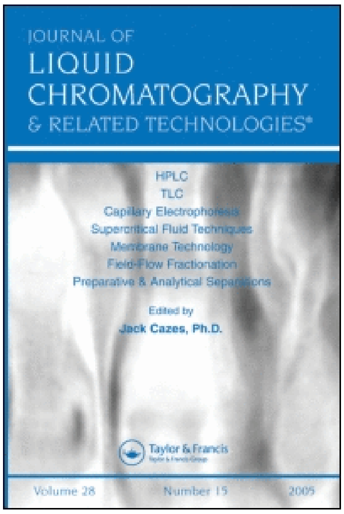

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Thin Layer Chromatographic Screening of Coal Liquids

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THIN LAYER CHROMATOGRAPHIC SCREENING OF COAL LIQUIDS

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ABSTRACT

Procedures are described for the thin layer chromatographic (TLC) analysis of coal-derived liquids. After solvent selection using Selectosol(1) radial TLC, a series of compounds typically found in coal liquids was used to demonstrate their elution behavior on silica gel. It was determined that unactivated (Brockman 4) silica plates series developed with isooctane/tetrahydrofuran (THF) (80:20, v/v) provided the best separation. The order of elution was saturate > hydroaromatic > polynuclear aromatic (PNA) > phenols $\geqslant$ nitrogen bases. The use of two-dimensional TLC with reverse phase and silica contiguous on the same plate (Whatman Multi-K) is discussed for the rapid separation and identification of coal liquid components. Trimethylsilyl ether derivatives were prepared of phenols and alcohols present in coal conversion products. This technique proved most useful in that the TMS-derivatives behaved similarly to their parent PNA, in order of elution, on silica plates using a moderately active mobile phase (isooctane:THF,80:20, v/v). TLC and the reactions described provide a semi-quantitative measure of the degree of hydrogenation of coal-derived liquids.

INTRODUCTION

As the fossil fuel industry develops within the United States and increases its ability to convert bituminous coal to cleaner burning solvent refined coal (SRC) and coal liquids, it becomes important to have a host of analytical methods for the analysis of such coal-derived materials. During coal liquefaction major compositional changes occur that affect the physical and chemical properties of the coal-derived recycle solvent that transports the coal through the process. Heteroatom removal such as hydrodenitrogenation, hydrodesulfurization and hydrogenation of polynuclear aromatics are some of the major reactions taking place within the recycle solvent. These compositional changes are of special interest because the amounts and kinds of species present relate to the potential of the solvent to donate or shuttle hydrogen. Coal conversion requires the transfer of hydrogen from the gas phase to the whole coal or its thermolysis products through the hydrogen donor solvent. If hydrogen cannot be shuttled from the gas phase _via_ the solvent to the coal components, regressive reactions (2) are believed to occur, such that "repolymerization" occurs to form much less tractable products.

The SRC-I process in particular requires a recycle solvent that will carry the coal (30-40 wt %) into the reactor, dissolve its thermolysis products, and shuttle hydrogen to free radical sites before regressive reactions occur. Then, the recycle solvent must regenerate itself _in situ_ with new gas phase hydrogen with the aid of coal minerals as catalyst. Another process, Exxon Donor Solvent, (EDS) (3) relies on removing the solvent from the main process stream and with a specific catalyst increases the hydrogen content, then returns a distillate portion to the process to continue liquefactio

This investigation has four major objectives:

1. Using TLC, screen coal liquids for the presence of various classes of organic compounds such as hydroaromatics, polynuclear aromatics (PNAs), phenols, and nitrogen compounds.

2. Determine the effectiveness of hydrogenation treatment of coal liquids by the conversion of aromatics to hydroaromatics and the reduction of heteroaromatic species by assessing the chromatogram for the relative intensity of fluoresence of these compound classes.

3. Use the data from TLC to determine suitable mobile phases for HPLC analysis of coal products for more efficient quantitation and quality control.

4. Examine the chromatographic behavior of trimethylsilyl (TMS) ether derivatives of phenols and alcohols. Determine if this procedure proves useful in characterization of these hydroxyl compounds on normal phase TLC and HPLC silica because the derivatives would have their polar functionality removed.

