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CHEMICAL SYSTEMS LABORATORY TECHNICAL REPORT

ARCSL-TR-82031

GAS-SOLID CHROMATOGRAPHY STUDIES USING ACTIVATED
CHARCOALS TREATED WITH 4-VINYLPYRIDINE

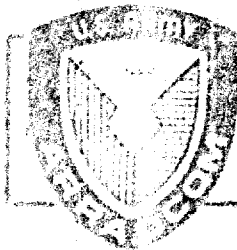
by

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October 1982

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US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARCSL-TR-82031	2. GOVT ACCESSION NO. AD-A122 284	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) GAS-SOLID CHROMATOGRAPHY STUDIES USING ACTIVATED CHARCOALS TREATED WITH 4-VINYLPYRIDINE		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Gerhard Magin Edward J. Poziomek		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS Commander, Chemical Systems Laboratory ATTN: DRDAR-CLB Aberdeen Proving Ground, Maryland 21010		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 1L161102A71A Tech Area B
11. CONTROLLING OFFICE NAME AND ADDRESS Commander, Chemical Systems Laboratory ATTN: DRDAR-CLJ-R Aberdeen Proving Ground, Maryland 21010		12. REPORT DATE October 1982
		13. NUMBER OF PAGES 25
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE NA
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) DTIC DEC 10 1982 H		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Activated charcoal Gas-solid chromatography 4-Vinylpyridine Reactive polymer		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The present paper reports the performance of a series of 4-vinylpyridine-impregnated charcoals as gas-solid chromatograph columns in the retention of water, a series of alcohols (methanol, ethanol, n-propanol, iso-propanol, n-butanol, tert-butanol), and several hydrocarbons (methane, ethane, propane, cyclopropane). The 4-vinylpyridine loading ranged up to 30% by weight. The activated charcoal was a coal-based one with a surface area of about 1000 sq m/gm. (Continued on reverse side)		

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20. ABSTRACT (Continued)

The use of activated charcoal in gas chromatography centers around the analysis of low boiling gases and hydrocarbons. Treatment of activated charcoal with 4-vinylpyridine led to decreases in both retention times and heats of adsorption for the organics examined. Increasing the 4-vinylpyridine content resulted in further decreases; an exception was noted with water, in which case a minimum in the retention time was noted with charcoals containing 3% to 5% 4-vinylpyridine.

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PREFACE

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GAS-SOLID CHROMATOGRAPHY STUDIES USING ACTIVATED CHARCOALS TREATED WITH 4-VINYLPYRIDINE

1. INTRODUCTION

Activated charcoals are characterized by large surface areas (400 to 1200 sq m/gm) and the presence of a variety of polar surface groups, such as hydroxyl, carbonyl, and carboxyl. These adsorbents have been used in gas-solid chromatography (GSC) for the analysis of permanent gases and hydrocarbons; a recent review is available.¹ It has also been reported that GSC techniques are useful in studying the oxidation of CO by a Cu/Cr/Ag catalyst supported on charcoal.² Because of their strong adsorptive characteristics, activated charcoals have been applied in GSC only for the analysis of compounds of low molecular weight. Attempted analysis of polar and hydrogen bonding compounds usually leads to peak tailing, irreversible adsorption, and/or "ghosting" phenomena. These problems have also been encountered with graphitized carbon blacks,³ but were largely eliminated by prior treatment of the carbons with hydrogen at 1000° C. The chemical nature of the surface of activated charcoal can be modified permanently by a vapor treatment with 4-vinylpyridine.⁴ This treatment apparently involves an adsorption polymerization, but the resulting surface was not fully characterized. Such surface treatments give rise to various possibilities of adjusting specific adsorptive forces, obtaining more homogeneous surfaces, and changing selectivity in GSC applications.

We describe here the characteristics and performances of 4-vinylpyridine-impregnated charcoals as GSC adsorbents with water, and alcohols and hydrocarbons of low molecular weight. Also, the effect of treating an activated charcoal with hydrogen at 440° C was examined in a limited fashion for purposes of comparison.

