AD-A063 587 DREXEL UNIV PHILADELPHIA PA F/G 7/4

MECHANISMS OF ACTIVATED CARBON DEGRADATION BY PERSPIRATION.(U)

JUL 77 L L PYTLEWSKI DAAA15-75-C-0195

UNCLASSIFIED DU-SW-3 ARCSL-CR-77034 NL

| OF |

AD A063587

END

DATE FILMED

3-79

DDC

LEVEL III

A038144

AD-E400109

CONTRACTOR REPORT ARCSL-CR-77034

MECHANISMS OF ACTIVATED CARBON DEGRADATION BY PERSPIRATION

Third Quarterly Progress Report

AD A063587

by

Dr. Louis L. Pytlewski

July 1977

DREXEL UNIVERSITY
Philadelphia, Pa. 19104

Contract DAAA15-75-C-0195

US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
Chemical Systems Laboratory
Aberdeen Proving Ground, Maryland 21010

Approved for public release; distribution unlimited

78 10 27 061

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

Destroy this report when it is no longer needed. Do not return it to the originator.

(1/2-in. O.D. by 6-in.

DISCLAIMER NOTICE

THIS DOCUMENT IS BEST QUALITY PRACTICABLE. THE COPY FURNISHED TO DDC CONTAINED A SIGNIFICANT NUMBER OF PAGES WHICH DO NOT REPRODUCE LEGIBLY.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER
ARCSL-CR-77034

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
MECHNAISMS OF ACTIVATED CARBON DEGRADATION BY PERSPIRATION

5. TYPE OF REPORT & PERIOD COVERED
~~Third~~ Quarterly Progress Report Jan 76 - Apr 76

6. PERFORMING ORG. REPORT NUMBER
DU-SW-3

7. AUTHOR(s)
Dr. Louis L. Pytlewski

8. CONTRACT OR GRANT NUMBER(s)
DAAA15-75-C-0195

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Drexel University
Philadelphia, PA 19104

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
1L762710A09506

11. CONTROLLING OFFICE NAME AND ADDRESS
Director, Chemical Systems Laboratory
Attn: DRDAR-CLJ-R
Aberdeen Proving Ground, MD 21010

12. REPORT DATE
Jul 1977

13. NUMBER OF PAGES
20

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)
Director, Chemical Systems Laboratory
Attn: DRDAR-CLW-P
Aberdeen Proving Ground, MD 21010
(CPO - Sheldon E. Day 671-2801)

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)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Synthetic sweat	Crown ether
Sweat poisoning	Silicone coating
Activated charcoal	Amino acids
Gas chromatography	Organic poisoning materials
CCl_4 pickup	Inorganic poisoning materials

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Sweat degradation of activated charcoal was studied by static and dynamic test methods. For the static tests, both untreated and treated charcoal was immersed in a synthetic sweat solution or an aqueous solution of the individual components of the synthetic sweat solution, dried at 70 °C for 12 hours, and then exposed to carbon tetrachloride vapors in a desiccator to determine capacity. The ratio of treated charcoal pickup to untreated charcoal pickup was used as a measure of poisoning effects. Dynamic tests used a gas chromatograph column (½" O.D. by 6" long) packed with activated charcoal. Synthetic

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

405 723

Item 20 continued

sweat solutions or solutions of the individual components were injected into the column to determine whether the charcoal would preferentially adsorb one or more components thus pinpointing the "poisoning" material or materials present in synthetic sweat. Conclusions from the studies were that, other than loss of capacity of the charcoal due to water, no single component or components could be identified as "poisoning materials." Specific conclusions from the static test data were that pretreatment of charcoal with silicone, crown ether, or pH 7 buffer solution all were effective in moderating the reduction of carbon tetrachloride pick up due to exposure to synthetic sweat. This was probably because the pretreatments protected the charcoal from contact with water in the synthetic sweat solutions. Results of the gas chromatography studies were inconclusive.

PREFACE

The work reported in this document was authorized by Task 1L762710A09506, Body Protection Investigations. It was carried out from January 1976 to April 1976.

