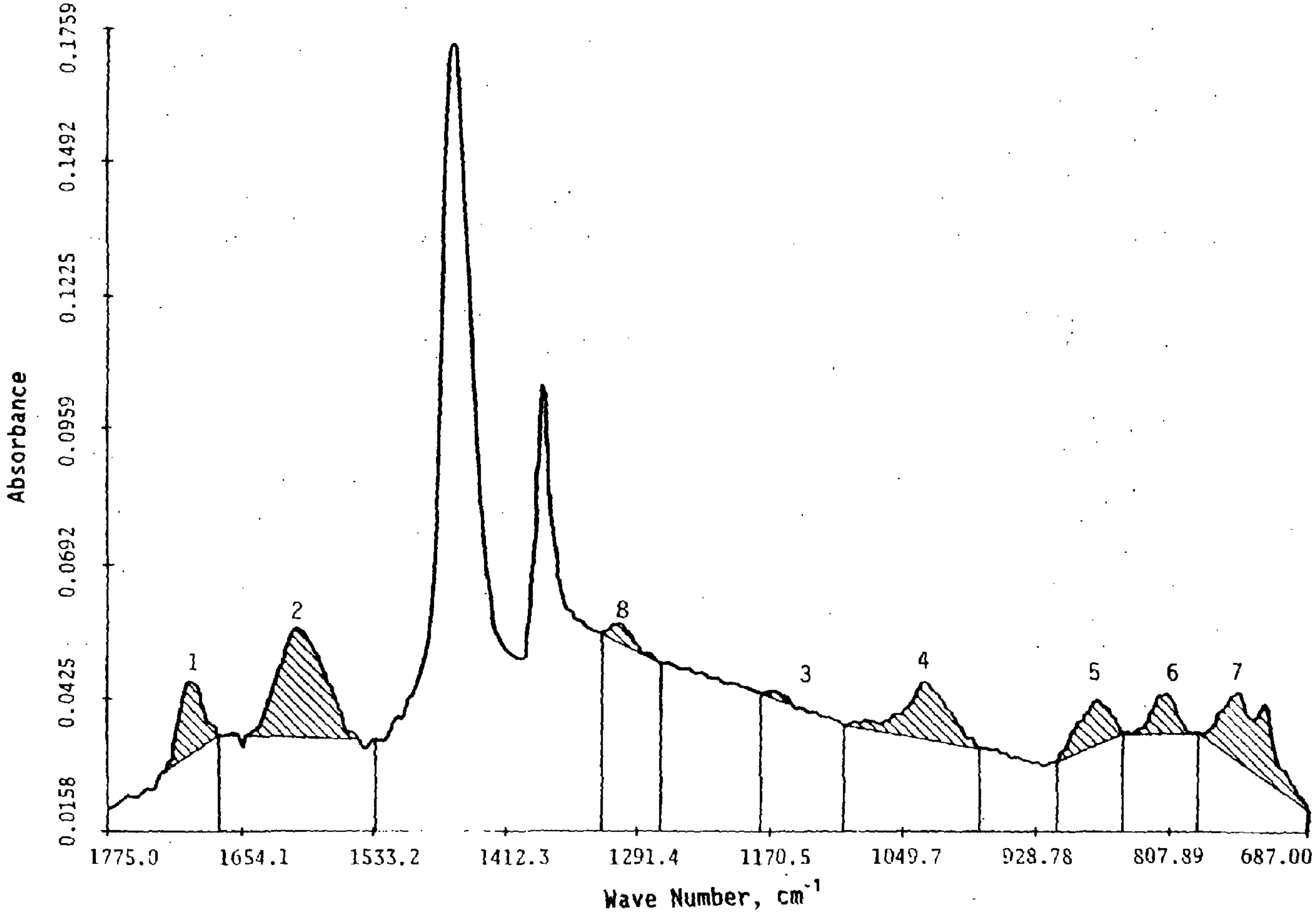

Figure 1. Example of an infrared spectrum for asphalt.

For IR spectral analyses, the asphalts were applied as a film to a KBr plate using a spatula bearing the neat hot asphalt. Sample scans were obtained by directing the infrared radiation through the films. Because absorbance is a function of film thickness, the thickness was adjusted so the peak at a wave number of 2926.6 cm^{-1} fell between 0.80 to 0.90 absorbance. This infrared region reflects the presence of strong C-H stretching groups which are common to all asphalts. Absorbance in this region is more strongly affected by film thickness than absorbance in the other regions, and thus it is assumed that a similar absorbance from asphalt to asphalt in this region is indicative of a uniform thickness, which is needed to compare asphalts. This region is not shown in figure 1.

The areas under the peaks for each region, as shown by the hatched areas in figure 1, are roughly proportional to the concentration of the given functional group. An infrared datum reported in this study for a given region is the ratio of the hatched area in that region to the total hatched area. It is assumed that changes in the total area from sample to sample are due to minor variations in asphalt film thicknesses and that using a ratio accounts for these variations. Thus the reported data are relative. A negative datum indicates a valley is between the pairs of wave numbers.

The rheological tests required the asphalt samples to be heated to a maximum of 275 °F (135 °C). This may have had a minor, unknown effect on the recovered asphalt properties. The HP-GPC technique and the IR spectral analysis only required a minor amount of heating to soften the samples.

2. Test Results

Penetration and viscosity data are given in table 4; HP-GPC data are given in table 5, and IR data are given in tables 6, 7, and 8.

Student's paired *t*-tests at a 95 percent confidence level and linear regression analyses were used to analyze the data. The paired *t*-test determines whether or not two data sets are significantly different when

Table 4. Penetration and viscosity data.

FHWA ID	Penetration, 25 °C (100 g, 5 s), 0.1 mm			Viscosity, 135 °C Centistokes			Viscosity, 60 °C Poise		
	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE
B5603	126	129	122	245	252	270	975	1006	1121
B5851	74	75	68	501	510	506	2229	2210	2181
B5856	62	66	68	617	634	685	3559	3554	4065
B5891	85	82	76	290	315	312	1259	1334	1397
B5901	147	149	155	226	237	234	580	632	576
B5928	67	67	76	432	477	418	2281	2398	1845
B5941	71	73	79	416	431	439	1996	2079	2005
B5947	70	75	84	302	311	322	1270	1351	1278
C8658	54	60	51	675	695	680	4346	4496	3928
C8724	67	67	70	614	648	657	3570	3860	3348
Avg =	82	84	85	432	451	452	2207	2292	2174
Std Dev =	60	60	61	331	340	346	2517	2598	2425

Before = Before Recovery
CH_2Cl_2 = Recovered from Methylene Chloride
TCE = Recovered from Trichloroethylene

Table 5. Gel permeation chromatography (HP-GPC) data.

FHWA ID	Percent Large Molecular Size			Percent Medium Molecular Size			Percent Small Molecular Size		
	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE
B5603	17.1	18.2	17.3	49.8	49.0	50.0	33.1	32.8	32.8
B5851	26.4	26.5	27.3	47.6	47.4	46.9	26.0	26.1	25.8
B5856	24.3	23.7	26.8	49.8	50.1	47.5	25.9	26.2	25.8
B5891	13.0	14.4	14.4	44.8	44.4	44.5	42.2	41.2	41.0
B5901	17.0	16.9	17.1	49.7	49.7	48.9	33.3	33.4	34.0
B5928	20.2	20.6	21.4	48.8	48.1	47.9	31.0	31.3	30.7
B5941	20.5	20.8	20.9	49.1	48.8	48.5	30.4	30.4	30.6
B5947	15.3	16.3	15.8	50.0	50.1	49.5	34.8	33.7	34.8
C8658	22.5	26.6	25.8	51.3	49.1	49.4	26.2	24.3	24.8
C8724	25.5	28.1	26.9	50.1	46.6	48.1	24.4	25.2	25.0
Avg =	20.2	21.2	21.4	49.2	48.3	48.1	30.7	30.5	30.5
Std Dev =	9.1	9.6	10.1	3.6	3.6	3.2	10.9	10.4	10.7

Table 6. Infrared (IR) data of the asphalts before recovery.