2. MATERIALS AND PROCEDURES

2.1 Charcoals.

Samples from a single lot of 12 to 30 mesh coal-base activated charcoal (surface area ca 1000 sq m/gm, CWS grade, Pittsburgh Activated Carbon Division, Calgon Corp) were utilized. Impregnation of the charcoal was accomplished according to a procedure reported previously.⁴ Essentially, it involved vapor adsorption of 4-vinylpyridine onto charcoal rotating in a flask.

2.2 Test Materials.

Methane, ethane, propane, cyclopropane, and butane were obtained from the Matheson Company, Inc. in CP grade. Methanol, ethanol, iso-propanol, n-propanol, n-butanol, and tert-butanol were reagent grade. Distilled water was also employed.

2.3 Column Packing Procedure.

Charcoal was added to the column from a funnel reservoir. A hand-held vibrator (Vibrocraft, Inc.) was utilized to ensure reproducible packing. Stainless-steel 1/4-inch OD columns in 30-cm lengths were employed. The effective packing length was near 29 cm. Obviously, the weight of charcoal required to fill the column varied because of density differences among the impregnated samples. For example, 3.90 gm of a 30% 4-vinylpyridine carbon or 2.61 gm of the unimpregnated material were needed to fill a 30-cm column.

2.4 Gas Chromatograph.

A 7620A series Hewlett Packard chromatograph was employed. The thermal conductivity detector was utilized for all of the experiments. The bridge current and thermal conductivity temperature were kept at 150 MA and 160°C, respectively. Helium was the carrier gas. A Hamilton microliter syringe (7101) and a Precision Sampling Corp. Pressure Lok gas syringe (1 cc) were used for the injection of liquids and gases, respectively.

3. CHARACTERISTICS AND PERFORMANCES OF GSC COLUMNS

3.1 Water.

A study was carried out on the performance of charcoal and 4-vinylpyridine-impregnated charcoals against water. Conditions included: 0.5 μ l water; injection port temperature, 140°C; column temperature, 120°C; and helium flow rate 40 ml/min. Plots of retention time, peak heights, peak areas, plate numbers, and tailing factors, each versus weight percent of the charcoal as 4-vinylpyridine, are given in figures 1 through 5. Typical water chromatograms obtained using unimpregnated charcoal and a 10% 4-vinylpyridine charcoal are given in figure 6.

Peak areas were determined by using a disc integrator unit. Retention times (t_R), tailing factors, and peak heights were calculated using conventional techniques as described in the chromatograph operating manual. The plate numbers were obtained from the formula $5.545 (t_R, \text{cm/half-width, cm})^2$.

The effect of conditioning time is evident in figure 1. Conditioning at 120°C for 2 hours was not found to give reproducible data. However, conditioning at 150°C overnight did, and this was adopted as a standard practice.

All data points represent averages from three to six determinations with the same column. Standard deviations for the various retention times were usually 0.01 to 0.02 minutes. Reproducibility between two columns prepared from the same charcoal was found to be acceptable. For example, two different columns of 2% 4-vinylpyridine charcoal gave the following pairs of average values: $t_R(\text{cm})$ - 0.89, 0.89; peak area - 680, 660; peak height - 53, 51.

3.2 Humidification Treatment.

The GSC characteristics of activated charcoal and 4-vinylpyridine-impregnated charcoals can be modified early by a simple humidification treatment. For example, columns of charcoal which had been utilized in obtaining the data for curve B of figure 1 were equilibrated with air at 80% RH and 75°F with the air drawn through the columns. The weight percent water pickup decreased with increasing 4-vinylpyridine content (table 1). The columns were then reconditioned at 150°C overnight in the chromatograph. As apparent in curve C (figure 1), the humidification treatment led to a general increase in the retention times for water. However, a minimum is still present; also, there is more scatter of the data.

3.3 Alcohols.

Dependence of retention time for several alcohols on percent 4-vinylpyridine contained in the charcoal adsorbent, boiling point of the hydroxylic compound, and number of carbon atoms in the hydroxylic material is evident in table 2. Chromatography conditions: 0.5 μ l alcohol; injection port, 155°C; column temperature, 150°C; helium flow rate, 60 ml/min.