CONTENTS

MECHANISMS OF ACTIVATED CARBON DEGRADATION BY PERSPIRATION

I. INTRODUCTION

A substantial number of investigations have been conducted on this problem during the past twenty five years by Edgewood Arsenal personnel and outside contractors.[1] Overall it is impossible to draw reasonable, workable conclusions from all of the published work heretofore presented. A great deal of the research is at best piecemeal and one often meets contradictions between investigators and within particular publications. Synthetic sweat formulations have been developed and there are significant variations in not so much the types of compounds but in their relative concentration.[*,2] None of the formulations have included body (sebaceous) oils. The substances present in largest amounts and common to most formulations are inorganic salts such as NaCl, KCl, $Ca_3(PO_4)_2$, $CaCO_3$, and $KHCO_3$. The organic material common to all formulations is lactic acid--but lower in concentration than NaCl by a factor of 0.05. Also common to all formulations as organic components and in concentrations approximately 10% of the lactic acid are urea, uric acid, formic acid, and glucose. Some formulations also contain very small amounts of organic acids particularly of the amino acid type and these number about twenty different kinds.

The great bulk of sweat studies were conducted using "synthetic sweats" and out of these have evolved two "schools of thought" about the effect of sweat on activated carbon. "School 1" propounds that it is not a "poisoning" which occurs but simply a matter of filling up the internal pores and covering over adsorptive sites in a carbon with sweat solution. From this approach the most often suggested cure for this problem centers on making the carbon hydrophobic yet retaining its gas adsorption capability. "School 2" says that there is a specific ingredient or collection of ingredients in sweat which poison (destroy) the internal adsorptive surface of a carbon. Attention here has focused on lactic acid. Obviously, the solution to this problem is to prevent lactic acid (and/or other "poisons") from getting to the activated carbon.

II. EXPERIMENTAL WORK AND RESULTS

Experiments were conducted in two areas of analysis; a. static tests -- Most of the experimental work done involved exposure of granular activated carbon (PAC Lot 7502) to various solutions and vapors using carbon tetrachloride (CCl_4) vapor adsorption as an indicator of loss in activity. b. Additionally, dynamic measurements were attempted using gas chromatography wherein columns were packed with activated carbon and sweat samples of various types (especially aqueous lactic acid) were injected onto the column.

*Owens, C., Private Communication, December 20, 1974

A. Static Tests

The static tests conducted involved using an enormous number of samples, typically sextuplicates for each experiment, along with controls for each kind of treated carbon. Experience has clearly shown that usual analytical procedures of duplicate and triplicate runs on a single sample are by no means enough when handling activated carbons. Enormous variations in a single batch of activated carbon have more often than not resulted in significant irreproducibility. It is strongly suspected that much of the earlier work on the sweat problem did not take this into account. (We have done copper and chromium analyses on ASC Whetlerite and found analytical deviations of $\pm 10\%$ between samples as large as 100 grams.) In this work, on many occasions control samples of PAC Lot 7502 have shown as high as a 50% variance in CCl_4 vapor uptake on a dry, untreated basis. Everything possible was done in an attempt to limit the effects of the intrinsic heterogeneity of activated carbon.

A typical experiment in our static system was conducted as follows: six, ten gram (g) samples of activated carbon were first heated at 110°C to constant weight at room temperatures. These samples were immersed in a synthetic sweat solution for ten minutes, dried at 70°C for 12 hours, reweighed to check for retained solution and then exposed to CCl_4 vapor in a desiccator for a 24 hour period after which the CCl_4 uptake was determined. Carbon samples were, at times, doubly soaked or treated successively with several solutions and distilled water with subsequent CCl_4 uptake determined. Activated carbons were on occasion also pre-treated with a hydrophobic silicone surfactant and various buffer solutions then exposed to sweat solutions and CCl_4 vapors. The following Table contains information (from left to right) as to type of treatment in column 1; column 2, grams of CCl_4 taken up per gram of carbon (dry); column 3, grams of sweat retained after drying per gram of carbon (dry); column 4, grams of water retained after drying per gram of carbon (dry); columns 5 and 6, ratio of CCl_4 uptake to weat retained; column 7, an activity of treated carbon index arrived at by the following:

