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A STUDY OF PHYSIOCHEMICAL FACTORS AFFECTING CHARCOAL ADSORPTION OF CONTAMINANTS IN MANNED SPACECRAFT ATMOSPHERE

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FINAL REPORT

Prepared Under Contract No. NAS 9-11049

for

National Aeronautics and Space Administration

Manned Spacecraft Center
Houston, Texas

**analytical
research
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inc.**

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by

C. L. Deuel

1666-F August 1971

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ABSTRACT

Data generated from a study of analytical stripping procedures for compounds adsorbed on charcoal, along with time and temperature variations in thermal-vacuum stripping are presented. Comparison of six storage materials and/or containers for maintaining contaminant free charcoal is made. There is a listing of more than twenty compounds apparently formed by catalytic action of charcoal on a prepared gas mixture.

Gas evolution studies from mass spectrometric examination of heated charcoal is summarized in a series of figures. A rather extensive program of development of adsorption isotherms with mathematical modeling, along with derivation of the mathematics involved is also listed. The results from application of predicted adsorption capacity of a prepared mixture indicates successful application of the mathematical modeling. There is also a brief study on the efficiency of adsorption-desorption of compounds on two charcoals of different origins as well as on 5A molecular sieve.

FOREWORD

This study was conducted in part at the analytical laboratories of Aerojet-General Corporation, Azusa, California, and at the facilities of Analytical Research Laboratories, Inc., Monrovia, California. The latter company is an independent laboratory formed by the technical staff of the Aerojet Laboratory when that company divested itself of chemical operations. Performance was under contract NAS 9-11049 for the Manned Spacecraft Center, Houston, Texas. This report includes the work begun 1 July 1970 and concluded on 31 July 1971. Mr. W. J. Rippstein of NASA was the technical monitor.

This project was under the direction of C. L. Deuel. Mass spectroscopists were D. L. Quick and N. W. Hultgren, gas chromatographers were H. C. Harper and C. L. Deuel, and N. W. Hultgren performed the mathematical studies along with data reduction. Mr. M. L. Moberg performed the adsorption-desorption study and was responsible for the overall direction of this program.

CONTENTS

TABLES

TABLES (Cont.)

FIGURES

FIGURES (Cont.)

I. INTRODUCTION

Activated charcoal's ability to adsorb large quantities of undesirable gasses is universally recognized, and has led to its general use for deodorizing and/or detoxifying man's air. The breathing canisters used for manned space flights have coupled charcoal with lithium hydroxide to maintain the purity of the enclosed atmosphere. The efficacy of this system can best be attested to by the fifteen Apollo flights to date. This thin layer of charcoal has not only provided "clean" air, it has captured a history of that portion of the flight in which it was used. As many of these breathing canisters as possible have been recovered following these flights, so that the contents of the canisters could be analyzed. These analyses have produced volumes of data, especially regarding desorbates from the charcoal. The increasing duration of man's habitation of closed environments, placing greater demands upon his air purification system, has emphasized the need for an evaluation of these data and of charcoal. For example, a large number of halogenated compounds (up to thirty per sample), and of C_2 - C_4 hydrocarbons, especially olefins, have been noted in post flight sampling. To establish the source of these materials, it is necessary to determine the reliability of the identity and quantity of compounds reported. Confidence in any given identity or quantitation is high, but there is the question of whether a given compound should stand alone, or be associated with a parent compound from which it may have been formed through charcoal exposure. Other questions that must be considered include, the desorption procedure, the choice of charcoal type, and pre-exposure treatment (with associated storage prior to use) of the charcoal to obtain a clean starting material. This program was designed to provide some answers to these questions, and to, hopefully, design a mathematical model to allow prediction of the capacity of charcoal for any given compound or groups of compounds.

It may be pertinent to consider just what activated charcoal is before studying these tests.

Ordinary charcoal contains a relatively nonporous surface, with little more surface area than is readily visible and with little more sorptive capacity than a stone. Heating this charcoal to 800-1000°C in a controlled, semi-oxidative atmosphere produces a new product. Large quantities of gasses are driven off, opening up interstitial molecular spaces. Continued heating further enlarges these spaces to form a system of macro, transitional, and micro pores. The end product is a porous mass with a large surface area per unit volume containing a complex series of hydrogen-oxygen radicals on the pore surface, providing high chemisorption bonding for any molecules extending into these pores. There is also a heterogeneous system of catalysts superimposed on the carbon structure through trace metals present in the original source. These changes allow charcoal to hold large quantities of adsorbates through chemisorption, polymerization, conversion of compounds to a less reactive or volatile state, and by adsorption in a monolayer over a surface of up to 10,000,000 square feet per pound (over 220 acres). This surface consists of macropores ($>$ 200Å diameter) that exert no appreciable effect on adsorption, transitional pores, 50-200Å wide, on which surface adsorption occurs, and micropores, $<$ 50Å, whose volumes may be filled with adsorbed material. These latter pores show a substantial increase in both adsorption energy and in adsorption potential as compared to corresponding values for the larger pores. The smallest of the micropores i. e. $<$ 10Å, may also exert a molecular sieve effect on exposed materials.

II. TECHNICAL DISCUSSION

A. CHARCOAL SELECTION

Activated charcoal may be prepared from nearly any organic material that may be charred. For these tests, three cocoanut shell and two petroleum base charcoals were selected. These charcoals are characterized as:

Designation	Manufacturer		Type	Area M^2/g	Mesh Size
AC	Barnebey-Cheney		Cocoanut	1000	6 x 10
VG	"	"	"	1700	6 x 10
GI	"	"	"	1700	8 x 12
888	Witco		Petroleum	1900	8 x 16
199	"		"	?	6 x 12

The type AC charcoal is presently in use in the Apollo breathing canisters. Even though large quantities of this type were available from previous canister use fresh stock was purchased to provide valid comparison with the other charcoals. Both the VG and GI type charcoals were recommended by Barnebey-Cheney as having considerably greater surface area, and consequently higher sorptive capacity. The type 888 charcoal is the starting material from which, by modifying with certain chemical additions, the adsorbate for radioactive iodine is prepared. The type 199 is prepared for Mil-C-17605B specifications for atmospheric purification. The latter charcoal was soon dropped from further testing because of considerable quantities of SO_2 that gradually diminished only through multiple stripping. Type 888 charcoal also desorbed a moderate quantity of SO_2, but was retained throughout the test program to provide a different type charcoal for comparitive testing. Bone charcoal, which contains nearly 80% inorganic salts, was not selected because of its low surface area and probable catalytic activity, a function of cation concentration. Similarly, graphitized carbon black was not selected because of its low surface area and, presumably, lower capacity.

The Barnebey-Cheney charcoals were received packed in double paper bags, while the Witco samples were in a large mouthed metal can closed with a single seal pressed lid. As received, these charcoals all contained a considerable number of organic adsorbates and just over 1% water. Typical "as received" organic contamination for each type were Witco 199, 3.38 µg/g, Witco 888 1.19 µg/g, Barnebey-Cheney AC 10.0 µg/g, VG 49.7 µg/g, and GI 71.6 µg/g.

B. INITIAL SAMPLE PREPARATION

Obviously, charcoal samples used for analytical adsorption-desorption studies must be "cleaned" before tests can be run. All such samples were subjected to a vacuum oven stripping prior to use. For this process, the charcoal was placed in a large evaporating dish in a vacuum oven at 160-170°C for 12-18 hours. This treatment reduced the contaminant levels of the charcoal to 0.08 to 0.3 µg/g on AC, 0.9 to 1.5 µg/g on GI, 4.3 µg/g on VG, 0.1 to 1.2 µg/g on 888 and 1.0 µg/g on type 199. While the ideal zero contaminant level was not achieved, residual contamination was considered sufficiently low for testing to proceed. All data from these tests labeled vac. oven or vac. oven stripped represent the residual contamination removed on the analytical vacuum rack following this vacuum oven treatment.

While it was recognized that "stripping" at 500-700°C would probably produce the zero contaminant level sought, this treatment was not attempted. Catalysis on charcoal surfaces generally increases exponentially at temperatures above 150-170°C, and this, coupled with the thermal degradation expected in subsequent regenerative steps would adversely affect the analytical creditability.

C. STRIPPING PROCESSES

The principle of gas chromatography is based upon the fact that when the external concentration of a gas is less than the vapor pressure of that quantity adsorbed, adsorbed material will be released to preserve equilibrium. For this reason low concentrations of material are readily moved in a dynamic system and the free mean path of a molecule restricts movement in a static vacuum system. Continuing the effort to effectively strip charcoal, a dynamic system was provided by a hot nitrogen gas stream. Nominal 20 gram samples of charcoal were placed in a 3/4" x 6" section of stainless steel tubing and closed by stainless steel reducing unions at either end. The charcoal was prevented from entering the open ends by a stainless steel screen. One end of the container was connected to a nitrogen supply by a length of 1/4" tubing. The sample container and upper two feet of supply line were wrapped with heating tape, then covered with asbestos tape. The system was heated to 160°C and gas flow was maintained at 400 cc/min. The purge gas was not trapped since these tests were not to determine the composition of removed contaminants, but rather to determine the composition of those contaminants not removed by purging. Following a 60 minute purge, the unit was removed from the line, the ends capped, and the sample container transferred to an inert atmosphere box for opening. Sample handling from this point was the same as for the Apollo breathing canister charcoals.

Table I presents the results of the hot nitrogen purge, with as received and vacuum oven stripped data presented for comparison. It is evident that the hot nitrogen purge partially cleaned the charcoal, but not as efficiently as the vacuum oven. It is interesting to note that a greater concentration of benzene and toluene were removed from the stripped samples than was apparently present in the original state. It seems likely that the ability to completely desorb these hydrocarbons is dependent upon the concentration of other contaminants. In a few instances, lower molecular weight hydrocarbons were generated by decomposition of more complex compounds and migration from the interstices of the adsorbent was effectively aided by purging. Other small variations are probably attributable to nonhomogeneity of the sample and/or represent the extent of analytical precision.

TABLE 1

ANALYSES OF DESORBATES FROM CANDIDATE CHARCOALS

(μg/g charcoal)

	Witco 888 Vacuum Oven Stripped	Witco 888 as Received	Witco 888 Hot N_2 Purge	AC Vacuum Oven Stripped	AC as Received	AC Hot N_2 Purge	VG Vacuum Oven Stripped	VG as Received	VG Hot N_2 Purge	GI Vacuum Oven Stripped	GI as Received	GI Hot N_2 Purge
Freon 11	0.03	-	-	-	0.12	-	-	1.89	-	-	4.0	-
Freon 113	-	0.067	-	0.03	0.2	0.013	0.0029	0.16	-	-	1.15	-
Trifluoromethane	-	-	-	-	-	-	-	-	-	-	0.27	-
Pentafluoroethane	-	-	-	-	-	-	-	-	0.94	-	-	-
Ethyl fluoride	trace	-	-	-	-	-	-	-	-	-	-	-
Difluoroethylene	-	-	-	-	-	-	-	-	0.076	-	-	-
Dimethyldifluorosilane	0.0018	-	-	-	-	-	-	-	0.14	-	-	-
Trifluoropropene	-	-	-	-	-	-	-	-	0.69	-	-	-
Trifluoropropane	-	-	-	-	-	-	-	-	0.065	-	-	-
Chloroform	-	-	-	-	-	-	-	2.3	-	-	-	-
Methylene chloride	-	-	-	0.014	0.66	-	-	19.3	-	-	12.3	-
Methyl chloride	-	-	trace	-	-	-	-	-	-	-	0.00013	-
1,1,1 Trichloroethane	-	0.00037	-	0.0021	0.067	-	-	0.31	-	-	0.5	-
Trichloroethylene	-	-	-	-	0.13	-	0.014	1.55	-	-	0.014	-
Tetrachloroethylene	-	-	-	-	0.05	-	-	-	0.61	-	0.035	-
Vinyl chloride	-	0.00002	-	-	-	-	-	-	-	-	-	-
Vinylidene chloride	0.0087	0.0025	-	0.0009	0.013	-	-	0.58	0.013	-	1.65	-
Trifluorochloroethylene	0.0029	-	-	-	-	-	-	0.011	-	-	-	-
Ethane	-	-	0.0072	-	-	0.0024	0.020	0.03	-	-	-	0.3
Propane	0.00003	0.00081	0.027	0.004	2.14	0.0011	0.0060	0.45	-	0.07	0.0028	0.076
Butane	0.0035	0.0051	0.0011	0.0043	0.55	0.0031	0.037	1.15	0.19	0.00085	10.2	0.27
Isobutane	-	-	-	0.0026	0.0046	-	-	2.99	-	-	0.011	-
Acetylene	-	-	0.00089	0.007	0.0073	0.00085	0.011	0.15	-	-	0.019	-
Ethylene	-	-	0.0011	0.0018	0.011	-	0.013	1.28	0.075	-	1.45	2.3
Propylene	-	-	0.077	0.052	0.18	0.02	1.1	0.33	-	-	1.25	3.5
Propadiene	-	-	0.00018	-	-	-	-	-	-	-	-	-
Methyl acetylene	0.0021	0.0035	-	0.0002	0.018	-	0.0033	0.18	3.0	-	0.038	-
1-Butene	0.0049	0.0041	0.057	0.019	0.57	0.014	0.31	1.72	1.1	0.015	0.2	1.6
2-Butene (cis)	0.057	0.0021	0.034	0.0069	0.041	0.0047	0.27	2.68	0.53	-	0.46	0.47
2-Butene (trans)	0.0024	-	-	-	0.0059	-	0.0046	-	-	0.00001	0.012	-
1,3 Butadiene	-	-	-	-	0.0021	-	-	0.29	-	-	-	-
1-Pentene	0.0032	0.00027	-	-	0.013	-	-	0.57	-	-	0.4	-
2-Pentene	-	-	-	0.0003	0.0038	-	-	0.23	-	-	0.24	-

TABLE 1 (Cont.)

(μg/g charcoal)

	Witco 888 Vacuum Oven Stripped	Witco 888 as Received	Witco 888 Hot N_2 Purge	AC Vacuum Oven Stripped	AC as Received	AC Hot N_2 Purge	VG Vacuum Oven Stripped	VG as Received	VG Hot N_2 Purge	GI Vacuum Oven Stripped	GI as Received	GI Hot N_2 Purge
Isoprene	-	-	-	0.0018	0.048	-	0.075	2.14	-	0.025	2.65	-
2-Hexene	-	-	0.0011	-	0.74	-	0.0022	0.1	0.018	-	0.17	0.0055
Cyclohexene	-	-	-	-	-	-	-	-	-	-	0.22	-
Styrene	-	-	-	0.00001	0.00009	-	-	0.0038	-	-	-	-
Cyclopentane	-	-	-	-	0.013	0.0057	0.0018	1.09	0.0013	-	-	0.44
Cyclohexane	0.0052	-	-	0.0003	0.0048	-	-	-	-	-	-	-
Methyl cyclopentane	-	-	0.034	0.0006	0.011	0.003	0.015	0.095	0.1	-	0.065	0.11
Methyl cyclohexane	-	0.0015	0.00014	0.0026	0.24	-	-	0.16	1.2	0.0019	0.95	-
Dimethyl cyclohexane	0.0055	-	-	0.00006	-	-	-	-	-	-	-	-
Benzene	0.011	0.0022	0.13	0.012	0.036	0.16	0.050	0.43	10.	0.45	7.7	5.0
Toluene	0.0018	0.0068	0.065	0.027	0.030	0.056	-	1.31	11.	0.1	16.5	0.93
m-Xylene	0.0013	0.00056	-	trace	trace	-	-	0.046	0.15	0.00075	0.21	0.012
o-Xylene	-	0.00064	0.003	0.00004	0.00004	-	-	0.026	-	0.0019	0.008	0.00032
p-Xylene	0.00019	0.00033	0.0014	-	-	0.0038	-	0.028	0.056	0.00001	0.10	-
Ethyl benzene	0.00009	-	-	0.00001	trace	-	-	0.02	-	-	-	0.041
C_9 Aromatics	0.0069	0.0008	-	0.0002	0.0002	-	-	0.014	0.25	0.001	0.075	0.064
C_{10} Aromatics	0.002	-	-	-	0.0012	-	0.0023	0.0073	0.016	0.003	0.0012	0.0041
Furan	0.0019	0.0044	0.004	0.0044	0.032	0.013	0.031	0.19	0.92	0.11	0.75	0.35
Tetrahydrofuran	-	-	-	-	-	-	-	0.015	-	-	-	-
Dioxane	0.00036	0.0017	-	0.0083	0.038	-	-	0.18	0.12	-	-	-
Methyl furan	-	-	-	-	-	-	-	-	0.25	-	-	-
Methyl alcohol	0.023	0.0032	0.28	0.01	2.83	0.015	1.7	-	-	-	0.075	1.9
Ethyl alcohol	0.0046	0.044	-	0.032	0.35	0.0085	0.035	2.49	-	0.0085	0.16	0.25
Allyl alcohol	-	0.0011	-	-	-	-	-	-	-	-	-	-
Propyl alcohol	-	-	-	0.00007	0.025	-	0.0025	-	-	-	-	-
Isopropyl alcohol	0.0037	0.0079	-	0.0008	0.13	0.028	0.0094	0.15	0.42	-	-	0.42
Butyl alcohol	-	0.0008	0.019	-	0.00003	-	0.0045	-	0.14	-	0.15	0.07
s-Butyl alcohol	0.0002	-	-	-	-	-	-	-	-	-	-	-
Isobutyl alcohol	0.00008	0.00047	0.0067	-	-	0.013	0.041	0.061	0.13	-	0.1	0.25
Isoamyl alcohol	-	-	-	0.00004	0.00005	-	-	0.011	-	-	-	-
Acetone	0.019	0.027	0.35	0.059	0.65	0.09	0.052	1.49	1.1	0.10	1.85	0.38
Methyl ethyl ketone	-	0.00007	-	-	-	-	0.017	-	0.1	-	0.085	-
Methyl propyl ketone	-	-	-	-	-	-	-	-	0.022	-	-	-
Methyl isobutyl ketone	0.024	0.0012	0.012	0.0003	0.014	0.00007	0.018	0.051	-	-	-	-

TABLE 1 (Cont.)

(μg/g charcoal)

	Witco 888 Vacuum Oven Stripped	Witco 888 as Received	Witco 888 Hot N_2 Purge	AC Vacuum Oven Stripped	AC as Received	AC Hot N_2 Purge	VG Vacuum Oven Stripped	VG as Received	VG Hot N_2 Purge	GI Vacuum Oven Stripped	GI as Received	GI Hot N_2 Purge
Dimethyl ether	-	-	0.0038	-	-	-	-	-	0.035	-	-	-
Acetaldehyde	-	0.0022	0.046	-	-	0.039	0.14	1.21	-	0.0022	5.2	-
Ethyl acetate	-	-	0.0039	0.0007	0.033	-	0.073	0.15	0.27	-	0.16	0.049
Butyl acetate	-	-	-	-	-	-	-	0.068	-	-	-	-
Acetonitrile	-	-	0.01	-	0.013	0.0004	-	0.054	0.092	0.0023	0.18	0.055
Dimethyl sulfide	-	-	-	-	-	-	-	-	-	0.005	-	0.66
Sulfur dioxide	<1	<1	<1	-	-	-	-	-	-	-	-	-
Carbon oxysulfide	-	-	-	-	-	-	-	-	0.15	-	-	-
Total	0.228	1.193	1.176	0.30	10.0	0.49	4.33	49.7	33.9	0.897	71.6	19.5

Considering the usefulness of displacement liquid chromatography and publications describing the "cleaning" of adsorbents with solvents, a study of solvent treatment of "as received" charcoal was made. Two solvents, methylisobutyl ketone (MIBK), and methanol were selected for their structural differences and adsorption isotherms. Also these solvents were repeatedly found in the desorbates of Apollo canister charcoals. Charcoal, in the "as received" condition, was placed in a soxhlet extraction thimble and refluxed for three hours with the selected solvent. The charcoal was then transferred to a vacuum oven to remove the solvent. Vacuum oven stripping was conducted at 150°C for 16 hours.

The data from these tests suggest relatively little success in the use of these displacement solvents for contaminant removal. Residual contaminant levels were not materially reduced and the contaminant picture was further complicated by apparent solvent degradation. Some of the results from these tests are presented in Tables 2 and 3.

TABLE 2

ANALYSIS OF VG CHARCOAL DESORBATE AFTER MIBK REFLUXING

(Refluxed 3 Hours with MIBK and Heated
16 Hours in Vacuum Oven at 150°C)

Major Constituents Found in the -190°C Collector	1st Lab Stripping μg/g Charcoal	2nd Lab Stripping μg/g Charcoal
Butane	17.	0.26
Propylene	5.0	2.1
1-Butene	12.0	7.5
Isoprene	2.0	1.3
Methylcyclopentane	3.4	0.5
Benzene	0.26	3.6
Toluene	2.3	2.8
Furan	1.1	0.26
Tetrahydrofuran	7.5	-
Methyl alcohol	5.0	2.1
Acetone	42.	18.
MIBK	35.	0.04
Acetaldehyde	5.3	3.9
Ethyl acetate	1.1	0.82
Others	8.	13.
Major Constituents in the -80°C Collector	36 mg/g	1 mg/g
MIBK + H_2O*		

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*Two phases, estimated 90% MIBK, 10% H_2O

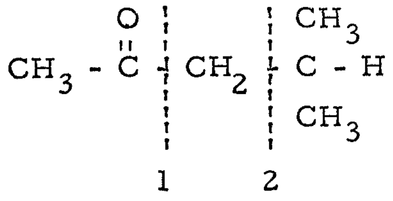
TABLE 3

ANALYSIS OF AC CHARCOAL DESORBATE AFTER MIBK REFLUXING

(Refluxed 3 Hours with MIBK and Heated
16 Hours in Vacuum Oven at 150°C)

Major Constituents	Mg Adsorbate/g Charcoal
Propylene	0.21
Butene-butane	0.25
Ethane	0.009
Ethylene	0.005
Isoprene	0.025
Hexene-2	0.065
Methyl cyclopentane	0.015
Methyl cyclohexane	0.006
Toluene	0.06
Acetone	0.23
Methyl isobutyl ketone	50.

These tables indicate that appreciable quantities of acetone, propylene, butenes, and butanes were formed on charcoal either during thermal-vacuum treatment or upon adsorption. These GC data were confirmed by mass spectrometry. Analysis of the MIBK used in this study is shown in Table 4. By examining the structure of MIBK,



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-H$$

it can be seen that by splitting the molecule at dashed line 2 (and transferring an hydrogen atom) acetone and propylene would be by-products. If the structure is severed at line 1, butenes and butanes could form depending on the type of rearrangement occurring. The remaining fragment might yield acetaldehyde or ethanol as logical products. Other similar reactions have been described in the literature. For example, the conversion of cyclopropane to propylene at 115°C on Linde 13X molecular sieve and the conversion of cyclohexanol to cyclohexene on firebrick at about 200°C have been studied rather thoroughly. From these data it is apparent that considerably more tests must be made before any extended conclusions can be formed regarding desorbates from Apollo charcoals.

An "as received" AC charcoal was soxhlet treated for three hours with methanol followed by a vacuum oven treatment for six hours at 150°C. Following this, the charcoal was further desorbed on the LTVS for one hour at 150°C. The effluent was collected and analyzed. The results given in Table 5 show large amounts of impurities.

TABLE 4

GAS CHROMATOGRAPHIC ANALYSIS OF MIBK CONTAMINANTS

Major Constituents	Weight in 1 µl of MIBK, µg
Propylene	0.003
1-Butene	0.003
Pentene-2	0.008
Benzene	0.03
m-Xylene	0.34
o-Xylene	0.24
Furan	0.06
Tetrahydrofuran	0.06
Methylfuran	0.06
Ethyl alcohol	0.11
Methyl alcohol	0.02
Acetone	0.21
Methyl ethyl ketone	0.27
Methyl propyl ketone	0.17
Ethyl acetate	0.17

TABLE 5

ANALYSIS OF AC CHARCOAL DESORBATE AFTER METHYL ALCOHOL REFLUXING

(Charcoal Refluxed 3 Hours with MEOH
and Heated 6 Hours in Vacuum Oven at 150°C)

Major Constituents in -190°C Trap	μg Adsorbate/g Charcoal
Freon 113	0.74
Tetrachloroethylene	5.5
Butane	0.21
1-Butene	0.33
Methylcyclopentane	0.56
Benzene	8.6
Toluene	6.0
Methyl alcohol	10.
Isopropyl alcohol	0.26
Acetone	2.3
MIBK	0.4
Acetaldehyde	5.0
Others	3.2
Contents of the -80°C Collector	2.9 mg/g charcoal

Superheated steam is occasionally used commercially to manufacture activated charcoal. As previously mentioned, the primary consideration of these tests were to determine whether stripping methods other than those used for Apollo charcoal samples would prove superior. A stripping study using steam at 160°C was made.. The test set up and procedure was the same as previously described for the hot nitrogen purge. Temperature control proved more difficult than with nitrogen so that only an average temperature of 160°C was maintained. The residual contaminants from these tests were 1.2 µg/g on AC charcoal, of which trichloroethylene, benzene, toluene, and acetone were the most prominent; 3.1 µg/g on GI charcoal, of which benzene was the principal contributor; 34. µg/g on VG charcoal of which there were many major constituents, and Witco 888 charcoal had 10.7 µg/g with acetone as the major contaminant. These data are presented in Table 6. It may be noted that this stripping method seems approximately equal to the hot nitrogen. An interesting observation with this series was that the residual water content did not substantially increase above the approximately 2% remaining after vacuum oven treatment.

Since none of the stripping methods investigated proved to be superior to the vacuum-thermal method initially adopted, variables in operational parameters were investigated.