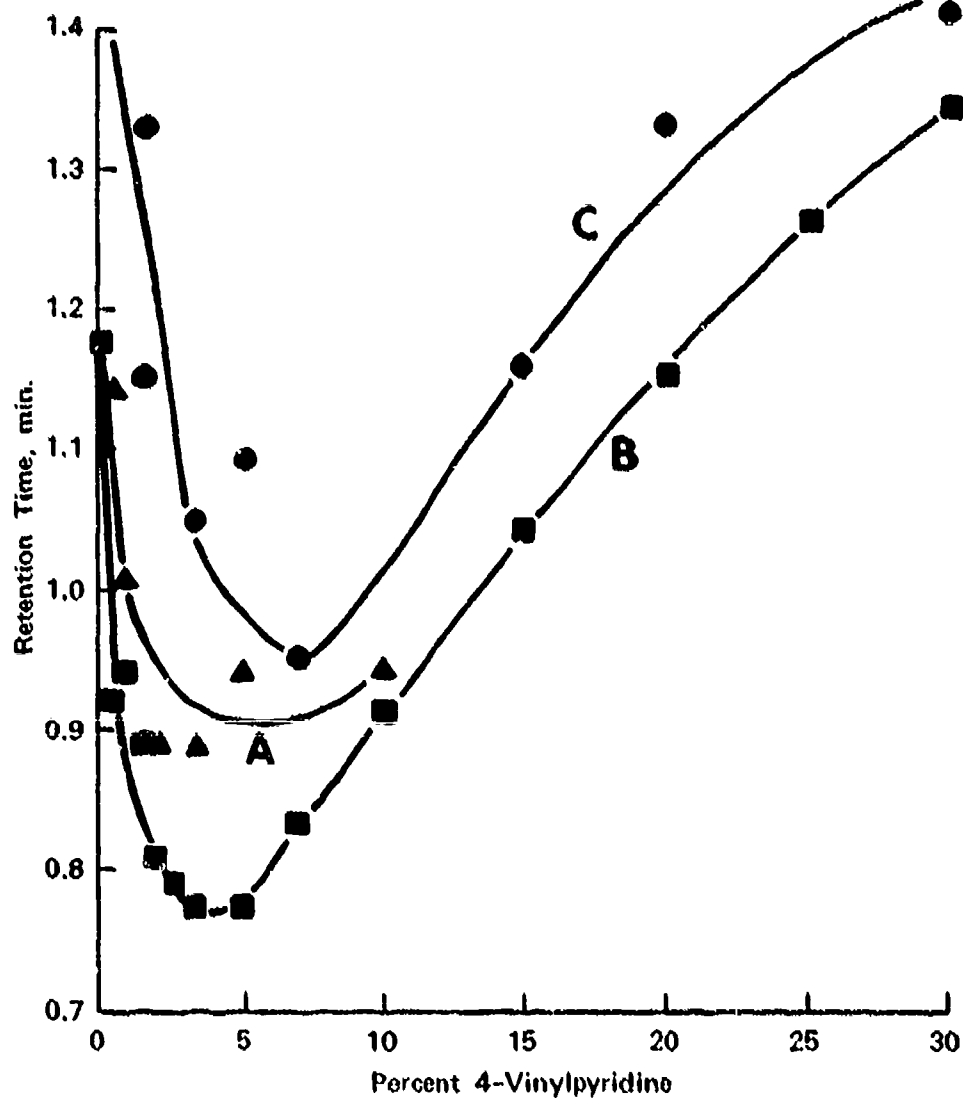


Figure 1. Retention Time of Water Versus Weight Percent of 4-Vinylpyridine Contained in the Charcoal Adsorbent

A, columns conditioned 2 hours, 120°C; B, columns conditioned overnight 150°C; C, columns used in B, then humidified to constant weight in 90% RH air and reconditioned again overnight at 150°C