FHWA ID	Spectral Region 1	2	3	4	5	6	7	8
B5603	-0.002	0.418	0.009	0.058	0.102	0.099	0.293	0.024
B5851	-0.004	0.283	0.018	0.113	0.105	0.107	0.347	0.031
B5856	-0.026	0.503	0.045	-0.052	0.042	0.103	0.351	0.033
B5891	-0.047	0.395	0.008	0.106	0.133	0.105	0.276	0.025
B5901	-0.038	0.344	0.010	0.149	0.101	0.090	0.317	0.027
B5928	-0.042	0.440	0.018	0.067	0.100	0.097	0.294	0.025
B5941	0.014	0.367	0.020	0.039	0.091	0.089	0.347	0.034
B5947	-0.052	0.400	-0.016	0.101	0.118	0.094	0.330	0.026
C8658	-0.103	0.504	0.050	0.003	0.058	0.112	0.345	0.031
C8724	-0.048	0.454	0.020	-0.013	0.081	0.105	0.372	0.029
Avg =	-0.035	0.411	0.018	0.057	0.093	0.100	0.327	0.028
Std Dev =	0.066	0.138	0.037	0.127	0.054	0.015	0.062	0.007

Table 7. Infrared (IR) data of asphalts recovered from methylene chloride (CH_2Cl_2).

FHWA ID	Spectral Region 1	2	3	4	5	6	7	8
B5603	0.020	0.396	0.023	0.111	0.093	0.102	0.235	0.021
B5851	-0.014	0.294	0.025	0.107	0.106	0.122	0.328	0.032
B5856	-0.051	0.497	0.037	0.000	0.055	0.109	0.327	0.025
B5891	-0.035	0.387	0.011	0.077	0.121	0.101	0.311	0.027
B5901	-0.052	0.388	-0.003	0.067	0.134	0.100	0.333	0.033
B5928	-0.020	0.421	0.023	0.056	0.097	0.093	0.303	0.026
B5941	-0.007	0.387	0.020	0.076	0.110	0.097	0.287	0.029
B5947	-0.050	0.394	-0.003	0.072	0.124	0.106	0.330	0.028
C8658	-0.104	0.492	0.046	-0.028	0.069	0.116	0.377	0.031
C8724	-0.013	0.480	0.039	-0.032	0.039	0.094	0.361	0.034
Avg =	-0.033	0.414	0.022	0.051	0.095	0.104	0.319	0.029
Std Dev =	0.068	0.124	0.033	0.104	0.063	0.019	0.079	0.008

Table 8. Infrared (IR) data of asphalt recovered from trichloroethylene (TCE).

FHWA ID	Spectral Region 1	2	3	4	5	6	7	8
B5603	0.030	0.428	0.025	0.064	0.067	0.108	0.254	0.024
B5851	-0.003	0.268	0.027	0.126	0.101	0.123	0.327	0.031
B5856	-0.024	0.454	0.052	-0.008	0.055	0.099	0.344	0.029
B5891	-0.038	0.394	0.013	0.087	0.124	0.105	0.291	0.024
B5901	-0.034	0.355	0.016	0.093	0.111	0.099	0.330	0.030
B5928	-0.006	0.439	0.021	0.035	0.076	0.100	0.307	0.027
B5941	0.013	0.368	0.022	0.053	0.105	0.114	0.300	0.026
B5947	-0.060	0.408	-0.014	0.126	0.128	0.105	0.282	0.025
C8658	-0.087	0.486	0.053	-0.021	0.062	0.107	0.371	0.029
C8724	-0.009	0.452	0.042	0.010	0.027	0.117	0.330	0.032
Avg =	-0.022	0.405	0.026	0.057	0.086	0.108	0.314	0.028
Std Dev =	0.069	0.126	0.040	0.105	0.066	0.016	0.067	0.006

Table 9. Statistical results comparing the asphalts recovered from the solvents to the asphalts before recovery.

	Methylene Chloride to Before Recovery			Trichloroethylene to Before Recovery		
Test	r^2	Slope	*t*	r^2	Slope	*t*
Pen 25 °C	0.99	0.99	2.215 NS	0.93	0.98	0.994 NS
Vis 60 °C	1.00	1.03	3.059 I	0.95	0.94	-0.363 NS
Vis 135 °C	1.00	1.03	4.927 I	0.98	1.04	2.862 I
LMS	0.91	1.01	2.404 I	0.96	1.08	3.832 I
MMS	0.60	0.77	-2.044 NS	0.78	0.78	-3.777 D
SMS	0.98	0.95	-0.961 NS	0.98	0.97	-0.939 NS
Region 1	0.67	0.85	0.345 NS	0.77	0.92	2.432 I
Region 2	0.91	0.85	0.411 NS	0.94	0.88	-0.982 NS
Region 3	0.71	0.75	1.121 NS	0.89	1.00	3.582 I
Region 4	0.55	0.61	-0.482 NS	0.76	0.70	-0.061 NS
Region 5	0.58	0.86	0.264 NS	0.52	0.89	-1.024 NS
Region 6	0.31	0.69	1.517 NS	0.09	0.32	2.581 I
Region 7	0.33	0.74	-0.760 NS	0.36	0.65	-1.476 NS
Region 8	0.13	0.44	0.073 NS	0.23	0.36	-0.753 NS
		$t_{0.05}$ = 2.262			$t_{0.05}$ = 2.262	

the data are paired or related.(7) If the absolute value of the *t* generated from the data is greater than the *t* at the 95 percent confidence level, defined as $t_{0.05}$, then there is a significant difference between the two data sets. In the tables of this report, "NS" means there was no significant difference between two data sets. In analyses comparing asphalts recovered from solvents to asphalts before recovery, "I" indicates the recovery process increased the property, and "D" indicates the recovery process decreased the property. In analyses comparing asphalts recovered from methylene chloride to asphalts recovered from trichloroethylene, the data for the asphalts recovered from trichloroethylene are used as the reference data because this is the standard solvent. Thus the analyses give the effects of changing from trichloroethylene to methylene chloride. The regressions indicate whether or not the two sets of data correlate.

Standard deviations (two $\text{sigma}_{\text{sample}}$) of the data sets are also included as supplementary information. Differences in standard deviations between the before and after recovery test data may indicate that a solvent is affecting the data, but the standard deviations were primarily included to determine the sensitivity of each test property to changes in the grade of asphalt, and whether this sensitivity could affect the conclusions of the other statistical analyses. Ninety-five percent of the data for the entire population of asphalts should fall within the average value plus and minus this standard deviation.

a. Results of the *t*-tests

Statistical results for the data comparisons between the samples recovered from the solvents and the samples before recovery, are given in table 9. Methylene chloride had no significant effect on the penetrations but slightly hardened the asphalts according to both viscosities. The HP-GPC data showed an increase in the LMS content, which complemented the changes in the viscosities. No corresponding significant decreases in the other two HP-GPC sizes were obtained. The IR data provided no significant differences, and thus did not explain the changes in the viscosities and LMS content.

Trichloroethylene had no effect on the penetrations or viscosities at 140 °F (60 °C), but slightly hardened the asphalts according to the viscosities at 275 °F (135 °C). As with methylene chloride, there was an increase in LMS content. This complemented the increases in viscosities at 275 °F (135 °C), but not the data for the two other rheological tests. The increase in the LMS content corresponded to a decrease in the MMS content.

The IR data for the asphalts recovered from trichloroethylene showed increases in regions 1 (C=O Carbonyl Stretch), 3 (Secondary and Tertiary C-O and S=O), and 6 (Aromatic). No corresponding significant decreases in the other regions were found. Increases in these regions, a sign of aromatic molecules being oxidized, could be expected based on the hardening shown by the viscosity at 135 °C and the HP-GPC data.

Table 10 shows the statistical results comparing the asphalts recovered from the two solvents. The only differences between the asphalts were in IR spectral regions 1 (C=O Carbonyl Stretch) and 5 (Polysubstituted Aromatic), which means that in general the solvents affected the asphalt properties similarly. The difference in region 1 was mainly related to the use of trichloroethylene. Table 9 indicates that this solvent increased the relative area in this region whereas methylene chloride had no effect. The significant difference in region 5, where the samples recovered from methylene chloride had a higher relative area, appeared to be related to minor effects produced by both solvents as neither solvent showed a significant effect in table 9. Although these differences in the IR data were found, there were no differences in the rheological or HP-GPC data.

b. Results of the Regressions and Analyses of the Standard Deviations

The coefficients of determination (r^2) for the regression analyses are also shown in tables 9 and 10. Meanings applied to these coefficients in this study are given in table 11. For high coefficients, the slopes in tables 9 and 10 generally approached one, indicating that either the solvent had no effect (where the *t*-value is NS), or the effect was similar from asphalt to

Table 10. Statistical results comparing the asphalts recovered from methylene chloride (CH_2Cl_2) to the asphalts recovered from trichloroethylene (TCE).