TABLE 6

RESIDUAL CONTAMINANTS ON SELECTED CHARCOALS FOLLOWING STEAM PURGING

AC Charcoal, Steam Strip	Mol-Wt	μg/g
Freon 22	86.50	0.016
Freon 113	187.39	0.033
1,1,1-Trichloroethane	133.42	0.012
Trichloroethylene	131.40	0.13
Tetrachloroethylene	165.85	0.062
Butane	58.12	0.0046
Propylene	42.08	0.0073
Methylacetylene	40.07	0.0033
1-Butene	56.10	0.0029
2-Butene (cis)	56.10	0.011
Isoprene	68.11	0.0018
Styrene	104.14	0.012
Decalin	138.25	0.00095
Benzene	78.11	0.10
Toluene	92.13	0.19
m-Xylene	106.16	0.017
o-Xylene	106.16	0.019
p-Xylene	106.16	0.013
Ethylbenzene	106.16	0.0092
C_9 Aromatics	120.19	0.024
Trimethylbenzene	120.19	0.0040
Mesitylene	120.19	0.0059
Indene	116.15	0.00065
C_{10} Aromatics	134.21	0.010
Naphthalene	128.16	0.00039
C_{11} Aromatics	148.24	0.0012
Tetrahydrofuran	72.10	0.027
Dioxane	88.10	0.013
Methylfuran	82.10	0.039
Ethyl alcohol	46.07	0.065
Isopropyl alcohol	60.09	0.029
Isobutyl alcohol	74.12	0.036
Acetone	58.08	0.15
Ethyl acetate	88.10	0.082
Propyl acetate	102.13	0.038
Butyl acetate	116.16	0.020
Unknown	0.0	0.00038
	Total	1.20408

TABLE 6 (Cont.)

GI Charcoal, Steam Strip	Mol-Wt		μg/g
Vinyl fluoride	46.04		0.0034
Tetrachloroethylene	165.85		0.0012
Vinylidene chloride	96.95		0.13
Dichlorodifluoroethane	134.94		0.016
Ethane	30.07		0.00021
Butane	58.12		0.13
Ethylene	28.05		0.11
Propylene	42.08		0.12
Methylacetylene	40.07		0.00021
1-Butene	56.10		0.40
2-Butene (cis)	56.10		0.046
1-Pentene	70.13		0.032
2-Pentene	70.13		0.046
Isoprene	68.11		0.13
2-Hexene	84.16		0.0095
Methylcyclopentane	84.11		0.042
Benzene	78.11		0.76
Toluene	92.13		0.27
p-Xylene	106.16		0.00063
Isobutyl alcohol	74.12		0.22
Acetone	58.08		0.052
Methyl ethyl ketone	72.10		0.20
Acetaldehyde	44.05		0.010
Ethyl acetate	88.10		0.34
		Total	3.05998

VG Charcoal, Steam Strip	Mol-Wt	μg/g
Freon 113	187.39	4.4
Trimethylfluorosilane	92.20	0.15
Trichloroethylene	131.40	1.2
Tetrachloroethylene	165.85	0.26
Ethane	30.07	0.078
Butane	58.12	0.36
Trimethylhexane	128.26	0.28
Acetylene	26.04	0.026
Propylene	42.08	0.58
Methylacetylene	40.07	0.00039
1-Butene	56.10	1.9
2-Butene (cis)	56.10	2.5
1-Pentene	70.13	0.43
Isoprene	68.11	2.5
Octyne	110.20	0.069
Styrene	104.14	0.00066

TABLE 6 (Cont.)

VG Charcoal, Steam Strip	Mol-Wt		µg/g
Methylcyclohexane	98.18		0.19
Benzene	78.11		0.66
Toluene	92.13		9.7
o-Xylene	106.16		0.0030
p-Xylene	106.16		0.0059
C_9 Aromatics	120.19		0.022
Cumene	120.20		0.028
C_{10} Aromatics	134.21		0.0097
Naphthalene	128.16		0.025
Furan	68.07		2.7
Dioxane	88.10		0.11
Methylfuran	82.10		0.11
Ethyl alcohol	46.07		0.040
Isopropyl alcohol	60.09		1.4
Isobutyl alcohol	74.12		0.018
Acetone	58.08		2.3
Methyl ethyl ketone	72.10		0.044
Methyl isobutyl ketone	100.16		0.42
Acetaldehyde	44.05		0.33
Methyl acetate	74.08		0.53
Ethyl acetate	88.10		0.17
Unknown	0.0		0.46
		Total	33.95276

Witco 888, Steam Strip		
Ethyl fluoride	48.06	0.093
Vinyl fluoride	46.04	0.0053
Ethane	30.07	0.022
Butane	58.12	0.0098
Acetylene	26.04	0.0055
Ethylene	28.05	0.095
Propylene	42.08	0.014
1-Butente	56.10	0.19
2-Butene (cis)	56.10	0.056
2-Butene (trans)	56.10	0.0050
1-Pentene	70.13	0.0092
2-Hexene	84.16	0.012
Octyne	110.20	0.013
Benzene	78.11	0.82
Toluene	92.13	0.12
m-Xylene	106.16	0.0012
o-Xylene	106.16	0.00044

TABLE 6 (Cont.)

Witco 888, Steam Strip	Mol-Wt	μg/g
p-Xylene	106.16	0.0052
Ethylbenzene	106.16	0.00064
C_9 Aromatics	120.19	0.0089
Furan	68.07	0.27
Dioxane	88.10	0.0043
Methylfuran	82.10	0.0094
Methyl alcohol	32.04	0.18
Ethyl alcohol	46.07	0.55
Isopropyl alcohol	60.09	0.080
n-Butyl alcohol	74.12	0.0033
t-Butyl alcohol	74.12	0.0040
Isobutyl alcohol	74.12	0.020
Acetone	58.08	7.7
Methyl ethyl ketone	72.10	0.00061
Methyl isobutyl ketone	100.16	0.11
Acetaldehyde	44.05	0.10
Ethyl acetate	88.10	0.015
Carbon oxysulfide	60.07	0.059
Sulfur dioxide	64.06	0.00073
C_{10} Aromatics	134.21	0.036
	Total	10.67471

D. TIME AND TEMPERATURE VARIABLES FOR ANALYTICAL STRIPPING

VG charcoal was selected for the initial stripping parameter variation tests since even after the conventional vacuum oven pretreatment it still contained more contamination than the other charcoals "as received". A portion of the data contained in Table 7 represent the analyses of the residual contamination found on Type VG charcoal after the standard vacuum oven activation procedure, i. e. 18 hours at 165°C. As may be noted, the apparent residual of 4.33 µg/g charcoal would still indicate this charcoal is furthest removed from the ideal zero level of any of the four tested. The material removed by this process was particularly high in unsaturates and in alcohol, with aromatics, ketones, and esters all at moderate levels.

The balance of Table 7 presents the analysis of material from the charcoal after it had been allowed to cool to ambient temperature for four hours before reheating to 160°C for one hour under hard vacuum. The total from this second stripping was 6.5 ug/g, or 151% of that removed by the first analytical strip. A closer look at the individual compounds shows that the major contributors are still unsaturates and alcohol, with a slight increase in esters. These are all compounds thought to be weakly adsorbed as compared to the aromatics. This same charcoal was then cooled to ambient temperature for an additional 18 hours before restripping. It will be noted that 0.6 ug/g of charcoal were removed, which is 14% of the quantity removed by the initial strip, and 5% of the total removed by the first two strips. There was still no noted increase in aromatics, but a continued high level of unsaturates and the appearance of Freon 113 in quantity not previously noted. The total removed by these three strippings was 11.5 ug/g. These figures show clearly that the hard vacuum-heating system found to remove 95+% of the contaminants from AC charcoal in one hour is wholly inadequate for Type VG charcoal, removing only 37% of the contaminants.

A second sample from the lot of VG Type charcoal previously subjected to vacuum oven pretreatment was stripped for one hour at 350°C on the vacuum rack. This high temperature treatment resulted in the collection of 11 µg/gm charcoal of desorbates. If it be assumed that the 11.5 µg/g removed by the three 160°C strippings represents 100%, then the one hour at 350°C resulted in the removal of 95+% of the total contaminants and compares favorably with the standard 160°C strip used for Type AC charcoal. A study of the data contained in Table 8 indicates a predominance of benzene (46% of the total), propylene, and methyl acetylene. The high benzene value would not be unusual if the charcoal were thoroughly stripped, however, this value is nearly 3-1/2 times that found in the three strippings at lower temperature. This finding gives rise to numerous questions regarding the possibility of compound formations, desorption and adsorption mechanics, stripping procedure, etc.

It is suggested that strongly adsorbed materials such as benzene "flood" the micro pores of charcoal while the less strongly bound compounds are more evenly distributed over the surface. Heating under vacuum allows the ready stripping of these surface adsorbed materials, while those "flooded" areas remain relatively undisturbed. If the heat and vacuum are interrupted, a portion of the remaining adsorbate then redistributes itself to the depleted sites developed on the surface, where it may be removed by a resumption of heat and vacuum. The performance of benzene would seem to lend credence to this hypothesis.

Table 9A contains the analysis of that material stripped from a sample of vacuum oven pretreated charcoal at 125°C for 18 hours. This long time-low temperature strip removed only 2.6 µg/g of contaminants, consisting mainly of benzene, acetone, and alcohol. Comparing this total to the 11+ µg/g known to be present (as shown in the grand totals of Table 7 the low efficiency of this method becomes evident.

TABLE 7

RESIDUAL CONTAMINANTS FOUND ON TYPE VG CHARCOAL AFTER MULTIPLE STRIPPING

VG CHARCOAL, VACUUM OVEN STRIP

COMPOUND	MW	UG/G
FREON 113	187.39	0.0029
TRICHLOROETHYLENE	131.40	0.014
ETHANE	30.07	0.20
PROPANE	44.09	0.0060
BUTANE	58.12	0.037
ACETYLENE	26.04	0.011
ETHYLENE	28.05	0.013
PROPYLENE	42.08	1.1
METHYLACETYLENE	40.07	0.0033
1-BUTENE	56.10	0.31
2-BUTENE (CIS)	56.10	0.27
2-BUTENE (TRANS)	56.10	0.0046
ETHYLACETYLENE	54.09	0.00028
ISOPRENE	68.11	0.075
2-HEXENE	84.16	0.0022
CYCLOPENTANE	70.13	0.0018
METHYLCYCLOPENTANE	84.11	0.015
BENZENE	78.11	0.050
C10 AROMATICS	134.21	0.0023
FURAN	68.07	0.031
METHYL ALCOHOL	32.04	1.7
ETHYL ALCOHOL	46.07	0.035

TABLE 7 (Cont.)

VG CHARCOAL, VACUUM OVEN STRIP

COMPOUND	MW	UG/G
N-PROPYL ALCOHOL	60.09	0.0025
ISOPROPYL ALCOHOL	60.09	0.0094
N-BUTYL ALCOHOL	74.12	0.0045
ISOBUTYL ALCOHOL	74.12	0.041
ACETONE	58.08	0.052
METHYL ETHYL KETONE	72.10	0.017
METHYL ISOBUTYL KETONE	100.16	0.018
ACETALDEHYDE	44.05	0.14
METHYL ACETATE	74.08	0.070
ETHYL ACETATE	88.10	0.073
PROPYL ACETATE	102.13	0.048
	TOTAL	4.33043

TABLE 7 (Cont.)

VG CHARCOAL, SECOND STRIP

COMPOUND	MW	UG/G
FREON 11	137.38	0.068
FREON 113	187.39	0.0067
VINYL CHLORIDE	62.50	0.025
ETHANE	30.07	0.71
PROPANE	44.09	0.052
BUTANE	58.12	0.67
ACETYLENE	26.04	0.0074
ETHYLENE	28.05	0.19
PROPYLENE	42.08	1.2
METHYLACETYLENE	40.07	1.6
1-BUTENE	56.10	0.19
2-BUTENE (CIS)	56.10	0.46
2-BUTENE (TRANS)	56.10	0.099
1-PENTENE	70.13	0.080
2-PENTENE	70.13	0.050
ISOPRENE	68.11	0.14
2-HEXENE	84.16	0.16
METHYLCYCLOPENTANE	84.11	0.022
METHYLCYCLOHEXANE	98.18	0.027
BENZENE	78.11	0.021
TOLUENE	92.13	0.0012
ETHYLBENZENE	106.16	0.0042

TABLE 7 (Cont.)

VG CHARCOAL, SECOND STRIP

COMPOUND	MW	UG/G
TRIMETHYLBENZENE	120.19	0.00008
FURAN	68.07	0.012
DIOXANE	88.10	0.0035
METHYL ALCOHOL	32.04	0.13
ETHYL ALCOHOL	46.07	0.094
ISOPROPYL ALCOHOL	60.09	0.0061
ISOBUTYL ALCOHOL	74.12	0.00019
ACETONE	58.08	0.0033
METHYL ETHYL KETONE	72.10	0.13
ACETALDEHYDE	44.05	0.018
ETHYL ACETATE	88.10	0.19
PROPYL ACETATE	102.13	0.15
ACETONITRILE	41.05	0.036
	TOTAL	6.54999

TABLE 7 (Cont.)

VG CHARCOAL, THIRD STRIP

COMPOUND	MW	UG/G
FREON 113	187.39	0.21
VINYLIDENE CHLORIDE	96.95	0.012
BUTANE	58.12	0.0032
N-HEPTANE	100.20	0.00002
PROPYLENE	42.08	0.13
METHYLACETYLENE	40.07	0.068
1-BUTENE	56.10	0.047
2-BUTENE (CIS)	56.10	0.0051
2-BUTENE (TRANS)	56.10	0.00083
ISOPRENE	68.11	0.016
METHYLCYCLOHEXANE	98.18	0.0065
BENZENE	78.11	0.037
TOLUENE	92.13	0.0011
FURAN	68.07	0.0050
DIOXANE	88.10	0.0060
ETHYL ALCOHOL	46.07	0.011
ISOPROPYL ALCOHOL	60.09	0.0026
ISOBUTYL ALCOHOL	74.12	0.013
ACETONE	58.08	0.0026
ACETALDEHYDE	44.05	0.0093
DIMETHYL SULFIDE	62.13	0.0093
	TOTAL	0.60199

TABLE 7 (Cont.)

VG CHARCOAL, STRIP 4, 350C

COMPOUND	MW	UG/G
METHYL CHLORIDE	50.49	0.0070
ETHANE	30.07	0.15
PROPANE	44.09	0.023
BUTANE	58.12	0.053
ISOBUTANE	58.12	0.011
ETHYLENE	28.05	0.0097
METHYLACETYLENE	40.07	0.67
1-BUTENE	56.10	0.013
2-BUTENE (CIS)	56.10	0.0054
2-BUTENE (TRANS)	56.10	0.075
ISOPRENE	68.11	0.029
CYCLOHEXENE	82.14	0.083
OCTYNE	110.20	0.0029
CYCLOPENTANE	70.13	0.00084
METHYLCYCLOPENTANE	84.11	0.0021
METHYLCYCLOHEXANE	98.18	0.033
BENZENE	78.11	3.8
TOLUENE	92.13	0.13
M-XYLENE	106.16	0.0055
P-XYLENE	106.16	0.0031
ETHYLBENZENE	106.16	0.0032
C9 AROMATICS	120.19	0.0051

TABLE 7 (Cont.)

VG CHARCOAL, STRIP 4, 350C

COMPOUND	MW	UG/G
MESITYLENE	120.19	0.038
INDENE	116.15	0.00038
NAPHTHALENE	128.16	0.037
FURAN	68.07	0.0031
METHYLFURAN	82.10	0.016
ETHYL ALCOHOL	46.07	0.048
N-PROPYL ALCOHOL	60.09	0.00009
ISOPROPYL ALCOHOL	60.09	0.016
ISOBUTYL ALCOHOL	74.12	0.0083
ACETONE	58.08	0.12
METHYL ETHYL KETONE	72.10	0.00075
METHYL ISOBUTYL KETONE	100.16	0.046
DIMETHYL ETHER	46.07	0.00009
ACROLEIN	56.06	0.037
ACETONITRILE	41.05	0.050
	TOTAL	5.52562

TABLE 8

RESIDUAL CONTAMINANTS FOUND ON TYPE VG CHARCOAL ON 350°C STRIPPING

VG CHARCOAL, HIGH TEMPERATURE STRIP

COMPOUND	MW	UG/G
TRIFLUOROPROPENE	96.05	0.013
METHYLENE CHLORIDE	84.94	0.00007
1,1,1-TRICHLOROETHANE	133.42	0.047
TRICHLOROETHYLENE	131.40	0.00015
TETRACHLOROETHYLENE	165.85	0.00023
ETHANE	30.07	0.043
PROPANE	44.09	0.026
BUTANE	58.12	0.090
TRIMETHYLHEXANE	128.26	0.052
ACETYLENE	26.04	0.0063
ETHYLENE	28.05	0.0039
PROPYLENE	42.08	1.1
METHYLACETYLENE	40.07	1.4
1-BUTENE	56.10	0.63
2-BUTENE (CIS)	56.10	0.58
2-BUTENE (TRANS)	56.10	0.0084
ETHYLACETYLENE	54.09	0.0018
2-PENTENE	70.13	0.11
ISOPRENE	68.11	0.42
2-HEXENE	84.16	0.051
CYCLOHEXENE	82.14	0.081
OCTYNE	110.20	0.029

TABLE 8 (Cont.)

VG CHARCOAL, HIGH TEMPERATURE STRIP

COMPOUND	MW	UG/G
STYRENE	104.14	0.13
METHYLCYCLOPENTANE	84.11	0.17
BENZENE	78.11	5.1
TOLUENE	92.13	0.10
M-XYLENE	106.16	0.038
P-XYLENE	106.16	0.024
ETHYLBENZENE	106.16	0.0032
C9 AROMATICS	120.19	0.011
FURAN	68.07	0.069
DIOXANE	88.10	0.075
ETHYL ALCOHOL	46.07	0.095
N-PROPYL ALCOHOL	60.09	0.12
ISOPROPYL ALCOHOL	60.09	0.089
ISOBUTYL ALCOHOL	74.12	0.13
ACETONE	58.08	0.11
METHYL ETHYL KETONE	72.10	0.00016
ACETALDEHYDE	44.05	0.19
ETHYL ACETATE	88.10	0.00029
	TOTAL	11.03804

TABLE 9A

RESIDUAL CONTAMINANTS FOUND ON TYPE VG CHARCOAL ON 125°C STRIPPING

VG CHARCOAL, LOW TEMPERATURE STRIP

COMPOUND	MW	UG/G
FREON 11	137.38	0.00003
1,1,1-TRICHLOROETHANE	133.42	0.19
TRICHLOROETHYLENE	131.40	0.026
TETRACHLOROETHYLENE	165.85	0.0052
PROPANE	44.09	0.00006
BUTANE	58.12	0.0014
METHYLACETYLENE	40.07	0.00024
1-BUTENE	56.10	0.019
2-BUTENE (CIS)	56.10	0.0026
ISOPRENE	68.11	0.021
OCTYNE	110.20	0.068
METHYLCYCLOPENTANE	84.11	0.00002
METHYLCYCLOHEXANE	98.18	0.030
BENZENE	78.11	1.2
TOLUENE	92.13	0.081
M-XYLENE	106.16	0.014
P-XYLENE	106.16	0.00025
C9 AROMATICS	120.19	0.044
C10 AROMATICS	134.21	0.064
NAPHTHALENE	128.16	0.012
C11 AROMATICS	148.24	0.017
FURAN	68.07	0.020

TABLE 9A (Cont.)

VG CHARCOAL, LOW TEMPERATURE STRIP

COMPOUND	MW	UG/G
DIOXANE	88.10	0.049
METHYL ALCOHOL	32.04	0.0092
ETHYL ALCOHOL	46.07	0.15
N-PROPYL ALCOHOL	60.09	0.059
N-BUTYL ALCOHOL	74.12	0.050
ISOBUTYL ALCOHOL	74.12	0.00089
ACETONE	58.08	0.35
METHYL ETHYL KETONE	72.10	0.0094
ACETALDEHYDE	44.05	0.020
ETHYL ACETATE	88.10	0.012
ACETONITRILE	41.05	0.053
UNKNOWN	0.0	0.038
	TOTAL	2.62642

After allowing a cooling period of two hours, the low temperature stripped sample was subjected to additional hard vacuum desorption at 160°C for one hour. This resulted in the collection of an additional 1.8 µg/g of contaminants. Table 9B contains this analysis. The total of 4.4 µg/g collected from the low temperature strip followed by the regular strip is in good agreement with the 4.3 µg/g recovered from the initial 160°C strip, apparently indicating that stripping at 125°C would require nearly 30 hours to remove the same quantity of contaminant that can be removed in one hour at 160°C.

The indication from this study of Type VG charcoal is that stripping at 350°C is more efficient than the lower temperature used to desorb the Apollo canister charcoal. Repeated desorption study of type AC charcoal during Apollo breathing canister tests indicates that this charcoal is 95+% desorbed by one hour at 160°C under hard vacuum, while type VG charcoal is only 35-40% desorbed by similar treatment. Possibly the comparison is not valid in that the type AC charcoal data were obtained from exposed charcoal containing relatively large quantities of adsorbates, while the type VG data were from a new sample and the contaminants consist of those apparently inherent to the preparation processes. To determine whether the other charcoals would desorb satisfactorily at 160°C from an initial unexposed state, type GI and 888 charcoals were subjected to temperature cycling similar to that of the type VG.

The type 888 charcoal stock was blended and a sample was prepared in the vacuum oven at 165°C for 16 hours. A fifty gram sample of this prepared charcoal was desorbed at 160°C for one hour on the analytical vacuum rack. The data from these desorptions are contained in Table 10. The sample was then allowed to stand for four hours at ambient temperatures before again heating to 160°C. The total from this second stripping was 0.16 µg/g, or 118% of that desorbed from the initial stripping. The desorbates remained essentially the same as removed by Strip 1, but with a ten fold increase in benzene and toluene. This same charcoal was then

TABLE 9B

RESIDUAL CONTAMINANTS FOUND ON TYPE VG CHARCOAL
REMOVED AT 160°C FOLLOWING 125°C STRIP

VG CHARCOAL, STANDARD STRIP FOLLOWING LOW TEMPERATURE STRIP

COMPOUND	MW	UG/G
FREON 22	86.50	0.00079
FREON 113	187.39	0.16
METHYLENE CHLORIDE	84.94	0.25
METHYL CHLORIDE	50.49	0.00020
1,1,1-TRICHLOROETHANE	133.42	0.051
TRICHLOROETHYLENE	131.40	0.24
TETRACHLOROETHYLENE	165.85	0.029
BUTANE	58.12	0.0081
TRIMETHYLHEXANE	128.26	0.014
PROPYLENE	42.08	0.00031
METHYLACETYLENE	40.07	0.0013
1-BUTENE	56.10	0.0018
2-BUTENE (CIS)	56.10	0.00015
2-BUTENE (TRANS)	56.10	0.00018
ISOPRENE	68.11	0.19
STYRENE	104.14	0.00012
METHYLCYCLOHEXANE	98.18	0.024
BENZENE	78.11	0.29
TOLUENE	92.13	0.17
M-XYLENE	106.16	0.00039
P-XYLENE	106.16	0.00033
ETHYLBENZENE	106.16	0.00090

TABLE 9B (Cont.)

VG CHARCOAL, STANDARD STRIP FOLLOWING LOW TEMPERATURE STRIP

COMPOUND	MW	UG/G
C9 AROMATICS	120.19	0.00011
ISOPROPYL ALCOHOL	60.09	0.13
ISOBUTYL ALCOHOL	74.12	0.0073
ACETONE	58.08	0.18
METHYL ETHYL KETONE	72.10	0.0013
METHYL PROPYL KETONE	86.13	0.034
ACETALDEHYDE	44.05	0.0030
METHYL ACETATE	74.08	0.022
ETHYL ACETATE	88.10	0.0082
BUTYL ACETATE	116.16	0.0029
	TOTAL	1.81708

TABLE 10

RESIDUAL CONTAMINANTS FOUND ON TYPE 888 CHARCOAL REMOVED BY MULTIPLE STRIPPING

888 CHARCOAL, VACUUM OVEN PREPARED

COMPOUND	MW	UG/G
TRIFLUOROMETHANE	70.02	TRACE
TRICHLOROETHYLENE	131.40	0.00013
VINYLIDENE CHLORIDE	96.95	0.00004
BUTANE	58.12	0.00003
ISOPENTANE	72.15	0.00076
PROPYLENE	42.08	0.00011
METHYLACETYLENE	40.07	0.00006
1-BUTENE	56.10	0.0048
METHYLCYCLOHEXANE	98.18	0.00072
BENZENE	78.11	0.0066
TOLUENE	92.13	0.0011
M-XYLENE	106.16	0.0027
P-XYLENE	106.16	0.0063
C9 AROMATICS	120.19	0.0067
C10 AROMATICS	134.21	0.0022
FURAN	68.07	0.0067
ETHYL ALCOHOL	46.07	0.0012
N-PROPYL ALCOHOL	60.09	0.00041
ISOBUTYL ALCOHOL	74.12	0.0012
ACETONE	58.08	0.091
METHYL ETHYL KETONE	72.10	0.00048
METHYL ISOBUTYL KETONE	100.16	0.00049

TABLE 10 (Cont.)

888 CHARCOAL, VACUUM OVEN PREPARED

COMPOUND	MW	UG/G
ACETALDEHYDE	44.05	0.00008
ETHYL ACETATE	88.10	0.00082
SULFUR DIOXIDE	64.06	TRACE
	TOTAL	0.13484

TABLE 10 (Cont.)

888 CHARCOAL, STRIP 2, 160C

COMPOUND	MW	UG/G
TRIFLUOROMETHANE	70.02	TRACE
TETRACHLOROETHYLENE	165.85	0.00055
VINYLIDENE CHLORIDE	96.95	0.0035
PROPANE	44.09	0.00005
BUTANE	58.12	0.00004
PROPYLENE	42.08	0.0019
METHYLACETYLENE	40.07	0.00002
1-BUTENE	56.10	0.025
2-BUTENE (TRANS)	56.10	TRACE
ISOPRENE	68.11	0.00004
METHYLCYCLOPENTANE	84.11	0.0066
METHYLCYCLOHEXANE	98.18	0.0036
BENZENE	78.11	0.062
TOLUENE	92.13	0.036
M-XYLENE	106.16	0.00011
O-XYLENE	106.16	0.00014
C9 AROMATICS	120.19	0.00005
C10 AROMATICS	134.21	0.00004
FURAN	68.07	0.00049
DIOXANE	88.10	0.00009
ETHYL ALCOHOL	46.07	0.0055
N-PROPYL ALCOHOL	60.09	0.00012

TABLE 10 (Cont.)

888 CHARCOAL, STRIP 2, 160C

COMPOUND	MW	UG/G
N-BUTYL ALCOHOL	74.12	0.00013
ISOBUTYL ALCOHOL	74.12	0.0080
ACETONE	58.08	0.0029
METHYL ISOBUTYL KETONE	100.16	0.00059
ACETALDEHYDE	44.05	0.0018
SULFUR DIOXIDE	64.06	TRACE
	TOTAL	0.15876

TABLE 10 (Cont.)