MATERIALS

TLC Equipment

All solvents were HPLC grade and were obtained from J. T. Baker Chemical Co., Phillipsburg, NJ. TLC plates were precoated 20 x 20 cm glass plates from the following manufacturers: Analtech, (Silica Gel GF, 6-613A, Reverse Phase - RPS, Alumina GF, 6-601A) Schleicher and Schull, Keene, NH, (Silica Gel G 1500), and Whatman Inc., Clifton, NJ (Multi-K Type CS5, KC_{18}/K5F). Plates were spotted with either Cordis Combs (Cordis Labs, P. O. Box 370428 Miami, FL) or Fisher graduated 3 x 10 μL TLC spotting micropipets. The developing chamber was a standard glass tank from Pioneer Scientific Company, Wilmington, DE. Model compounds examined in this report were obtained from a number of sources. The majority of standards were obtained from a library of compounds accumulated over the past years from various coal research laboratories. Ultra-pure samples of 1-azafluoranthene, 7-azafluoranthene and 4-azapyrene were obtained from M. Zander of Rütgerswerke, Akteingesellschaft, Castrop - Rauxel, West Germany. Hexamethyldisilizane was obtained from Supelco, Inc., Belfonte, PA.

Coal-derived liquids were obtained from the Air Products and Chemicals Inc., Coal Process Development Unit (CPDU), pilot plant at the Allentown PA facility. The sample designated Feed Liquid was subjected to hydrogenation at 1.39×10^7 Pa, 415°C and a linear space velocity of 0.5 h^{-1}, and produced the Product Liquid sample. Recycle solvents were obtained from the Catalytic Inc., Wilsonville, AL SRC-I, 6-Ton per day Pilot Plant.

The coal liquids were separated into saturate, aromatic, phenolic and nitrogen base fractions by solvent extraction and column chromatographic techniques (4). See Figures 1a and b.

Instrumentation

High Performance Liquid Chromatography (HPLC) was performed on a Beckman-Altex Liquid Chromatograph equipped with Model 110A and Model 100 dual pumps, a Model 323, 254 nm fixed wavelength detector and a Hitachi Model 100-40 variable wavelength spectrophotometer. An Altex Model 500 Autosampler equipped with a 50 μL loop was used to standardize all sample injections. For normal phase operations, the Altex Ultrasphere 5μ silica column was equipped with an Altex Li/Chrosorb SI 60, 10μ precolumn while for reverse phase chromatography an Altex Ultrasphere ODS 5μ column was used.

Infrared spectra were obtained on a Perkin-Elmer Model 457 infrared spectrophotometer. Samples were run as dilute carbon disulfide solutions in a Research and Industrial Instruments Co., (England) variable pathlength cell using air as a reference.

METHODS

Thin Layer Chromatography - Solvent Screening

The S and S Selectosol system was used to determine optimum solvent composition for analysis. This system employs small fiber wicks, spotted with the appropriate organic mixture to be separated in contact with a standard Silica GF TLC plate. A wick is dipped

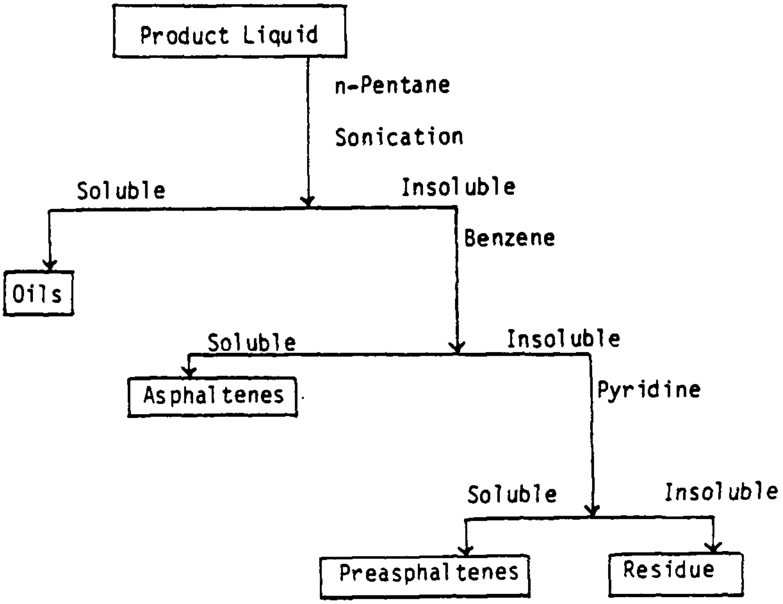


FIGURE 1a. Solvent Separation Scheme for a Product Liquid

into a solvent well and the components of the mixture separate as concentric circles on the plate. This technique is called radial TLC.