$$\frac{\text{number in column 2}}{0.842} \times (\text{number in column 5}) \times 100$$

where 0.842 is the $\frac{g\ CCl_4}{g\ \text{carbon dry}}$ for plain, activated, dry carbon. The higher this number, the better the carbon responds after treatments. All carbons were PAC Lot 7502.

Table

Sweat Degradation Experiments on Various Treated and Untreated Carbons

Type of Treatment	$\frac{g\ CCl_4}{g\ carbon\ dry}$	$\frac{g\ sweat}{g\ carbon\ dry}$	$\frac{g\ H_2O}{g\ carbon\ dry}$	$\frac{g\ CCl_4}{g\ sweat}$	$\frac{g\ CCl_4}{g\ H_2O}$	Carbon resistance to sweat and/or H_2O
1) PAC 7502; no treatment Reference carbon	0.842					
2) Siliconized -- outer surface coating						
a) no treatment	0.557					
b) H_2O soak only	0.427					
c) sweat soak only	0.481					
3) PAC 7502; impregnated with individual components of synthetic sweat--dried at 70°C then sweat treated						
a) Uric acid	0.442	0.257		1.72		90
b) Lactic acid	0.508	0.116		4.38		264
c) Formic acid	0.425	0.289		1.47		74
d) $CaCO_3$	0.492	0.184		2.67		156
e) $KHCO_3$	0.449	0.177		2.54		135
f) NaCl	0.480	0.166		2.89		165
g) Synthetic sweat	0.661	0.182		3.63		285
h) H_2O, then sweat	0.705	0.111		6.35		532
i) Urea	0.427	0.200		2.14		108
j) l-serine	0.408	0.231		1.77		86

Table, Continued

Type of Treatment	$\frac{g\ CCl_4}{g\ carbon\ dry}$	$\frac{g\ sweat}{g\ carbon\ dry}$	$\frac{g\ H_2O}{g\ carbon\ dry}$	$\frac{g\ CCl_4}{g\ sweat}$	$\frac{g\ CCl_4}{g\ H_2O}$	Carbon resistance to sweat and/or H_2O
3) Continued						
k) dl-alanine	0.481	0.095		5.06		289
l) 1-aspartic acid	0.281	0.023		12.20		407
m) Glucose	0.286	0.023		12.40		421
n) Glutamic acid	0.310	0.042		7.38		272
o) 1-proline	0.250	0.057		4.39		130
p) 1-histidine	0.214	0.133		1.61		41
q) 1-arginine	0.246	0.155		1.59		46
r) Glucosamine	0.211	0.240		0.83		22
s) 1-lysine	0.230	0.177		1.30		36
t) dl-citrulline	0.282	0.214		1.32		44
u) 1-valine	0.320	0.195		1.64		62
v) 1-leucine	0.283	0.241		1.17		39
w) dl-phenylalanine	0.427	0.074		5.77		293
x) d-ribose	0.207	0.155		1.34		33
y) Glycine	0.180	0.242		0.74		16
4) PAC 7502 (pre-treated with pH 10 buffer)						
a) Control--no other treatment	0.415					
b) Synthetic sweat treated	0.313	0.198		1.58		59
c) H_2O treated; no sweat	0.345		0.144		2.40	98