Test	r^2	Slope	t
Pen 25 °C	0.94	1.00	-0.266 NS
Vis 60 °C	0.93	1.11	1.091 NS
Vis 135 °C	0.97	1.02	-0.148 NS
LMS	0.94	1.02	-0.441 NS
MMS	0.63	1.43	0.646 NS
SMS	0.99	1.02	-0.328 NS
Region 1	0.90	1.04	-3.065 D
Region 2	0.85	1.06	1.057 NS
Region 3	0.83	0.92	-1.471 NS
Region 4	0.68	1.20	-0.598 NS
Region 5	0.89	1.00	2.671 I
Region 6	0.09	3.57	-1.129 NS
Region 7	0.70	1.39	0.817 NS
Region 8	0.57	1.82	1.077 NS

$t_{0.05} = 2.262$

Table 11. Meanings for regression analyses.

Regression, r^2	t-test	Conclusion
High, ≥ 0.81	NS	Data are similar.
High, ≥ 0.81	I (or D)	Data has increased (or decreased) in a correlated manner. A slope of one indicates a parallel shift of the data.
Low, < 0.81	NS	Effect of solvent varies from asphalt to asphalt.
Low, < 0.81	I (or D)	Data has increased (or decreased) overall but the effect varies from asphalt to asphalt.

asphalt (where the *t*-value is I or D). For low coefficients, the slopes tend to deviate from one, which indicates the data is scattered. Overall, neither solvent appeared to be more advantageous based on these analyses, although the slightly higher coefficient in table 9 for the penetration data of the asphalts recovered from methylene chloride appears to match a visual analysis of the data. By examining table 4, the penetrations for the asphalts recovered from methylene chloride appear to be slightly closer to the penetrations of the asphalts before recovery than those recovered from trichloroethylene.

As shown by tables 9 and 10, penetration, both viscosity tests, LMS content, and the SMS content consistently provided the highest coefficients. The MMS content had lower coefficients. This was attributed to the small variation in the MMS content from asphalt to asphalt, as shown by the small standard deviations in table 5. This low variation indicates that the usefulness of the MMS content for comparing asphalts may be very limited.

Spectral regions had high to low coefficients. Many of the low coefficients also appeared to be the result of very little variation in the data from asphalt to asphalt. Tables 6 through 8 show that regions 6 (Aromatic) and 8 (Aromatic Amine C-N or Oxidized Nitrogen N-O), in particular, had small standard deviations.

Overall, the data indicated that methylene chloride can be used in the recovery process as this solvent performed as well as trichloroethylene and most effects on asphalt properties were either insignificant or slight.

3. Repeatability Study

a. Reserve Asphalts

The two reserve samples of each asphalt were not needed in the previous part of the study, so it was decided to determine the repeatability of the recovery process by recovering the reserve samples for five out of the ten asphalts. The objective of this part of the study was to compare the properties of these asphalts after recovery to the properties previously found after recovery. Both solvents were used.

Penetration and viscosity results are given in tables 12 and 13. In these tables, both the data for the reserve samples after recovery, and the data previously measured after recovery and reported in table 4, are given. HP-GPC and IR results for the reserve asphalts after recovery are given in tables 14 through 16. HP-GPC and IR data previously measured after recovery are given in tables 5, 7, and 8 and were not recopied.

Because the reserve asphalt samples had been stored 6 weeks (in closed tins in the laboratory), it was decided to check their penetrations before dissolving and recovering them. These penetrations are also shown in table 12 under the two columns labeled "Before Recovery." A comparison of these penetrations to the previous penetrations before recovery indicated that asphalts B5603, B5891, and B5901 hardened. There were also slight differences between the penetrations of the two reserve samples for asphalts B5603 (112 versus 118) and B5891 (71 versus 78). These discrepancies, which may have been due in part to reheating the asphalts before penetration testing, indicated that the repeatability of the methods could not be properly evaluated using these samples, and the intended analyses were eliminated. However, the penetration data does show that changes in properties due to reheating and storage can be as significant as changes resulting from the use of solvents.

Because the penetrations before recovery were obtained for the reserve asphalt samples, the penetrations after recovery could be compared to them. Table 17 shows the effect of the solvents on penetration. As with previous analyses, neither solvent had an effect on penetration. Regressions were eliminated because of the limited amount of data.

The two sets of data for the reserve samples after recovery could also be compared, and table 18 shows the statistical results. The analyses indicate that the properties were not significantly different except for the MMS

Table 12. Repeatability Study - Penetrations at 25 °C, 0.1 mm.

		Samples Recovered from Methylene Chloride		Samples Recovered from Trichloroethylene	
Asphalt	Data Set	Before Recovery	After Recovery	Before Recovery	After Recovery
B5603	previous	126	129	126	122
	reserve	112	114	118	110
B5891	previous	85	82	85	76
	reserve	71	75	78	72
B5901	previous	147	149	147	155
	reserve	138	133	136	134
B5928	previous	67	67	67	76
	reserve	63	62	64	64
C8658	previous	54	60	54	51
	reserve	54	53	53	58

Table 13. Repeatability Study - Viscosities.

		Viscosity at 60 °C, P		Viscosity at 135 °C, Cst	
		Samples Recovered from		Samples Recovered from	
Asphalt	Data Set	Methylene Chloride	Trichloro-ethylene	Methylene Chloride	Trichloro-ethylene
B5603	previous	1006	1121	252	270
	reserve	1154	1268	265	284
B5891	previous	1334	1397	315	312
	reserve	1610	1755	318	336
B5901	previous	632	576	237	234
	reserve	694	744	242	252
B5928	previous	2398	1845	477	418
	reserve	2819	3109	470	503
C8658	previous	4496	3928	695	680
	reserve	5740	5241	770	759

Table 14. Repeatability Study - Gel permeation chromatography (HP-GPC) for the reserve asphalts recovered from the solvents.

FHWA ID	Percent Large Molecular Size		Percent Medium Molecular Size		Percent Small Molecular Size	
	CH_2Cl_2	TCE	CH_2Cl_2	TCE	CH_2Cl_2	TCE
B5603	20.1	20.3	47.5	47.3	32.4	32.4
B5891	14.0	14.7	44.0	43.7	42.0	41.6
B5901	18.4	18.7	48.8	48.3	32.8	33.0
B5928	21.1	20.9	47.7	47.5	31.2	31.6
C8658	29.6	29.6	45.3	44.6	25.1	25.8
Avg =	20.6	20.8	46.7	46.3	32.7	32.9
Std Dev =	11.3	10.9	3.9	4.0	12.1	11.3

Table 15. Repeatability Study - Infrared (IR) data for reserve asphalts recovered from methylene chloride (CH_2Cl_2).

FHWA ID	Spectral Region 1	2	3	4	5	6	7	8
B5603	-0.011	0.411	0.033	0.089	0.093	0.107	0.260	0.020
B5891	-0.035	0.435	0.008	0.099	0.115	0.096	0.256	0.026
B5901	-0.074	0.373	0.022	0.102	0.112	0.105	0.330	0.030
B5928	-0.055	0.444	0.011	0.130	0.098	0.095	0.244	0.033
C8658	-0.123	0.565	0.030	0.048	0.059	0.135	0.252	0.035
Avg =	-0.060	0.445	0.021	0.094	0.095	0.108	0.268	0.029
Std Dev =	0.085	0.144	0.022	0.059	0.045	0.032	0.070	0.012

Table 16. Repeatability Study - Infrared (IR) data for reserve asphalts recovered from trichloroethylene (TCE).

FHWA ID	Spectral Region 1	2	3	4	5	6	7	8
B5603	-0.001	0.405	0.029	0.107	0.078	0.110	0.250	0.021
B5891	-0.062	0.396	0.009	0.126	0.145	0.118	0.248	0.021
B5901	-0.037	0.359	0.011	0.118	0.111	0.109	0.305	0.025
B5928	-0.026	0.448	0.012	0.095	0.096	0.101	0.237	0.036
C8658	-0.135	0.593	0.042	-0.007	0.065	0.139	0.272	0.030
Avg =	-0.052	0.440	0.021	0.088	0.099	0.115	0.262	0.027
Std Dev =	0.102	0.182	0.029	0.109	0.062	0.029	0.054	0.013

Table 17. Repeatability Study - Statistical results comparing the reserve asphalts recovered from the solvents to the reserve asphalts before recovery.