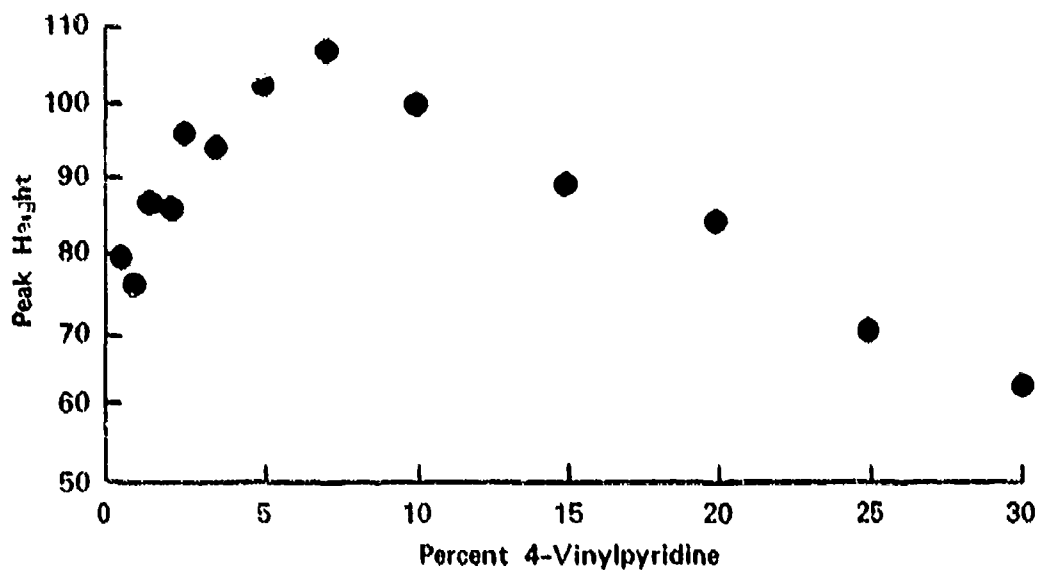


Figure 2. Peak Heights of Water Pulses Versus Weight Percent of 4-Vinylpyridine Contained in Charcoal Adsorbent

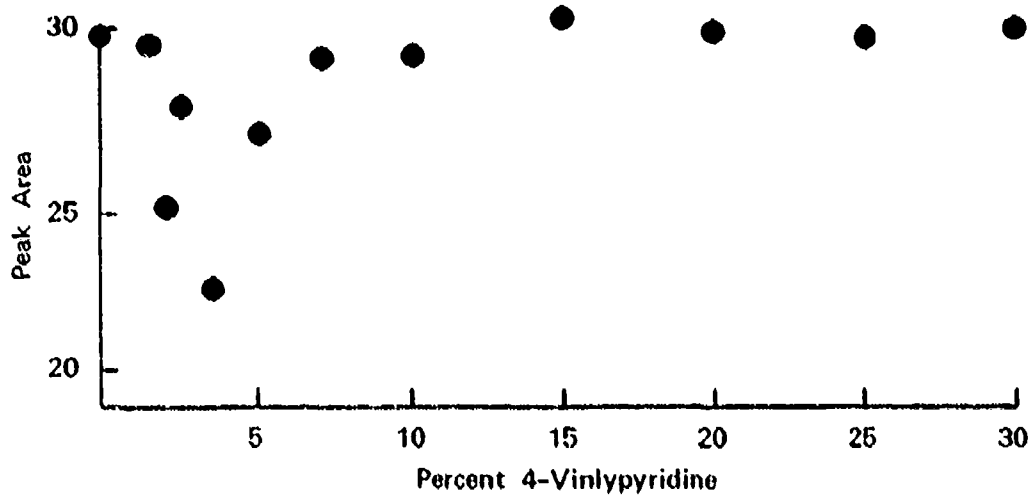


Figure 3. Peak Areas of Water Pulses Versus Weight Percent of 4-Vinylpyridine Contained in Charcoal Adsorbent

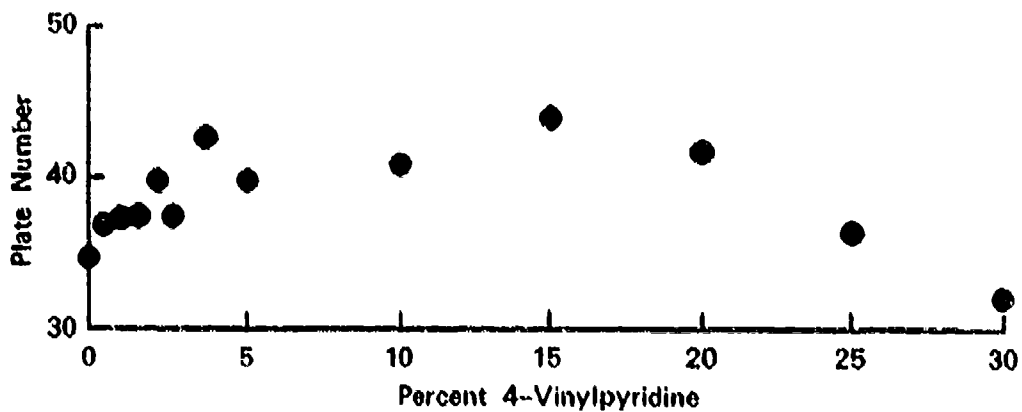


Figure 4. Plate Numbers of Charcoal Columns Versus Weight Percent of 4-Vinylpyridine Contained in Charcoal Adsorbent (Water Pulse Experiments)

