

SILYLATION OF ASPHALTS WITHIN GLC COLUMNS. EFFECTS ON INVERSE GLC DATA AND INFRARED SPECTRA

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INTRODUCTION

Inverse gas-liquid chromatography (IGLC) has indicated differences in the chemical composition of whole asphalts (1-4) as well as fractions from asphalts (1, 5). IGLC measures interactions between the functional groups of volatile test compounds and functional groups in the liquid phase, which in our studies is asphalt. The asphalt may be analyzed either as-received or after an in-column oxidation procedure.

Asphalt contains many types of functional groups that may exhibit selective affinity for specific test compounds. The identification of selective interactions between functional groups of asphalts and test compounds would provide interpretive information about IGLC data and its relation to the chemical composition of asphalts. Such information is important because previous work has established empirical correlations between IGLC data for specific test compounds and in-use performance (4) or accelerated weathering durability (2, 3).

One approach to the identification of IGLC interactions is selective blocking of functional groups in the asphalt. Work with other materials has shown that silylating reagents are reactive toward certain functional groups containing active hydrogens. Such groups are known to be present in asphalts. These active hydrogen groups are believed to interact strongly with certain test compounds used in IGLC. In the present study *N,O*-bis(trimethylsilyl)acetamide (BSA) was used to silylate these groups in asphalts. Using a novel approach, silylation is conveniently carried out *in situ* by injecting BSA directly into the IGLC column. Independent work published after completion of this study made use of in-column silylation of volatile solutes (6).

In the present study, IGLC data were obtained on a number of oxidized and unoxidized asphalts that had been silylated. These data are compared with data from samples before silylation.

Infrared spectra were obtained on asphalts recovered from the columns. These spectra are correlated with IGLC data to provide information about functional group interactions between test compounds and asphalts.

EXPERIMENTAL

Apparatus and Procedure

IGLC data were obtained on a Beckman GC-2A gas chromatograph.* Columns were prepared using $\frac{1}{8}$ -inch by 12 $\frac{1}{2}$ -foot aluminum tubing packed with 1 part asphalt on 10 parts by weight of 20-40 mesh Fluoropak 80. Columns were conditioned at 130°C for at least 6 hours, using a helium inlet gauge pressure of 15 psi. Following conditioning, test compounds (0.1 μ l) were then

*Mention of specific products or brand names is made for information only and does not imply endorsement by the Bureau of Mines.

introduced separately and retention times determined. In this study, two columns were prepared from each asphalt. One column was used to obtain test compound retention data on the original asphalt followed by in-column silylation after which retention data were again obtained. The second column was oxidized by the introduction of air under conditions previously reported (2, 3), and retention data were obtained. This was followed by in-column silylation, and retention data were again obtained.

Silylation. - The in-column silylation of asphalt samples was performed in a manner similar to that used to treat column packing supports to prevent "tailing of peaks" from polar materials (7-10). The column to be treated was heated to 160° C while blanketing with helium carrier gas. Four portions of BSA were then injected at 30-minute intervals, the first portion being 200 μ l and the remainder being 100- μ l quantities. One hour after injection of the final portion, the temperature was lowered to 130° C and held overnight (at least 15 hours) to elute excess BSA and reaction by-products. Inverse GLC data were then obtained.

Infrared Spectra. - Infrared spectra were obtained with a Perkin-Elmer Model 521 double-beam spectrophotometer using solvent compensation. Asphalt samples were recovered from the IGLC packing for infrared study with CCl_4 using a modified Soxhlet extraction. The solution obtained was adjusted so that the asphalt concentration was 20g/l. The spectra were obtained on these solutions using 1 cm sodium chloride cells.

Materials. - N,O-Bis(trimethylsilyl)acetamide (BSA) and hexamethyldisilazane (HMDS) were used as received from Pierce Chemical Company. Wilmington (Calif.) asphalt (11) and two asphalts, D and J, from the Zaca-Wigmore Experimental Road Test (12) were used in this study. The former was prepared in this laboratory, and the latter two were furnished by the Materials Division of the Bureau of Public Roads.