888 CHARCOAL, STRIP 3, 160C

COMPOUND	MW	UG/G
METHYLENE CHLORIDE	84.94	0.00019
BUTANE	58.12	0.00009
1-PENTENE	70.13	0.00003
2-PENTENE	70.13	0.012
METHYLCYCLOPENTANE	84.11	0.00003
BENZENE	78.11	0.00075
TOLUENE	92.13	0.00059
METHYL ALCOHOL	32.04	0.0015
ETHYL ALCOHOL	46.07	0.00010
N-PROPYL ALCOHOL	60.09	0.00009
ISOPROPYL ALCOHOL	60.09	0.00019
ACETONE	58.08	0.0038
ACETALDEHYDE	44.05	TRACE
SULFUR DIOXIDE	64.06	TRACE
	TOTAL	0.01892

TABLE 10 (Cont.)

888 CHARCOAL, STRIP 4, 350C

COMPOUND	MW	UG/G
ETHANE	30.07	0.00029
BUTANE	58.12	0.00060
ETHYLENE	28.05	0.00024
PROPYLENE	42.08	0.00018
BENZENE	78.11	0.021
TOLUENE	92.13	0.0035
FURAN	68.07	0.00010
ETHYL ALCOHOL	46.07	0.0022
ISOPROPYL ALCOHOL	60.09	0.00034
ISOBUTYL ALCOHOL	74.12	0.00010
ACETONE	58.08	0.012
METHYL ISOBUTYL KETONE	100.16	0.0031
SULFUR DIOXIDE	64.06	TRACE
	TOTAL	0.04368

cooled to ambient temperature for 18 hours before again stripping at 160°C. The first two strippings had apparently resulted in relatively "clean" charcoal since the third desorption resulted in a total contaminant level of only 0. 02 ug/g consisting principally of Pentene 2. After cooling to ambient temperature for two hours, the charcoal was again desorbed, but at 350°C for one hour. The total contaminant level is still quite low, but is twice that desorbed from the third 160° strip. Fifty percent of this high temperature desorbate consists of benzene. It is interesting to note that sulfur dioxide was found to be present in all four of the desorbates, indicating a remarkable tenacity for this compound.

To compare the cumulative temperature cycling with a single high temperature strip, a second vacuum oven prepared sample was stripped at 350°C for one hour. Table 11 presents the result of this desorption. The total desorbed is 150% of the total removed from a similar sample by the four strippings described. This increase is primarily contained in a 30 fold increase in benzene, accompanied by appreciable increases in isoprene and methyl cyclopentane. Benzene accounted for 48% of the total desorbate, which compares remarkably well with the 46% benzene noted in the 350° strip of VG charcoal.

A sample of GI charcoal was prepared and vacuum desorbed with temperature cycling and the four stage stripping just described for the 888 charcoal. Table 12 shows a contaminant level from the second strip 68% of that indicated from the initial stripping, with benzene still accounting for 70% of the desorbate. The third stripping at 160°C, resulted in the closest approach to the ideal zero level of contamination yet obtained. There was no contamination noted except for a trace of benzene at a level far too low for quantitation. This same sample, cooled and restripped at 350°, showed a contamination level of 0. 05 μg/g, or roughly the level obtained from type 888 after the same treatment. Table 12 shows this contamination to be mainly attributable to a benzene increase to 0. 021 μg/g and to an unexplained

TABLE 11

RESIDUAL CONTAMINANTS FOUND ON TYPE 888 CHARCOAL REMOVED BY 350°C THERMAL-VACUUM STRIPPING

888 CHARCOAL, HIGH TEMPERATURE STRIP

COMPOUND	MW	UG/G
VINYLIDENE CHLORIDE	96.95	0.0083
PROPANE	44.09	0.0039
METHYLACETYLENE	40.07	0.00050
ISOPRENE	68.11	0.025
OCTYNE	110.20	0.0025
METHYLCYCLOPENTANE	84.11	0.051
METHYLCYCLOHEXANE	98.18	0.0093
BENZENE	78.11	0.26
TOLUENE	92.13	0.046
M-XYLENE	106.16	0.00008
O-XYLENE	106.16	TRACE
MESITYLENE	120.19	0.011
FURAN	68.07	0.0022
DIOXANE	88.10	0.00011
METHYLFURAN	82.10	0.00084
METHYL ALCOHOL	32.04	0.019
ETHYL ALCOHOL	46.07	0.043
ISOPROPYL ALCOHOL	60.09	0.00063
ACETONE	58.08	0.038
ACETALDEHYDE	44.05	0.0070
ACETONITRILE	41.05	0.0025
DIMETHYL SULFIDE	62.13	0.00073

TABLE 11 (Cont.)

888 CHARCOAL, HIGH TEMPERATURE STRIP

COMPOUND	MW	UG/G
SULFUR DIOXIDE	64.06	0.00004
	TOTAL	0.53721

TABLE 12

RESIDUAL COMTAMINANTS FOUND ON TYPE GI CHARCOAL REMOVED BY MULTIPLE STRIPPING

GI CHARCOAL, VACUUM OVEN PREPARED

COMPOUND	MW	UG/G
FREON 113	187.39	0.00098
TETRACHLOROETHYLENE	165.85	0.00010
VINYLIDENE CHLORIDE	96.95	0.00044
PROPANE	44.09	0.0058
BUTANE	58.12	0.010
METHYLACETYLENE	40.07	0.017
1-BUTENE	56.10	0.0038
METHYLCYCLOHEXANE	98.18	0.00059
BENZENE	78.11	1.4
TOLUENE	92.13	0.0068
O-XYLENE	106.16	0.00045
P-XYLENE	106.16	0.00002
MESITYLENE	120.19	0.00093
FURAN	68.07	0.00031
ETHYL ALCOHOL	46.07	0.0015
ACETONE	58.08	0.047
METHYL ISOBUTYL KETONE	100.16	0.0016
ACROLEIN	56.06	TRACE
ETHYL ACETATE	88.10	0.00004
	TOTAL	1.52086

TABLE 12 (Cont.)

GI CHARCOAL, STRIP 2, 160C

CCMPOUND	MW	UG/G
METHYLENE CHLORIDE	84.94	0.012
TETRACHLOROETHYLENE	165.85	0.0013
BUTANE	58.12	0.00022
METHYLACETYLENE	40.07	0.00041
1-BUTENE	56.10	0.00005
METHYLCYCLOHEXANE	98.18	0.064
BENZENE	78.11	0.71
TOLUENE	92.13	0.16
M-XYLENE	106.16	0.0015
O-XYLENE	106.16	0.00053
ETHYLBENZENE	106.16	0.0035
C9 AROMATICS	120.19	0.0055
FURAN	68.07	0.0038
METHYL ALCOHOL	32.04	0.011
ACETONE	58.08	0.071
	TOTAL	1.04431

TABLE 12 (Cont.)

GI CHARCOAL, STRIP 3, 160C

COMPOUND	MW	UG/G
	TOTAL	0.0

TABLE 12 (Cont.)

GI CHARCOAL, STRIP 4, 350C

COMPOUND	MW	UG/G
FREON 11	137.38	0.00013
FREON 113	187.39	0.017
1,1,1-TRICHLOROETHANE	133.42	0.00020
BUTANE	58.12	0.00026
METHYLACETYLENE	40.07	0.0020
OCTYNE	110.20	0.00037
METHYLCYCLOHEXANE	98.18	0.00022
BENZENE	78.11	0.021
TOLUENE	92.13	0.0090
FURAN	68.07	0.00041
ACETONE	58.08	0.00080
	TOTAL	0.05160

appearance of Freon 113 at a concentration of 0.017 µg/g. A 350°C stripping of vacuum oven prepared type GI charcoal was not performed.

The VG charcoal sample subjected to a vacuum oven preparation, followed by three successive strippings at 160°, followed by a fourth stripping at 350°C was left in storage in the sealed evacuated flask for one month after the fourth strip. It was then subjected to an additional 160°C strip. Table 13, containing the analysis of this stripping, shows this sample to still contain a residual contamination of 0.1 µg/g of which more than half is benzene. These data clearly indicate the improbability of completely stripping charcoal by these relatively gentle means.

It has been demonstrated that some polymerization on charcoal may be expected if it is heated above 150°C in air. This effect is probably minimized during moderately hard-vacuum rack stripping. However, charcoal as a catalyst is well documented, especially with trace metal salts present. Cocoanut charcoal, because of its plant origin contains a number of trace metals. Possibly the appearance of such large numbers of olefins, known to be rather active and subject to ready polymerization, may be explained by catalysis on charcoal.

E. MASS SPECTROMETRIC STUDIES OF GAS EVOLUTION

Concurrently with these studies, a series of tests using mass spectrometry for measuring gas evolution from small samples of charcoal were made. With this system, it was thought possible to follow total gas evolution, identify types of gas evolved, and determine the relative cleanliness of charcoals.

Small samples of charcoal were crushed in aluminum foil to avoid contamination, placed in a glass capillary within a ceramic probe, and inserted into the analytical section of a CEC 21-204 Mass Spectrometer. The capillary was temperature programmed and a recording of total ion current made as a function of the gas evolution. The area described by the curve represents the amount of gas evolved. While analyses can be made

TABLE 13

RESIDUAL CONTAMINANTS FOUND ON TYPE VG CHARCOAL AFTER MULTIPLE STRIPPING AND STORAGE UNDER VACUUM

VG CHARCOAL AFTER 4 WEEKS STORAGE IN VACUUM FLASK AFTER STRIPPING

COMPOUND	MW	UG/G
1,1,1-TRICHLOROETHANE	133.42	TRACE
PROPANE	44.09	.0059
BUTANE	58.12	.0091
PROPYLENE	42.08	.0086
1-BUTENE	56.10	.00044
2-BUTENE (CIS)	56.10	.0080
2-BUTENE (TRANS)	56.10	.00007
1-PENTENE	70.13	.0032
BENZENE	78.11	.059
TOLUENE	92.13	.00005
FURFURAL"	96.08	.00027
N-PROPYL ALCOHOL	60.09	.0026
ISOBUTYL ALCOHOL	74.12	.0015
ACETONE	58.08	.00008
	TOTAL	.09863

of the evolved products at selected times, only several scans were run for these tests. Figure No. 1 represents the results obtained without charcoal. The probe itself evolves a small amount of gas. At about 330°C the probe evolved high boiling substances from previous work. Figure No. 2 was a trial run in which a sample of Apollo Type AC charcoal was used. Large amounts of gas were given off. As the temperature increased, the rate of gas evolution decreased to a minimum near 170°C, then with a further temperature increase the rate of gas evolution again increased. The significance of these data are uncertain although the temperature programming was not as uniform as desired. An improvement in temperature control should be made if possible. Figure No. 3 is a repeat run on the same sample of charcoal used in Figure No. 2 and shows essentially no further desorption. The test shown in Figure No. 4 was designed to illustrate semiquantitative capabilities. Approximately 0.7 mg of Barnebey-Cheney VG charcoal "as received" was used. Figure No. 5 was obtained by using 2.9 mg of the same charcoal. These data show that about four times as much gas is being evolved from an equivalent increase in mass of charcoal. Again, the interpretation of the rise in gas evolution above 150°C is open to question. Figure No. 6 is a repeat of the sample used in Figure No. 5. For this test however, the sample was held at 300°C for 15 minutes.

Figure 7 shows the results of heating approximately 2.3 mg of Witco 199 charcoal in the mass spectrometer solids probe. The major gas evolved is SO_2. The relative amounts of SO_2 and the temperature are plotted as a function of time. This high SO_2 content prompted the removal of type 199 from further testing. Tables 14 and 15 have been included to illustrate the relative cleanliness of this charcoal. Figure 8 shows the curve for GI charcoal in which one of the major compounds has been tentatively identified as lauric acid, $CH_3(CH_2)_{10}COOH$. The mass spectrum is consistent with this identification and it would be a likely component of

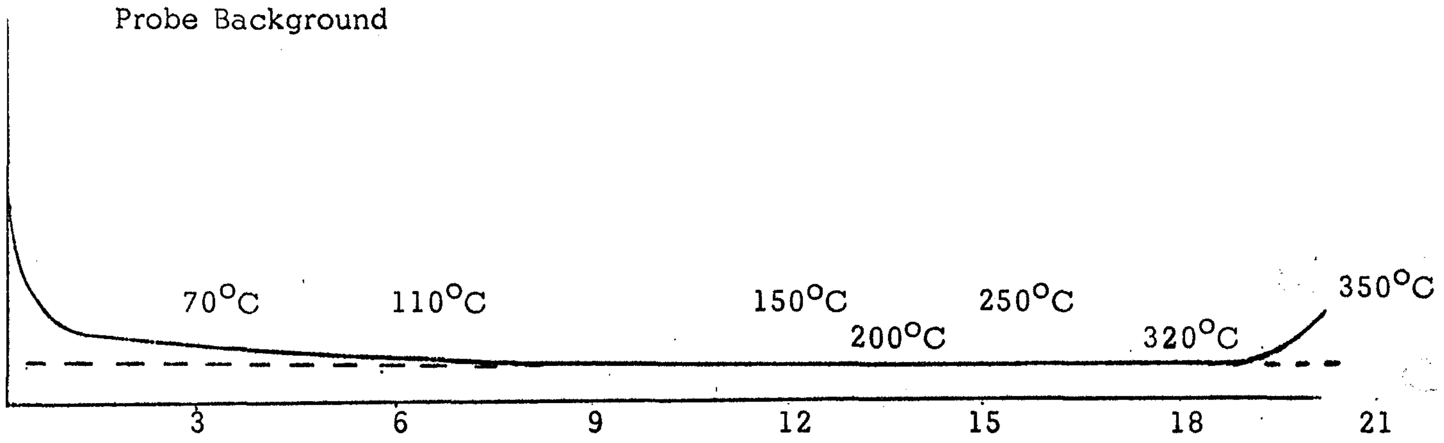

Probe Background

Figure 1

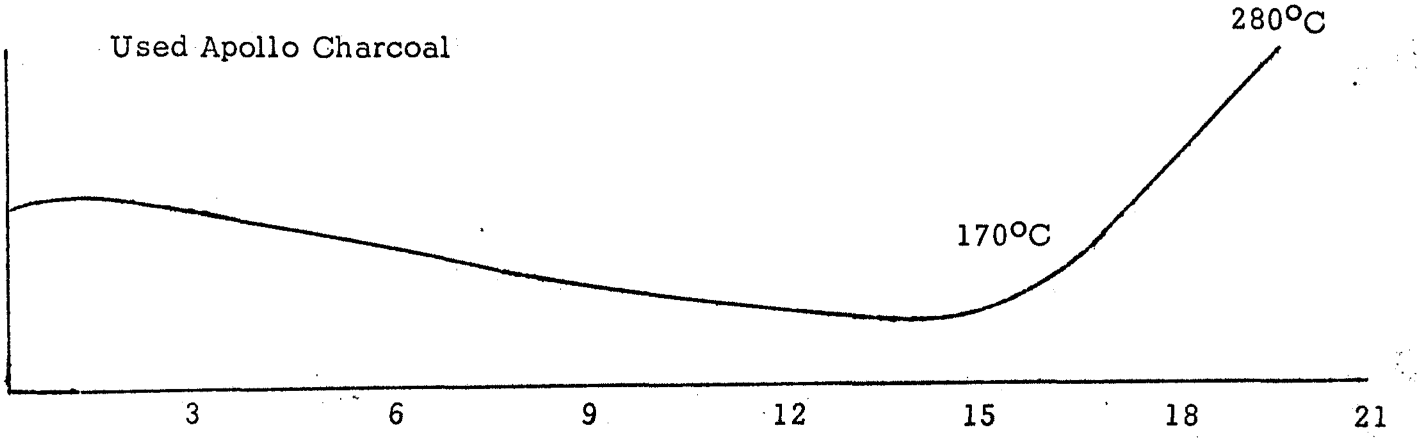

Used Apollo Charcoal

Figure 2

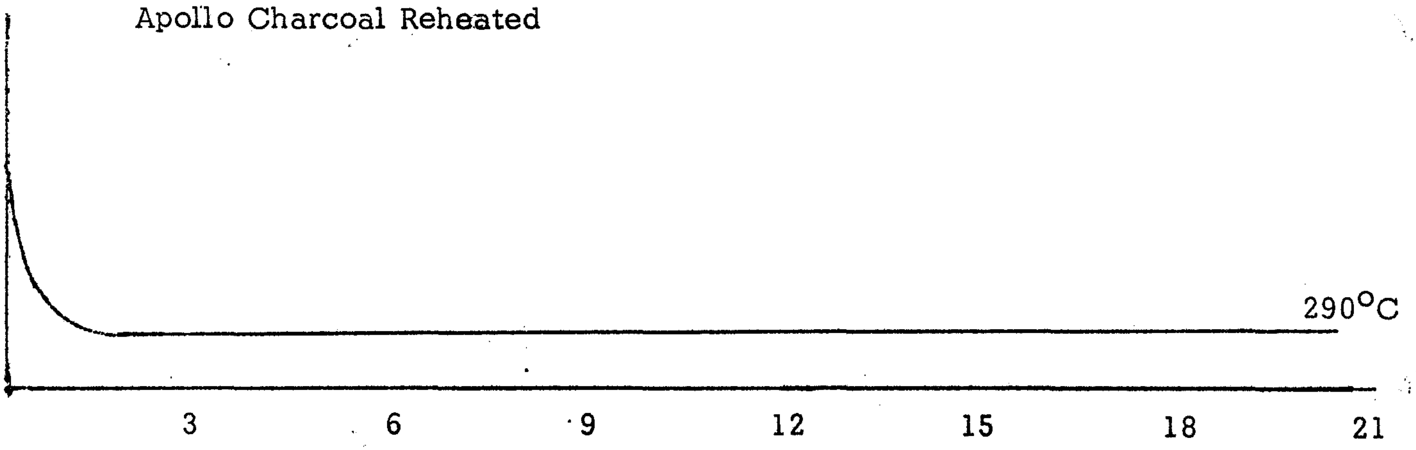

Apollo Charcoal Reheated

Figure 3

MS Total Ion Scans

0.7 mg VG Charcoal, as received

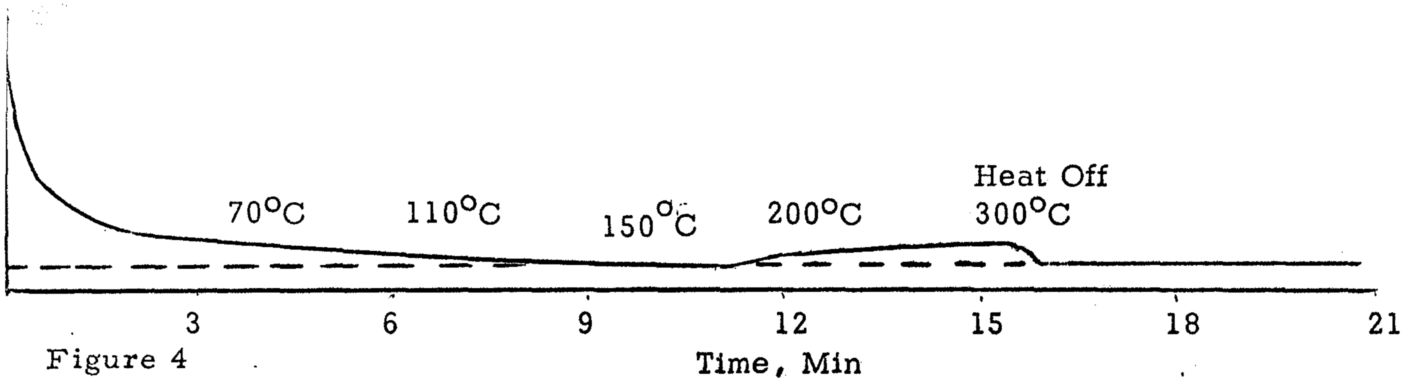


Figure 4

2.9 mg VG Charcoal, as received

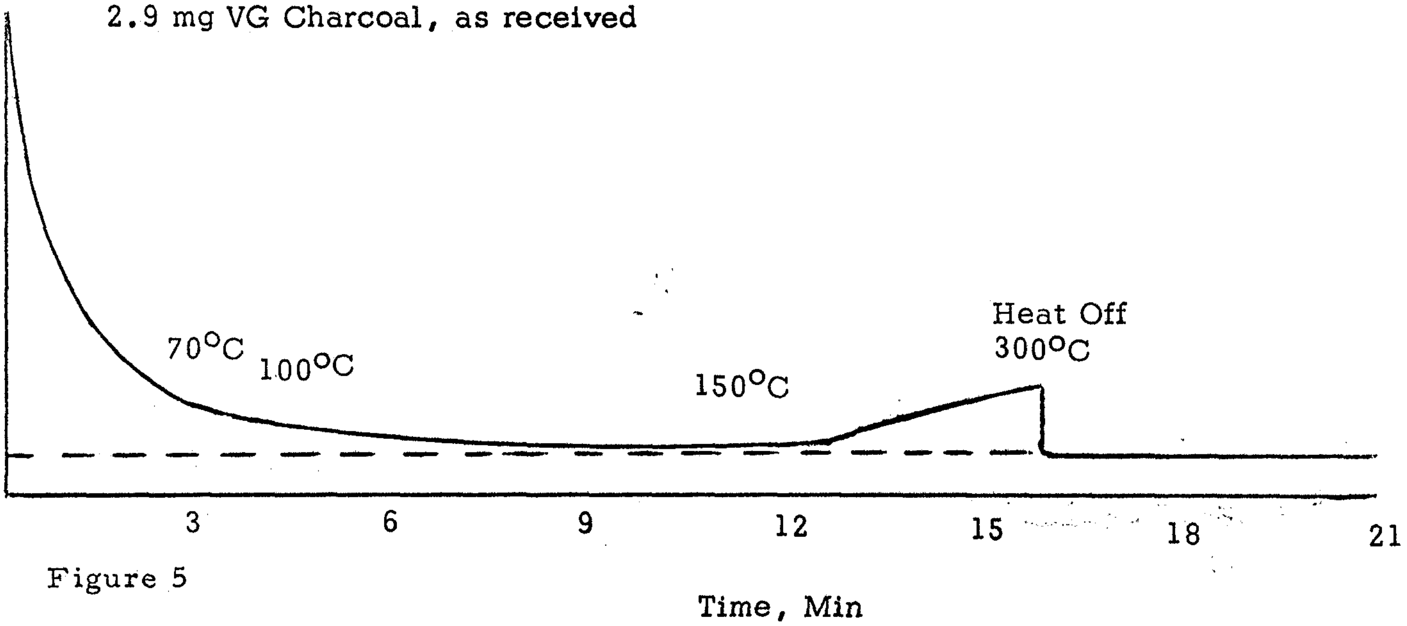


Figure 5

2.9 mg VG Charcoal, above sample reheated

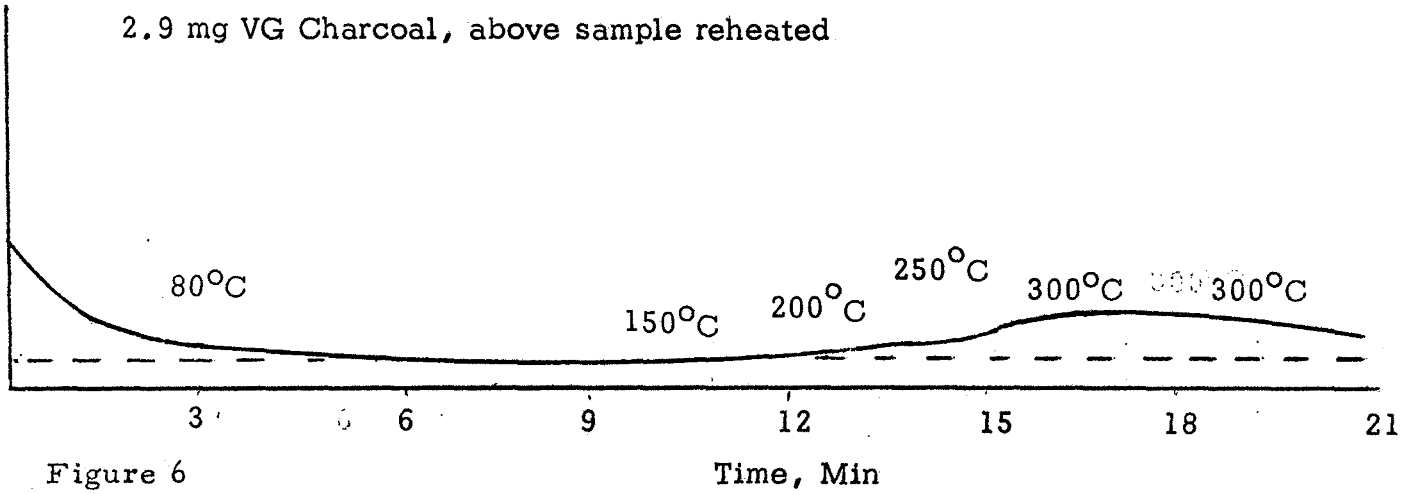


Figure 6

MS Total Ion Scans

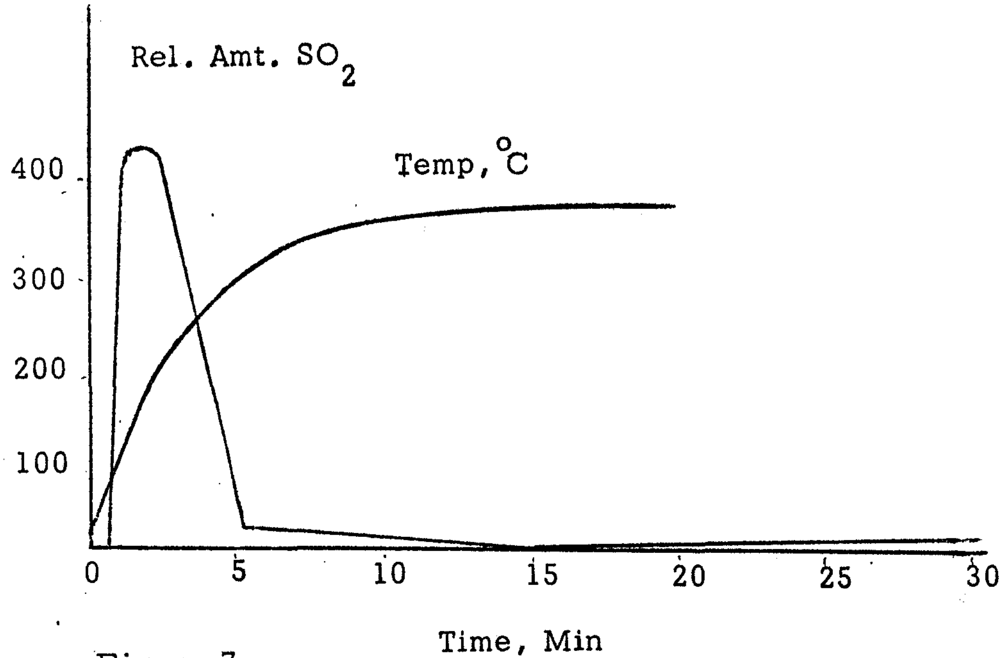


Figure 7

Evolution of SO_2 from Witco 199

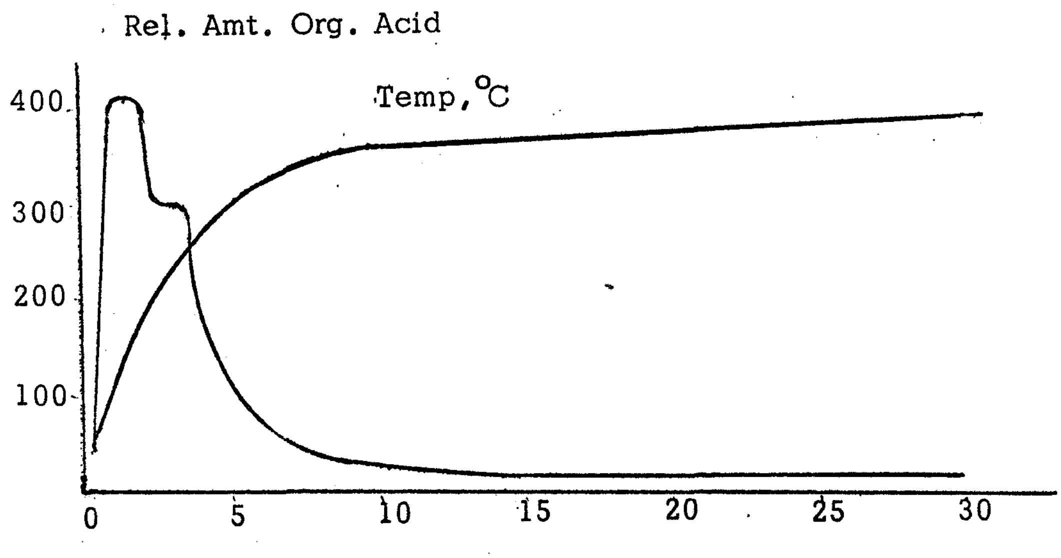


Figure 8

Evolution of Organic Acid (Lauric?) from GI Charcoal

TABLE 14

CONTAMINANTS FOUND ON AS RECEIVED WITCO 199 CHARCOAL

WITCO 199 AS RECEIVED

COMPOUND	MW	UG/G
FREON 11	137.38	0.63
FREON 113	187.39	1.3
1,1,1-TRICHLOROETHANE	133.42	0.0054
TRICHLOROETHYLENE	131.40	0.032
VINYLIDENE CHLORIDE	96.95	0.021
TRIFLUOROCHLOROETHYLENE	116.48	0.054
PROPANE	44.09	0.00012
ISOBUTANE	58.12	0.00011
N-HEPTANE	100.20	0.0024
TRIMETHYLHEXANE	128.26	0.0034
PROPYLENE	42.08	0.0037
METHYLACETYLENE	40.07	0.00035
1-BUTENE	56.10	0.013
2-BUTENE (CIS)	56.10	0.010
2-BUTENE (TRANS)	56.10	0.00033
1-PENTENE	70.13	0.017
ISOPRENE	68.11	0.024
METHYLCYCLOHEXANE	98.18	0.0023
BENZENE	78.11	0.050
TOLUENE	92.13	0.079
M-XYLENE	106.16	0.00004
FURAN	68.07	0.0024

TABLE 14 (Cont.)