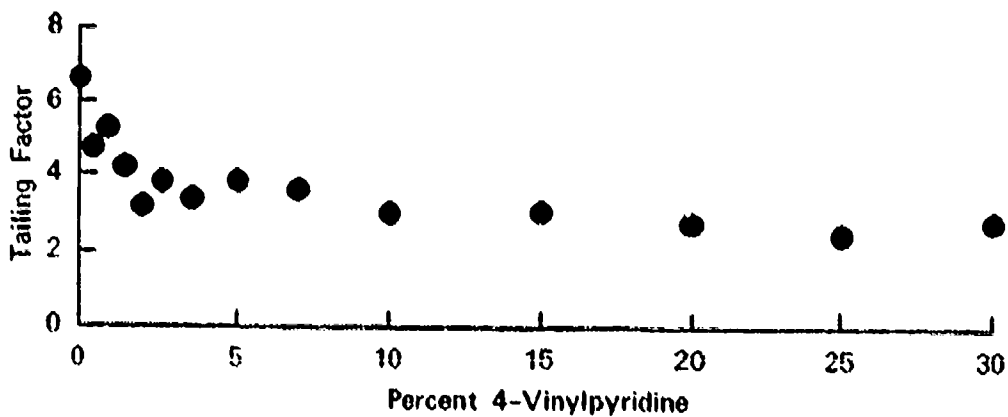


Figure 5. Tailing Factors from Water Chromatograms Versus Weight Percent of 4-Vinylpyridine Contained in Charcoal Adsorbent