TLC - One and Two Dimensional

One and two-dimensional TLC employing conventional elution was carried out in a standard rectangular glass tank. All standard compounds were dissolved in methylene chloride, the concentrations ranging from 0.05 to 3.5 mg/mL.

TLC plates employed in conventional, one-dimensional chromatography were scored to provide 8 channels, 2.4 cm wide prior to use. The origin was spotted with 10 μL of sample from a Cordis Comb. If multiple applications were used, the spot was allowed to dry prior

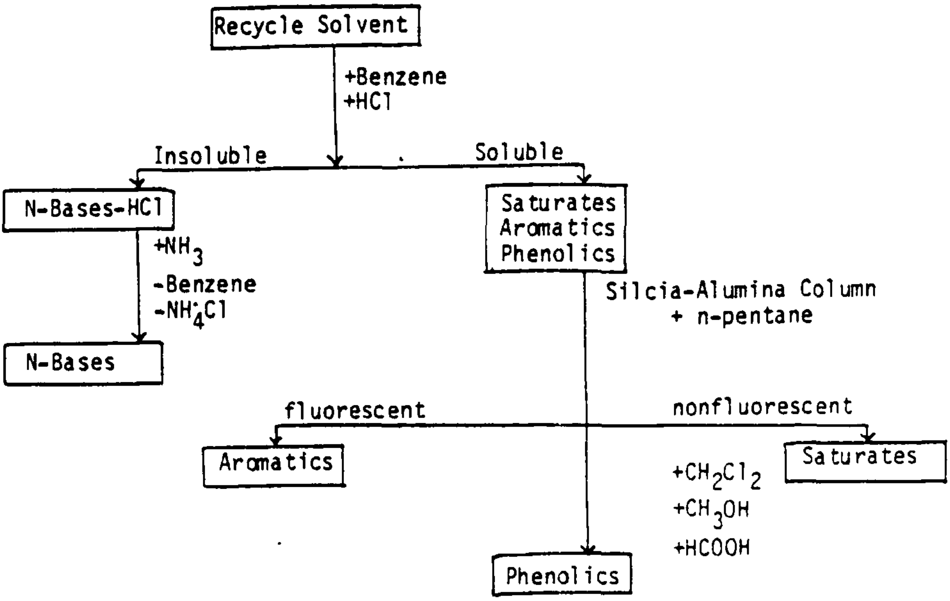


FIGURE 1b. Column Chromatographic Separation Scheme for Separation into Nitrogen Bases, Saturates Aromatics and Phenolics.

to the next application. Spotting of the Whatman Multi-K plate was done with the Fisher 30 X 10µL TLC spotting micropipets by applying a 10µL spot onto the reverse phase portion of the plate. A blow dryer was used to dry the spot prior to the application of the next component. Multiple development was used to concentrate the area of the spots for each chromatogram. Spots were allowed to rise with the developing solvent, the TLC plate was removed from the chamber, dried and returned to the chamber for further development using the following intervals, 1/5, 2/5, 3/5, 4/5, and up to 19 cm on the TLC plate. The chromatograms were visualized using the natural fluorescence of many of the components under 366 nm uv radiation or 254 nm in the case of the silica gel GF plates. Phenols were visualized by spraying the appropriate plates with 0.1 M NaOH solutions of Fast Blue Salt B. This diazo reagent reacts with phenols by coupling para to the OH group to produce a purple spot. Most nitrogen heterocycles were fluorescent under long wave ultraviolet radiation and those that did not fluoresce were sprayed with a 0.1 N $AgNO_3/NH_3$ solution to produce a black spot when exposed to visible light.

All chromatograms were photographed using a Minolta SRT 101 single lens reflex camera with a Rokkor-PF f 1.7, 55 mm lens. Ektrachrome ASA 400 film was found to be satisfactory for recording all chromatograms under long or short wave ultraviolet radiation. The camera was mounted on a tripod and equipped with a cable release. Exposure times were 1/30 s for 254 nm light and 1/8 s for 366 nm light.