WITCO 199 AS RECEIVED

COMPOUND	MW	UG/G
METHYL ALCOHOL	32.04	0.015
ETHYL ALCOHOL	46.07	0.0033
ISOPROPYL ALCOHOL	60.09	0.0031
ACETONE	58.08	0.071
METHYL ISOBUTYL KETONE	100.16	0.0071
ACETALDEHYDE	44.05	0.056
METHYL ACETATE	74.08	0.0030
ETHYL ACETATE	88.10	0.0061
SULFUR DIOXIDE	64.06	~ 1
	TOTAL	3.38141

TABLE 15

CONTAMINANTS FOUND ON WITCO 199 CHARCOAL AFTER VACUUM OVEN STRIPPING

WITCO 199 AFTER VAC OVEN -

COMPOUND	MW	UG/G
FREON 11	137.38	0.00073
FREON 113	187.39	0.00013
DIMETHYLDIFLUOROSILANE	96.16	0.00066
TRIFLUOROCHLOROETHYLENE	116.48	0.00010
PROPANE	44.09	0.0033
BUTANE	58.12	0.0027
PROPYLENE	42.08	0.0026
1-BUTENE	56.10	0.0019
2-BUTENE (CIS)	56.10	0.011
2-BUTENE (TRANS)	56.10	0.00005
CYCLOHEXANE	84.16	0.00023
BENZENE	78.11	0.00013
TOLUENE	92.13	0.00051
O-XYLENE	106.16	0.00004
C9 AROMATICS	120.19	0.0015
MESITYLENE	120.19	0.00017
C10 AROMATICS	134.21	0.0084
FURAN	68.07	0.00092
METHYL ALCOHOL	32.04	0.010
ETHYL ALCOHOL	46.07	0.0035
ACETONE	58.08	0.0011
SULFUR DIOXIDE	64.06	~ 1
	TOTAL	1.04971

cocoanut oil. Figure 9 shows the amount of CO_2 evolved from GI and AC charcoals as a function of temperature. Each data point is measured at approximately 10 minute intervals. The sample of charcoal (~1 g) was inserted in a special inlet on the CEC 21-130 mass spectrometer and heated under controlled conditions. Pressure was measured with a Wallace and Tiernan gauge. After each measurement the evolved gases were evacuated and analyzed on the mass spectrometer. After the first 2 data points the evolved gases were essentially pure CO_2.

These series of experiments indicate that the mass spectrometric studies on total gas evolution or of a specific compound can be a useful means of characterizing charcoal performance under controlled conditions.

F. LONG TERM STORAGE TESTS

To investigate storage methods for maintaining clean charcoal until ready for use, long term storage tests were instituted. One pound bulk samples of each charcoal were vacuum-oven treated for 18 hours at 165°C. Two samples of each type were placed under desiccator storage over anhydrous magnesium perchlorate (J. T. Baker's Anhydrone). One desiccator was flushed with nitrogen before sealing, while the other was evacuated to less than 5 microns before sealing. Bags were formed from Marvelseal B-117E by heat sealing rolled edges. Weighed samples were added to these bags under an inert atmosphere and the bags sealed, again using heat sealed rolled edges. The fourth storage system consisted of 1 quart size triple seal cans containing the bulk of the prepared charcoal under an inert atmosphere. As a control, 10 gram samples of each charcoal were sealed in glass ampoules under a nitrogen atmosphere. These samples were all subjected to 16 week's storage. Following appropriate exposure, these samples were transferred in a dry box with a nitrogen atmosphere to vacuum flasks for desorption at 160°C in the usual manner. The results from these storage tests are contained in Tables 16-19 but may be summarized as follows:

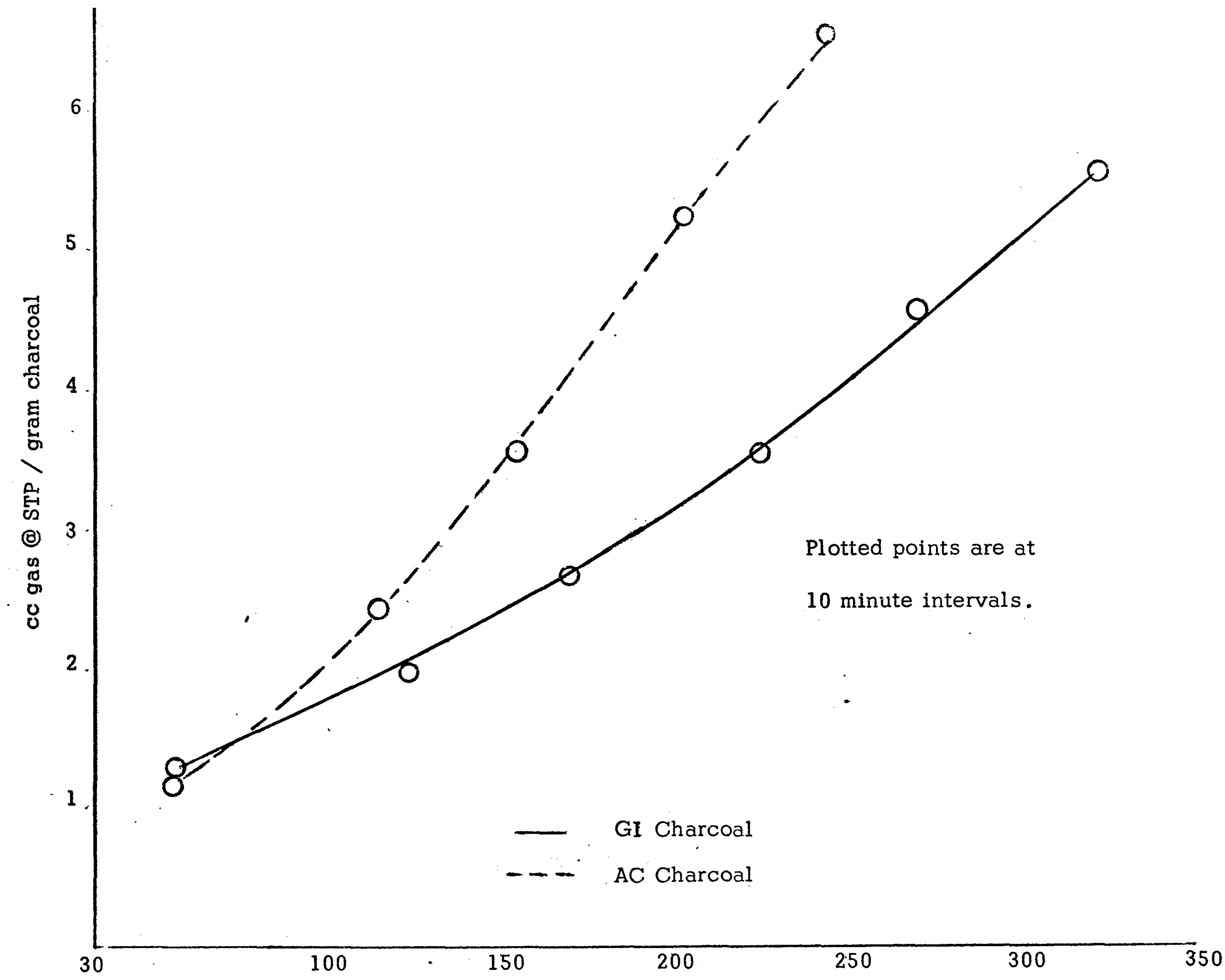


Figure 9

Figu

Gas Evolution vs Temperature for AC and GI Charcoals

Summary of Long Term Storage Results

(Total Residual Contamination, $\mu g/g$)

	Storage Method				
Charcoal Type	Marvel Seal	Triple Seal Can	Vac. Desiccator	Desiccator	Ampoule
AC	0.89	0.61	0.71	1.16	2.96
GI	0.41	0.69	1.64	2.75	6.11
VG	2.06	6.77	Lost	3.88	9.67
888	Lost	3.13	3.22	8.5	4.95

Two glass evacuated receivers containing the desorbates from one 888 sample and one VG sample were accidentally broken before the sample could be analyzed. The loss of these two samples was regrettable but did not affect the over all storage picture. As the above summary indicates, the paper backed marvel seal bag and the triple sealed can were about equal in ability to maintain low contamination levels. The samples stored in the desiccators were, with the exception of AC charcoal, all more contaminated than would normally be expected. It is probable, however, that these results reflect the relative adsorption potential of these charcoals. This observation is assuming that the higher level of desorbates were removed from the anhydrone desiccant which had not been degassed prior to use. The very high values for glass ampoule storage are unexplained except for residual contamination of the ampoule before use. The ampoules were new, clean, and dry, and were not knowingly exposed to solvents. The VG and GI charcoals both showed benzene as the most prominent contaminant, while acetone made up 50-90% of the desorbate from AC and 888 charcoals. As a control sample, ampoule storage was obviously unsuccessful.

TABLE 16

RESIDUAL CONTAMINANTS FROM AC CHARCOAL AFTER LONG TERM STORAGE TESTS

AC CHARCOAL, TRIPLE SEAL CAN STORAGE

COMPOUND	MW	UG/G
CHLOROFORM	119.39	.051
1,2-DICHLOROETHANE	98.97	.00027
TRIFLUOROCHLOROETHYLENE	116.48	.038
ETHANE	30.07	.00021
PROPANE	44.09	.0070
BUTANE	58.12	.023
ACETYLENE	26.04	.0043
ETHYLENE	28.05	.00057
METHYLACETYLENE	40.07	.014
1-BUTENE	56.10	.087
2-BUTENE (CIS)	56.10	.085
2-BUTENE (TRANS)	56.10	.010
1-PENTENE	70.13	.074
2-PENTENE	70.13	.036
ISOPRENE	68.11	.0066
2-HEXENE	84.16	.0038
BENZENE	78.11	0.100
ISOPROPYL ALCOHOL	60.09	.0051
ISOBUTYL ALCOHOL	74.12	.0080
ACETONE	58.08	.052
	TOTAL	.60729

TABLE 16 (Cont.)

AC CHARCOAL, MARVELSEAL B-117E BAG STORAGE

COMPOUND	MW	UG/G
VINYL CHLORIDE	62.50	.00029
VINYLIDENE CHLORIDE	96.95	.0090
DICHLOROBENZENE	147.01	.15
ETHANE	30.07	.00037
PROPANE	44.09	.016
BUTANE	58.12	.0012
ACETYLENE	26.04	.0048
ETHYLENE	28.05	.0065
METHYLACETYLENE	40.07	.0013
1-BUTENE	56.10	.028
2-BUTENE (CIS)	56.10	.013
2-BUTENE (TRANS)	56.10	.00007
1-PENTENE	70.13	.0030
ISOPRENE	68.11	.0033
2-HEXENE	84.16	.0085
METHYLCYCLOHEXANE	98.18	.029
BENZENE	78.11	.095
C10 AROMATICS	134.21	.00003
NAPHTHALENE	128.16	.0075
FURAN	68.07	.0052
DIOXANE	88.10	.029
METHYLFURAN	82.10	.0067

TABLE 16 (Cont.)

AC CHARCOAL, MARVELSEAL B-117E BAG STORAGE

COMPOUND	MW	UG/G
ACETONE	58.08	.030
METHYL ETHYL KETONE	72.10	.014
METHYL ISOBUTYL KETONE	100.16	.00056
ETHYL ACETATE	88.10	.43
	TOTAL	.88739

TABLE 16 (Cont.)

AC CHARCOAL, VACUUM DESICCATOR STORAGE OVER ANHYDRONE

COMPOUND	MW	UG/G
FREON 11	137.38	.074
METHYLENE CHLORIDE	84.94	.0097
METHYL CHLORIDE	50.49	.00003
1,1,1-TRICHLOROETHANE	133.42	.00035
TRICHLOROETHYLENE	131.40	.0050
VINYLIDENE CHLORIDE	96.95	.00007
TRIFLUOROCHLOROETHYLENE	116.48	.013
ETHANE	30.07	.00004
PROPANE	44.09	.00056
BUTANE	58.12	.0027
TRIMETHYLHEXANE	128.26	.00093
ACETYLENE	26.04	.0056
ETHYLENE	28.05	.0032
METHYLACETYLENE	40.07	.0010
1-BUTENE	56.10	.038
2-BUTENE (CIS)	56.10	.010
2-BUTENE (TRANS)	56.10	.00088
2-PENTENE	70.13	.00006
METHYLCYCLOHEXANE	98.18	.00054
BENZENE	78.11	.43
TOLUENE	92.13	.0011
M-XYLENE	106.16	.00008

TABLE 16 (Cont.)

AC CHARCOAL, VACUUM DESICCATOR STORAGE OVER ANHYDRONE

COMPOUND	MW	UG/G
O-XYLENE	106.16	.00009
P-XYLENE	106.16	.00009
MESITYLENE	120.19	.00002
FURAN	68.07	.0090
ETHYL ALCOHOL	46.07	.059
ISOBUTYL ALCOHOL	74.12	.0012
ACETONE	58.08	.043
METHYL ETHYL KETONE	72.10	.010
METHYL ISOBUTYL KETONE	100.16	.00007
	TOTAL	.71536

TABLE 16 (Cont.)

AC CHARCOAL, DESICCATOR STORAGE OVER ANHYDRONE AND UNDER N_2 ATOMOSPHERE

COMPOUND	MW	UG/G
METHYL CHLORIDE	50.49	.00019
1,1,1-TRICHLOROETHANE	133.42	.018
TRICHLOROETHYLENE	131.40	.0045
VINYLIDENE CHLORIDE	96.95	.00055
PROPANE	44.09	.0038
BUTANE	58.12	.0044
METHYLACETYLENE	40.07	.0023
1-BUTENE	56.10	.017
2-BUTENE (CIS)	56.10	.017
2-BUTENE (TRANS)	56.10	.00043
1-PENTENE	70.13	.0050
METHYLCYCLOHEXANE	98.18	.00056
BENZENE	78.11	.97
TOLUENE	92.13	.0036
P-XYLENE	106.16	.0028
C9 AROMATICS	120.19	.00031
C10 AROMATICS	134.21	.00003
FURAN	68.07	.023
METHYLFURAN	82.10	.0046
METHYL ALCOHOL	32.04	0.00010
ISOPROPYL ALCOHOL	60.09	.0035
N-BUTYL ALCOHOL	74.12	TRACE

TABLE 16 (Cont.)

AC CHARCOAL, DESICCATOR STORAGE OVER ANHYDRONE AND UNDER N_2 ATMOSPHERE

COMPOUND	MW	UG/G
ISOBUTYL ALCOHOL	74.12	.0017
ACETONE	58.08	.071
METHYL ETHYL KETONE	72.10	.0039
ACETONITRILE	41.05	.00020
	TOTAL	1.16025

TABLE 16 (Cont.)

AC CHARCOAL, GLASS AMPOULE STORAGE

COMPOUND	MW	UG/G
FREON 11	137.38	.031
1,2-DICHLOROETHANE	98.97	.0021
TRICHLOROETHYLENE	131.40	.0014
BUTANE	58.12	.0043
PROPADIENE	40.06	.00004
1-BUTENE	56.10	.0024
1-PENTENE	70.13	.0077
BENZENE	78.11	.016
TOLUENE	92.13	.029
M-XYLENE	106.16	.00002
O-XYLENE	106.16	.00082
P-XYLENE	106.16	.00065
INDENE	116.15	.00048
C10 AROMATICS	134.21	.00082
ETHYL ALCOHOL	46.07	.00075
N-BUTYL ALCOHOL	74.12	.00087
ACETONE	58.08	2.7
METHYL ETHYL KETONE	72.10	.10
METHYL ISOBUTYL KETONE	100.16	.0044
ETHYL ACETATE	88.10	.054
	TOTAL	2.95875

TABLE 17

RESIDUAL CONTAMINANTS FROM GI CHARCOAL AFTER LONG TERM STORAGE TESTS

GI CHARCOAL, MARVELSEAL B117E BAG STORAGE

COMPOUND	MW	UG/G
FREON 113	187.39	.0023
METHYLENE CHLORIDE	84.94	.084
TRICHLOROETHYLENE	131.40	.00027
TRIFLUOROCHLOROETHYLENE	116.48	.00088
PROPANE	44.09	.00004
BUTANE	58.12	.00015
HEXANE	86.17	.0012
PROPYLENE	42.08	.015
1-BUTENE	56.10	.021
2-BUTENE (CIS)	56.10	.00027
2-HEXENE	84.16	.00005
CYCLOPENTANE	70.13	.00012
METHYLCYCLOHEXANE	98.18	.012
BENZENE	78.11	.11
TOLUENE	92.13	.038
M-XYLENE	106.16	.00003
P-XYLENE	106.16	.00003
C9 AROMATICS	120.19	.00006
MESITYLENE	120.19	.00002
FURAN	68.07	.014
METHYL ALCOHOL	32.04	.021
ETHYL ALCOHOL	46.07	.018

TABLE 17 (Cont.)

GI CHARCOAL, MARVELSEAL B117E BAG STORAGE

COMPOUND	MW	UG/G
ISOPROPYL ALCOHOL	60.09	.028
ACETONE	58.08	.038
METHYL ETHYL KETONE	72.10	.00004
ETHYL ACETATE	88.10	.0038
	TOTAL	.40993

TABLE 17 (Cont.)

GI CHARCOAL, TRIPLE SEAL CAN STORAGE

COMPOUND	MW	UG/G
FREON 113	187.39	.00056
HEXAFLUOROETHANE	138.01	.0018
METHYLENE CHLORIDE	84.94	.027
TRICHLOROETHYLENE	131.40	.19
TETRAFLUOROCHLOROETHANE	136.52	.00045
TRIFLUOROCHLOROETHYLENE	116.48	.0088
ETHANE	30.07	.0059
BUTANE	58.12	.0054
ACETYLENE	26.04	.019
ETHYLENE	28.05	.012
PROPYLENE	42.08	.072
1-BUTENE	56.10	.0050
2-BUTENE (CIS)	56.10	.0017
2-BUTENE (TRANS)	56.10	.024
METHYLCYCLOHEXANE	98.18	.0036
BENZENE	78.11	.00054
TOLUENE	92.13	.025
O-XYLENE	106.16	.00011
P-XYLENE	106.16	.00003
C10 AROMATICS	134.21	.00007
FURAN	68.07	.012
METHYLFURAN	82.10	.10

TABLE 17 (Cont.)

GI CHARCOAL, TRIPLE SEAL CAN STORAGE

COMPOUND	MW	UG/G
ETHYL ALCOHOL	46.07	.034
ISOBUTYL ALCOHOL	74.12	.0023
ACETONE	58.08	.069
METHYL ETHYL KETONE	72.10	.058
ETHYL ACETATE	88.10	.018
ACETONITRILE	41.05	.00035
	TOTAL	.69407

TABLE 17 (Cont.)

GI CHARCOAL, VACUUM DESICCATOR STORAGE OVER ANHYDRONE

COMPOUND	MW	UG/G
CHLOROFORM	119.39	.0050
METHYLENE CHLORIDE	84.94	TRACE
1,1,1-TRICHLOROETHANE	133.42	.0088
TRICHLOROETHYLENE	131.40	.031
FLUOROCHLOROETHYLENE	80.50	.00035
PROPANE	44.09	.15
BUTANE	58.12	.0034
METHYLACETYLENE	40.07	TRACE
1-BUTENE	56.10	.0073
2-BUTENE (CIS)	56.10	.021
2-BUTENE (TRANS)	56.10	.0012
1-PENTENE	70.13	.094
2-PENTENE	70.13	.0017
ISOPRENE	68.11	.0013
METHYLCYCLOHEXANE	98.18	.030
BENZENE	78.11	.84
TOLUENE	92.13	.042
O-XYLENE	106.16	.0011
MESITYLENE	120.19	.0023
C10 AROMATICS	134.21	.00006
FURAN	68.07	.084
ETHYL ALCOHOL	46.07	.018

TABLE 17 (Cont.)

GI CHARCOAL, VACUUM DESICCATOR STORAGE OVER ANHYDRONE

COMPOUND	MW	UG/G
ISOPROPYL ALCOHOL	60.09	.0017
ISOBUTYL ALCOHOL	74.12	.0044
ACETONE	58.08	.28
METHYL ETHYL KETONE	72.10	.0057
ACETONITRILE	41.05	.012
	TOTAL	1.64132

TABLE 17 (Cont.)

GI CHARCOAL, DESICCATOR STORAGE OVER ANHYDRONE AND UNDER N_2 ATMOSPHERE

COMPOUND	MW	UG/G
1,1,1-TRICHLOROETHANE	133.42	.074
TRICHLOROETHYLENE	131.40	.012
BUTANE	58.12	.0074
1-BUTENE	56.10	.021
2-BUTENE (CIS)	56.10	.0016
2-BUTENE (TRANS)	56.10	.00021
1-PENTENE	70.13	.066
ISOPRENE	68.11	.011
2-HEXENE	84.16	.00037
METHYLCYCLOHEXANE	98.18	.046
BENZENE	78.11	1.7
TOLUENE	92.13	.11
P-XYLENE	106.16	.00048
C9 AROMATICS	120.19	.0057
FURAN	68.07	.11
DIOXANE	88.10	.00077
ETHYL ALCOHOL	46.07	.29
ISOPROPYL ALCOHOL	60.09	.0068
ISOBUTYL ALCOHOL	74.12	.046
ACETONE	58.08	.26
METHYL ETHYL KETONE	72.10	.0010
ACETONITRILE	41.05	.0083
	TOTAL	2.7469

TABLE 17 (Cont.)

GI CHARCOAL, GLASS AMPOULE STORAGE (N2 ATMOSPHERE)

COMPOUND	MW	UG/G
CHLOROFORM	119.39	.0072
METHYL CHLORIDE	50.49	.0029
TRICHLOROETHYLENE	131.40	0.100
TRIFLUOROCHLOROETHYLENE	116.48	1.4
ETHANE	30.07	TRACE
PROPANE	44.09	.00081
BUTANE	58.12	.074
TRIMETHYLHEXANE	128.26	.066
ACETYLENE	26.04	.23
ETHYLENE	28.05	.0072
METHYLACETYLENE	40.07	.0021
1-BUTENE	56.10	.048
2-BUTENE (CIS)	56.10	.58
2-BUTENE (TRANS)	56.10	.031
1-PENTENE	70.13	.066
ISOPRENE	68.11	.019
2-HEXENE	84.16	.032
CYCLOPENTANE	70.13	.013
METHYLCYCLOHEXANE	98.18	0.100
BENZENE	78.11	1.5
TOLUENE	92.13	.16
ETHYLBENZENE	106.16	.0014

TABLE 17 (Cont.)