Test	Methylene Chloride to Before Recovery t	Trichloroethylene to Before Recovery t
Pen 25 °C	-1.752 NS	-0.679 NS
	$t_{0.05}$ = 2.776	$t_{0.05}$ = 2.776

Table 18. Repeatability Study - Statistical results comparing the reserve asphalts recovered from methylene chloride (CH_2Cl_2) to the reserve asphalts recovered from trichloroethylene (TCE).

Test	t
Pen 25 °C	-0.121 NS
Vis 60 °C	-0.148 NS
Vis 135 °C	-0.903 NS
LMS	-1.151 NS
MMS	3.259 I
SMS	-0.765 NS
Region 1	-0.614 NS
Region 2	0.492 NS
Region 3	0.053 NS
Region 4	0.353 NS
Region 5	-0.485 NS
Region 6	-2.177 NS
Region 7	0.825 NS
Region 8	1.262 NS

$t_{0.05} = 2.776$

content, although the difference between the MMS content averages in table 14 is only 0.4 percent, which probably has little practical significance. There were no changes in any of the other data, and thus the test results overall agreed that the two solvents affected the asphalt properties similarly.

The *t*-test conclusions for the IR regions 1 and 5 in table 18 are different from those given in table 10, whereas they should be the same. Even though some of the reserve asphalts hardened, which makes the data less than optimal, the differences between the conclusions in these tables appear to indicate that at least one solvent had a slightly different effect on the IR data when the recoveries were repeated. The conclusions for the other IR regions, rheological tests, and the HP-GPC technique, except for the MMS content, were in agreement.

(Note: The conclusions in table 10 were generated using the 10 asphalts. However, the same *t*-test conclusions were obtained after eliminating the five asphalts not used in this part of the study and repeating the *t*-tests.)

Finally, a large discrepancy was noticed in table 13 between the two viscosities at 140 °F (60 °C) for asphalt B5928 recovered from trichloroethylene (1845 Poise versus 3109 Poise). This was not related to the hardening problem alone. The softening that occurred with the "previous" asphalt sample and the hardening of the "reserve" asphalt sample is also part of the discrepancy. For this asphalt, the recovery process using trichloroethylene was not repeatable.

b. Additional Tests

Because of the problems with the reserve samples, it was decided to further evaluate the repeatability of the recovery processes. Fifteen samples of the Exxon AC-20 (B5941) were poured into 3-fluid ounce tin containers. Penetrations were performed on all samples and they were then sorted into three groups such that the groups had equal average penetrations and standard deviations. Five samples were used to measure properties before recovery, five were recovered from methylene chloride, and five were recovered from trichloroethylene. The data are shown in tables 19 through 23. During one recovery, the Abson flask broke, and a "before recovery" sample was used as a replacement. This left only four samples for this group. No reserve samples had been poured from the bulk supply of the asphalt, and it was felt that all samples should be taken at the same time because heating is involved. One operator performed all recoveries.

The statistical results are shown in table 24. For this data, either a pooled formula or separate variance t-test was used, whichever one was applicable. The separate variance formula is used when the variances of the two data sets are not equal. The $t_{0.05}$ value varies with whichever t-test is used and the degrees of freedom (not given in this report).

Various significant differences were found, but many of these differences have little practical significance. In most comparisons, the averages were very close, but small variations in the data led to the significant differences. For example, table 19 indicates that the samples recovered from methylene chloride had an average penetration of 72. This was statistically less than the average penetration of 75 for the samples before recovery. The largest differences between the before and after data were with the viscosities, where methylene chloride provided data closer to the data before recovery.

Tables 19 and 20 show that methylene chloride provided lower standard deviations than trichloroethylene for the rheological and HP-GPC data, which indicates that the process using methylene chloride is more repeatable. Table 20 also shows that for this asphalt, the HP-GPC technique was a very precise technique as the standard deviations are low compared to the average values.

As with the previous analyses in tables 9 and 10, the significant changes in table 24 for the rheological and HP-GPC data due to the recovery processes show hardening or increased molecular structuring. However, these changes did not necessarily complement each other. The effect can be significant for one

Table 19. Penetration and viscosity data for asphalt B5941.

	Penetration, 25 °C (100 g, 5 s), 0.1 mm			Viscosity, 135 °C Centistokes			Viscosity, 60 °C Poise		
	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE
	76	71	79	419	439	445	1999	2227	2149
	76	73	73	418	429	454	2025	2117	2243
	75	72	74	422	442	463	2031	2223	2367
	76	73	72	418	431	468	2018	2170	2457
	71	71	71	--	439	457	--	2226	2332
Avg =	75	72	74	419	436	457	2018	2193	2310
Std Dev =	4	2	6	4	11	18	28	97	236

Before = Before Recovery
CH_2Cl_2 = Recovered from Methylene Chloride
TCE = Recovered from Trichloroethylene

Table 20. Gel permeation chromatography (HP-GPC) for asphalt B5941.

	Percent Large Molecular Size			Percent Medium Molecular Size			Percent Small Molecular Size		
	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE
	18.9	19.3	18.9	49.7	49.5	49.5	31.4	31.2	31.6
	18.7	19.1	19.6	49.7	49.5	49.3	31.6	31.4	31.1
	18.9	19.3	18.7	49.3	49.5	49.7	31.5	31.3	31.7
	18.9	19.4	19.5	49.6	49.4	49.3	31.5	31.2	31.2
	--	19.6	19.5	--	49.4	49.3	--	31.1	31.2
Avg =	18.9	19.3	19.2	49.6	49.5	49.4	31.5	31.2	31.4
Std Dev =	0.2	0.4	0.8	0.4	0.1	0.4	0.2	0.2	0.5

Table 21. Infrared (IR) data of asphalt B5941 before recovery.

	Spectral Region							
	1	2	3	4	5	6	7	8
	-0.009	0.370	0.038	0.107	0.122	0.105	0.236	0.029
	0.032	0.402	0.017	-0.031	0.135	0.110	0.308	0.025
	0.019	0.379	0.029	0.069	0.145	0.103	0.233	0.024
	0.006	0.424	0.010	0.029	0.115	0.106	0.285	0.023
Avg =	0.012	0.394	0.024	0.044	0.129	0.106	0.266	0.025
Std Dev =	0.035	0.049	0.025	0.118	0.027	0.006	0.074	0.005

Table 22. Infrared (IR) data of asphalt B5941 recovered from methylene chloride (CH_2Cl_2).

	Spectral Region							
	1	2	3	4	5	6	7	8
	0.021	0.406	0.015	0.017	0.114	0.128	0.268	0.030
	0.013	0.363	0.020	0.082	0.108	0.118	0.272	0.025
	0.022	0.355	0.016	0.064	0.101	0.125	0.290	0.027
	-0.008	0.363	0.027	0.010	0.141	0.121	0.311	0.036
	0.048	0.355	0.027	0.060	0.102	0.119	0.264	0.026
Avg =	0.019	0.368	0.021	0.047	0.113	0.122	0.281	0.029
Std Dev =	0.040	0.043	0.012	0.063	0.033	0.008	0.039	0.009

Table 23. Infrared (IR) data of asphalt B5941 recovered from trichloroethylene (TCE).

	Spectral Region							
	1	2	3	4	5	6	7	8
	0.034	0.403	0.025	0.083	0.120	0.100	0.220	0.015
	0.019	0.386	0.016	0.096	0.127	0.098	0.239	0.020
	-0.000	0.353	0.013	0.089	0.139	0.101	0.273	0.032
	0.044	0.395	0.025	0.118	0.116	0.082	0.202	0.017
	0.029	0.392	0.023	0.107	0.104	0.096	0.230	0.017
Avg =	0.025	0.386	0.020	0.099	0.121	0.095	0.233	0.020
Std Dev =	0.033	0.039	0.011	0.028	0.026	0.015	0.053	0.014

Table 24. Statistical results for asphalt B5941 comparing the samples recovered from the solvents to the samples before recovery, and the samples recovered from the solvents to each other.