Table, Continued

Type of Treatment	g CCl_4 / g carbon dry	g sweat / g carbon dry	g H_2O / g carbon dry	g CCl_4 / g sweat	g CCl_4 / g H_2O	Carbon resistance to sweat and/or H_2O
5) PAC 7502; impregnated with selected individual components and dried at 52°C then sweat treated						
a) Control--no treatments	0.382					
b) Control--no treatments	0.545					
c) dl-citrulline	0.310	0.131		2.37		87
d) l-histidine	0.251	0.276		0.91		27
e) l-leucine	0.265	0.241		1.10		35
f) dl-phenylalanine	0.288	0.266		1.08		37
g) d-ribose	0.203	0.340		0.60		14
h) Glycine	0.256	0.317		0.81		24
i) Glucose	0.291	0.253		1.15		40
j) Lactic acid	0.313	0.106		2.95		110
k) l-proline	0.358	0.104		3.46		147
l) Formic acid	0.315	0.198		1.59		59
m) l-serine	0.375	0.083		4.52		201
n) Uric acid	0.323	0.160		2.02		77
o) Urea	0.342	0.129		2.65		108

Table, Continued

Type of Treatment	$\frac{g\ CCl_4}{g\ carbon\ dry}$	$\frac{g\ sweat}{g\ carbon\ dry}$	$\frac{g\ H_2O}{g\ carbon\ dry}$	$\frac{g\ CCl_4}{g\ sweat}$	$\frac{g\ CCl_4}{g\ H_2O}$	Carbon resistance to sweat and/or H_2O
6) PAC 7502; pre-treated with pH 10 buffer--a repeat of #4 above						
a) Control--no treatments	0.397					
b) H_2O soak only	0.341		0.131		2.60	105
c) Synthetic sweat only	0.303	0.162		1.87		67
7) PAC 7502; pre-treated with pH 7 buffer						
a) Control--no sweat or H_2O soaking	0.542					
b) H_2O soak only	0.467		0.078		6.02	334
c) Synthetic sweat only	0.402	0.121		3.31		158
8) Random con-trol--clean PAC 7502 (CCl_4 only)	0.551					

Table, Continued

Type of Treatment	$\frac{g\ CCl_4}{g\ carbon\ dry}$	$\frac{g\ sweat}{g\ carbon\ dry}$	$\frac{g\ H_2O}{g\ carbon\ dry}$	$\frac{g\ CCl_4}{g\ sweat}$	$\frac{g\ CCl_4}{g\ H_2O}$	Carbon resistance to sweat and/or H_2O
9) PAC 7502; pretreated with pH 3 buffer						
a) Control--no sweat or H_2O soaking	0.375					
b) H_2O soak only	0.300		0.124		2.42	86
c) Synthetic sweat only	0.261	0.150		1.74		54
10) PAC 7502; pretreated with pH 1 buffer						
a) Control--no sweat or H_2O soaking	0.329					
b) H_2O soak only	0.311		0.052		5.98	221
c) Synthetic sweat only	0.269	0.097		2.76		88
11) PAC 7502; pretreated with Dibenzo-18-crown-6 ether						
a) Control--no sweat or H_2O soaking	0.240					
b) H_2O soak only	0.226		0.006		37.0	993
c) Synthetic sweat only	0.242	0.003		77.3		2221

Table, Continued

Type of Treatment	g CCl_4 / g carbon dry	g sweat / g carbon dry	g H_2O / g carbon dry	g CCl_4 / g sweat	g CCl_4 / g H_2O	Carbon resistance to sweat and/or H_2O
12) PAC 7502; a control, a H_2O soaked, and a synthetic sweat soaked carbon were placed in a drying oven at 52°C --after the days indicated CCl_4 adsorption measurements were made						
a) One day at 52°C						
1. Control	0.886					
2. H_2O only	0.812		0.212		3.83	369
3. Sweat only	0.763	0.274		2.78		252
b) Four days at 52°C						
1. Control	0.815					
2. H_2O only	0.818		0.004		204.5	19867
3. Sweat only	0.809	0.025		32.0		3075
c) Five days at 52°C						
1. Control	0.751					
2. H_2O only	0.648		0.001		602.7	46384
3. Sweat only	0.623	0.019		32.5		2405