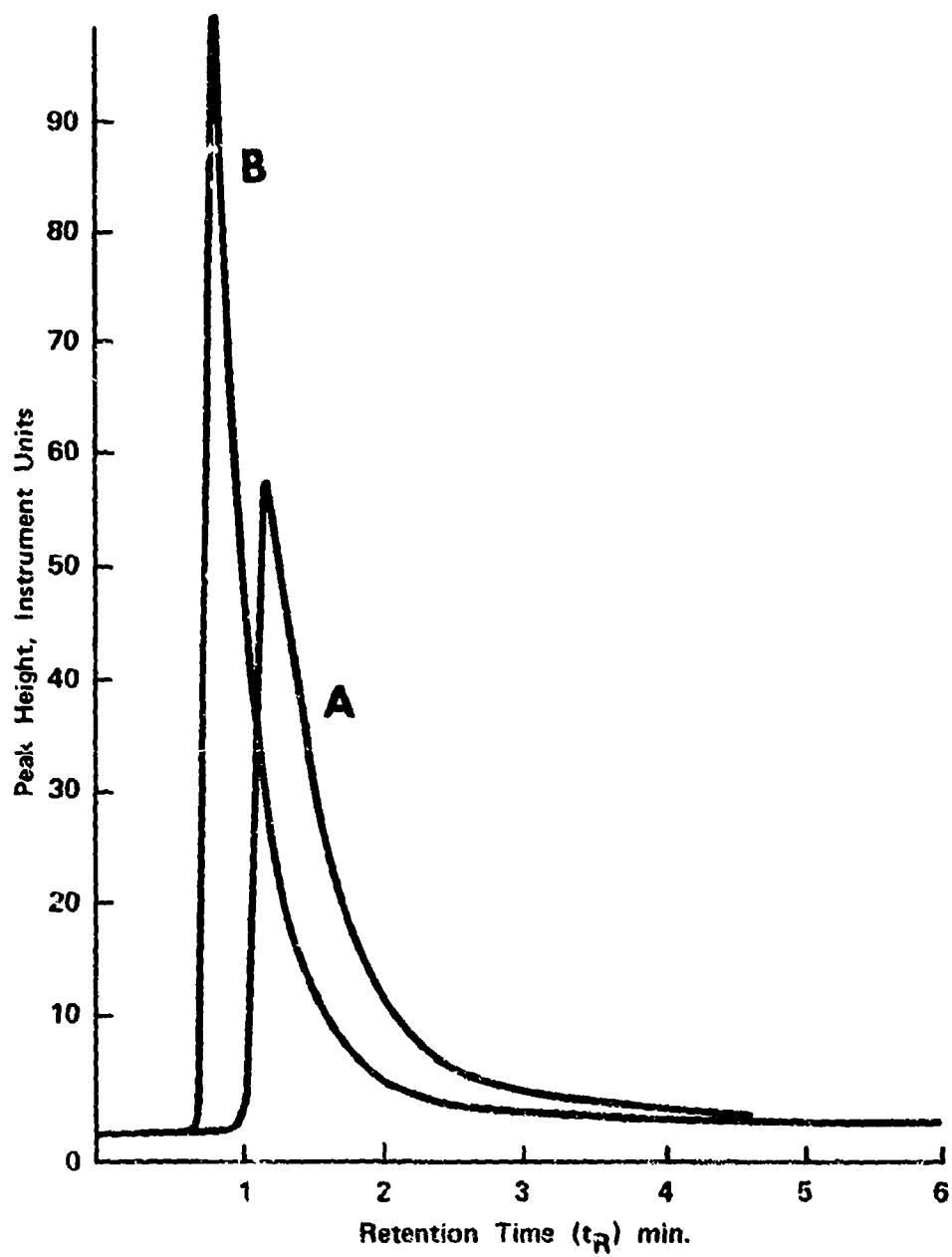


Figure 6. Water Chromatograms, Curve A, Unimpregnated Charcoal,
Curve B, 10% 4-Vinylpyridine

Table 1. Equilibrium Adsorption of Water Vapor* by a 4-Vinylpyridine Impregnated Charcoal

4-Vinylpyridine impregnant	Water adsorbed
%	%
0	38.5
0.5	37.6
0.8	37.1
1.5	35.6
3.4	34.3
5.0	32.9
10	26.8
15	19.2
20	12.6
25	9.1
30	9.2

*From 80% RH air

Table 2. Retention Times of Hydroxylic Compounds

Hydroxylic compound		Retention time (t_R) min adsorbent		
Name	Boiling point	4-Vinylpyridine on charcoal		
		0	3.4	25
	$^{\circ}\text{C}$		%	
H ₂ O	100	0.47	0.24	0.30
CH ₃ OH	65	1.96	1.11	0.70
C ₂ H ₅ OH	78.5	14.5	5.80	2.27
n-C ₃ H ₇ OH	97.1	-	30.9	9.45
iso-C ₃ H ₇ OH	82.4	-	-	6.35
n-C ₄ H ₉ OH	117.5	-	-	44.6
tert-C ₄ H ₉ OH	82.2	-	-	14.9

Plots of $\ln t_R$ versus number of carbons (hydroxylic compound) are linear for each of the charcoals examined. Slopes (and correlation coefficients) for the 0%, 3.4% and 25% 4-vinylpyridine carbons are 1.71 (0.9954), 1.62 (0.9998), and 1.26 (0.9937). The slope (and correlation coefficient) for the 25% 4-vinylpyridine carbon, leaving out the point for water, are 1.39 (0.9981).

3.4 Hydrocarbons.

A study was carried out with hydrocarbons for determination of the heats of adsorption of various carbons. To illustrate relative charcoal performance, retention time dependence for several charcoals at a column temperature of 110°C is given in table 3. Chromatographic conditions: 1.0 ml hydrocarbon gas; injection port, 155°C; helium flow rate, 60 ml/min.

Table 3. Retention Times of Hydrocarbons on 4-Vinylpyridine Impregnated Charcoal Columns at 110°C

Hydrocarbon	Retention time (t_R), min adsorbent		
	4-Vinylpyridine on charcoal		
	0	3.4	10
		%	
CH ₄	0.09	0.10	0.03
C ₂ H ₆	2.39	1.17	0.60
C ₃ H ₈	21.7	9.42	3.74
Cyclopropane	15.7	6.71	3.14

Also, data obtained at various column temperatures for t_R of cyclopropane versus percent 4-vinylpyridine loading are given in figure 7.