	Methylene Chloride to Before Recovery		Trichloroethylene to Before Recovery		Methylene Chloride to Trichloroethylene	
Test	*t*	($t_{0.05}$)	*t*	($t_{0.05}$)	*t*	($t_{0.05}$)
Pen 25 °C	-2.622 D	(2.306)	-0.589 NS	(2.306)	-1.231 NS	(2.604)*
Vis 60 °C	7.641 I	(2.623)*	5.471 I	(2.750)*	-2.049 D	(2.306)
Vis 135 °C	5.608 I	(2.365)	9.433 I	(2.661)*	-4.577 D	(2.306)
LMS	4.802 I	(2.365)	2.053 NS	(2.642)*	0.499 NS	(2.306)
MMS	-1.176 NS	(2.960)*	-1.260 NS	(2.365)	0.478 NS	(2.623)*
SMS	-3.822 D	(2.365)	-1.098 NS	(2.587)*	-0.915 NS	(2.306)
Region 1	0.414 NS	(2.365)	1.039 NS	(2.365)	-0.513 NS	(2.306)
Region 2	-1.667 NS	(2.365)	-0.549 NS	(2.365)	-1.349 NS	(2.306)
Region 3	-0.403 NS	(2.365)	-0.504 NS	(2.365)	0.167 NS	(2.306)
Region 4	0.102 NS	(2.365)	1.827 NS	(3.000)*	-3.378 D	(2.306)
Region 5	-1.442 NS	(2.365)	-0.912 NS	(2.365)	-0.855 NS	(2.306)
Region 6	6.494 I	(2.365)	-2.567 D	(2.365)	6.807 I	(2.306)
Region 7	0.815 NS	(2.365)	-1.554 NS	(2.365)	3.289 I	(2.306)
Region 8	1.403 NS	(2.365)	-1.383 NS	(2.365)	2.360 I	(2.306)

* Separate Variance Formula

or more measurements, but not for all measurements. There was a good agreement between the rheological and HP-GPC data for the comparison between the asphalts recovered from methylene chloride and the asphalts before recovery, but not for the other two comparisons.

Table 24 also shows that there was little agreement between the changes in the IR data and the rheological or HP-GPC data. For example, with methylene chloride there was an increase in region 6 (Aromatic) while for trichloroethylene there was a decrease in region 6, yet both solvents increased the viscosities.

A second asphalt (Chevron AC-5, B5901) was also evaluated, but only the penetrations and viscosities were measured. The data are given in table 25 and the statistical results in table 26. The asphalts recovered from methylene chloride provided data closer to the data before recovery and lower standard deviations; therefore, it was the better solvent. The *t*-test conclusions are biased because of the unequal standard deviations provided by the three groups. For example, the samples recovered from methylene chloride had an average penetration of 151. This was statistically less than the average penetration of 156 for the samples before recovery. The samples recovered from trichloroethylene had an average penetration of 149. This was not statistically less than the average penetration of 156 for the samples before recovery. Again, the significant changes in the rheological data due to the recovery processes show hardening.

Data from this repeatability study indicated that methylene chloride was the better solvent. Both solvents tended to harden the asphalts slightly, but methylene chloride showed less hardening and more repeatable results from replicate to replicate.

Table 25. Penetration and viscosity data for asphalt B5901.

	Penetration, 25 °C (100 g, 5 s), 0.1 mm			Viscosity, 135 °C Centistokes			Viscosity, 60 °C Poise		
	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE
	158	155	167	223	230	230	545	576	553
	156	149	149	222	231	239	550	587	622
	156	150	137	223	233	251	547	590	696
	156	151	144	222	230	246	549	584	665
	152	151	146	221	229	247	547	578	666
Avg =	156	151	149	222	231	243	548	583	648
Std Dev =	4	5	22	2	3	17	4	12	111

Before = Before Recovery
CH_2Cl_2 = Recovered from Methylene Chloride
TCE = Recovered from Trichloroethylene

Table 26. Statistical results for asphalt B5901 comparing the samples recovered from the solvents to the samples before recovery, and the samples recovered from the solvents to each other.

Test	Methylene Chloride to Before Recovery		Trichloroethylene to Before Recovery		Methylene Chloride to Trichloroethylene	
	t	($t_{0.05}$)	t	($t_{0.05}$)	t	($t_{0.05}$)
Pen 25 °C	-3.111 D	(2.306)	-1.372 NS	(2.703)*	0.509 NS	(2.703)*
Vis 60 °C	12.708 I	(2.306)	3.735 I	(2.776)*	-2.299 NS	(2.750)*
Vis 135 °C	10.844 I	(2.306)	5.492 I	(2.750)*	-3.193 D	(2.703)*

* Separate Variance Formula

PHASE II - HARDENED ASPHALTS

1. Materials and Test Procedures

The 11 materials identified in table 27 were used to determine the suitability of methylene chloride to recover hardened asphalts. Methylene chloride was found to be a suitable solvent in Phase I; however, because most asphalts to be recovered are hardened in the mixing plant and inservice, this phase was deemed necessary.

Two of the asphalts used in Phase I were aged using the thin film oven (TFO) procedure (AASHTO T 179 and ASTM D 1754). These two asphalts, along with another asphalt used in Phase I, were also used in the three plant-produced loose mixtures, which were obtained from State highway agencies for another FHWA study.(6) Cores from three aged pavements and three coating grade roofing asphalts were also evaluated.

For loose mixtures and cores, only properties after recovery can be obtained. The properties of the asphalts before recovering them from the mixtures are unknown and can not be obtained. Where differences in properties after recovery are found, there is no basis for choosing which solvent has less of an effect on the property, except if the HP-GPC or IR methods provide an unusual result or indicate a solvent was not completely removed from an asphalt.

The tests and statistical analyses used in Phase I were also used in this Phase. The asphalts were extracted from the loose mixtures and cores using the centrifuge method (Method A of AASHTO T 164 and ASTM D 2172). The mixtures were first placed in solvent for one-half hour. The effluent was removed and the aggregates were washed with 200 ml of solvent until the extract was clear. This required four to five washings depending on the mixture. The number of washings did not vary with the type of solvent.

Table 27. Materials used in Phase II.

FHWA ID	Type of Material	Comments
C8658	TFO Asphalt	Asphalt used in Phase I
C8724	TFO Asphalt	Asphalt used in Phase I
C8658	Loose Mixture	Asphalt used in Phase I
C8724	Loose Mixture	Asphalt used in Phase I
B5928	Loose Mixture	Asphalt used in Phase I
B5965	Pavement Core	US-30, NE (6 years old)
B5966	Pavement Core	I-270, MD (19 years old)
B5967	Pavement Core	Gaithersburg, MD (Local Road, 2 yrs)
B5950	Coating Grade Roofing Asphalt	GS Roofing Products Co. Plant, Ennis, TX (from Gulf States Refining Co., Houston, TX)
B5951	Coating Grade Roofing Asphalt	GS Roofing Products Co. Plant, Shreveport, LA (from Berry Refining Co., Tuscaloosa, AL)
B5952	Coating Grade Roofing Asphalt	GS Roofing Products Co. Plant, Peachtree City, GA (from Hunt Oil Co., Stevens, AR)

Table 28. Percent asphalt content by weight of the total mixture.

FHWA ID	Percent Asphalt Content using Methylene Chloride	Percent Asphalt Content using Trichloroethylene
C8658	7.20	7.19
C8724	6.84	6.85
B5928	5.56	5.68
B5965	6.09	6.08
B5966	7.75	7.82
B5967	6.59	6.73
Avg.	6.67	6.73

2. Test Results for the Aged Paving Grade Asphalts

The asphalt contents for the six extractions (three loose mixtures and three cores) are shown in table 28. These data do not clearly show that one solvent is more efficient for removing asphalt than the other. This efficiency was not thoroughly evaluated and it was not the intent of this study to do so. However, the efficiency of a solvent to remove an asphalt could affect the properties after recovery if, for example, one solvent was better able to remove strongly adsorbed polar asphalt groups. Additional information on the suitability of methods to determine asphalt contents has been reported elsewhere.(8)

Penetration and viscosity data are given in table 29; HP-GPC data in table 30, and IR data in tables 31 through 33. The data for the coating grade roofing asphalts were not included in these tables because their properties were radically different from those of the paving grade asphalts. Paired *t*-tests, regression analyses, and standard deviations were again used to analyze the data.