Liquid Chromatography

In comparing the TLC retardation factors (R_f) for silica plates with HPLC retention times, the Beckman-Altex liquid chromatograph was equipped with the 5 μ ultrasphere silica column and isocratically eluted with 80% isooctane, 20% THF at a flow rate of 1 mL/min. The ODS column was eluted with 95% methanol and 5% water run isocratically at a flow rate of 1 mL/min. All retention times are reported as relative to point of sample injection.

Trimethylsilyl Derivatives (5,6)

Silyl derivatives were prepared by adding to a 50 mL side arm filtering flask in turn, 50 mg of the phenol, or alcohol or coal liquid, 5 mL of benzene, 0.5 mL of hexamethyldisilizane and 50 μL of pyridine - d_5. The flask was fitted with a Bunsen valve to release solvent pressure and to keep moisture out. A neoprene stopper wrapped with Teflon sheet was used to seal the flask. The mixture was gently refluxed and swirled on a hot plate for 0.5 to 2 hours. Longer times were used to allow coal-derived phenols to react. After the reflux period, the mixture was transferred to a 100 mL round bottom flask *via* a 1 mL benzene wash and the mixture frozen in liquid nitrogen to remove benzene by sublimation under vacuum. Dry nitrogen gas was then bled into the flask, and 2 mL of CS_2 added.

The sample was examined by infrared spectrophotometry for disappearance of the OH absorption band at 3600 cm^{-1} characteristic of monomeric (non-hydrogen bonded) hydroxyls.

RESULTS AND DISCUSSION

Solvent Selection

One objective was to determine the best solvent system for separating coal-derived liquids on TLC so that the results could be applied to HPLC analysis. A wide range of solvents and solvent mixtures was examined using the S & S Selectasol system. On Silica gel GF, the following solvents were investigated: isooctane, tetrahydrofuran (THF), benzene, methanol and methylene chloride. The solvent system that best separated a total coal liquid that boils up to 450°C was isooctane/THF (80:20, v:v).

Activation of TLC Plates:

We determined that activation (water content) of the silica plates played a reverse role in our separations. Highly activated plates, with low water content, were difficult to maintain and did not provide the best separation. Table 1 gives the results of

TABLE 1

Comparison of Activated and Unactivated Silica

Compound	R_f Activated	R_f Unactivated	Ratio: $\frac{R_f\ U}{R_f\ A}$
1-Pyrenol	0.34	0.38	1.1
Fluorene	0.65	0.72	1.1
Phenanthrene	0.59	0.67	1.1
Acenaphthene	0.68	0.78	1.1

comparing activated versus nonactivated TLC plates. We estimate that our highest activity achieved was nearly Brockman 1 (∿1% H_2O) and the best operational plates had Brockman 3-4 (∿8% H_2O). Table 1 also shows that the ratio R_f unactivated/R_f activated remains essentially constant for the compounds tested, showing that the difference in R_f value is due to the nonactivation of the plate rather than an effect due to the component.

With this information we chromatographed over 40 compounds as TLC standards. The majority of compounds chromatographed are known components of coal liquids. Table 2 lists selected standard compounds, their structures, and R_f values. As can be seen from Table 2, aromatic compounds with no functional groups possess the highest R_f value while phenols and nitrogen-heterocycles possess relatively low R_f values.

The value of TLC as a screening tool for complex coal liquids is due to the fact that the R_f values can be quickly determined and easily measured. Table 3 shows that hydroaromatics elute first followed by aromatics (PNA's) with phenols and nitrogen hetrocycles a close third and fourth, respectively.

Since the R_f value depends on interactions between solute and solvent and between solute and adsorbent, the R_f values in Table 3 provide good working ranges. Compounds such as phenols which can associate with the adsorbent have relatively low R_f values, while hydroaromatics and PNA's elute faster. Examination of the R_f values for carbazole (0.49) and N-ethylcarbazole (0.59) shows that when the N-H on carbazole is changed to an N-Et, the R_f value is increased. N-Ethylcarbazole's attraction for the polar silica adsorbent is a dipole-dipole interaction which is weaker than hydrogen bonding of an NH. Hydroaromatics have larger R_f values than aromatics because of a stronger solvent attraction for the former compounds than for the latter group.