GI CHARCOAL, GLASS AMPOULE STORAGE (N2 ATMOSPHERE)

COMPOUND	MW	UG/G
C9 AROMATICS	120.19	.18
C10 AROMATICS	134.21	.35
FURAN	68.07	.22
ETHYL ALCOHOL	46.07	.10
N-PROPYL ALCOHOL	60.09	.027
ISOPROPYL ALCOHOL	60.09	.082
N-BUTYL ALCOHOL	74.12	.0038
ISOBUTYL ALCOHOL	74.12	.30
ACETONE	58.08	.18
METHYL ETHYL KETONE	72.10	.18
METHYL ISOBUTYL KETONE	100.16	.00007
ETHYL ACETATE	88.10	.00070
BUTYL ACETATE	116.16	.00012
ACETONITRILE	41.05	TRACE
	TOTAL	6.11201

TABLE 18

RESIDUAL CONTAMINANTS FROM VG CHARCOAL AFTER LONG TERM STORAGE

VG CHARCOAL, MARVELSEAL B-117E BAG STORAGE

COMPOUND	MW	UG/G
CHLOROFORM	119.39	.00003
METHYL CHLORIDE	50.49	.00089
1,1,1-TRICHLOROETHANE	133.42	.026
TRICHLOROETHYLENE	131.40	.00022
TETRACHLOROETHYLENE	165.85	TRACE
VINYL CHLORIDE	62.50	.0045
CHLORODIFLUOROETHYLENE	98.50	.0047
ETHANE	30.07	.40
PROPANE	44.09	.29
BUTANE	58.12	.13
ISOBUTANE	58.12	.014
2,2,5-TRIMETHYLHEXANE	128.26	.0056
ACETYLENE	26.04	.012
ETHYLENE	28.05	.0022
PROPADIENE	40.06	.00043
METHYLACETYLENE	40.07	.32
1-BUTENE	56.10	.053
2-BUTENE (CIS)	56.10	.11
2-BUTENE (TRANS)	56.10	.019
1-PENTENE	70.13	.0021
ISOPRENE	68.11	.0014
2-HEXENE	84.16	.0011

TABLE 18 (Cont.)

VG CHARCOAL, MARVELSEAL B-117E BAG STORAGE

COMPOUND	MW	UG/G
METHYLCYCLOPENTANE	84.11	.0085
METHYLCYCLOHEXANE	98.18	.0015
BENZENE	78.11	.54
TOLUENE	92.13	.039
M-XYLENE	106.16	.00069
O-XYLENE	106.16	.00026
P-XYLENE	106.16	.0012
C9 AROMATICS	120.19	.0053
FURAN	68.07	.020
DIOXANE	88.10	.00001
ISOBUTYL ALCOHOL	74.12	.0027
ACETONE	58.08	.029
BUTYL ACETATE	116.16	.00058
ACETONITRILE	41.05	.0095
	TOTAL	2.06293

TABLE 18 (Cont.)

VG CHARCOAL, TRIPLE SEAL CAN STORAGE

COMPOUND	MW	UG/G
METHYLENE CHLORIDE	84.94	.0042
TRICHLOROETHYLENE	131.40	.073
TRIFLUOROCHLOROETHYLENE	116.48	.31
FLUOROCHLOROETHYLENE	80.50	.0013
ETHANE	30.07	.23
PROPANE	44.09	.066
BUTANE	58.12	.082
TRIMETHYLHEXANE	128.26	.0068
ACETYLENE	26.04	.063
ETHYLENE	28.05	.15
METHYLACETYLENE	40.07	TRACE
1-BUTENE	56.10	.16
2-BUTENE (CIS)	56.10	.11
2-BUTENE (TRANS)	56.10	.017
1-PENTENE	70.13	.099
ISOPRENE	68.11	.040
2-HEXENE	84.16	.073
METHYLCYCLOHEXANE	98.18	.0040
BENZENE	78.11	.42
TOLUENE	92.13	.013
C9 AROMATICS	120.19	.00020
C10 AROMATICS	134.21	.00020

TABLE 18 (Cont.)

VG CHARCOAL, TRIPLE SEAL CAN STORAGE.

COMPOUND	MW	UG/G
FURAN	68.07	.011
ISOPROPYL ALCOHOL	60.09	.049
ISOBUTYL ALCOHOL	74.12	.037
ACETONE	58.08	4.7
METHYL ETHYL KETONE	72.10	.014
ACETONITRILE	41.05	.013
	TOTAL	6.76948

TABLE 18 (Cont.)

VG CHARCOAL, DESICCATOR STORAGE OVER ANHYDRONE AND UNDER N_2 ATMOSPHERE

COMPOUND	MW	UG/G
FREON 11	137.38	.57
FREON 113	187.39	1.6
CHLOROFORM	119.39	.022
METHYL CHLORIDE	50.49	.00031
1,1,1-TRICHLOROETHANE	133.42	.23
TRICHLOROETHYLENE	131.40	.099
ETHANE	30.07	.00081
PROPANE	44.09	.026
BUTANE	58.12	.034
ACETYLENE	26.04	.0081
PROPYLENE	42.08	.056
METHYLACETYLENE	40.07	.00001
1-BUTENE	56.10	.043
2-BUTENE (CIS)	56.10	.085
2-BUTENE (TRANS)	56.10	.013
2-HEXENE	84.16	.0016
METHYLCYCLOHEXANE	98.18	.063
BENZENE	78.11	.42
TOLUENE	92.13	.060
P-XYLENE	106.16	.00003
C9 AROMATICS	120.19	.0049
C10 AROMATICS	134.21	.00005

TABLE 18 (Cont.)

VG CHARCOAL, DESICCATOR STORAGE OVER ANHYDRONE AND UNDER N_2 ATMOSPHERE

COMPOUND	MW	UG/G
FURAN	68.07	.032
DIOXANE	88.10	TRACE
ETHYL ALCOHOL	46.07	.043
ISOBUTYL ALCOHOL	74.12	.0067
ACETONE	58.08	.48
METHYL ETHYL KETONE	72.10	.00031
ACETONITRILE	41.05	.0053
	TOTAL	3.88452

TABLE 18 (Cont.)

VG CHARCOAL, GLASS AMPOULE STORAGE (N2 ATMOSPHERE)

COMPOUND	MW	UG/G
FREON 11	137.38	.64
FREON 21	102.92	.039
FREON 113	187.39	.00021
METHYL CHLORIDE	50.49	.00087
1,1,1-TRICHLOROETHANE	133.42	.18
TRICHLOROETHYLENE	131.40	.98
TRIFLUOROCHLOROETHYLENE	116.48	.47
ETHANE	30.07	.018
PROPANE	44.09	.36
BUTANE	58.12	.50
ACETYLENE	26.04	.0023
METHYLACETYLENE	40.07	.00059
1-BUTENE	56.10	.18
2-BUTENE (CIS)	56.10	.51
2-BUTENE (TRANS)	56.10	.088
ISOPRENE	68.11	.66
2-HEXENE	84.16	.00052
STYRENE	104.14	.0012
METHYLCYCLOHEXANE	98.18	.068
BENZENE	78.11	3.0
TOLUENE	92.13	.23
M-XYLENE	106.16	.015

TABLE 18 (Cont.)

VG CHARCOAL, GLASS AMPOULE STORAGE (N2 ATMOSPHERE)

COMPOUND	MW	UG/G
O-XYLENE	106.16	.0074
P-XYLENE	106.16	.031
ETHYLBENZENE	106.16	.00002
C9 AROMATICS	120.19	.13
C10 AROMATICS	134.21	.013
FURAN	68.07	.053
ETHYL ALCOHOL	46.07	.011
ISOPROPYL ALCOHOL	60.09	.35
ISOBUTYL ALCOHOL	74.12	.048
ACETONE	58.08	.88
METHYL ETHYL KETONE	72.10	.11
ETHYL ACETATE	88.10	.070
ACETONITRILE	41.05	.056
	TOTAL	9.66855

TABLE 19

RESIDUAL CONTAMINANTS FROM 888 CHARCOAL AFTER LONG TERM STORAGE

888 CHARCOAL, TRIPLE SEAL CAN STORAGE

COMPOUND	MW	UG/G
FREON 113	187.39	2.7
METHYLENE CHLORIDE	84.94	.0033
TRICHLOROETHYLENE	131.40	.0030
TRIFLUOROCHLOROETHYLENE	116.48	.0059
ETHANE	30.07	.015
PROPANE	44.09	.0018
BUTANE	58.12	.0014
ACETYLENE	26.04	.00061
ETHYLENE	28.05	.0052
PROPYLENE	42.08	.0043
1-BUTENE	56.10	.0016
2-BUTENE (CIS)	56.10	.0020
2-BUTENE (TRANS)	56.10	.00087
ISOPRENE	68.11	.0016
METHYLCYCLOPENTANE	84.11	TRACE
BENZENE	78.11	.13
TOLUENE	92.13	.13
M-XYLENE	106.16	.00002
O-XYLENE	106.16	.00004
FURAN	68.07	.00007
ETHYL ALCOHOL	46.07	.012
ISOPROPYL ALCOHOL	60.09	.0025

TABLE 19 (Cont.)

888 CHARCOAL, TRIPLE SEAL CAN STORAGE

COMPOUND	MW	UG/G
ISOBUTYL ALCOHOL	74.12	.010
ACETONE	58.08	.030
METHYL ETHYL KETONE	72.10	.037
METHYL ACETATE	74.08	.00026
ETHYL ACETATE	88.10	.0018
SULFUR DIOXIDE	64.06	.00002
	TOTAL	3.13423

TABLE 19 (Cont.)

888 CHARCOL, VACUUM DESICCATOR STORAGE OVER ANHYDRONE

COMPOUND	MW	UG/G
FREON 11	137.38	.50
FREON 113	187.39	.19
METHYLENE CHLORIDE	84.94	.37
1,1,1-TRICHLOROETHANE	133.42	.19
TRICHLOROETHYLENE	131.40	.085
ETHANE	30.07	.00017
PROPANE	44.09	.00032
BUTANE	58.12	.0036
PROPADIENE	40.06	.00059
1-BUTENE	56.10	.041
2-BUTENE (CIS)	56.10	.072
2-BUTENE (TRANS)	56.10	.0055
1-PENTENE	70.13	.011
ISOPRENE	68.11	.40
METHYLCYCLOHEXANE	98.18	.013
BENZENE	78.11	.046
TOLUENE	92.13	.021
M-XYLENE	106.16	.0012
C9 AROMATICS	120.19	.0017
FURAN	68.07	.018
DIOXANE	88.10	.0037
ETHYL ALCOHOL	46.07	.061

TABLE 19 (Cont.)

888 CHARCOL, VACUUM DESICCATOR STORAGE OVER ANHYDRONE

COMPOUND	MW	UG/G
N-PROPYL ALCOHOL	60.09	.00053
ISOPROPYL ALCOHOL	60.09	.041
ISOBUTYL ALCOHOL	74.12	.0038
ACETONE	58.08	1.1
METHYL ETHYL KETONE	72.10	.058
METHYL ISOBUTYL KETONE	100.16	.00070
ETHYL ACETATE	88.10	.026
SULFUR DIOXIDE	64.06	TRACE
	TOTAL	3.21927

TABLE 19 (Cont.)

888 CHARCOAL, DESICCATOR STORAGE OVER ANHYDRONE AND UNDER N_2 ATMOSPHERE

COMPOUND	MW	UG/G
ETHYL FLUORIDE	48.06	.00051
1,1,1-TRICHLOROETHANE	133.42	TRACE
TRICHLOROETHYLENE	131.40	.39
ETHANE	30.07	.034
PROPANE	44.09	.035
BUTANE	58.12	.19
ISOPENTANE	72.15	.0024
ACETYLENE	26.04	.0041
ETHYLENE	28.05	.035
PROPYLENE	42.08	.27
METHYLACETYLENE	40.07	.022
1-BUTENE	56.10	3.2
2-BUTENE (TRANS)	56.10	.086
1-PENTENE	70.13	.40
ISOPRENE	68.11	.042
2-HEXENE	84.16	.070
METHYLCYCLOHEXANE	98.18	.079
BENZENE	78.11	.28
TOLUENE	92.13	.12
M-XYLENE	106.16	.0070
O-XYLENE	106.16	.00059
P-XYLENE	106.16	.00002

TABLE 19 (Cont.)

888 CHARCOAL, DESICCATOR STORAGE OVER ANHYDRONE AND UNDER N_2 ATMOSPHERE

COMPOUND	MW	UG/G
ETHYLBENZENE	106.16	TRACE
C10 AROMATICS	134.21	.013
FURAN	68.07	.013
DIOXANE	88.10	.030
METHYL ALCOHOL	32.04	1.5
ETHYL ALCOHOL	46.07	.80
ISOPROPYL ALCOHOL	60.09	.20
ISOBUTYL ALCOHOL	74.12	.011
ACETONE	58.08	.55
METHYL ETHYL KETONE	72.10	.063
METHYL ISOBUTYL KETONE	100.16	.061
ETHYL ACETATE	88.10	.0023
ACETONITRILE	41.05	.080
	TOTAL	8.54191

TABLE 19 (Cont.)

888 CHARCOAL, GLASS AMPOULE STORAGE

COMPOUND	MW	UG/G
CHLOROFORM	119.39	.25
METHYL CHLORIDE	50.49	.049
1,1,1-TRICHLOROETHANE	133.42	.22
ETHANE	30.07	.058
PROPANE	44.09	.24
ACETYLENE	26.04	.0040
PROPYLENE	42.08	.0045
METHYLACETYLENE	40.07	.053
1-PENTENE	70.13	.030
2-PENTENE	70.13	.38
ISOPRENE	68.11	.069
2-HEXENE	84.16	.28
CYCLOPENTANE	70.13	.0040
CYCLOHEXANE	84.16	.16
BENZENE	78.11	.19
FURAN	68.07	.067
ISOPROPYL ALCOHOL	60.09	.18
ISOBUTYL ALCOHOL	74.12	.037
ACETONE	58.08	2.4
METHYL ETHYL KETONE	72.10	.067
ETHYL ACETATE	88.10	.084
SULFUR DIOXIDE	64.06	.089
	TOTAL	4.9531

A more accelerated storage test was performed on the cloth backed metallized bags used to wrap Apollo canisters. Samples of each of the four charcoals were sealed in bags made by rolling and heat sealing the edges in the same way in which the Marvel Seal bags were made. These bags were placed in a desiccator over an open petri dish containing equal parts of ethylene dichloride, n-pentane, and tetrahydrofuran for one week. The adsorption through these bags was so great that quantitation was not attempted with the desorbates. It was noted that the metallizing had broken away from the cloth whenever the material was creased, folded, or bent over a sharp radius. As a non-permeable cover for charcoal samples, this material appears to be unsuitable.

G. COMPOUND CONVERSION STUDY

The continued appearance of appreciable quantities of C_2-C_4 hydrocarbons, a myriad of halogenated hydrocarbons, and the results listed earlier in this report on the MIBK stripping strongly imply that compound conversions must be occurring on the charcoal, either directly during adsorption or through the influence of heat during stripping procedure.

To demonstrate this conversion, and air mixture of approximately 7 ft^3 @ 1500 psig containing 1 cc of equal parts (by volume) of methyl ethyl ketone, methyl isobutyl ketone, and Freon 113 (contaminated with a small quantity of isopropyl alcohol) was prepared. To this mixture, a quantity of propadiene approximately equal to the weight of Freon 113 was added. These materials were selected to insure that double bonding was present to make fragmenting easier and, of course, to provide the compound suspected as being the parent of the majority of halogenated compounds found in the Apollo studies.

Fresh vacuum oven stripped samples of 888 and AC charcoals were obtained. Two stainless steel tubes approximately 4" in length by 1/2" in diameter were packed with each charcoal type. These tubes contained nominally 3 grams of 888 and 4 grams of AC charcoal. The charcoal was retained with glass wool plugs on either end. To one end of each tube, a micrometer valve was attached. The other end of the tube was attached to a manifold and, in turn, attached to the sample gas bottle. The flow rate through each tube was adjusted to 250 cc/min. The prepared sample was exhausted after 4 hours' flow time, indicating 60 liters of gas had flowed through each charcoal sample. The valves were closed and the sample tubes were returned to a dry box for transfer to stripping flasks. Stripping was performed at 160°C in the usual manner on one sample of each charcoal, and at 350°C on the other sample. The selection of the two stripping temperatures was to determine whether the higher temperature caused greater compound conversion. These samples were each run by g. c. with mass spectrometer peak scanning for positive identification. To insure that the fraction alloted to the mass spectrometer was large enough to be readily seen, a large fraction of the desorbate was run each time. This sized sample caused overloading of the electrometer system of the gas chromatograph, rendering quantitation somewhat questionable, but did allow positive mass spectrometric identity. The number and apparent quantity of compounds apparently formed were greater than had been anticipated.

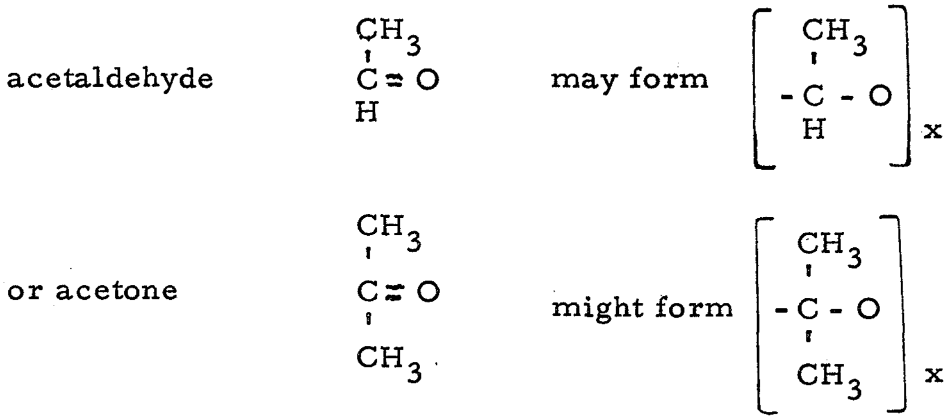
To verify the reproducibility of these data, a second gas sample, slightly more dilute than the first, on a second set of charcoals was prepared and run. These samples were desorbed and analyzed in the same manner as before.

Table 20 contains the listing of those compounds removed from the charcoal samples other than those comprising the test gas mixture. The compound recovered in greatest abundance is trifluorochloroethylene. This compound appears regularly in Apollo canister studies and must stem from Freon 113. Trifluoroethylene and 3- chloropropene were found in nearly all samples. Dichlorodifluoroethylene and chlorofluoroethylene were found on type AC charcoal only.

Even though isopropyl alcohol was a part of the test gas, it was present only as a minor contaminant of Freon 113. The quantity recovered in 7 out of the 8 samples was up to 1000 times the quantity added.

Butane and the butenes are regularly present in vacuum-oven cleaned charcoal, but in levels below 0.1 ug total in charcoal samples of this size. These values were greater by factors of up to 10,000 in all eight samples for the butenes, and in 6 samples for butane. Ethane, ethylene, acetylene, and the others of these lighter hydrocarbons were present in most samples, but at levels of questionable significance.

The acetone-acetaldehyde values were both elevated, and the fact that they were not found together on any one charcoal column may be significant. In nearly any case where a double bond can be converted to a single one, polymerization probably occurs. Thus,



acetaldehyde $\overset{CH_3}{\underset{H}{C}}=O$ may form $\left[-\overset{CH_3}{\underset{H}{C}}-O\right]_x$

or acetone $\overset{CH_3}{\underset{CH_3}{C}}=O$ might form $\left[-\overset{CH_3}{\underset{CH_3}{C}}-O\right]_x$

which may be a significant type of reaction in the appearance or absence of aldehydes or ketones.

A signal identified by mass spectrometric examination as ethylene oxide was noted only on the AC charcoals stripped at 350°C.

As stated, the concentration of test gas was so great that peaks could not be easily quantitated and resolution suffered badly. These conditions were chosen, however, to provide an overabundance of material for reactants, and to insure that these would be sufficiently large signals for unequivocal mass spectrometric identification.

While the quantity of apparently newly formed compounds was greater at 350° stripping than at 160°, they were not significantly

TABLE 20

COMPOUNDS, OTHER THAN TEST GAS, RECOVERED FROM CHARCOAL, ($g \times 10^{-6}$)

	Run 1				Run 2			
	Type AC		Type 888		Type AC		Type 888	
	160°	350°	160°	350°	160°	350°	160°	350°
Trifluoroethylene	1.12	0.70	0.0046	0.037	-	3.7	2.0	0.61
3-Chloropropene	21.5	43.6	7.25	55.6	35.2	102.	2.3	4.5
Trifluorochloroethylene	279.	3075.	247.	1010.	387.	354.	240.	399.
Dichlorodefluoroethylene	0.012	0.70	-	-	0.66	41.	-	-
Chlorofluoroethylene	0.40	-	-	-	-	6.3	-	-
Ethane	0.43	0.36	0.022	5.56	-	2.8	0.28	17.4
Butane	11.2	15.2	1.48	-	-	7.4	22.3	2.82
Isobutane	0.60	-	-	-	-	-	-	-
Acetylene	0.47	0.45	0.01	0.052	-	2.3	0.035	1.02
Ethylene	0.29	0.97	0.028	-	-	5.6	4.5	-
Propylene	-	-	-	-	24.2	-	-	-
1-Butene	23.6	3.18	3.62	7.7	9.2	44.5	1.20	14.4
2-Butene (cis)	18.5	2.91	15.8	10.8	29.4	102.	5.51	0.69
2-Butene (trans)	-	-	-	-	-	-	13.	-
1-Pentene	-	-	-	-	-	-	29.	-
2-Pentene	-	-	-	-	-	-	24.	-
Isopropyl alcohol*	125.	48.	362.	944.	158.	-	64.	69.
Isobutyl alcohol	-	-	-	-	-	-	2.0	-

---

*Isopropyl alcohol was added but in much lower quantity.

TABLE 20 (Cont.)

	Run 1				Run 2			
	Type AC		Type 888		Type AC		Type 888	
	160°	350°	160°	350°	160°	350°	160°	350°
Acetone	-	9.7	-	90.	40.5	-	-	-
Acetaldehyde	125.	-	17.5	-	-	-	-	-
Ethylene oxide	-	103.	-	-	-	91.	-	-
Wt. Charcoal, g	4.3	5.4	3.3	3.1	4.4	5.7	2.9	3.0

greater to conclude that stripping temperature initiates these compound changes. For further evidence, recovery studies made on charcoal held at 25°C and at 50°C provided some additional substantiation.

The formation of so many compounds in significant quantity using a simple gas mixture immediately offers a probable explanation for the many halogenated materials as well as compounds not readily associated with human habitation or the Apollo spacecraft found in the Apollo breathing canister desorption studies, as well as offering a plausible reason for the lack of some compounds that might reasonably be expected. At the same time, it becomes evident that only an involved computer study could trace all of these compounds through the many possible chemical reactions to obtain the parent compound and a true atmospheric profile.

A minimal effort was made to determine whether trichloroethylene, $CHCl{=}CCl_2$, reacts readily with AC charcoal and lithium hydroxide. The following mixtures were sealed in glass capillary tubes:

1. AC charcoal
2. AC charcoal and trichloroethylene
3. AC charcoal and lithium hydroxide
4. Lithium hydroxide and trichloroethylene
5. AC charcoal, lithium hydroxide, and trichloroethylene

These mixtures were maintained at room temperature for 48 hours, then heated to 170°C for 30 minutes just prior to mass spectrometric analysis of the gas phase. No evidence of dichloroacetylene was noted at M. S. detection levels. These tests were not run under dynamic conditions, and in the absence of carbon dioxide, water, or other halogen or hydrocarbon materials, therefore it can only be stated that trichloroethylene does not readily react with lithium hydroxide or AC charcoal.

H. DEVELOPMENT OF ADSORPTION ISOTHERMS AND MATHEMATICAL MODELING

The analysis of the adsorption of air-borne contaminants on a charcoal bed is identical to the analysis required for gas-solid chromatography. The charcoal bed is considered to be a chromatographic column on which a "frontal analysis" is being made. The column is considered to be clean at the outset when an air flow containing a mixture of contaminants is started through the column. In the ideal case, the exit gas will be clean for a certain length of time, after which there will be a sudden "step" in which the least strongly adsorbed contaminant is evolved. This will be followed by another "step" in which a mixture of the two least strongly adsorbed contaminants are evolved. A series of steps ensues until the adsorbent is completely saturated and the composition of the exit gas equals the composition of the input gas. The charcoal no longer serves its purpose as an air purifier when the first breakthrough occurs. Some discussion of the mathematics involved follows:

The equations for the concentration profile of adsorbates on an adsorbent bed as a function of time and distance, have only been solved for specific examples. However, certain specific assumptions lead to great simplification of the equations. The following development is based on the derivations in Hougen and Watson (Reference 11), amended for multi-component systems.

If longitudinal diffusion is negligible compared to the gas flow rate, then a system of "n" equations can be written, one for each component:

$$(1) \quad G y_i dt = G\left(y_i + \frac{\partial y_i}{\partial z} dz\right) dt + p_B dz \frac{\partial w_i}{\partial t} dt + p_G F_e \frac{\partial y_i}{\partial t} dt\, dz$$

This equation represents the material balance for a section of bed of thickness "dz," and unit cross sectional area where,

G = mass velocity of carrier gas, g/cm^2-sec
p_B = bulk density of charcoal adsorbent, g/cm^3
p_G = gas density, g/cm^3
F_e = external void fraction of bed
t = time, sec
w_i = adsorbate content of component "i" on charcoal, g/g solid

y_i adsorbate content of component "i" in gas, g/g carrier
z distance in bed in direction of flow, cm.

The first term (to the left of the equal sign) in equation (1) represents the mass of component "i" entering the volume element of charcoal in time dt, the second term represents the mass leaving, the third represents the change in the amount present on the solid and the fourth term represents the change in quantity in the gas phase.

For the case of steady flow where the pore volume of the bed is negligible, compared to the volume of gas which has been passed through the bed, the last term can be dropped. Then equation (1) can be rewritten:

$$(2) \quad -G \frac{\partial y_i}{\partial z} = p_B \frac{\partial w_i}{\partial t}$$

This is the general equation that must be solved. Now assumptions concerning the kinetics of adsorption must be made. Frequently it can be assumed that the rate of adsorption is proportional to the "driving force," as is the case where mass transfer through a gas film is the controlling factor.

$$(3) \quad R_i = K_i A_B (p_i - p_i^*)$$

where:

R_i = rate of adsorption of component "i", moles/cm^3-sec
K_i = adsorption constant of component "i", moles/cm^2-sec-torr
A_B = external area of charcoal, cm^2/cm^3
p_i = partial pressure of component "i", in carrier gas, torr
p_i^* = partial pressure of component "i" in carrier gas in equilibrium with the amount that is actually present on the charcoal, torr.