The statistical results shown in table 34 indicate that the asphalts recovered from methylene chloride had lower penetrations and larger relative areas in IR regions 3 (Secondary and Tertiary C-O and S=O) and 7 (Mono-substituted Aromatic C-H). No corresponding significant decreases in other IR regions were obtained. These differences in the effects of the two solvents could not be adequately explained because of the absence of test data before recovery and the lack of agreement between the results of the tests. For example, the viscosities and HP-GPC data agreed with each other but not with the penetration data, although the average difference in penetration as shown by table 29 was only 4 dmm. A further complication is that the results in table 34 do not exactly match the results given for the virgin paving grade asphalts in tables 10 and 18. However, for the two asphalts subjected to the TFO conditioning, table 29 shows that the penetrations of the asphalts recovered from methylene chloride were closer to the penetrations before recovery, and therefore was the better solvent in these two cases.

Table 29. Penetration and viscosity data for the aged paving grade asphalts.

FHWA ID	Penetration, 25 °C (100 g, 5 s), 0.1 mm			Viscosity, 135 °C Centistokes			Viscosity, 60 °C Poise		
	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE
C8658 TFO	36	38	43	1059	1081	1110	11057	11668	11673
C8724 TFO	40	41	47	985	1032	1026	9485	10328	9777
C8658 Mix	--	36	40	--	1152	1210	--	13461	13185
C8724 Mix	--	36	37	--	1149	1223	--	13916	14149
B5928 Mix	--	32	36	--	751	780	--	10513	10114
B5965 Core	--	11	18	--	1561	1522	--	123980	108504
B5966 Core	--	17	19	--	1624	1722	--	53866	50413
B5967 Core	--	18	21	--	1291	1299	--	37325	34706
Avg =	--	29	33	--	1205	1237	--	34382	31565
Std Dev =	--	23	23	--	569	581	--	79055	68687

Before = Before Recovery
CH_2Cl_2 = Recovered from Methylene Chloride
TCE = Recovered from Trichloroethylene

Table 30. Gel permeation chromatography (HP-GPC) data for the aged paving grade asphalts.

FHWA ID	Percent Large Molecular Size			Percent Medium Molecular Size			Percent Small Molecular Size		
	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE
C8658 TFO	31.2	31.5	32.5	44.1	43.9	43.1	24.5	24.6	24.3
C8724 TFO	30.5	32.7	32.4	44.8	43.4	43.3	24.7	24.0	24.4
C8658 Mix	--	33.8	33.7	--	42.8	42.4	--	23.4	23.9
C8724 Mix	--	34.0	34.3	--	42.4	42.2	--	23.5	23.5
B5928 Mix	--	26.2	25.3	--	43.9	44.3	--	30.0	30.4
B5965 Core	--	35.0	35.4	--	44.2	43.7	--	20.7	20.9
B5966 Core	--	30.8	30.4	--	44.8	44.8	--	24.4	24.7
B5967 Core	--	30.7	30.4	--	42.7	42.9	--	26.6	26.7
Avg =	--	31.8	31.8	--	43.5	43.3	--	24.7	24.9
Std Dev =	--	5.5	6.3	--	1.7	1.8	--	5.4	5.5

Table 31. Infrared (IR) data of the two TFO asphalts before recovery.

FHWA	Spectral Region							
ID	1	2	3	4	5	6	7	8
C8658 TFO	-0.063	0.445	0.050	0.048	0.043	0.094	0.356	0.028
C8724 TFO	-0.021	0.508	0.043	0.017	0.030	0.081	0.315	0.028

Table 32. Infrared (IR) data of the aged paving grade asphalts recovered from methylene chloride (CH_2Cl_2).

FHWA	Spectral Region							
ID	1	2	3	4	5	6	7	8
C8658 TFO	-0.074	0.466	0.063	0.065	0.043	0.097	0.323	0.017
C8724 TFO	-0.031	0.487	0.055	0.018	0.039	0.109	0.299	0.024
C8658 Mix	-0.013	0.273	-0.005	0.520	-0.018	0.066	0.157	0.020
C8724 Mix	0.002	0.255	-0.009	0.503	-0.022	0.065	0.186	0.019
B5928 Mix	0.067	0.318	0.024	0.209	0.084	0.089	0.190	0.021
B5965 Core	0.211	0.288	0.006	0.177	0.065	0.058	0.170	0.025
B5966 Core	0.102	0.261	0.040	0.265	0.050	0.074	0.180	0.028
B5967 Core	0.071	0.298	-0.004	0.405	0.022	0.062	0.128	0.017
Avg =	0.042	0.331	0.021	0.270	0.033	0.078	0.204	0.021
Std Dev =	0.181	0.185	0.057	0.380	0.075	0.037	0.138	0.008

Table 33. Infrared (IR) data of the aged paving grade asphalts recovered from trichloroethylene (TCE).

FHWA ID	Spectral Region 1	2	3	4	5	6	7	8
C8658 TFO	-0.073	0.465	0.054	0.071	0.050	0.113	0.294	0.026
C8724 TFO	-0.028	0.457	0.052	0.052	0.043	0.103	0.297	0.024
C8658 Mix	-0.024	0.244	-0.011	0.574	-0.016	0.061	0.146	0.027
C8724 Mix	0.002	0.249	-0.015	0.558	-0.039	0.068	0.157	0.020
B5928 Mix	0.049	0.330	0.017	0.234	0.075	0.083	0.193	0.019
B5965 Core	0.211	0.297	0.008	0.142	0.063	0.061	0.193	0.025
B5966 Core	0.047	0.170	0.021	0.176	0.033	0.428	0.109	0.016
B5967 Core	0.073	0.302	-0.008	0.405	0.023	0.068	0.120	0.018
Avg =	0.032	0.314	0.015	0.277	0.029	0.123	0.189	0.022
Std Dev =	0.174	0.205	0.054	0.419	0.078	0.249	0.145	0.008

Table 34. Statistical results comparing the aged paving grade asphalts recovered from methylene chloride (CH_2Cl_2) to the aged paving grade asphalts recovered from trichloroethylene (TCE).

Test	r^2	Slope	*t*
Pen 25 °C	0.97	1.01	-5.657 D
Vis 60 °C	1.00	1.15	1.524 NS
Vis 135 °C	0.98	0.99	-1.993 NS
LMS	0.98	0.90	0.072 NS
MMS	0.80	1.02	1.310 NS
SMS	0.99	0.99	-2.247 NS
Region 1	0.95	1.06	1.398 NS
Region 2	0.89	0.95	1.370 NS
Region 3	0.96	1.07	3.052 I
Region 4	0.95	0.93	-0.363 NS
Region 5	0.94	0.99	1.171 NS
Region 6	0.01	2.40	-1.034 NS
Region 7	0.85	1.03	5.844 I
Region 8	0.29	-5.05	-0.224 NS

$t_{0.05} = 2.365$

The regression analyses in table 24 indicated that all of the properties correlated to a high degree, except IR regions 6 (Aromatic) and 8 (Aromatic Amine C-N or Oxidized Nitrogen N-O). As previously stated, the relative areas in these two regions tend to vary little from asphalt to asphalt, and thus low coefficients of determination could be expected. As shown in table 33, core number B5966 provided an outlier in region 6, which could not be explained.

The standard deviations were also reviewed. The standard deviations in table 30 again show that the variations in the MMS content from asphalt to asphalt were low.

Properties for the virgin asphalts were compared to those for the aged asphalts to determine generalized differences in properties. Compared to the virgin asphalts in tables 4 and 5, the aged asphalts had a lower average penetration, a higher average viscosity at both temperatures, a higher average LMS content, and lower average MMS and SMS contents. Thus the physical properties complemented each other in that each showed hardening or molecular structuring. These results were as expected.

Differences between the IR data of the virgin and aged asphalt groups were also examined, and they were found to vary with the solvent. However, by reviewing both data sets, trends in the data could be established. These trends indicated increases in regions 1 (C=O, Carbonyl Stretch) and 4 (Primary C-O, S=O) with age, and decreases in the other regions, although the decrease in region 3 (Secondary & Tertiary C-O, S=O) was slight. This result should not be considered conclusive because the asphalts in these two groups differed, and the aged asphalts are probably not representative of aged asphalts in general according to chemical properties. Further discussions on this data and the IR test are given in appendix A.

Additional supplementary analyses showing the effects of TFO conditioning and mix plant aging are given in appendix B.