TABLE 2

Retardation Factors for Silica Plates Using Isooctane/THF (80:20, V/V)

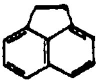
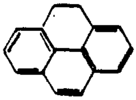
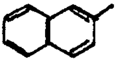
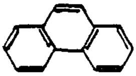
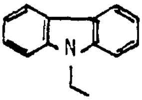
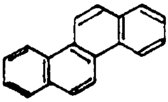
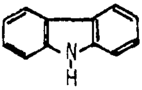
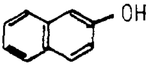
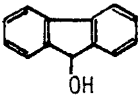
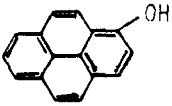
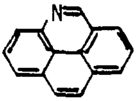
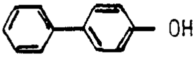
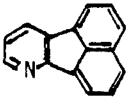
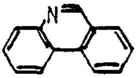
Compound	R_f	Structure
Acenaphthene	0.78	
4,5-Dihydropyrene	0.69	
2-Methylnaphthalene	0.67	
Phenanthrene	0.67	
N-Ethylcarbazole	0.54	
Chrysene	0.50	
Carbazole	0.44	
2-Naphthol	0.42	
9-Fluorenol	0.40	
1-Pyrenol	0.34	
4-Azapyrene	0.34	
p-Phenylphenol	0.33	
7-Azafluoranthene	0.32	
Phenanthridene	0.22	

Table 3

Means, Standard Deviations and Ranges of R_f Values for Classes of Standard Compounds

Class	R_f (mean)	s	Range	Number of Compounds
Hydroaromatics	0.75	0.05	0.80-0.69	7
Aromatics (PNA's)	0.60	0.11	0.74-0.32	9
Phenols	0.37	0.09	0.46-0.16	11
Nitrogen Heterocycles	0.30	0.19	0.54-0.00	22

Effectiveness of Hydrotreating of a Coal Liquid

We applied this TLC screening technique to the evaluation of the effectiveness of hydrogenation of coal liquids obtained from the CPDU facility at APCI. In Table 4, the sample designated Product Liquid was a liquid obtained from the CPDU after being subjected to hydrogenation.

The bands at R_f values 0.13 and from 0.23 to 0.36 in the Feed Liquid were identified as phenols by spraying with Fast Blue Salt B. Figure 2, a photograph of the TLC plate, shows a darker region of the spots at R_f values of 0.78 and 0.82. These values are within the range for hydroaromatics (See Table 2). As discussed previously, the presence of hydroaromatics in a product liquid is particluarly important in the maintenance of a good recycle solvent in the conversion of coal to a clean burning fuel.

Comparison of TLC and HPLC

Our work with the ODS plates involved characterization of PNA's using a reverse phase mode. The Selectasol system was used to determine that a solvent mixture of methanol: water (95:5, v/v)

TABLE 4

TLC R_f Values of Feed and Hydrotreated Product Liquids Using Isooctane/THF (80:20, v/v)

Product Liquid	Feed Liquid
0.82	0.77
0.78	0.64
0.75	0.36
0.64	0.34
0.21	0.29
0.17	0.27
-	0.25
-	0.23
-	0.19
-	0.13

provided optimum chromatographic resolution. Table 5 shows results from TLC and HPLC using methanol:water on ODS stationary phases. It must be kept in mind that the greater the R_f value for TLC, the faster the elution on HPLC. Thus, in both cases using ODS Stationary phase, two-ring compounds (naphthalene) elute first followed by three-ring compounds (phenanthrene and anthracene) with the remaining four-ring (pyrene) compounds eluting last. In going from TLC to HPLC, we have found it necessary to decrease the strength of the solvent by raising the concentration of water.

Table 6 shows the results of transferring the TLC data on silica plates to HPLC on a silica column.

Figure 3 is a graph of the data and shows the linear relationship achieved between TLC and HPLC retention values for the comparison. Deviations from linearity are due to variations in the adsorbent, primarily from differences in particle sizes and packing density.