At low partial pressures (where the ideal gas law holds and the total pressure approximately equals the carrier gas partial pressure),

$$(4) \quad p_i = P y_i M_G / M_i$$

where:

P = total pressure, torr
M_i = molecular weight of component i
M_G = molecular weight of carrier gas

Then equation (3) may be rewritten,

$$(5) \quad R_i = K_i A_B P M_G (y_i - y_i^*)/M_i = p_B \frac{\partial w_i}{\partial t} / M_i$$

Equations (2) and (5) may be rewritten,

$$(6) \quad \frac{\partial y_i}{\partial z} = - a_i (y_i - y_i^*)$$

$$(7) \quad \frac{\partial w_i}{\partial t} = b_i (y_i - y_i^*)$$

where:

$$(8) \quad a_i = P K_i A_B M_G / G$$

$$(9) \quad b_i = P K_i A_B M_G / p_B$$

The solution of equations (6) and (7) depends upon the value of w_i as a function of all y_i^*. K_i could also be a function of y_i^*. The relationships $w_i = f_i\,(y_i^*, y_2^* \ldots . y_n^*)$ are just the mathematical description of the adsorption isotherms for the charcoal of a multicomponent system. Adsorption isotherms obeying the Langmuir law for mixtures yield the relationship:

$$(10) \quad w_i = C_i y_i^* / (1 + \sum_{i=1}^{n} C_i y_i^*)$$

where:

C_i is the Langmuir constant for the pure component adsorbed on the charcoal.

In summary, to completely determine the concentration profile of the adsorbates on a charcoal bed as a function of distance and time, equations (6) and (7) must be solved for each component. The functional relationship between w_i and y_i^* (the equilibrium adsorption isotherm) must be estimated or known, and the initial concentration profile in the gas and the charcoal must be known at time = 0. The solution of the equations is greatly simplified if the breakthrough profile for each component is assumed to be completely sharp. Published tables and graphs are available for special cases of the one-component system. A computer is almost a necessity for the case of several components.

Some specific solutions of the general equation may be derived as follows:

J. Wilson (Reference 2) developed a particular solution to equation 2 above

$$-G \frac{\partial y_i}{\partial z} = p_B \frac{\partial w_i}{\partial t}$$

assuming that the adsorption isotherms are linear (i. e. , the amount adsorbed is proportional to the pressure of the adsorbate), that instantaneous equilibrium is achieved, and that diffusion is negligible.

This theory predicts that a series of sharp bands forms down the length of the column. For example, considering the case for one component, methanol in an inert gas stream at a concentration of 0. 01 µl STP/cc (10 ppm) and a temperature of 100°C. Reference to its adsorption isotherm will show that the calculated charcoal capacity at this concentration is about 175 µl gas STP/g charcoal. If it is assumed the carrier gas flow rate is 2 l/min then 20 µl/min of methanol (2 l/min x 0. 01 µl/cc) must be adsorbed. This requires 0. 114 g charcoal (20 µl/min ÷ 175 µl/g charcoal) to adsorb the amount of methanol in one minutes' flow or 6. 84 g of adsorbent is required for each hour.

Figure 10 shows the idealized concentration of methanol on a charcoal adsorbent as a function of bed depth at succeeding times. The dashed curves show the effect of diffusion causing the adsorption front to spread. The 6. 84 g of charcoal should last one hour before the full concentration of 10 ppm of methanol breaks through, although there will be some loss through the diffused front. The required amount of charcoal is

$$W = \frac{tVc^{o}}{f(c^{o})}$$

where:

W = weight of adsorbent required, g
t = time to breakthrough, min
V = flow rate, cc/min
c^{o} = concentration of adsorbate in carrier gas, µl/cc
$f(c^{o})$ = concentration of adsorbate on charcoal at equilibrium with gas phase concentration c^{o}, µl/g charcoal.

If the input methanol concentration suddenly drops to zero and the adsorption isotherm for methanol is a straight line, i. e. , $f(f)\ ^{o}/c^{o} =$ constant, the velocity and shape of the concentration profile traveling through the adsorption bed will remain unchanged. This is illustrated by the solid lines in Figure 11. If $f(c^{o})/c^{o}$ is not constant, but increases as "c^{o}" decreases (the profile travels more slowly for a decrease in "c^{o}"), the front will tend to remain sharp. This is caused by the tendency of the faster high concentration regions to overtake the regions of low concentration. The same effect in the rear causes a tailing as the rapid-moving high concentration regions pull away from the slow-moving low concentration region. Figure 12 is taken from Wilson (Reference 2) and shows the concentration profiles for a mixture of adsorbates. Figures 12b, c, and d show what the profile would be for the same amount of each component taken separately. It is assumed that the adsorption isotherm for a mixture is calculable from those for the pure components and that the same amount of each substance is present. The adsorption isotherm for each substance is different. There is an abrupt step in the concentration profile at each point where a component has been completely adsorbed. As time progresses the distance between steps increases. The front of each step is traveling faster than the front

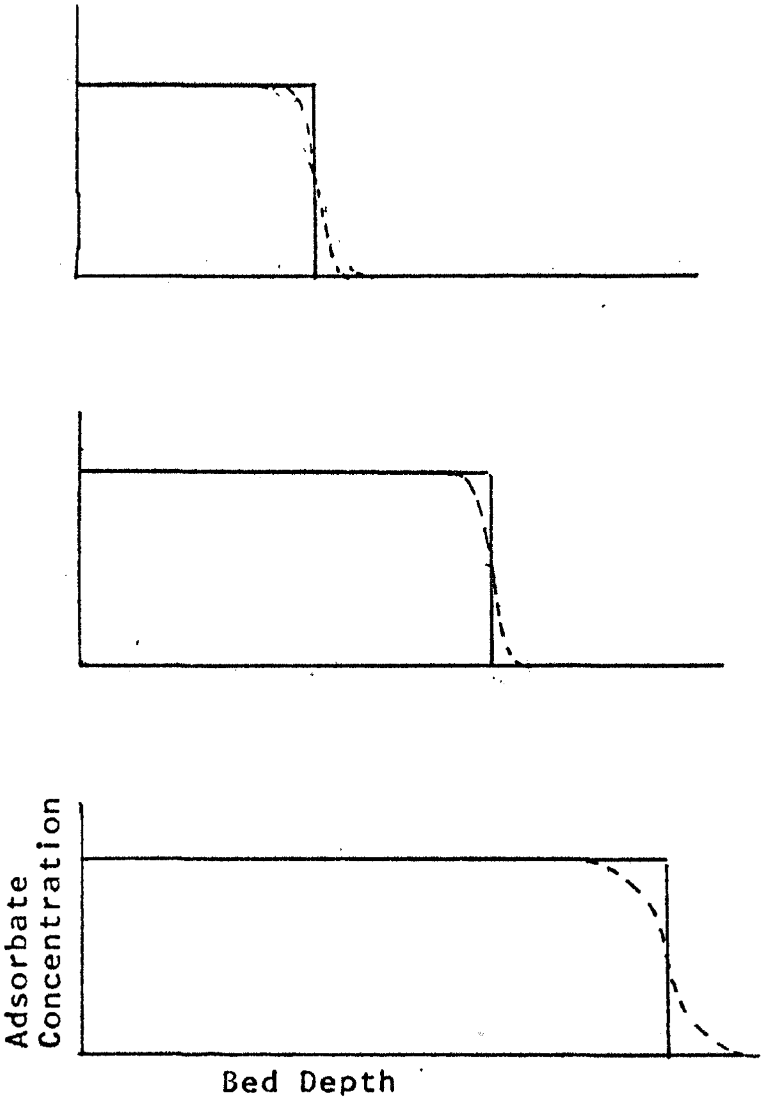


Figure 10. Idealized Concentration Profile of Adsorbate on Charcoal Bed at Three Successive Time Intervals

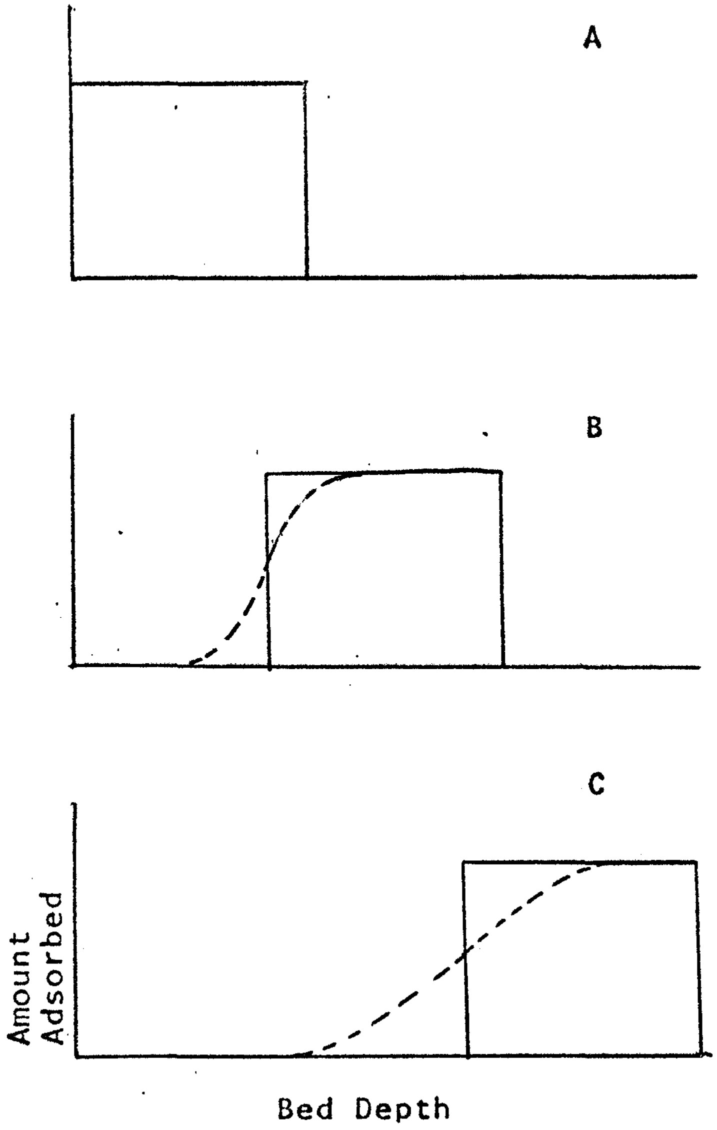


Figure 1.1. Elution of Single Component From Charcoal Bed

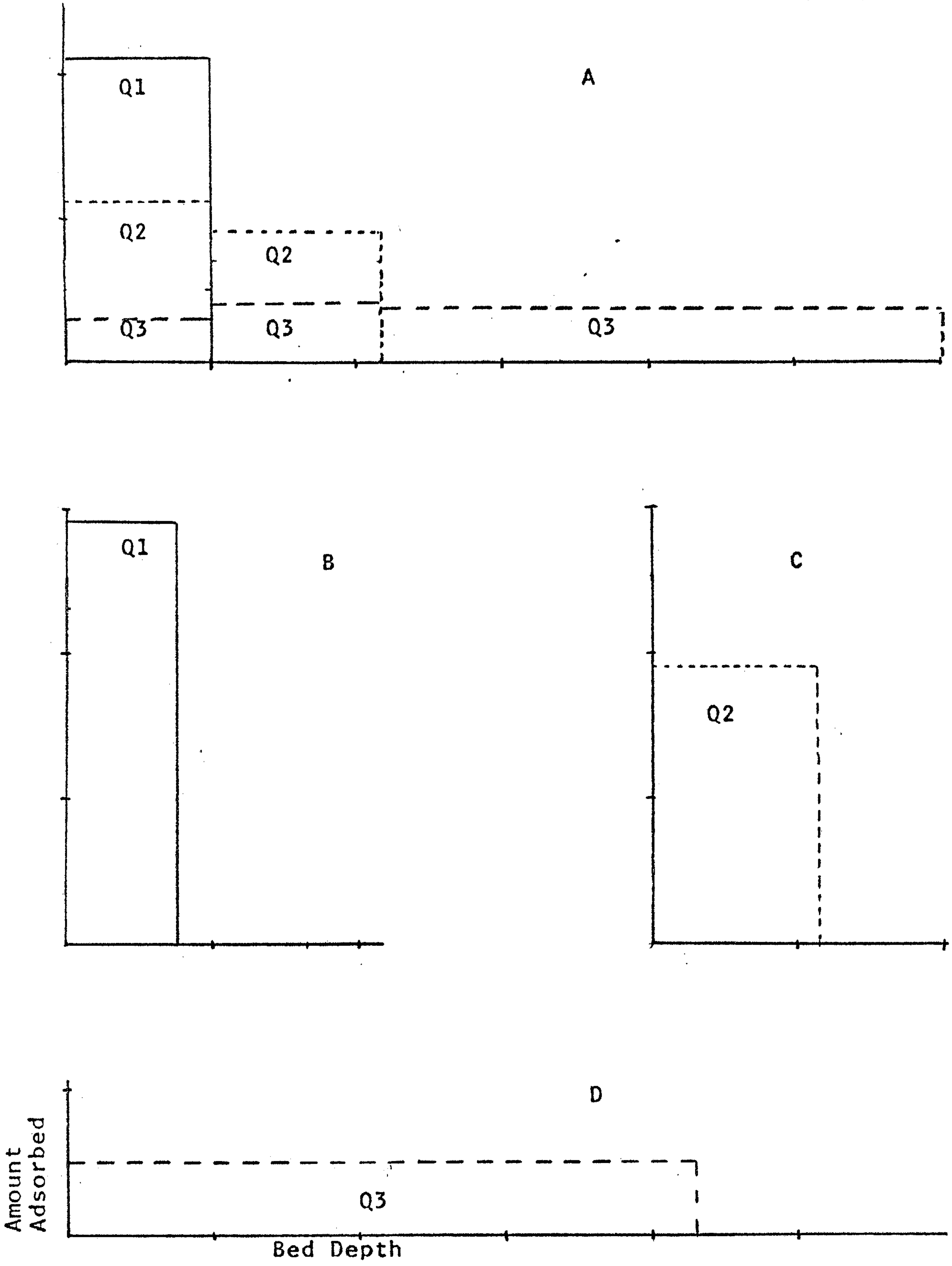


Figure 12. Adsorption Profiles of Mixture and of Individual Components

of the step to its left. The height of each step stays the same. All the above analyses consider the ideal case of linear adsorption isotherms and negligible diffusion.

Figure 13 shows the change with time of the concentration profile of a two component mixture. It is assumed that the inflowing gas stream had a constant concentration of two adsorbates until the profile in Figure A is built up. The adsorbate concentration is then cut to zero and the charcoal bed proceeds to act as a gas chromatograph and separate the two components as in Figures B, C, and D. Again, these profiles assume linear adsorption isotherms and no diffusion.

The calculation of these profiles and of their rate of travel depends upon being able to evaluate the adsorption isotherm of each component as a function of the concentration of all other components present. D. De Vault (Reference 3) corrected Wilson's equations for multiple adsorption. The solution is as follows: Let a volume "V" of carrier gas containing "n" impurities of initial concentrations "c_1^o, c_2^o, ... c_n^o" pass through an absortive bed of mass "M" per unit length. Let "Q_i" be the amount of component "i" adsorbed per unit length and let the adsorption isotherm be expressed as $Q_i = M f_i (c_1, c_2, \ldots c_n)$.

There will be a series of boundaries traveling down the column as in Figure 12a. Let "x_j" be the distance down the column of the boundary for which component "j" disappears. Let the subscript "a" apply to conditions just to the left of the boundary and the subscript "b" apply to conditions to the right. Define.

$$f_{ai} = f_i(c_{a1}, c_{a2}, \ldots ; c_{an}), \text{ etc.}$$

The substance "j" which disappears at each boundary will be the one for which f_{ai}/c_{ai} is largest.

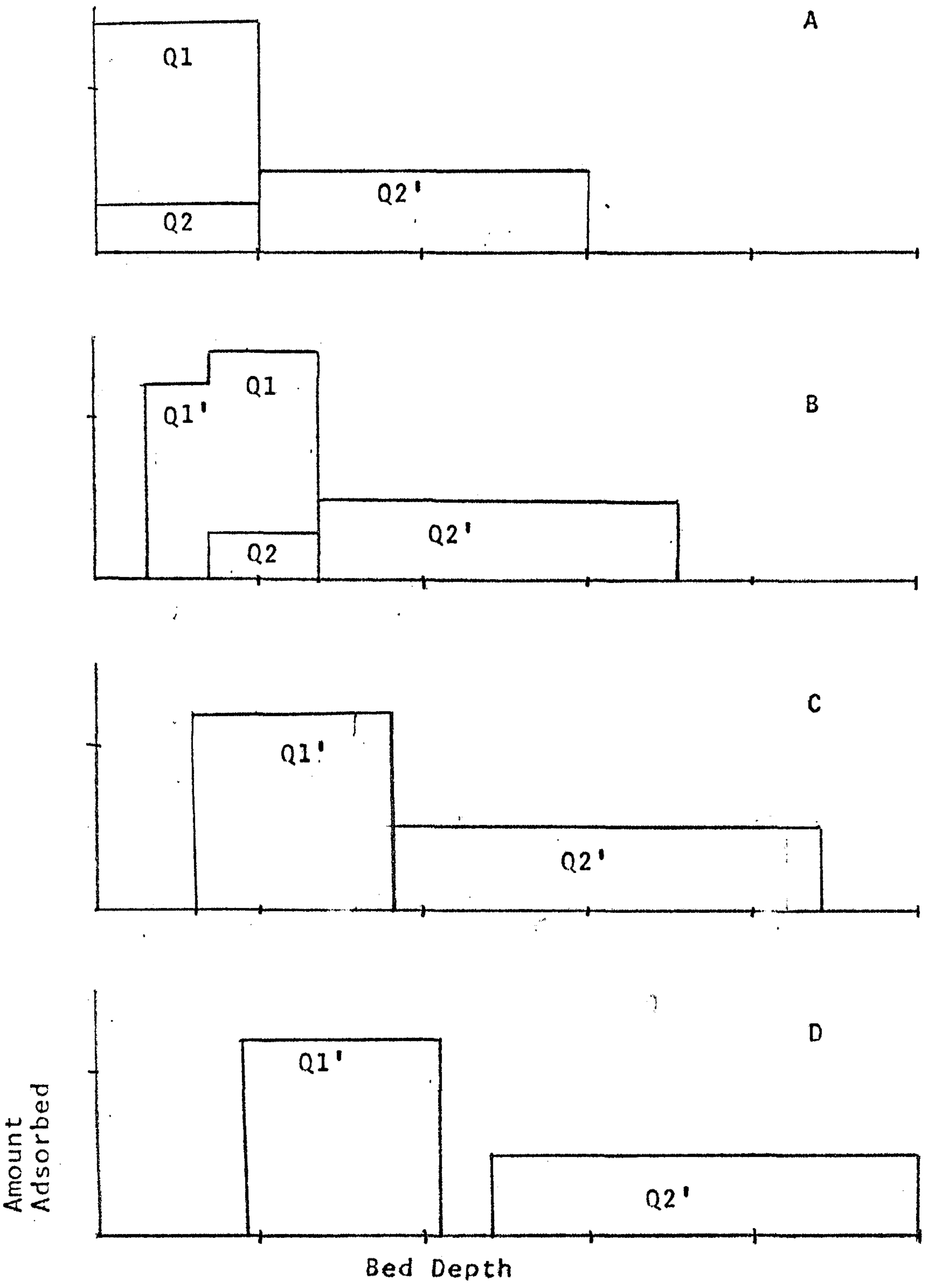


Figure 13. Elution of Two-component Mixture from Adsorbent Bed as Function of Time

There will be a series of simultaneous equations to be solved at each boundary. $x_j = V/(Mf_{aj}/c_{aj})$

$$\frac{f_{a1} - f_{b1}}{c_{a1} - c_{b1}} = \frac{f_{a2} - f_{b2}}{c_{a2} - c_{b2}} = \ldots\ldots = \frac{f_{aj}}{c_{aj}} = \ldots\ldots = \frac{f_{an} - f_{bn}}{c_{an} - c_{bn}}$$

For a given f_{aj}/c_{aj} there will be only one set of values for "c_{bi}" to solve these n-1 equations for the n-1 c_{bi} to the right of the boundary at x_j.

The above equations assume that the concentration in the gas phase is negligible compared to the concentration adsorbed. Note that the velocity of the step front is inversely proportional to f(c)/c. This signifies that for ordinary isotherms which are concave downwards ($f''(c) < 0$), fronts of high concentration travel faster than fronts of low concentration. This tends to counteract any diffusion and to sharpen advancing fronts, while tending to form tails on the rear of chromatograph peaks.

All the solutions of breakthrough patterns involve a knowledge of the adsorption isotherm of each component as a function of the concentrations of all the components.

There are several ways to measure adsorption isotherms. Perhaps the most common is a static method in which a weighed quantity of adsorbent is equilibrated with a known amount of adsorbate. The partial pressure and the amount adsorbed give one point on an adsorption isotherm. A second method is to run a flow measurement in which a carrier gas containing the adsorbate at a known partial pressure is flowed through a bed of adsorbent until breakthrough occurs. The amount that has been adsorbed is calculated from the volume of gas that has flowed, and a single point on the adsorption isotherm has been measured. This is the method that most directly models the characteristics of an air purification system. A third method is discussed below in which a complete curve can be calculated from one experiment in which the adsorbent is treated as a standard chromatographic column.

Huber and Keulemans (Reference 4) derive the equation:

$V_R(c) = mf'(c) + V_D$,

$V_R(c)$ is the retention volume for tail of a chromatographic peak corresponding to a gas phase concentration of "c"

m is the mass of the solid phase

$f'(c)$ is the derivative of the adsorption isotherm evaluated at concentration "c"

V_D is the dead space volume of the column.

This equation says in effect, that the time required for a point on the tail of a chromatograph peak to pass through the column is proportional to the slope of the adsorption isotherm at the point corresponding to the concentration in the tail. There are a range of concentrations in the tail.

It follows from this equation that the adsorption isotherm can be found by integrating the tail of the chromatographic peak according to the next equation

$$f(c) = \int_0^c f'(c)dc = \int_0^c \left(\frac{V_R - V_D}{m}\right)dc.$$

The results are reproducible within 10-20%.

V_D is very small compared to $V_r(c)$ in the case of activated charcoal and can be neglected. In the case of a linear adsorption isotherm (the amount adsorbed is directly proportional to the partial pressure) and equilibrium kinetics, the retention volume for a chromatographic column can be seen to equal the breakthrough volume.

The above technique was used to measure the adsorption isotherms on a series of compounds at various temperatures on several charcoals. Six inch gas chromatographic columns 1/8" OD were filled with approximately 0. 15 g of charcoal (sieved to Tyler screen size of 65-100) and heated overnight in a vacuum oven at 160°C. For the AC' charcoal, 0. 142 g were used with a nitrogen carrier gas flow of 30 cc/min STP. This allows a column residence time of about 0. 6 sec, much longer than the nominal residence time of 0. 06 seconds suggested by Barnebey-Cheney for carbon air purifiers. Injections of microliter (gas volume) amounts of methane, propane, methanol, butane, and 2-methyl butane (isopentane) were made at a column temperature of 160°C and the chromatographic peaks were recorded. Peaks for methane occurred at too low a retention time for accurate measurements. The ethane peak was nearly symmetrical. The peaks for the other compounds had fairly sharp fronts and long tails, as expected for compounds with concave adsorption isotherms.

The following table gives some typical retention times of the peak maxima and the times at which the tails were no longer significant:

Compound	Amount Injected, ug gas STP	Peak Height, Inches	Retention Time, Min. Peak, max.	Retention Time, Min. End of Tail
CH_4	6	6. 0	0. 1	0. 15
C_3H_8	6	1. 6	2. 9	3. 2
CH_3OH	9. 55	5. 3	5. 8	35.
C_4H_{10}	3. 18	3. 4	24. 5	38
C_5H_{14}	6	1. 45	150	200

Figure 14-17 show the results of isotherm experiments using these techniques.

Adsorption isotherms have been calculated from the retention volumes of isopentane, butane, propane, and methanol at 160 and 100°C on AC charcoal. The retention time for butane at 100°C is 4 hours for 0. 142 g of AC charcoal.

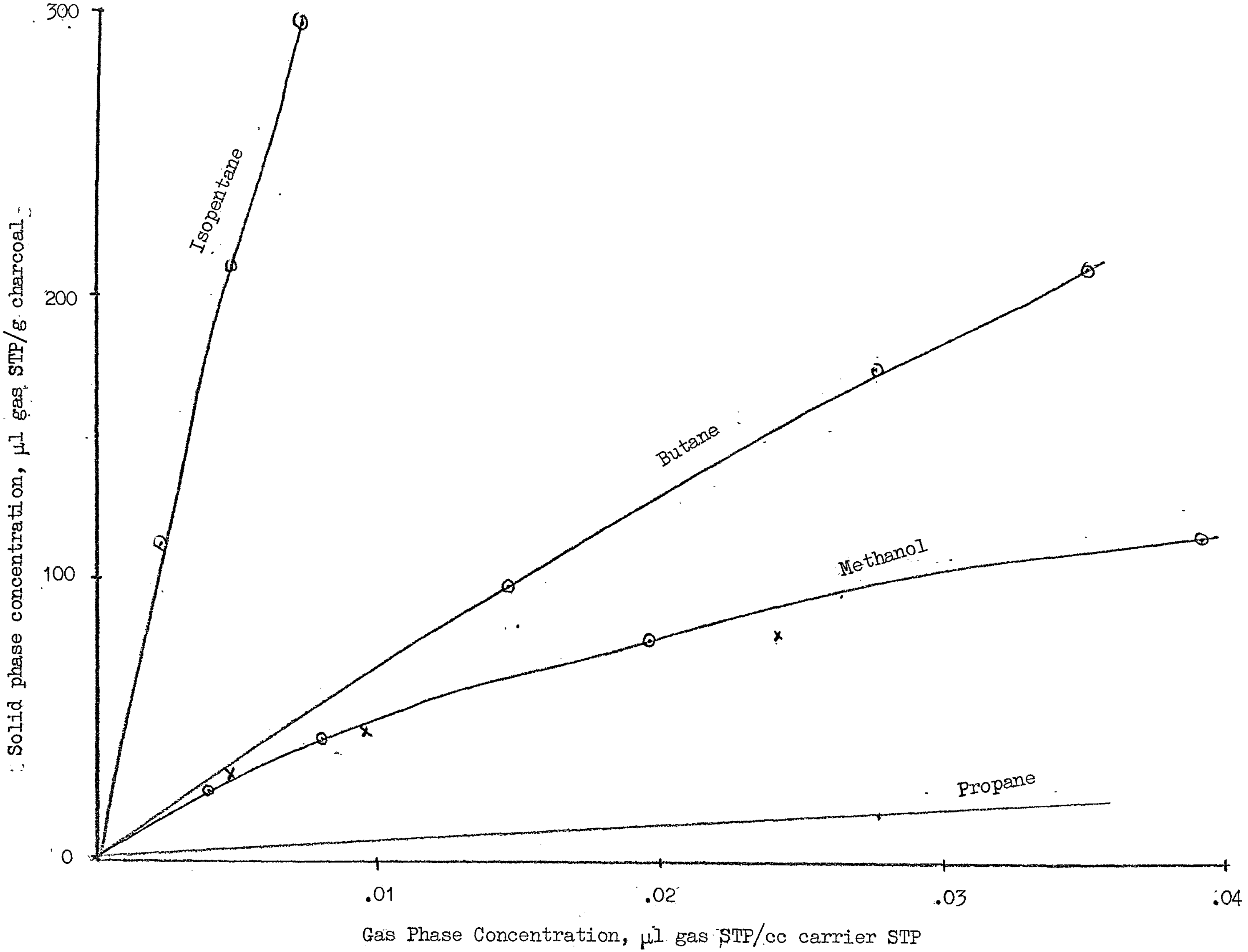


Figure 14. Adsorption Isotherms on AC Charcoal at 160 C.