3. Test Results for the Coating Grade Roofing Asphalts

The data for the three coating grade roofing asphalts are given in tables 35 through 39. Viscosities at 140 °F (60 °C) could not be obtained using any AASHTO T 202 (ASTM D 2171) viscometer available for this study (including an Asphalt Institute 400R). Viscosities at 275 °F (135 °C) were erratic, although a visual examination of the data for each asphalts in table 35 shows that the asphalts recovered from methylene chloride provided viscosities closer to the viscosities before recovery. A review of the penetration, HP-GPC, and IR data, and the *t*-test results shown in table 40, indicated that test results overall agreed that both solvents had little to no effect on the asphalt properties. The data were too limited to perform regression analyses.

Compared to the virgin or aged paving grade asphalts in tables 4, 5, 29, and 30, the roofing asphalts had a significantly higher average viscosity at 275 °F (135 °C), a higher average LMS content, and lower average MMS and SMS contents. Thus these physical properties complemented each other in that each showed hardening or molecular structuring. Based on expected relationships between penetration and viscosity for paving grade asphalts, the roofing asphalts had relatively high penetrations compared to the viscosities at 275 °F (135 °C). The penetrations of the aged paving grade asphalts and the roofing asphalts were similar, yet the roofing asphalts had viscosities at 275 °F (135 °C) which were an order of magnitude greater than those of the paving grade asphalts. These results were as expected.

A comparison of the IR data of the roofing asphalts to the paving grade asphalts is not presented. The data were too limited to evaluate changes in chemical properties.

Table 36 again shows that the standard deviations for the MMS content were very low. This was previous reported for the paving grade asphalts. Tables 5, 30, and 36 show that with increased molecular structuring, the standard deviations for the other two size contents decreased, and they were very low for the roofing asphalts. However, the crude sources of the roofing asphalts

Table 35. Penetration and viscosity data for the coating grade roofing asphalts.

FHWA ID	Penetration, 25 °C (100 g, 5 s), 0.1 mm			Viscosity, 135 °C Centistokes		
	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE
B5950	23	21	24	18620	24835	33102
B5951	16	20	22	36809	38510	28840
B5952	20	20	22	38508	41082	29121
Avg =	20	20	23	31312	34809	30354
Std Dev =	7	1	2	22049	17466	4767

Before = Before Recovery
CH_2Cl_2 = Recovered from Methylene Chloride
TCE = Recovered from Trichloroethylene

Table 36. Gel permeation chromatograph (HP-GPC) data for the coating grade roofing asphalts.

FHWA ID	Percent Large Molecular Size			Percent Medium Molecular Size			Percent Small Molecular Size		
	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE	Before	CH_2Cl_2	TCE
B-5950	53.8	55.2	53.2	31.3	30.2	31.4	14.9	14.6	15.4
B-5951	51.1	51.4	51.6	32.1	31.9	31.8	16.8	16.7	16.6
B-5952	52.2	52.5	52.9	31.3	30.9	30.5	16.5	16.5	16.6
Avg =	52.4	53.0	52.6	31.6	31.0	31.2	16.1	15.9	16.2
Std Dev =	2.7	3.9	1.7	0.9	1.7	1.3	2.0	2.3	1.4

Table 37. Infrared (IR) data for coating grade roofing asphalts before recovery.

FHWA ID	Spectral Region 1	2	3	4	5	6	7	8
B-5950	0.133	0.356	-0.018	0.043	0.105	0.059	0.288	0.034
B-5951	0.126	0.359	0.033	-0.057	0.121	0.092	0.309	0.018
B-5952	0.132	0.341	0.043	0.002	0.128	0.088	0.254	0.012
Avg =	0.130	0.352	0.019	-0.004	0.118	0.080	0.284	0.021
Std Dev =	0.008	0.019	0.065	0.101	0.024	0.036	0.056	0.023

Table 38. Infrared (IR) data for coating grade roofing asphalts recovered from methylene chloride (CH_2Cl_2).

FHWA ID	Spectral Region 1	2	3	4	5	6	7	8
B-5950	0.160	0.389	-0.032	0.006	0.125	0.087	0.243	0.022
B-5951	0.111	0.358	0.025	-0.027	0.127	0.102	0.280	0.024
B-5952	0.113	0.336	0.025	0.005	0.123	0.111	0.268	0.019
Avg =	0.128	0.361	0.006	-0.005	0.125	0.100	0.264	0.022
Std Dev =	0.055	0.053	0.066	0.038	0.004	0.024	0.038	0.005

Table 39. Infrared (IR) data of coating grade roofing asphalts recovered from trichloroethylene (TCE).

FHWA ID	Spectral Region 1	2	3	4	5	6	7	8
B-5950	0.144	0.376	-0.018	-0.006	0.124	0.076	0.282	0.022
B-5951	0.123	0.322	0.024	0.019	0.125	0.095	0.274	0.017
B-5952	0.125	0.359	0.023	-0.003	0.125	0.081	0.286	0.004
Avg =	0.131	0.352	0.010	0.003	0.125	0.084	0.281	0.014
Std Dev =	0.023	0.055	0.048	0.027	0.001	0.020	0.012	0.019

Table 40. Statistical results comparing the roofing asphalts recovered from the solvents to the roofing asphalts before recovery, and the roofing asphalts recovered from the solvents to each other.

	Methylene Chloride to Before Recovery	Trichloroethylene to Before Recovery	Methylene Chloride to Trichloroethylene
Test	t	t	t
Pen 25 °C	0.378 NS	1.964 NS	-7.000 D
Vis 135 °C	2.530 NS	-0.124 NS	0.697 NS
LMS	1.818 NS	0.495 NS	0.607 NS
MMS	-2.077 NS	-1.280 NS	-0.475 NS
SMS	-1.512 NS	0.658 NS	-2.000 NS
Region 1	-0.159 NS	0.061 NS	-0.286 NS
Region 2	0.747 NS	0.018 NS	0.505 NS
Region 3	-4.588 D	-1.672 NS	-0.709 NS
Region 4	-0.069 NS	0.200 NS	-0.463 NS
Region 5	0.968 NS	1.027 NS	0.277 NS
Region 6	3.790 NS	0.622 NS	2.256 NS
Region 7	-1.135 NS	-0.155 NS	-1.308 NS
Region 8	0.054 NS	-2.178 NS	1.692 NS
	$t_{0.05}$ = 4.303	$t_{0.05}$ = 4.303	$t_{0.05}$ = 4.303

are unknown, and thus it is unknown whether they are representative of roofing asphalts in general.

None of the data for the hardened asphalts indicated that methylene chloride could not be used in the recovery process.

SUMMARY AND CONCLUSIONS

The objective of this in-house study was to determine if methylene chloride (CH_2Cl_2) can be used to recover asphalts by the Abson Method (AASHTO T 170 and ASTM D 1856), and to compare its effects on recovered binder properties to those of trichloroethylene (C_2HCl_3). The repeatability of the recovery process using both solvents was also determined by recovering replicate asphalt samples.

Current nationally standardized test procedures (AASHTO and ASTM) do not allow methylene chloride in the Abson Method. Several State highway agencies use methylene chloride in the vacuum extraction procedure, and thus including this solvent in the Abson Method would be beneficial. However, there is no published data indicating the suitability of this solvent for recovering asphalts. ASTM proposes to include methylene chloride in the Abson Method in 1990.

Both virgin paving grade asphalts and hardened asphalts were used in this evaluation. Hardened asphalts consisted of paving grade asphalts aged by the thin film oven (TFO) procedure (AASHTO T 179 and ASTM D 1754), paving grade asphalts extracted from aged loose mixtures and cores, and coating grade roofing asphalts. The following tests were performed before and after recovery, using trichloroethylene and methylene chloride as solvents:

- Penetration at 77 °F (25 °C), (100 g, 5 s), (AASHTO T 49 and ASTM D 5).(2,3)
- Absolute Viscosity at 140 °F (60 °C), (AASHTO T 202 and ASTM D 2171).(2,3)
- Kinematic Viscosity at 275 °F (135 °C), (AASHTO T 201 and ASTM D 2170).(2,3)
- High Pressure Gel Permeation Chromatography (HP-GPC).(5,6)
    - Large Molecular Size (LMS).
    - Medium Molecular Size (MMS).
    - Small Molecular Size (SMS).
- Infrared (IR) Spectral Analysis.(6)
    - Eight Regions of Spectra.