Calculation of the Specific Interaction Coefficient (I_g)

Specific interaction coefficients for the test compounds were calculated according to the following equation:

$$I_g = 100 [\log V_g (\text{test compound}) - \log V_g (\text{hypothetical n-paraffin})].$$

I_g is different from the interaction coefficient (I_p) used in earlier work (1) in that specific retention volume (V_g) rather than corrected retention volume (V_R^0) is used in the calculations. The specific interaction coefficient thus obtained is a measure of interactions between the chemical functionalities of the asphalt and the test compound.

RESULTS AND DISCUSSION

Effect of Silylation on Inverse GLC Retention Data

Treatment of an inverse GLC column at 160° C with either HMDS or BSA resulted in a rapid reaction. By observing changes in the IR spectra of recovered asphalts following silylation, BSA was found to be more reactive than HMDS and, therefore, was chosen for further studies. Attempts to silylate asphalt samples in solution, using either BSA or HMDS, were unsuccessful because of slow reaction due to low boiling points of the solvents.

Data in Table I show that the specific interaction coefficients for phenol and propionic acid decrease on silylation. The interaction coefficients for acidic test compounds, particularly phenol, have been shown to correlate with service performance in both accelerated weathering and road test studies (2-4). Values of the I_g on all asphalts (oxidized or not) fall into narrow ranges for both test compounds after silylation. The range for phenol on silylated, as-received asphalts is 112 to 117; that for silylated-oxidized asphalts is 113 to 117. Ranges for propionic acid were 65 to 67 and 69 to 71, respectively. As a net result, all of the silylated asphalts are indistinguishable by these two test compounds. These data indicate that certain functional groups

TABLE I. - Comparison of specific interaction coefficients for asphalts, oxidized asphalts, and trimethylsilyl derivatives of both

Test compound	Asphalt sample ^a	Specific interaction coefficients (I _g)											
		W	WS	WO	WOS	D	DS	DO	DOS	J	JS	JO	JOS
Phenol		129	112	161	113	136 134	116 113	154 155	117 115	120	117	160	115
Propionic acid		94	67	108	71	97 --- ^b	65 65	154 157	71 69	72	65	99	71
Formamide		150	142	172	165	155 157	--- ^b 150	188 187	183 185	126	128	155	153

^a W, D, and J refer to Wilmington (Calif.) asphalt, asphalt D and asphalt J, respectively. S designates a sample silylated with BSA, and O designates a column-oxidized sample. Separate determinations on different samples of asphalt D are shown.

^b This value was not obtained.

that form on oxidation and interact strongly with phenol and propionic acid are blocked by silylation. Silylation also appears to block a portion of the strongly interacting groups present in as-received asphalts.

Phenols and carboxylic acids are compound types present in asphalts. These compound types contain active hydrogens and are believed to interact strongly with the test compounds phenol and propionic acid in IGLC columns via hydrogen bonding. Silylating reagents such as BSA form ethers and esters with phenols and carboxylic acids, respectively, thus reducing their ability to hydrogen bond. Therefore, it is concluded that the phenolic and carboxylic acid OH groups in asphalts are silylated by the technique used in this study, thus strongly suggesting that decreases in the I_g values for the test compounds phenol and propionic acid result from silylation of these groups.

Data in Table I show that even though the I_g values for phenol and propionic acid after silylation have narrow ranges the values are still high. These high, relatively constant values indicate that the silylated asphalt samples contain approximately the same concentration of other types of functional groups that interact with phenol or propionic acid.

The formamide I_g values (Table I) for oxidized or silylated-oxidized asphalts are in the same range (155 to 188, compared to 153 to 185). Ranges for as-received and silylated asphalts are also comparable, these being 127 to 157 and 128 to 150, respectively. Because the specific interaction coefficients for formamide decrease only slightly on silylation, it appears that formamide does not interact appreciably with groups that can be silylated. The carbonyl group is a major type of functional group formed on oxidation (13) that is not silylated with BSA by the current technique. Carbonyl groups have been shown (14) to interact strongly with formamide in GLC determinations. Because oxidized asphalts (whether silylated or not) have higher I_g values than corresponding unoxidized samples, and because carbonyl groups are polar functions formed on oxidation which are not silylated, it is concluded that carbonyl groups contribute appreciably to I_g values for formamide.