Table, Continued

Type of Treatment	$\frac{g\ CCl_4}{g\ carbon\ dry}$	$\frac{g\ sweat}{g\ carbon\ dry}$	$\frac{g\ H_2O}{g\ carbon\ dry}$	$\frac{g\ CCl_4}{g\ sweat}$	$\frac{g\ CCl_4}{g\ H_2O}$	Carbon resistance to sweat and/or H_2O
12) Continued						
a) Seven days at 52°C						
1. Control	0.810					
2. H_2O only	0.809		0.001		596	57264
3. Sweat only	0.802	0.019		41.5		3953
b) Twelve days at 52°C						
1. Control	0.835					
2. H_2O only	0.802		0.002		370.4	35280
3. Sweat only	0.772	0.018		41.9		3842
13) PAC 7502; same as experiment #12 except samples were double soaked in H_2O and sweat--dried at 52°C						
a) One day at 52°C						
1. Control	0.691					
2. H_2O only	0.590		0.109		5.41	379
3. Sweat only	0.523	0.128		4.09		254
b) Four days at 52°C						
1. Control	0.571					
2. H_2O only	0.578		0.035		16.7	1146
3. Sweat only	0.556	0.029		19.1		1261

Table, Continued

Type of Treatment	$\frac{g\ CCl_4}{g\ carbon\ dry}$	$\frac{g\ sweat}{g\ carbon\ dry}$	$\frac{g\ H_2O}{g\ carbon\ dry}$	$\frac{g\ CCl_4}{g\ sweat}$	$\frac{g\ CCl_4}{g\ H_2O}$	Carbon resistance to sweat and/or H_2O
13) Continued						
c) Six days at 52°C						
1. Control	0.634					
2. H_2O only	0.631		0.008		78.9	5913
3. Sweat only	0.601	0.021		28.6		2041
d) Eight days at 52°C						
1. Control	0.605					
2. H_2O only	0.614		0.006		102.3	7460
3. Sweat only	0.582	0.020		29.1		2011
e) Eleven days at 52°C						
1. Control	0.631					
2. H_2O only	0.616		-----		-----	----
3. Sweat only	0.631	0.025		25.2		1889

Note: sweat (plain H_2O vs. sweat)= -4.5%

B. Gas chromatography, carbon, and sweat.

It was felt that packing a gas chromatographic column with granular activated carbon and injecting sweat solution and components of synthetic sweat solutions onto the column might result in a workable partitioning. Such could allow for a determination, under dynamic flow conditions, of the relative retention times of the important species present, especially in real human sweat. It was found that a ¼" O.D. stainless steel column shortened to six inches in length was necessary to get anything to arrive at the flame ionization detector. This response did not occur until the column temperature reached approximately 250°C. It was obvious that the one rather broad band we obtained was due to decomposition of several organic compounds in our synthetic sweat sample.

III. DISCUSSION

In almost every experiment the synthetic sweat solution produced a reduction in the CCl_4 adsorptive capacity of an activated carbon which was only slightly larger than that of water alone. At no time, however, could one be inspired to use the word "poisoning." Typically, a loss of 4.5% of adsorptive capacity occurred due to sweat treatment when compared to the effects of water alone on PAC 7502 carbon. Two sets of experiments were conducted wherein the sweat residuals were allowed, at 52°C, to sit in the carbon over a period of 10 to 12 days. At the same time dry controls, and carbons treated with distilled water were run alongside the sweat treated carbons. The CCl_4 adsorption for all three types of samples exactly paralleled each other over this time period; the difference appearing only as retained solids in the sweat treated carbon.

Furthermore, aqueous solutions of lactic acid did not produce any sign of a deleterious effect on activated carbon studied and, if our system of classification as shown in columns two and seven of the table has any meaning we would have to place lactic acid in a neutral category. Column seven contains a number for each individual experiment in an attempt to indicate a degree of resistance to removal of adsorptive capacity by a particular kind of treatment or sequence of treatments; the higher the number, the greater the resistance to degradation by the carbon. Large numbers are not as significant in extracting useful information from the experiments as extremely small numbers--numbers less than 100. With this in mind it is noticed that a preponderance of such numbers are obtained for a large percentage of the amino acids, uric acid, and formic acid. Column seven also shows that in a study of the effect of pH buffered carbon on synthetic sweat using pH 10, 7, 3, and 1 buffers that the pH 7 buffer clearly stands out as significantly better than the rest.