3.5 Heats of Adsorption.

Heats of adsorption of various compounds on the 4-vinylpyridine-impregnated charcoals and the unimpregnated charcoal are listed in table 4. These were calculated from slopes of $\ln t_R$ versus $1/T_{abs}$. The temperatures chosen ranged from 70°C to 170°C, depending on the compound being examined. For a particular compound, the difference between highest and lowest temperatures was at least 40°C. Three to four temperatures were examined. Correlation coefficients for the straight line plots were never less than 0.995. Normally, values of better than 0.999 were obtained.

3.6 Comparison of Activated Charcoals.

The performance of three activated carbons as column materials was compared with water, methanol, and ethane (table 5). Two of the carbons were samples of the Pittsburgh Activated Carbon Division, BPL and CWS grades. The third carbon (CWSH) was CWS grade, pretreated with hydrogen at 440°C. Chromatographic conditions included: 0.5 μ l water, 0.5 μ l methanol, 1.0 μ l ethane; injection port, 155°C; column temperatures chosen from 110° to 160°C; helium flow rate, 60 ml/min.

4. RESULTS AND DISCUSSION

The 4-vinylpyridine treatment decreased the capacity for equilibrium adsorption of the charcoal (table 1) and the retention times for the alcohols and hydrocarbons (tables 2 and 3). Surface area effects were not determined. Hydrogen treatment also led to a reduction in

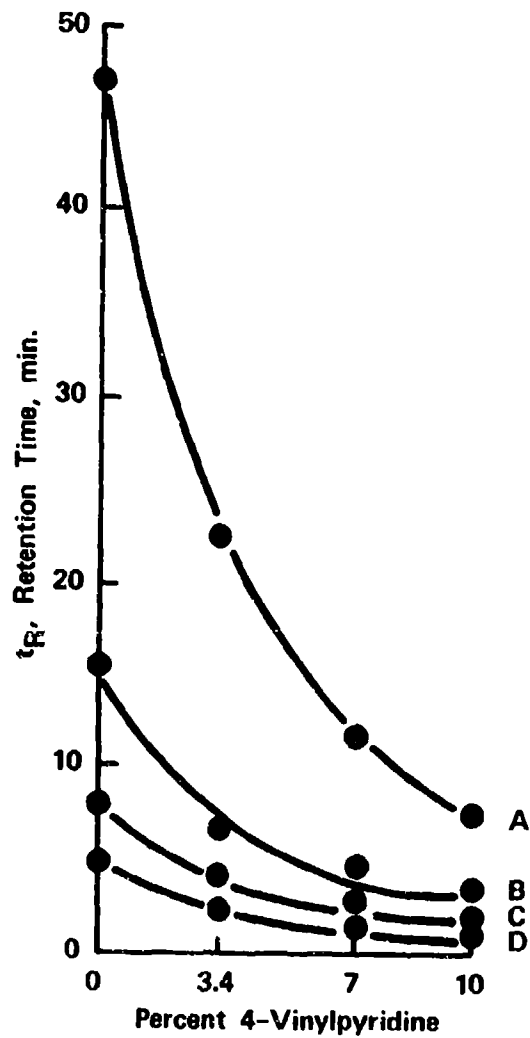


Figure 7. Plot of Retention Time of Cyclopropane Versus Weight Percent of 4-Vinylpyridine Contained in Charcoal Adsorbent.

Column temperatures: A, 80°C; B, 110°C; 130°C; D, 150°C

Table 4. Heats of Adsorption of Various Compounds on 4-Vinylpyridine Impregnated Charcoals

Compound	Adsorbent 4-vinylpyridine on charcoal		
	0	3.4	10
		%	
H ₂ O ^b	9.5 ^a	9.7 ^a	8.4
CH ₃ OH	9.9	-	10.4
C ₂ H ₅ OH	12.8	-	12.2
n-C ₃ H ₇ OH	-	-	13.0
iso-C ₃ H ₇ OH	-	-	12.2
CH ₄	6.0	6.1	5.3
C ₂ H ₆	7.5	7.0	6.5
C ₃ H ₈	9.8	9.1	8.5
Cyclopropane ^c	9.7	8.7	8.2

^a Chromatographic experiments performed at an He flow rate of 40 ml/min. All other runs were at 60 ml/min.