The IR spectral analysis shows changes in chemical properties, while the rheological tests and the HP-GPC technique show changes in physical properties. Ethyl alcohol was not added to either solvent as is at times the practice. The conclusions from this study are:

1. The data indicate that methylene chloride can be used to recover asphalts by the Abson Method.

2. Both solvents had some statistically significant effects on some asphalt properties, but neither solvent can be recommended over the other. For practical purposes, such as quality control testing and evaluating aged pavement properties, both solvents appear suitable for use in the recovery method.

3. For the two asphalts where replicate samples were tested, methylene chloride was the better solvent in that the replicate samples recovered using this solvent provided more consistent data from sample to sample.

4. When a physical property for a set of asphalts did significantly change because of the recovery process (either solvent), the change showed hardening or increased molecular structuring of the asphalts. When there was no significant change, the physical property for an individual asphalt could increase, decrease, or be unaffected.

5. The physical properties which were significantly affected by the solvents varied with the solvent and with the particular set of asphalts being evaluated (virgin paving grade, aged paving grade, roofing, or subgroup used in the repeatability study). The hardening (or structuring) was not consistently shown by any given asphalt property from data set to data set.

6. For any given set of asphalts, the changes in physical properties did not necessarily complement each other. Hardening (or structuring) could be shown by one or more properties, but not by all properties. However, a perfect agreement between these properties should not be expected because most of the

statistically significant changes in the properties were very slight, and the physical properties (penetration, viscosities, and HP-GPC size contents) are not surrogates for each other.

7. Differences between the physical properties of the three main sets of asphalts complemented each other (virgin paving grade versus aged paving grade versus roofing asphalts). As the penetration decreased, viscosity increased, LMS content increased, and the MMS and SMS contents decreased. Based on typical relationships between viscosity and penetration for paving grade asphalts, the roofing asphalts had relatively high viscosities at 275 °F (135 °C) compared to their penetrations. These results were as expected.

8. For any given set of asphalts, the variation in the MMS content from asphalt to asphalt was very low, which means that the usefulness of the MMS content for comparing different asphalts may be very limited.

9. As with the physical properties, the IR functional groups that were significantly affected by the recovery process varied with the solvent and with the particular set of asphalts being evaluated.

10. Changes in the IR data could not in general be related to the changes in the rheological or HP-GPC data, and no trends were evident. The IR technique used in this study appears to have poor reproducibility.

11. For any given set of asphalts, the variations in the IR data of regions 6 (Aromatic) and 8 (Aromatic Amine C-N or Oxidized Nitrogen N-O) from asphalt to asphalt generally were very low, which means that the usefulness of these two regions for comparing different asphalts may be very limited.

12. The penetration data of one set of asphalts used in the repeatability study showed that the penetrations of some asphalts can be significantly affected by routine handling (storage and reheating).

(Note: Extraction and recovery testing using any solvent can at least partially reverse steric hardening, so the recovered properties of aged pavement binders may not exactly match true in-situ properties. This effect was not evaluated in this study and is generally not considered in routine testing. The changes in properties due to the reversal of steric hardening are probably much greater than any effects the solvents had on the properties in this study.)

RECOMMENDATIONS

1. It is recommended that methylene chloride be included in the Abson Method for recovering asphalts (AASHTO T 170 and ASTM D 1856).

2. The repeatability study was limited. It is recommended that either AASHTO or ASTM sponsor round robin testing to determine the precision and bias of the Abson Method using both trichloroethylene and methylene chloride.

3. The standard deviations for all three HP-GPC size contents were lower for the aged paving grade asphalts compared to the virgin asphalts, and they were very low for the roofing asphalts. The data in this study is too limited to draw a definite conclusion, but the suggested decrease in the variation in the data with hardening warrants further study.

4. The infrared (IR) spectral technique, its reproducibility, and the assumptions used in analyzing the data should be evaluated. The potential of this technique for evaluating asphalts is as yet unfilled.

APPENDIX A: EVALUATION OF IR DATA

The data for the aged paving grade asphalts in tables 32 and 33 were compared to the data for the virgin asphalts in tables 7 and 8. The data for the TFO asphalts were eliminated from this analysis because these asphalts were also used in two of the mixtures. For the asphalts recovered from methylene chloride, aging increased the relative area in regions 1 and 4, decreased the relative area in regions 2, 5, 6, 7, and 8, and had no effect on region 3. For the asphalts recovered from trichloroethylene, aging increased the relative area in region 4, decreased the relative area in regions 2, 3, 5, 7, and 8, and had no effect on regions 1 and 6. If the datum of core B5966 in region 6, which may be an outlier, is eliminated from table 33, then region 6 would also decrease. Although the aged asphalts probably do not represent aged asphalts in general, the differences between the data for the two solvents were unexpected. Where the discrepancies occurred, this would mean that aging was not as important as other factors on these functional groups, although this is possible.

The above changes in the IR regions due to aging do not necessarily agree with the effects of the solvents on the IR data in this report; however, the changes in asphalt chemistry that lead to hardening in the recovery process may not be exactly the same as those that lead to aging in mixtures and cores. The value of the IR test is that it should be able to chemically sort out different types of hardening. Residual solvent left in the recovered samples could also affect the IR results. However, no residual solvent was found in the asphalts when their IR spectra were checked for solvent peaks.

To determine possible causes of the discrepancies between the effects of the solvents, ranges in the IR data were examined. Table 41 shows the acceptable ranges for each region when testing replicate samples of any single asphalt.(6) The ranges (highest value minus the lowest value) for all 10 virgin paving grade asphalts taken from table 6 are also given. Comparing the two sets of ranges indicates that for the majority of the regions, the reproducibility of the method appears to be poor. The acceptable ranges for repeated measurements on a given asphalt are high compared to the ranges for the 10 asphalts, which varied from an AC-5 to an AC-40. This may be one reason for the discrepancies noted above and the lack of consistency of the IR results in this study.

A 95-percent confidence range is also shown in table 41. This range was computed by multiplying the standard deviations in table 6 by two. This also indicates that the reproducibility of the method is poor.

The ranges generated by the four replicate samples of asphalt B5941 are also shown in table 41. For this asphalt, the data did not meet the acceptable range for region 1, and were slightly out of range for regions 2 and 4. Data for the remaining five regions were within the limits. This was the only asphalt used in this study where replicate samples were tested by the IR technique. For most regions, these ranges are also high compared to the ranges for the ten asphalts.

Table 41. Comparison of ranges for the eight infrared (IR) regions.

Infrared Region	Acceptable Range for Replicates(6)	Range for the Ten Asphalts (Table 6)	Confidence Range Computed from the Ten asphalts (Table 6)	Range for Asphalt B5941 (Table 21)
1	0.022	0.117	0.132	0.041
2	0.051	0.221	0.276	0.054
3	0.040	0.066	0.074	0.028
4	0.135	0.201	0.254	0.138
5	0.047	0.091	0.108	0.030
6	0.018	0.023	0.030	0.007
7	0.107	0.096	0.124	0.075
8	0.018	0.010	0.014	0.006

APPENDIX B: EFFECTS OF TFO AND MIX PLANT AGING

By statistically comparing the HP-GPC data of asphalts C8658 and C8724 in tables 5 and 30, it was found that TFO aging increased the LMS content and decreased the MMS content of the two asphalts subjected to this process. The SMS content did not significantly change. These conclusions were valid for all three data sets (data before recovery and both sets of data after recovery.) Changes in the IR data, using tables 6, 7, 8, 31, 32, and 33, due to the TFO varied with the data set and the asphalt, and no generalized conclusions could be made. These conclusions are based on only two asphalts and thus must not be considered definitive.

Another comparison of the HP-GPC data in the tables 5 and 30 shows that the three asphalts extracted from the loose mixtures had higher LMS contents and lower MMS and SMS contents compared to the corresponding virgin asphalts. For the IR data in tables 7, 8, 32, and 33, the only significant changes were decreases in regions 2 (Unsaturated C=O and C=C Olefinic Stretch) and 7 (Monosubstituted Aromatic C-H) with aging. These conclusions were valid for both data sets after recovery, but must not be considered definitive because of the limited number of asphalts.

As shown by table 29, the TFO asphalts had slightly higher penetrations and lower viscosities compared to the corresponding asphalts from the plant-produced loose mixtures. Differences could be expected because TFO aging only approximates the hardening that occurs during the mixing process, plus both the asphalts and the mixtures were stored in the FHWA laboratory for 2 years. Differences in the rates of hardening during storage may have occurred. Again, these conclusions are based on only two asphalts and thus must not be considered definitive.

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