Effect of Silylation on Infrared Spectra

Infrared spectra of dilute solutions of trimethylsilylacetamide, a silylated asphalt, and an asphalt are shown in Figure 1. The infrared band at 3610 cm^{-1} has been assigned to the free phenolic OH stretching band (15). Based on work in this laboratory, the band at 3540 cm^{-1} has been assigned to the free carboxylic acid OH stretching band. The band at 3420 cm^{-1} is attributed to the free amide NH stretching band of trimethylsilylacetamide. The latter assignment was made on the basis of trapping the effluent from silylation reactions and comparing its infrared spectrum with that of trimethylsilylacetamide obtained by hydrolysis of BSA. These spectra were essentially identical. The band at 3420 cm^{-1} appeared within the known range for NH stretching of amides. The infrared spectrum for BSA has no such band.

The infrared spectra of silylated asphalts show that silylation significantly decreases the absorbance in the 3610 and 3540 cm^{-1} regions. Little, if any, trimethylsilylacetamide remains in the asphalt sample after silylation. This is demonstrated by the absence of a sharp band in the silylated asphalt spectrum in the 3420 cm^{-1} region. The infrared data are summarized in Table II. In all cases, decreases in absorbances for free phenolic and carboxylic acid OH groups are evident after silylation, indicating that most of these groups react with BSA. Previous discussion of IGLC data concluded that silylation blocks phenolic and carboxylic acid OH groups in asphalt and that these groups probably interact strongly with phenol and propionic acid in IGLC columns. The infrared spectra show that free phenolic and carboxylic acid OH groups are essentially eliminated by silylation.

When free carboxylic acid and phenolic OH absorbance values for as-received asphalts are compared with values for oxidized asphalts, decreases in absorbance values for Wilmington

TABLE II. Comparison of infrared spectra of asphalt samples

Sample ^b	Absorbance ^a	
	Free phenolic OH, 3610 cm ⁻¹	Free carboxylic OH, 3540 cm ⁻¹
W	0.130	0.045
WS	<0.005 ^c	<0.005
D	0.097	0.028
DS	0.019	<0.005
J	0.035	0.020
JS	0.009	0.006

WO	0.070	0.028
WOS	<0.005	<0.005
DO	0.111	0.034
DOS	0.017	<0.005
JO	0.015	0.009
JOS	0.006	<0.005

^aThe values given are for 20g/l solutions of the sample in CCl₄ using 1 cm cells without solvent compensation. They were determined by the base-line technique.

^bSee footnote from Table I for sample designation

^cThe lower limit of detectability was about 0.005 absorbance units.

asphalt and asphalt J are observed. These results seem contradictory to the conclusion that increased concentrations of phenolic and carboxylic acid OH groups relate to the increase in I_g values for phenol and propionic acid. However, it has been shown previously (15) that column oxidation of asphalts results in a decrease of free OH absorbance while hydrogen-bonded OH absorbance increases significantly. Much of this hydrogen bonding remains intact even in dilute solutions so that the net result is a loss of free OH absorbance even though the total OH in the sample has increased. Upon silylation a general decrease is noted in the hydrogen-bonded absorbance; however, no quantitative determination could be made of the hydrogen-bonded region (about $3500\text{--}2500\text{ cm}^{-1}$) because it is overlapped by the C-H stretching region.

Repeatability of the Silylation Technique

Two separate packings were prepared, using asphalt D as the substrate. Two columns of each packing were processed in the manner described in the Experimental section. The data, included in Table I, show a maximum variation in specific interaction coefficients for a given test compound on duplicate asphalt samples of three I_g units. This is within the normal variation on duplicate runs of the same sample. The preliminary indication is that the technique gives reproducible results.