Two experiments were conducted using pretreated carbons; one coated with a silicone grease only on the outer surface of the carbon granule, the other impregnated with an organic "molecular sieve" compound called Dibenzo-18-crown-6-ether. It was felt that the crown ether might exclude water and many sweat compounds from the micropores but still allow for unhindered gaseous adsorption.

The silicone treated carbon again showed up well in resisting water adsorption, especially the water in synthetic sweat solutions. Previous experiments involving this degree of success were indicated in the second quarterly report. Many former studies report on the use of hydrophobic silicone coatings with variable success.*,**,*** It is felt that the wide variation in results of such earlier studies was due to the use of silicones in solution or as adsorbed gases which result in plugging up the carbon's internal pores to varying degrees. It is strongly suggested that more attention be given to the use of externally applied hydrophobic surface coatings as a means of at least delaying the effects of sweat.

Although the crown ether impregnated carbon showed a drop off in adsorption of CCl_4 on a dry carbon of about 70% it is noteworthy that synthetic sweat and water were hardly retained by this carbon and the value in the table, column seven is extraordinarily large for the synthetic sweat treated carbon. With more time it is felt that significant overall improvements could be made here.

More attention should be given to a complete chromatographic study of sweat and carbon. Recent advances in instrumentation in an area called "High Pressure Liquid Chromatography" should produce very useful results in the entire sweat problem.

In conclusion, we have not observed anything one could call a unique "sweat poisoning" associated with degradation of activated carbon by the components of synthetic sweat, other than acid degradation, and this is already well known in the chemistry of activated carbons.

Aqueous lactic acid appears to be entirely neutral in its effect on CCl_4 adsorption by tested activated carbons. Given the right conditions, hydrophobic coatings, such as silicones and fluorocarbon surfactants, should produce a carbon which significantly resists sweat degradation.

* Brillinger, J.H. Report on Active Duty Training. SAREA-DE-DP, September 6, 1972

** Brillinger, J.H. Report on Active Duty Training. SAREA-DE-DP, September 25, 1973

*** Warren, R. Inhouse Report. Chemical Sweat Poisoning Study, April-May, 1973

LITERATURE CITED

1. Redd, R. J. CWL Technical Memorandum 32-25, Study of Methods for Reducing the Sweat Poisoning of Activated-Charcoal-Impregnated Protective Clothing. 2 December 1957. UNCLASSIFIED Report.

2. Frank, G. B., Bruic, R. P. Special Scientific Report, Edgewood Arsenal. Preparation of a Synthetic Sweat, February, 1953. UNCLASSIFIED Report.

DISTRIBUTION LIST

Recipient	No. of Copies
Administrator Defense Documentation Center Attn: Accessions Division Cameron Station Alexandria, VA 22314	12
Commander/Director Chemical Systems Laboratory Attn: DRDAR-CLW-P/Mr. Sheldon E. Day Aberdeen Proving Ground, MD 21010	20
Chief, Research Division Attn: DRDAR-CLB-CA/Dr. Epstein	1
DRDAR-CLB-PA/Dr. Jonas	1
Chief, Developmental Support Division Attn: DRDAR-CLJ-L	3
DRDAR-CLJ-R	2
Chief, Physical Protection Division	1
Chief, Individual Protection Branch	1
Mr. Sheldon E. Day, Contract Project Officer Individual Protection Branch Physical Protection Division	5
Record Copy - Individual Protection Branch Physical Protection Division	1
Commander US Army Natick Research and Development Command Attn: DRXNM-VCC	1
DRXNM-VMP/Dr. Richard Macnair	1
DRXNM-TRL Natick, MA 01760	1
Commander US Army Development and Readiness Command Attn: DRCDE-DW-S Alexandria, VA 22333	2