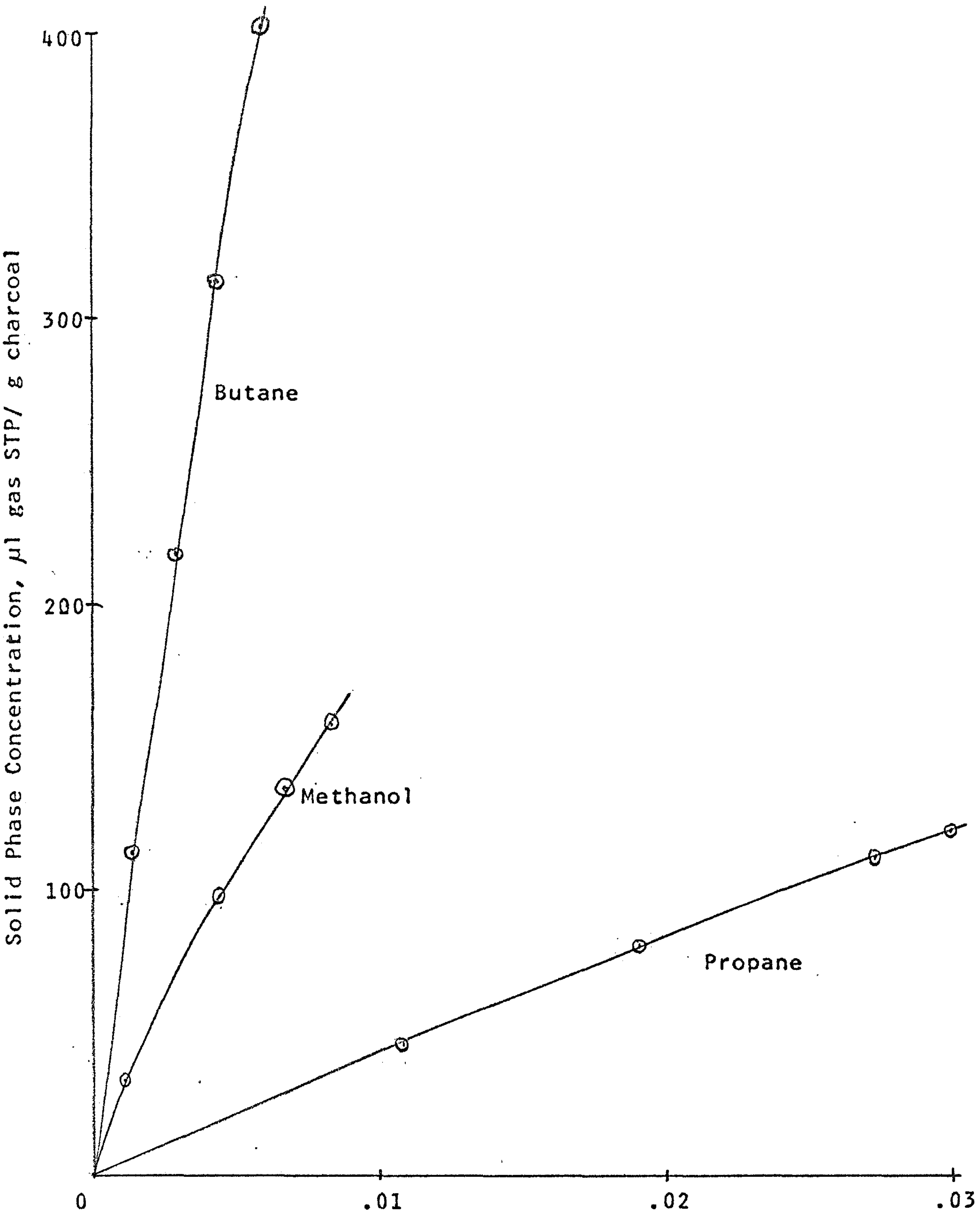


Figure 15. Adsorption Isotherms on AC Charcoal at 100°C.

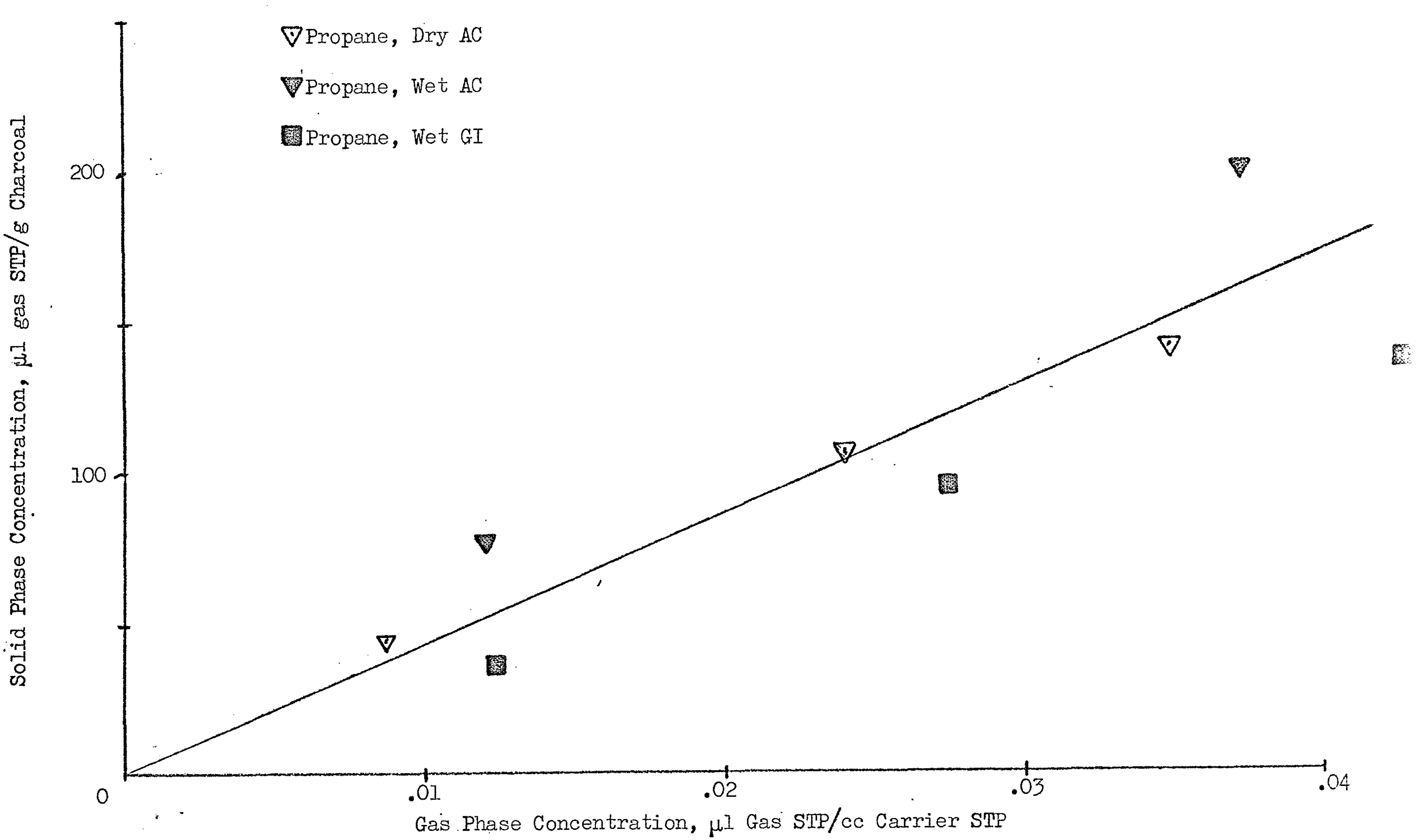


FIGURE 16. Adsorption Isotherms Of Propane On Charcoal At 100°C

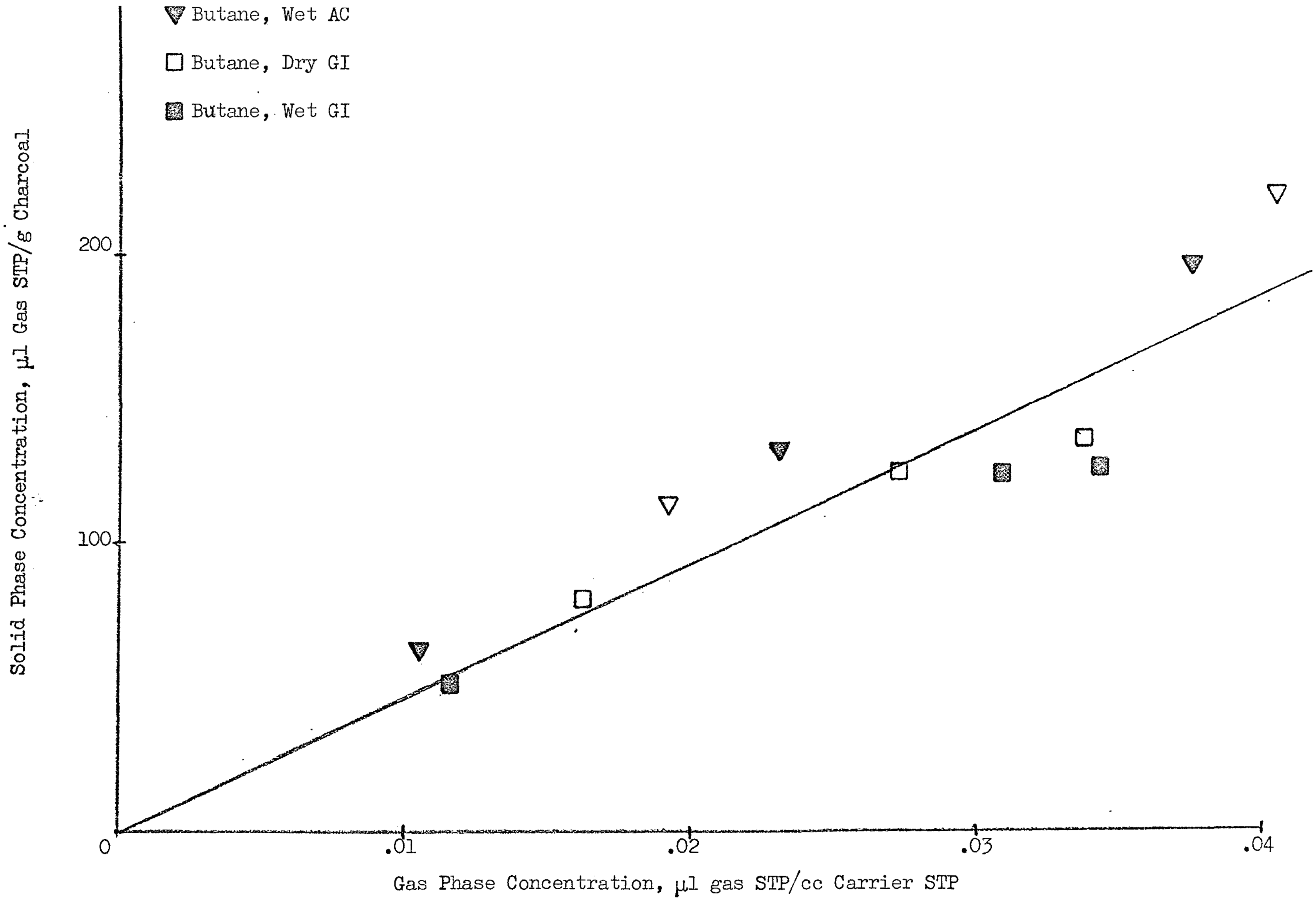


FIGURE 17. Adsorption Isotherms Of Butane On Charcoal At 160°C

Adsorption isotherms were measured for propane, methanol, and butane at 160°C on GI charcoal. The results were virtually identical to those for AC charcoal at the same temperature. Since GI charcoal is reported to have a nominal area of 1700 m^2/g compared to 1100 m^2/g for AC charcoal, it was expected that the retention times would have increased in the ratio 1.7/1.1. This lack of increase has yet to be explained.

The saturation of nitrogen carrier with water at ambient temperature seems to have minimal effect upon measured adsorption isotherms. Types AC and GI charcoals were subjected to wet and dry carriers at 100°C and 160°C with no differences in adsorption isotherms of either propane or butane noted. Figures 16 and 17 show the isotherms calculated. Seven run configurations were made as follows:

TEST GAS	CHARCOAL TYPE	CARRIER	TEMPERATURE
Propane	AC	Dry	100°
Propane	AC	Wet	100°
Propane	GI	Wet	100°
Butane	AC	Dry	160°
Butane	AC	Wet	160°
Butane	GI	Dry	160°
Butane	GI	Wet	160°

A survey of the literature indicates that the most generally successful correlation of adsorption isotherms is given by the Polanyi isotherm. Grant and Manes (Reference 5) apply it with good success to low pressures and super-critical temperatures of N_2, CH_4, A, H_2, and Ne on activated carbon and in silica gels.

Lockheed (Reference 6) and Edgewood Arsenal (Reference 7) have been using it to correlate the adsorption of various compounds on carbon.

The basic assumption of the Polanyi isotherm is that the free energy required to transfer a small amount of adsorbate from the adsorbent to the liquid at the same temperature is a function only of the volume that has been adsorbed (or the amount of surface of the charcoal that has been covered assuming that this is a function of the volume). This is expressed by the equation.

$$q = f\,(RT \ln p^{o}/p)$$

where:

q = the amount adsorbed, ml liquid/g adsorbent
T = absolute temperature, ^{o}k
p^{o} = vapor pressure of adsorbate at temperature T
p = partial pressure of adsorbate over adsorbent.

This implies that if "q" is determined at one temperature for a series of pressures "p" and is plotted against $\frac{RT}{B} \log p^{o}/p$ (the Polanyi potential) a curve will be formed which is the same for all other possible combinations of "p" and "T" for that adsorbent. The "affinity coefficient", "B", is a parameter (presumed independent of p and T) that makes the curves for different adsorbates fall on top of one another. It has been found empirically that in many cases there is a B which is different for each substance and will superimpore the curves for many substances on the same adsorbate. Many different correlations have been attempted between B and the physical properties of the adsorbent. One of the most common is to let $B = V_m$, the molal volume at the boiling point. The physical picture becomes ambiguous at temperatures above the boiling point, and particularly so above the critical point.

It is unlikely that the density of the adsorbate on the charcoal surface is equal to its liquid density, hence, the surface coverage is open to question. Furthermore, the meaning of p^{o} at temperatures above critical is open to question. The general practice has been to extrapolate log p^{o} linearly with $1/T$ and to assume the density of the adsorbate is that of the liquid at the boiling point. These techniques frequently do give surprisingly good correlations. In summary, in decreasing order of desirability there are several correlations that can be made for one-component adsorptions.

1. For each component and charcoal of interest measure the adsorption isotherms over the temperatures and pressures of interest. This involves no assumptions.

2. For each component and charcoal of interest measure the adsorption isotherms at one temperature over a range of pressures. A plot of "q" against $T \log p^o/p$ will give a different curve for each adsorbate - adsorbent pair that will predict adsorption for temperatures other than those that have been measured. This involves the basic Polanyi isotherm assumptions.

3. For one particular charcoal - adsorbate pair measure the adsorption isotherm at one temperature. Plot "q" against $\frac{T}{B} \log p^o/p$ let $B = 1$. This is the standard curve. For a different adsorbate on the same charcoal measure only a few points on the isotherm and calculate the value of B that most nearly superimposes these points on the standard curve. This method requires the decision as to what density should be used to convert adsorbed weight to adsorbed volume when different substances are used. No assumptions are made about B except that it exists and is constant for each adsorbate, adsorbent pair.

4. Prepare a standard curve as in 3. Assume that B is equal to molal volume at the boiling point.

The prediction of the adsorptive capacity of charcoal for one component of a mixture in the presence of the others is an important part of this work. In the last few years there have been several attempts for which moderate to good success has been claimed. Grant and Manes (Reference 5) consider that the adsorbate on the surface of the charcoal acts like and ideal solution and that the partial pressure of component "i" can be expressed as

$$p_i = X_i p_{oi}(V_T)$$

where:

p_i = partial pressure of component "i"
X_i = mole fraction of component "i" in the adsorbate
V_T = total volume of adsorbate mixture per gram of charcoal
$p_{oi}(V_T)$ = partial pressure that component "i" would have if other components were not present and the charcoal had adsorbed an amount V_T of component "i".

If "n" components are present, "n" partial pressures in the vapor phase are given, and the adsorption isotherms for the pure components are available, then the solution of "n" simultaneous equations will yield the adsorptive capacity of the charcoal for each component.

The method involves certain assumptions about the applicability of the Polanyi adsorption isotherms and the additivity of adsorbed volumes. Deviations between predicted and measured values of the order of 20 percent are reported.

It is clear that the method cannot be correct in all cases. An example would be the case where one adsorbent reacts with another in such a way that it enhances the adsorption of the other. This method always predicts a decrease in adsorptive capacity.

A series of experiments involving the effects of temperature and moisture on the adsorption of ethane and propane were made. A column consisting of 1.25 g of finely ground GI type charcoal was loaded with varying quantities of test gas through a sample loop. The carrier (and purge gas) was nitrogen flowing at 30 cc/min. Moisture variations were studied by duplicate test runs, using dry nitrogen for one and water saturated nitrogen for the other. Saturation was achieved by bubbling the carrier through a fritted glass gas scrubber immersed in water. Adsorption isotherms were calculated from the shape of the chromatographic peaks. Data for the concentrations corresponding to the chromatographic peaks are tabulated in Table 21. The information presented illustrates several of the variations obtainable from isotherm data. These include, gas phase concentration of sample at the peak of the detector response, the calculated concentration of adsorbed gas in equilibrium with the gas phase concentration at the peak of the detector response, the ratio between the solid and gas phase concentrations, the Polanyi adsorption potential using the molar volume at the boiling point of the sample, ratio of the vapor pressure of the sample to the partial pressure of the sample, and the calculated adsorption capacity of the charcoal for the liquefied sample at the test temperature.

The fitting of the Polanyi equation is somewhat questionable (Column 7, Table 21) since the temperature at which molar volume is to be taken is not strictly defined. Apparently success in applying the Polanyi equation is in selecting a temperature for molar volume that will enable plots of adsorption vs. the Polanyi potential to fall upon a single line. For presentation the molar volume at the boiling point of the sample gas was chosen. However, the charcoal temperature or sample melting point could have been chosen which might position the data points in Figure 18 closer to a single line. The temperatures involved in these studies are above the critical temperature of ethane. Vapor pressures were extrapolated from a straight line plot of log p vs. 1/T. The data thus generated for use in the calculation of the Polanyi potential were:

Sample	V_m, cc/mole	Vapor Pressure in Atmospheres at 34°C	50°C	100°C
Ethane	52.5	49	66	180
Propane	74.5	15.4	44	-

Figure 18 shows the adsorption plotted against the Polanyi potential, $(T/V_m) \log (p^o/p)$. Figure 19 illustrates the same adsorption values graphed with $(5) \log (p^o/p)$. The numerical value of 5 provides an absisissa with an equivalent (and readily comparable) range for the two plots.

TABLE 21

FLOW EXPERIMENTS OF ETHANE AND PROPANE ON BARNEBEY-CHENEY GI CHARCOAL

Sample	Temp, °C	Sample Size, µl, STP	Retention time, Min. (1)	C x 10^3 µl/cc (2)	F(C) µl/g (3)	F(C)/C cc/g (4)	A (5) mol °C/ml	log p^o/p (6)	q x 10^6 ml/g (7)
Dry Ethane	35	14.5	4.2	408	43.2	106	29.7	5.08	100
	34	14.5	4.0	202	26.7	132	31.5	5.40	62
	34	2.9	4.3	51	6.5	127	34.6	5.98	15
	50	14.5	2.2	255	23.0	90	33.3	5.41	54
	52	7.2	2.3	148	12.7	86	34.8	5.65	30
	100	7.2	0.8	193	8.7	45	42.3	5.97	20
Wet Ethane	50	29.0	1.8	409	40.1	98	32	5.21	95
	50	14.5	2.3	252	21.4	85	33.3	5.42	50
	48	7.2	2.4	166	13.6	82	34.5	5.60	32
	50	2.9	2.3	92	6.6	72	36.1	5.85	15
Dry Propane	50	14.5	45.0	21	31.8	1512	25.4	5.87	105
	100	14.5	9.1	105	31.0	295	28.0	5.62	105
	100	14.5	7.5	56	19.4	346	29.5	5.90	64
	100	7.2	9.0	45	12.6	280	30.0	5.99	42
Wet Propane	50	14.5	40.0	23	32.0	1390	25.3	5.83	105
	50	7.0	54.0	17	24.5	1441	25.8	5.96	82
	50	2.9	56.0	8.1	11.6	1440	27.3	6.27	39

---

(1) From time of introduction to peak of detector response.
(2) C = concentration of sample at time of peak of detector response in µl sample/cc of carrier.
(3) F(C) = calculated concentration of sample adsorbed on charcoal in equilibrium with gas phase at C in µl sample/g charc
(4) F(C)/C = equilibrium constant or ratio of (3):(2) i.e. (µl sample/g charcoal)/(µl sample/cc carrier)
(5) A = Polanyi adsorption potential $(^T/V_m)$ log (p^o/p) where T = Temperature, °K, V_m = molar volume sample at boiling poi
p^o = vapor pressure of sample at T, p = partial pressure of sample.
(6) p^o/p = ratio of vapor pressure of sample to its partial pressure.
(7) q = quantity of sample adsorbed/gm charcoal in cc of liquid/gm charcoal.