^b Heats of adsorption for water using 0.8% and 25% 4-vinylpyridine charcoal were 9.4 and 9.6 kcal/mole, respectively.

^c Heat of adsorption using 7% 4-vinylpyridine charcoal was 8.3 kcal/mole.

Table 5. Comparison of the Performance of Three Activated Carbons as GSC Column Materials With Water, Methanol, and Ethane

Column temperature °C	Retention time			Plate numbers of carbons			
	BPL	CWS	CWSH	BPL	CWS	CWSH	
		min					
		Water					
110	0.46	-	0.29	32	-	34	
130	0.27	0.31	0.20	27	29	29	
150	0.17	0.18	0.13	24	22	20	
160	0.15	0.13	-	20	18	-	
(ΔH, kcal/mole)	(7.7)	(9.7)	(6.6)				
		Methanol					
110	-	-	3.91	-	-	79	
130	3.12	3.04	2.15	69	50	74	
150	1.78	1.66	1.27	67	49	71	
160	1.42	1.30	-	66	45	-	
(ΔH, kcal/mole)	(9.1)	(9.9)	(9.0)				

Table 5. Continued

Column temperature °C	Retention time			Plate numbers of carbons		
	BPL	CWS	CWSH	BPL	CWS	CWSH
		min				
		Ethane				
110	2.72	2.26	1.90	55	42	53
130	1.65	1.34	1.18	52	40	48
150	1.02	0.84	0.77	48	33	45
160	-	0.76	0.66	-	35	43
(ΔH , kcal/mole)	(7.9)	(7.4)*	(7.1)			

*Repeat run for purpose of checking reproducibility also gave 7.4.

retention times (as shown in table 5 with a CWS grade charcoal), but the effects do not appear as dramatic. The 4-vinylpyridine treatment suppressed to a great extent the tailing normally observed with activated charcoals (figures 5 and 6). As mentioned earlier, activated charcoals are normally used for the analysis of permanent gases and hydrocarbons; difficulties are encountered with polar and hydrogen bonding compounds. It is obvious that a simple treatment involving vapor adsorption of 4-vinylpyridine onto the charcoal offers the possibility of extending the utility of activated charcoals in GSC. The 4-vinylpyridine treatment was initially of interest because of chemical reactivity considerations,⁴ however, it would be important to examine the effects of treating charcoal with other monomers as well. If polymerization occurs, the treatment may be a "permanent" one. Different surface characteristics should result depending on the choice of monomer.

No attempt was made to prevent water from being adsorbed on the wall of the stainless-steel columns. Trace quantities of water have been determined by Kaiser⁵ using carbosieve B, a highly nonpolar carbon (water is quickly eluted without tailing before methane). Kaiser found that quartz tubing adsorbs water less than either glass or stainless steel. Extreme caution must be used in handling carbosieve B. Oxidation of the surface causes peak tailing to occur. Considerable tailing is observed in any event with water.

In the present study the effect of particle size on column performance was not examined. The charcoal was used as received. Its low cost is an attractive feature. For an extended study with a particular activated charcoal, it is recommended that sufficient quantity be purchased to eliminate differences in the nature of the charcoal which might be found among particular lots of the same grade.

The effects on retention times noted with increasing 4-vinylpyridine content are undoubtedly due to a reduction of active surface area or suppression of active sites. An interesting anomaly involves water. The retention times decrease with increasing 4-vinylpyridine content up to 3 to 4 percent then increase (figure 1). A minimum was also observed in a plot of peak areas of water pulses versus weight percent of 4-vinylpyridine contained in the charcoal. The possibility exists that clustering or molecular arrangement of the vinylpyridine molecules produces centers which facilitate the adsorption of water through hydrogen bonding.

The presence of the vinylpyridine appears to give rise to surface homogeneity in terms of the pyridine taking up the most strongly specific adsorptive sites. However, the pyridine nitrogens which are apparently available⁴ form a surface which appears more specific for water adsorption as the concentration of 4-vinylpyridine increases, this despite the fact that the equilibrium absorption capacity for water (table 1) decreases.

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