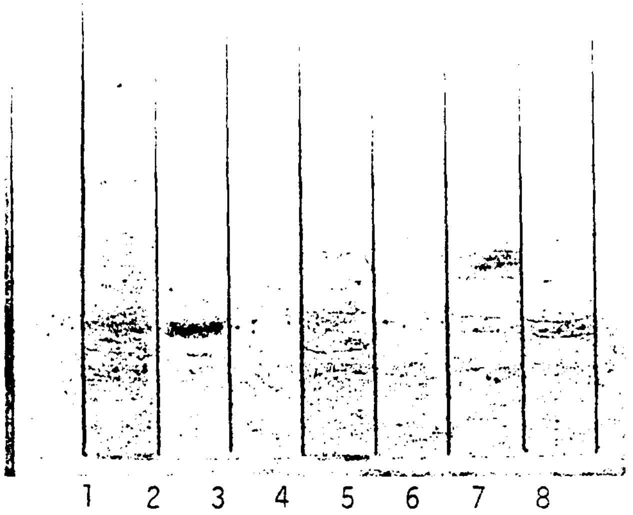


FIGURE 2. Thin Layer Chromatogram of:
1. Pyrene
2. Impure 1-Pyrenol
4. Anthracene
5. Feed Liquid
6. Fluorene
7. Impure Indole
8. 1-Acenaphthenol

For example, the silica in the Altex silica column has 80 A pore diameters and 5μ particle sizes while the Silica on Analtech Silica Gel G plates has 60 A pore diameters and 11μ particle sizes. Packing in a column for HPLC is extremely tight, usually made under 10000 psi, while the TLC plates have the adsorbent bound by gypsum.

Alumina coated TLC plates were investigated and showed no real improvement over the results obtained by silica-coated plates. Because some liquids contain a mixture of acidic, basic and neutral components, silica provides the best compromise on the activity of the adsorbent.

TABLE 5

Comparison of Retention (R_f, t_R) Results of TLC and HPLC On ODS Stationary Phases Using $CH_3OH:H_2O$

Compound	TLC R_f (95:5, v/v)	HPLC t_R (min.) (85:15, v/v, 1.0 mL/min)
Naphthalene	0.56	5.9
Phenanthrene	0.42	9.1
Anthracene	0.41	10.1
Fluoranthene	0.38	11.9
Pyrene	0.37	13.3
1,2 Benzofluorene	0.32	16.8
Chrysene	0.31	17.5

TABLE 6

Comparison of Retention Data of TLC and HPLC on Silica Stationary Phases Using Isooctane/THF

	R_f (80:20 v/v)	T_R (90:10, v/v)
Acenaphthene	0.77	3.75
Fluorene	0.72	3.80
Phenanthrene	0.67	4.30
Anthracene	0.67	3.85
Pyrene	0.64	3.85
1,2-Benzofluorene	0.57	4.20
Fluoranthene	0.55	4.80
Chrysene	0.50	5.10
Coronene	0.32	5.55

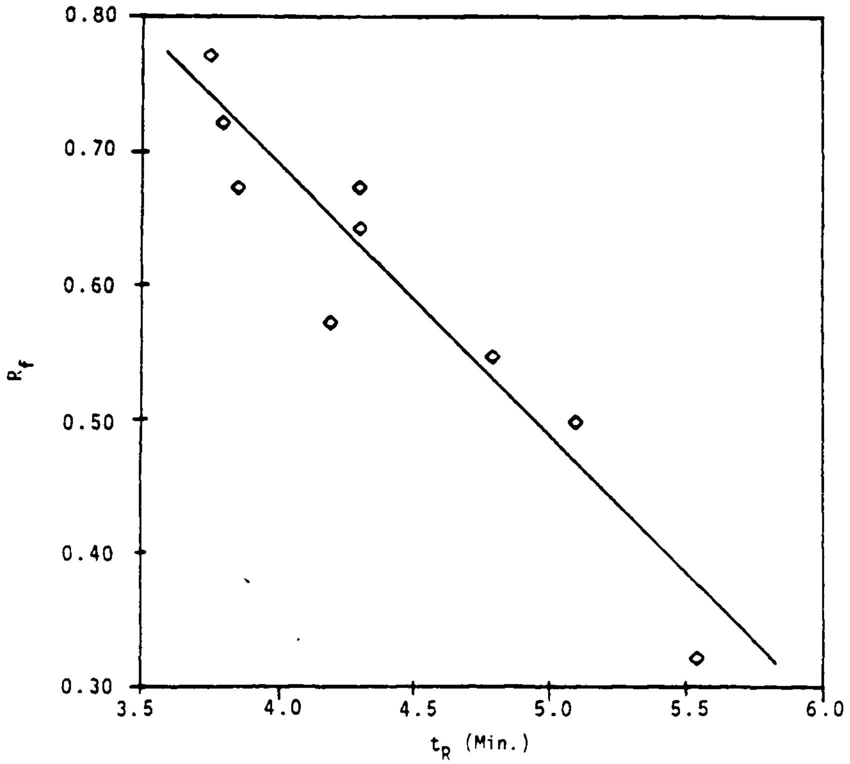


FIGURE 3 Graph of Comparison of Retention Data for TLC and HPLC on Silica Stationary Phases Using Isooctane:THF