SUMMARY AND CONCLUSIONS

Silylation of an asphalt within an IGLC column offers a convenient means to study asphalt functionality. More specifically, the reagent, BSA, reacts with most of the phenolic and carboxylic acid hydroxyl groups present in either as-received or column-oxidized asphalts. Comparison of infrared spectra before and after silylation substantiates this conclusion.

Silylation reduces the phenol and propionic acid I_g values on both oxidized and unoxidized asphalts to a common value characteristic for each individual test compound. This results from the blocking of the carboxylic acid and phenolic OH groups in the asphalts. These groups are believed to be the ones by which phenol and propionic acid differentiate among asphalts. The functional groups which interact strongly with formamide remain after silylation. These groups appear to be carbonyl functions.

The silylation technique should be applicable to investigations of the chemical structure of macromolecules and nonvolatile materials.

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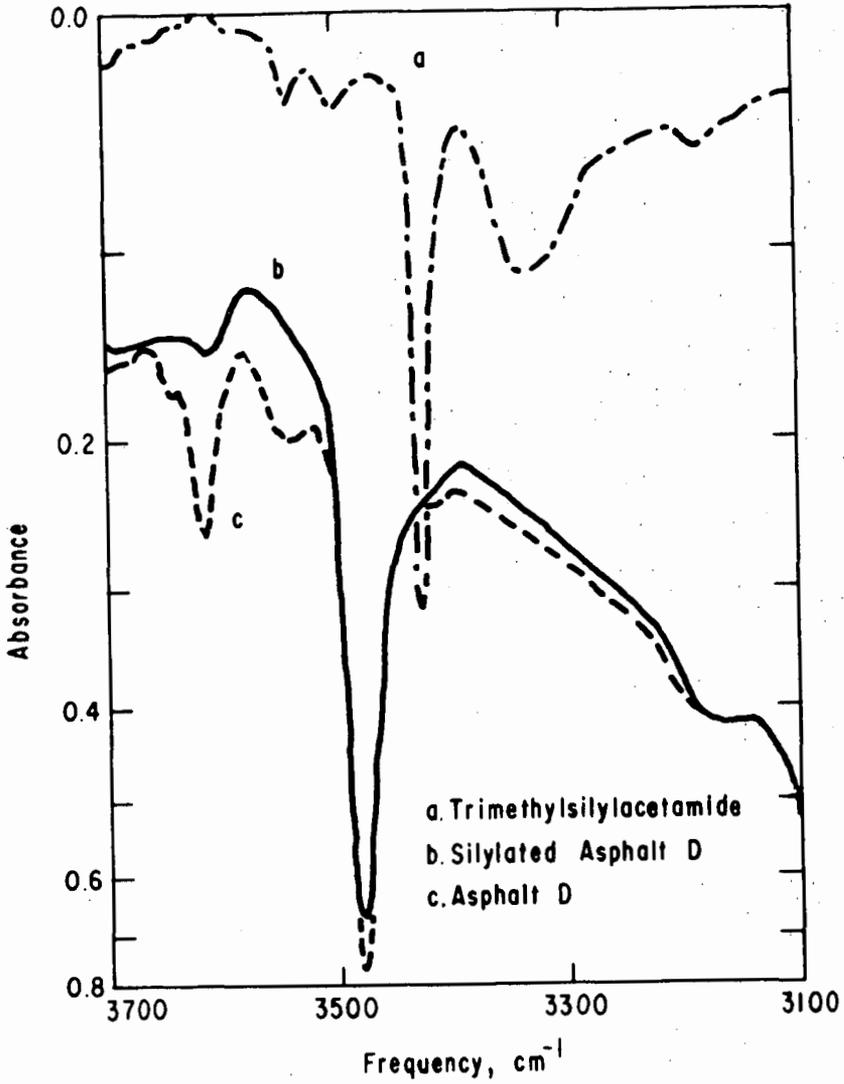


Figure 1. Infrared Spectra of Trimethylsilylacetamide, Silylated Asphalt D, and Asphalt D