Two Dimensional TLC

The Whatman Multi-K plate is manufactured in such a way that a 3 x 20 cm strip of the plate consisting of octadecylsilane groups bonded to Si-O-Si-C groups on silica gel is contiguous with a 17 x 20 cm hard silica surface. Samples were spotted on the ODS portion of the plate and allowed to elute using methanol/water (90:10, v/v). Plates were developed 16 cm up the plate, then removed from the tank and dried. After drying the plates were turned 90° for normal phase elution in the isooctane/THF (80:20, v/v) solvent. Results of a typical run on the Multi-K plate are shown in Figure 4. Those compounds that do not separate on the ODS portion of the plate separate on the silica portion. Table 7 shows R_f values measured for the elution on the ODS portion of the plate and the silica portion.

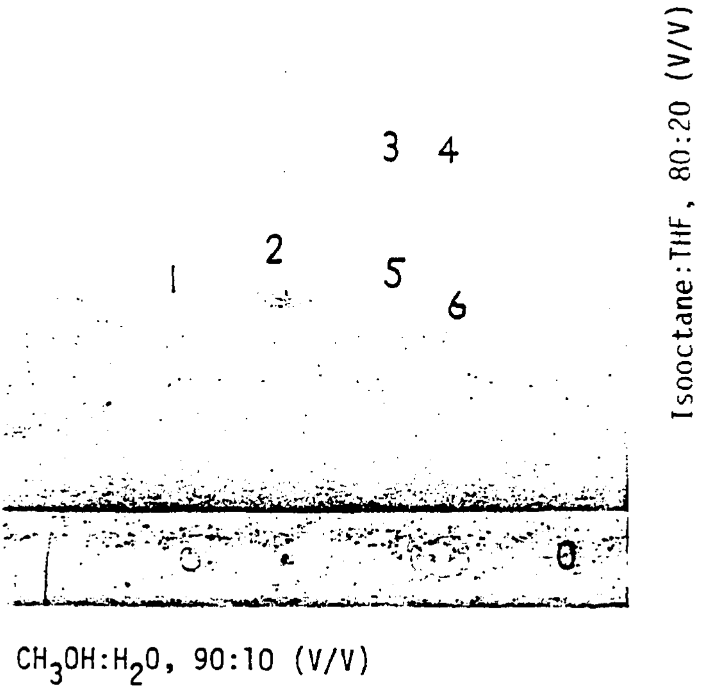


FIGURE 4. Two Dimensional Thin Layer Chromatogram Using Whatman Multi-K Plate. Spots are indentified as:

1. 2-Naphthol
2. Phenanthrene
3. Acenaphthene
4. Pyrene
5. 4-Azapyrene
6. 1-Azafluoranthene

TABLE 7

R_f Values for Selected Compounds on ODS and Silica Sections of Whatman Multi-K Plate

Compound	Color of Fluoresence (366 nm)	R_f ODS (CH_3OH/H_2O)	R_f Silica Isooctane/THF)
2-Naphthol	-	0.73	0.39
Phenanthrene	purple	0.56	0.63
Acenaphthene	-	0.41	0.73
Pyrene	blue	0.38	0.68
4-Azapyrene	green	0.36	0.32
1-Azafluoranthene	yellow	0.32	0.41

One must be careful in comparing R_f values for silica on the Analtech plate with the silica layer from the Whatman Multi-K plate. There are two reasons for differences in adsorbent power:

1. Pore and particle size differences in silica gel vary from one manufacturer to another.
2. By using an aqueous solvent in one dimension on the Whatman Multi-K plate, the silica was more deactivated than the Analtech plate. Thus a compound such as 2-naphthol, which can hydrogen bond to silica, had a higher R_f value on the aqueous solvent-preconditioned Whatman Multi-K plate.

Table 8 shows the R_f values for selected compounds on the Analtech silica plate and the silica portion of the Whatman Multi-K plate using the same solvent system.

Table 8 shows that for the compounds selected, the order of elution is predictable with both plates. The hydroaromatics elute first, followed by the aromatics, N-ethylcarbazole before carbazole and highly associated compounds like 2-Naphthol eluting slowly. The fact that phenanthridene elutes last on both plates is due to a weaker solute-solvent interaction as described earlier.

TABLE 8

Comparison of R_f Values on Analtech Silica and Whatman Multi-K Silica using Isooctane/THF (80:20, v/v)

Compound	R_f Analtech	R_f Whatman
Acenaphthene	0.77	0.88
1,2-Dihydropyrene	0.69	0.86
Anthracene	0.67	0.82
N-Ethylcarbazole	0.54	0.80
Carbazole	0.44	0.64
2-Naphthol	0.42	0.62
Phenanthridene	0.22	0.54

It was not our intended purpose to rate TLC plates from different manufacturers as both plates will give excellent results for different applications. The chromatographer must make the decision as to which type of plate to use for a particular application.

TMS Derivatives of Phenols and Alcohols

Phenols and alcohols cannot be easily chromatographed by HPLC using normal silica columns due to irreversible hydrogen-bonding on the adsorbent. We therefore prepared TMS derivatives of several hydroxyl compounds found in coal liquids to overcome this irreversible bonding. The infrared spectra of all derivatives showed the lack of the unassociated OH band at 3600 cm^{-1} and the presence of several bands at 1247, 850 and 754 cm^{-1}, all assigned to - $Si(CH_3)_3$, 1080 cm^{-1} assigned to - SiOR and 939 cm^{-1} assigned to SiOAr in the case of TMS phenols (7). Table 9 shows R_f values of these TMS derivatives as well as their parent hydroxyl compounds and their parent PNA's.

Table 9

R_f Values of TMS Derivatives Using Isooctane/THF (80:20, v/v)

Compound	$R_{f(OH)}$	$R_{f(TMS)}$	$R_{f(PNA)}$
p-Phenylphenol	0.33	0.65	0.74
1-Acenaphthenol	0.35	0.75	0.77
9-Fluorenol	0.40	0.73	0.72
2-Naphthol	0.42	0.70	0.62
Phenol	0.44	0.65	1.0*
Recycle Solvent A	0.42 to 0.22	0.75 to 0.69	0.75 to 0.53

*Inferred due to volatility of benzene on TLC plates.

The data in Table 9 show that conversion of the hydroxyl groups in the coal derived products makes the TMS ether derivative behave like the parent PNA on a silica plate. For example, the R_f value for 9-fluorenol is 0.40, while the R_f value for its TMS derivative is 0.73 which is nearly identical to the R_f value for fluorene (0.72). The structural change upon derivatization removes the ability of the compound to hydrogen bond to the silica and lowers the dipole-dipole interactions between the derivative and silica due to the three bulky methyl groups bonded to silicon. The TMS derivative is completely reversible to the original hydroxyl compound by reaction with water. Further investigation into the nature of the chromatography of TMS derivatives of hydroxyl compounds using TLC and HPLC is needed.

CONCLUSION

We have demonstrated that thin layer chromatography on silica gel can be effective as a rapid and semi-quantitative measure of the degree of hydrogenation of coal-derived liquids. In particular, hydrogenation and loss of hydroxyl (phenols) can be profiled by a side-by-side comparison of feed and product with the results recorded by photographic techniques. TLC, under the conditions described, provides a relative first measure of the hydrogen donor quality of coal-derived recycle solvents. The formation of a trimethylsilyl (TMS) derivative of the hydroxyl functional group has resulted in more predictable R_f values that are very similar to their parent aromatic nucleus on normal phase silica gel. Over spraying the TMS derivatives with Fast Blue Salt B aids in their location for spot removal by preparative techniques. Because the TMS derivative is completly reversible to the original hydroxyl with water, compounds can be recovered after separations.

Our results also confirm the use of S & S Selectosol radial TLC as a rapid screening tool for determinating the proper solvent combination for binary and ternary HPLC gradient elution chromatography.

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