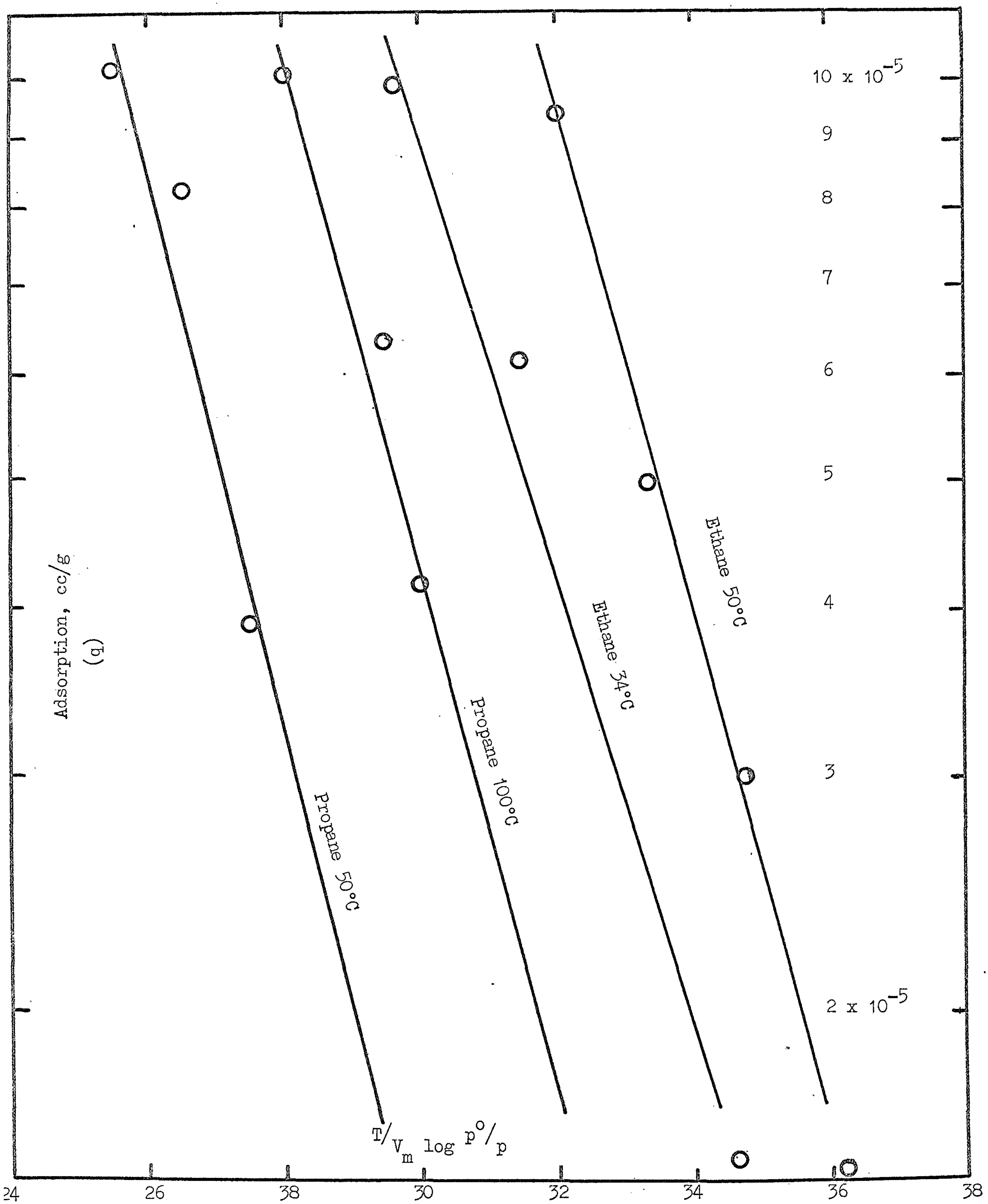


Figure 18: POLANYI POTENTIAL OF ETHANE AND PROPANE VS. ADSORPTION AT VARIOUS TEMPERATURES

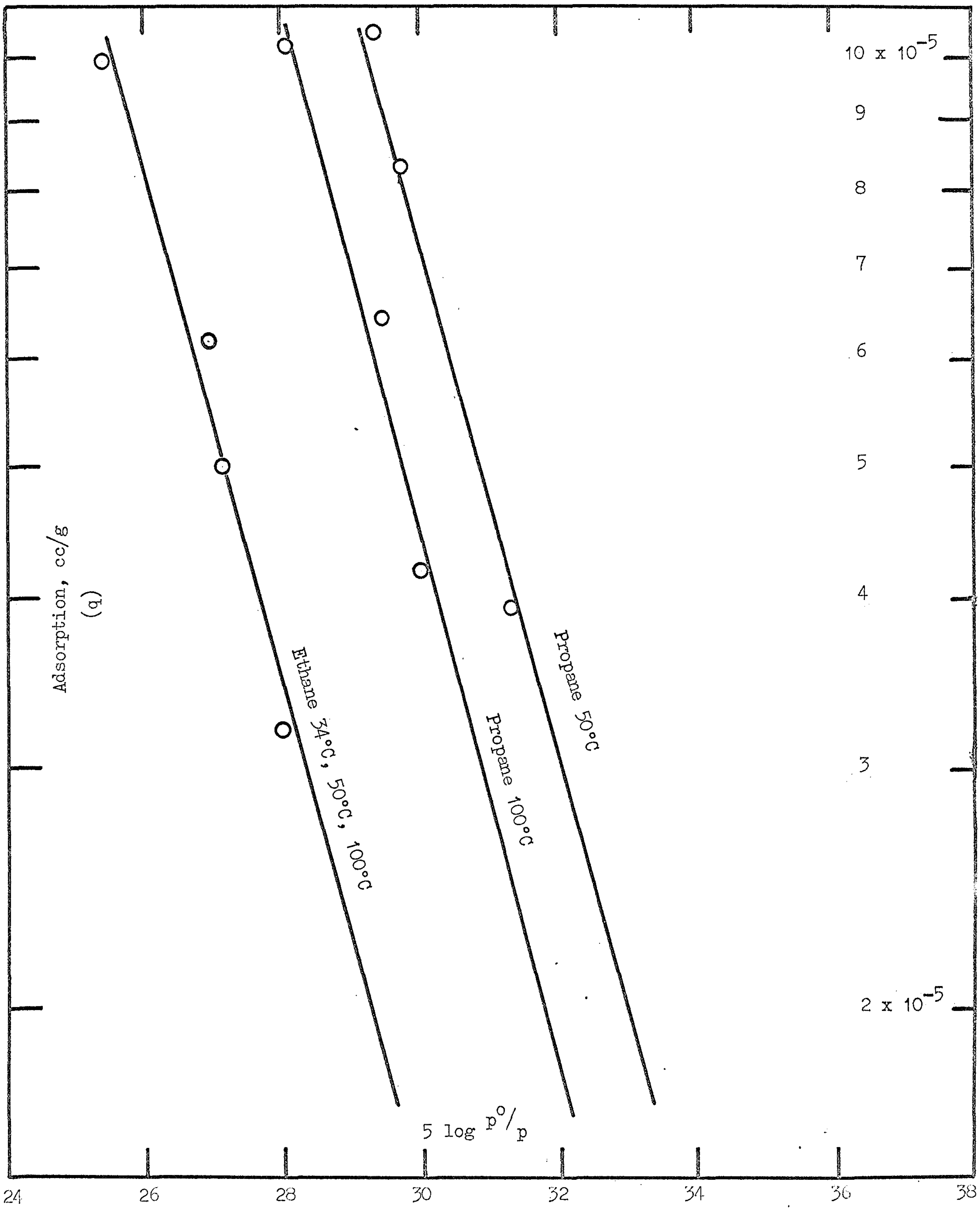


Figure 19: ADSORPTION OF ETHANE AND PROPANE AT VARIOUS TEMPERATURES VS. 5 LOG OF RATIO OF VAPOR PRESSURE OF SAMPLE TO ITS PARTIAL PRESSURE

For this particular series, it is apparent that temperature dependence is better fitted by Figure 19 for both ethane and propane. In no case does the presence or absence of moisture seem to have any noticeable effect upon the adsorption capacity of GI charcoal for the selected components. This may be due to the fact that the adsorption of water on charcoal does not follow typical isotherms. There is very little adsorption until a relative humidity of about 40% is reached. At this point there is a sharp rise in the amount of water adsorbed.

A series of flow experiments in which 55 ppm mixture of benzene in nitrogen and of ethanol in nitrogen were passed through 0.142 g of AC charcoal in a small chromatograph column at temperatures of 100° and of 30°C. Breakthrough times were monitored with a flame ionization detector. Flow rates varied from 200 to 300 cc/min. Despite the contact time of only .03 sec the breakthroughs were reasonably sharp, requiring only about 20 minutes from base to peak after a retention time of ten hours. This fact would seem to indicate that equilibrium was attained. For one sample of benzene adsorbed at 30°C, the weight gain of the charcoal was measured and found to agree with the calculated weight gain of 22.4 mg.

A test was made in which the benzene nitrogen mixture was flowed until breakthrough. Then the mobile phase was switched to an ethanol-nitrogen mixture and breakthroughs for the ethanol were measured. The breakthrough time was lowered about 40% by the presence of the benzene. Table 22 shows some of the results.

Figure 20 is a summary of some of the measured adsorption isotherms plotted as a function of the Polanyi potential. It can be seen that there seem to be three distinct groups of points. The first group consists of the saturated hydrocarbons: propane, butane, and isopentane.

TABLE 22

RESULTS OF BREAKTHROUGH RUNS WITH BENZENE AND WITH ETHANOL IN N_2 CARRIER

(0.142 g AC Charcoal)

	T °C	V cc/min	t min	w µg/g	q cc/g	A mol-T/cc
55 ppm Benzene	100	300	188	76	0.094	17.2
Clean charcoal	30	200	644	175	0.210	10.7
55 ppm Ethanol	100	200	12	2.0	0.0027	27.2
Clean charcoal	30	200	300	48.7	0.066	16.0
Sat. with 55 ppm benzene	30	200	176	28.5	-	-

T = column temperature, °C

V = flow volume, std cc/min

t = time, min

w = weight adsorbed/weight charcoal, µg/g

q = volume adsorbed/weight charcoal, cc/g

A = Polanyi potential, $(T/V_m) \log (P°/P)$.

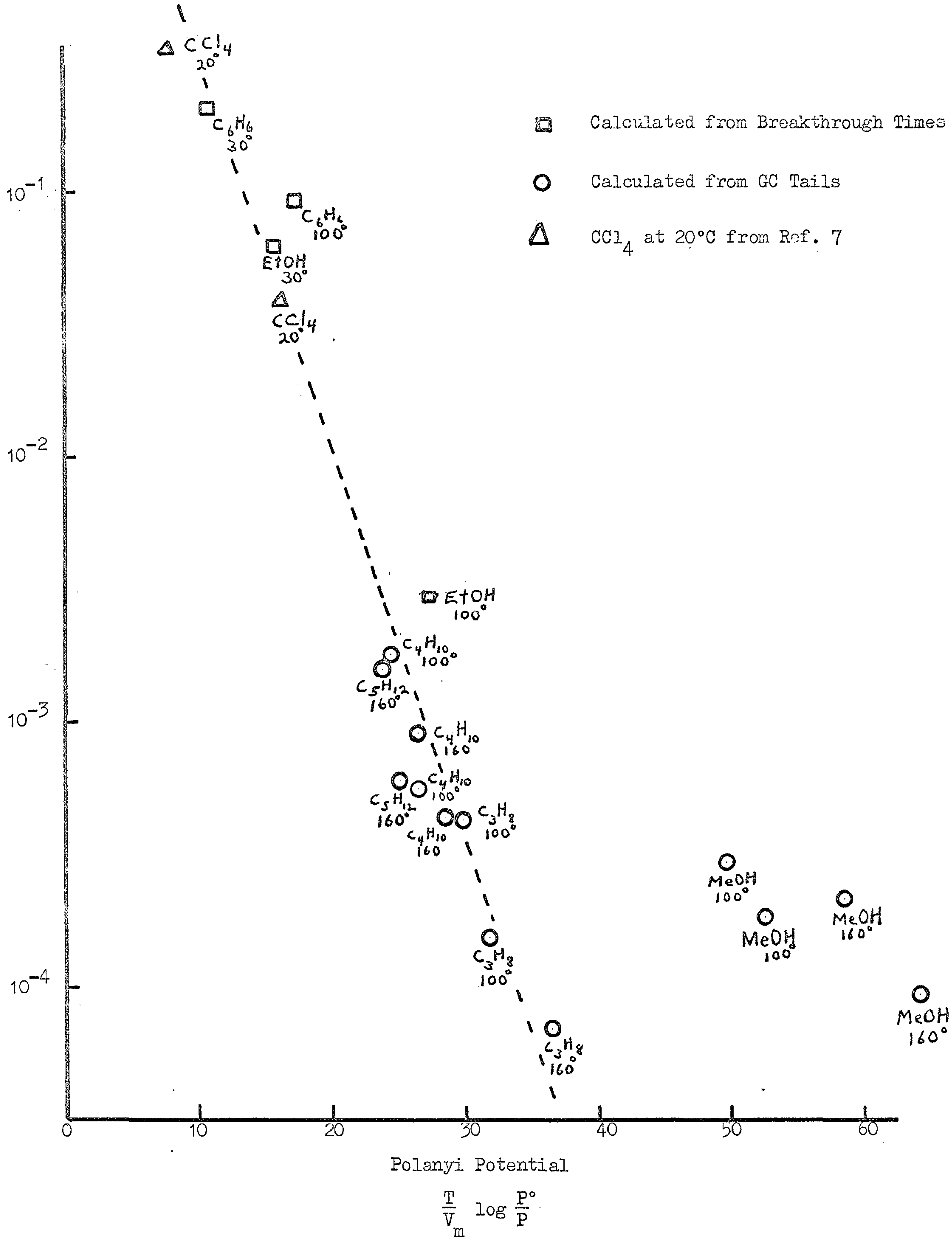


Figure 20. POTENTIAL PLOT FOR AC AND GI CHARCOALS

These points were calculated from the tails of their gas chromatograph peaks. The group generally lies consistently below the other two groups, indicating less adsorption. This can be explained by the assumption that the kinetics of the process are important. If the charcoal surface has a significant fraction of micropores that require some time for the adsorbate to enter, it may be flushed past by the carrier gas before being adsorbed, thus reducing the apparent adsorptivity of the charcoal. This reduction would be an error on the side of safety. On the other hand, the methanol data, forms a group that is more strongly adsorbed for a given Polanyi potential than would be expected from the data of the first group. There are two reasons suggested for this phenomena. First, the methanol molecule is smaller in size than the other compounds under consideration and therefore more able to enter the micropores. Second, the methanol molecule is much more polar than the others and probably requires a different B than its molal volume for a good correlation. However, the methanol data do correlate fairly well with the benzene and ethanol data which were derived from breakthrough experiments. It may be that the micropores were filled by benzene and ethanol because of the long time in which the carbon is exposed to the vapor in these experiments, and the micropores were filled with methanol because of its small size. As a matter of interest, two points representing CCl_4 are calculated from the data supplied in (Reference 7).

A brief test was performed to study the adsorptive capacity of charcoal for a prepared gas mixture. This mix contained Freon 12, Freon 113, benzene, ethyl alcohol, and acetone. Because of the rather enormous adsorptive capacity of charcoal, concentrations of material in the ppm range would be impractical for testing. Several hundred cubic feet of carrier and days of exposure would be required to effect saturation. Therefore the mixture prepared consisted of 25 cubic feet of nitrogen with approximately 200 ppm of each component. Since desorption of the charcoal would provide more material than could be practically managed, was trapped in two serially placed high efficiency Schultz traps immersed in liquid nitrogen. The desire to eliminate condensed oxygen problems prompted the choice of nitrogen carrier. A weighed quantity of charcoal was placed in a glass U-tube giving a L/D ratio of 12/1. This tube was placed in an oven controlled @ 35°C ± 0.5°C and connected to the mixture supply line and traps. The gas sample container was heated with an infrared lamp to minimize adsorption of the "contaminants." A flow rate of 250 cc/min. for 40 hours was predetermined as the adsorbent saturation point. Following emptying of the gas bottle, the tube was closed and the charcoal weighed to determine the quantity adsorbed. The contents of the cold traps were analyzed to determine material that had not been retained.

The cold trap analysis indicated that a total of 1470 µg had passed through the charcoal, representing only 0.036% of the total compounds mixed in the nitrogen. This analysis is summarized as follows:

Compound	Wt. in ug	% of Total
Freon 12	427	29.1
Freon 113	686	46.7
Benzene	7	0.5
Ethyl Alcohol	269	18.3
Acetone	80	5.4
Total	1469	100.0

These results indicate that the calculated capacity was essentially confirmed by experiment. While in actual service, the charcoal will adsorb other atmospheric contaminants and give a "breakthrough" earlier than determined by experimentation, predictability is still reasonable within controlled contaminant concentration limits.

I. ADSORPTION-DESORPTION STUDIES

A series of experiments were made to determine the relative recovery of five compounds from adsorbents and cryogenic trapping. The selected compounds were among those commonly found as spacecraft atmospheric contaminants, i.e., Freon 12, Freon 113, benzene, ethyl alcohol, and acetone. Approximately equal volumes of each (several microliters) were added to a metal cylinder and diluted with nitrogen to a pressure sufficient for the complete test series c. f., 10 liters.

An accurately measured sample of this mixture, chromatographically analyzed and the quantities of each component reported in micrograms, was used for reference.

A U-tube containing previously stripped charcoal or molecular sieve adsorbent was placed into the glass high vacuum system. A known volume of the reference gas was added to a glass cylinder located in such a manner that this sample could be cycled through the adsorbent and returned to the glass cylinder. A Töepler pump, with a volume of approximately 300 cc, was used for this recycling. At least 100 cycles were used for each study. Several tests with greater than 200 cycles were performed but no increase in quantity of gas adsorbed was observed. The adsorbate was maintained at 25°C for one test series and approximately 55°C for a second test series. All fittings and valves were fabricated from teflon or viton, including the fitting connections, in order to reduce external influence from addition or subtraction of impurities. Essentially a sample of known volume and chemical composition was dynamically exposed to an adsorbent for a period of more than two hours per test. Flow rate of gas through the adsorbent tube averaged about 1 liter per minute with dwell time greater than 10 seconds through an adsorbent path greater than 10 inches in length.

The same system was used for circulating another sample of the mixture through a glass Schultz trap immersed in liquid nitrogen. Recovery of added material through the cryogenic system was better than 89% of the starting material. While other tests with selected compounds have reported recoveries exceeding 95%, it is believed that the flow characteristics of these tests more nearly resemble actual atmospheric circulation systems. Operational parameters are presented in Table 23A and are the numbers related to the indicated superscripts of Table 23B.

Several observations are reasonably evident from these brief tests. First, the recoveries noted in Table 23B are considerably lower than originally anticipated. Unfortunately the sample size selected for the reference mixture was between 5 and 10% of the volume of each test gas. This amplifies errors that might result in comparing small and large signal responses. The quantities of each component are larger by at least two orders of magnitude than usually measured in trace analytical studies and linearity over more than three orders of magnitude using ionization detection is somewhat questionable. Volumetric dilutions were used in making the original mixture resulting in a moderate inbalance of components. Another important factor affecting the observed concentration was apparent adsorption of acetone and the alcohols on the walls of the reference sample cylinder. Desorption was not apparent during sampling. All manipulations were accomplished in the high vacuum rack system and, while adsorption is minimized in such a system, the recycling portion of the rack is neither heated nor stripped during the adsorption study. A more intensive study should include correction of the above weaknesses.

Second, the study was primarily designed for recovery data. Quantitative analysis for new compounds from degradation or recombination of free radicals formed on the active catalytic adsorption surfaces was obtained but the chromatograms were not optimized for a careful kinetics study. Apparently some synergism occurs on the active surfaces and fewer components in the starting mixture would greatly aid in giving more precise kinetics data. Only an estimate of the amount of ethyl acetate was made and products of ester decomposition were not observed because of the initial concentration in the starting material and the retention time interference from other components. Because measurement of degradation products was not a primary goal of the test series, only one analytical column was used for desorbate analyses. Multiple signal responses observed at certain retention times were rather common and quantitation was difficult for each signal using a single column.

It would appear that retention of various compound types is quite variable on molecular sieve material and degradation was greater than expected. Charcoal is apparently less selective and has a greater capacity than zeolitic type material. Undoubtedly, pore size has a marked effect on selectivity and total capacity of the adsorbate as well as cation concentration and subsequent catalytic decomposition. Other catalytic studies should be made in addition to these efforts.

Materials not adsorbed or eluted from charcoal were minimal as seen in the last column of Table 23B. Adsorption at 55°C was approximately the same as at 25°C with no noticeable increase in number or amount of newly formed products. In fact, a slight trend toward greater retention at the elevated temperature was observed.

TABLE 23A

CONDITIONS ASSOCIATED WITH TABLE 23B

(1) Compounds selected as representative atmospheric contaminants-methyl alcohol, isopropyl alcohol, ethyl acetate were impurities in the selected adsorbates. One sample source was used for all tests. The compounds were diluted with nitrogen.

(2) Approximately 300 cc of the 1000 cc starting volume were recycled by Töeplering more than 100 cycles for each test.

(3) The desorption process was essentially the one used for Apollo canister manipulation.

(4) Cryogenic collection was accomplished by cycling through a Schultz trap with Töepler operation.

(5) Fresh sieve material was placed in the adsorption loop and vacuum-thermal treated following the Apollo analytical procedure (13.1 g of material used).

(6) AC Apollo charcoal was material that had been purchased for these tests and had been thermally-vacuum stripped (9.9 g of material used).

(7) 888 Witco charcoal is a high surface area petroleum product supplied for air purification systems (6.7 g of material used).

(8) Micrograms of compound in selected volumes of sample.

(9) Weight percent of recovered material compared to the reference sample. All sample volumes used for each test were equated to the volume (STP) of reference material used, i.e.; reference material 26.7 cc, AC charcoal 575 cc, 888 charcoal 575 cc, molecular sieve 287 cc, cryogenic collection 575 cc.

(10) Percent recovery is based on total µg recovered from each test to sample composition before testing (reference sample).

(11) Products apparently formed on the adsorbent surfaces.

(12) Percent of formed products to recovered products would be an indication of percent degradation.

TABLE 23B

RECOVERY STUDY OF SELECTED COMPOUNDS(1)

Gas Mixture Recycled(2) Through Collector at 25°C,
Desorbed at 150°C(3)

Adsorbate	Reference Sample µg(8)	Cryogenic Collection(4) µg	Cryogenic Collection(4) wt-%(9)	5A Molecular Sieve(5) µg	5A Molecular Sieve(5) wt-%	AC Apollo Charcoal(6) µg	AC Apollo Charcoal(6) wt-%	888 Witco Charcoal(7) µg	888 Witco Charcoal(7) wt-%
Freon 12	161	160	100	4.2	2.6	55	34	43	27
Freon 113	136	76	56	66	49	10	7.4	36	26
Methyl alcohol*	1.1	-	-	0.44	40	0.04	3.6	0.04	3.6
Benzene	24	23	96	21	87	13	54	13.7	57
Ethyl alcohol	2.5	1.9	76	1.9	76	0.65	26	0.17	6.8
Isopropyl alcohol*	1.0	0.79	79	1.0	100	0.80	80	0.5	50
Acetone	2.5	0.87	35	3.5	> 100	1.5	60	3.1	> 100
Ethyl acetate*	0.50	0.40	80	~ 0.4	~ 80	≈ 0.4	~ 80	~ 0.4	~ 80
Total	329	293	89(10)	98.4	30	81.5	25	96.9	30

*Present as an impurity

Desorbates Not Found In Starting Material(11)	Cryogenic Collection µg	Cryogenic Collection % of Recovered Material	5A Molecular Sieve µg	5A Molecular Sieve % of Recovered Material	AC Apollo Charcoal µg	AC Apollo Charcoal % of Recovered Material	888 Witco Charcoal µg	888 Witco Charcoal % of Recovered Material
Chlorotrifluoroethylene	-	-	-	-	< 0.001	-	-	-
Dichlorodifluoroethylene	-	-	0.70	0.58	0.027	0.03	-	-
1,2 Dichloroethane	-	-	2.5	2.1	-	-	-	-
Vinylidenechloride	-	-	0.47	0.39	-	-	0.10	0.10
Ethane	-	-	0.05	0.004	0.007	0.009	0.003	0.003
Propane	-	-	1.5	1.2	-	-	-	-
n-Butane	-	-	0.47	0.39	0.008	0.01	-	-
Acetylene	-	-	0.22	0.18	0.15	0.19	0.01	0.01
Ethylene	0.004	0.002	0.16	0.13	0.69	0.86	0.04	0.04
Propylene	-	-	< 0.01	< 0.01	-	-	0.50	0.50
Methyl acetylene	-	-	0.19	0.15	-	-	-	-
2-Butene (cis)	-	-	0.25	0.21	0.003	0.004	-	-
2-Butene (trans)	-	-	0.20	0.17	-	-	-	-
Total Compared to Original Composition			6.7	2.4	0.90	0.3	0.2	0.2
% of Recovered Material(12)				6.8		1.1		0.7

Gas Mixture Recycled Through Collector at 55°C,

Desorbed at 150°C

Adsorbate	Reference Sample	AC Apollo Charcoal		888 Witco Charcoal		Cryogenic Collection Serially Following AC Charcoal Test	
	μg	μg	wt-%	μg	wt-%	μg	wt-%
Freon 12	161	52	32	43	27	0.10	0.06
Freon 113	136	20	15	105	77	0.24	0.18
Methyl alcohol*	1.1	0.10	10	0.01	1.0	-	-
Benzene	24	13	55	18	75	0.02	0.10
Ethyl alcohol	2.5	0.55	22	0.47	19	-	-
Isopropyl alcohol*	1.0	0.80	80	5.2	52	-	-
Acetone	2.5	0.15	6.0	0.21	8.4	0.12	-
Ethyl acetate*	0.50	~ 0.40	~ 80	~ 0.40	~ 80	-	-
Total	329	87	26.4	172	52.3	0.48	0.15

---

*Present as an impurity

Desorbates Not Found In Starting Material	μg	% of Recovered Material	μg	% of Recovered Material	μg	% of Recovered Material
Dichlorodifluoroethylene	0.03	0.03	-	-	-	-
Chlorotrifluoroethylene	0.54	0.62	0.56	0.33	-	-
Vinylidene chloride	-	-	0.004	-	-	-
Ethane	0.14	0.16	0.005	-	-	-
n-Butane	0.02	0.02	-	-	-	-
Ethylene	0.01	0.01	0.05	0.03	-	-
Propylene	< 0.001	-	0.91	0.54	-	-
Acetylene	0.08	0.09	0.04	0.03	-	-
Methylacetylene	-	-	0.08	0.05	-	-
Acetaldehyde	-	-	0.14	0.08	-	-
Total Amount Compared to Original Composition	0.83	0,25	1.78	0.54	-	-
% of Recovered Material		1.0		1.03		

III. CONCLUSIONS

The efforts to obtain an absolutely "clean" charcoal for a zero starting point indicate that charcoal samples are never completely stripped by the relatively modest laboratory methods. When quantities of adsorbates are large enough, the error introduced by starting contamination and by incomplete stripping is negligible. For trace adsorption use, however, significant error is possible. Difficulty in stripping is probably caused by in situ polymerization of adsorbates and by the apparently high energy requirements for removing material from the micropore structure. Of the methods tested, the 160°C, high vacuum system currently in use is as efficient as any for type AC charcoal. Higher surface area charcoals are more completely stripped at 350°C.

For storage of clean charcoal, there seems to be little to choose between the Marvel seal B-117E manufactured by Ludlow Corporation of Holyoke, Massachusetts and triple sealed metal cans such as "paint" cans. The Vacuum conventional desiccator probably would have been successful if the dessicant (anhydrone) was vacuum-thermally stripped before use. The metallized cloth used for Apollo canister shipping is very poor and too permeable to volatile organic materials for good isolation.

The choice of AC charcoal for spacecraft use has been a fortuitous choice so far as analytical use is concerned. This charcoal was most easily stripped of those tested, and was the easiest to keep relatively clean. As an adsorbant, however, it seems to have less capacity or activity than the other three tested materials. In terms of adsorptive potential, these charcoals would probably be rated in descending order as 888 > VG > GI > AC. The surface areas of 1000 m^2/g for AC compared to 1700 m^2/g for VG and GI charcoals, and 1800 m^2/g for 888 is a reasonable explanation for this observation.

Exposure of small samples of charcoal to a simple mixture of one freon, one hydrocarbon, and two ketones in air produced more than twenty compounds other than those added. The quantity varied from slightly more than might have been expected as residual contamination on the charcoal to large quantities of halogenated materials. These results indicate that more work is necessary to study the catalytic effect of charcoal on exposed materials. Without this type of investigation, the necessity of obtaining either a different adsorbant or an improved means for analtyical desorption of charcoal is evident if unbiased data are to be obtained.

The technique of using the retention time and shape of the tail of a component on a charcoal chromatograph column at elevated temperature is a rapid, effective way of deriving an adsorption isotherm for the charcoal. There are some indications that this method may tend to underrate the capacity of the charcoal, but this is a positive safety error if the charcoal is being used for a purification system.

The Polanyi adsorption isotherm provides a good correlation for most of the measured data, if B, the adsorption affinity, is measured for each component of interest.

The estimation of B as the molar volume provides a reasonable value if data are not otherwise available. Abnormal fluids such as water, methanol, or highly associated molecules must be separately considered. Simultaneous adsorption of several components does affect the capacity of the charcoal for any one. It is reasonable to follow the proposal of Myers and Prausnitz (Reference 8) and postulate that the partial pressure of the adsorbate in the vapor phase of an adsorbed mixture is equal to the product of the mole fraction of the adsorbate in the charcoal and the partial pressure the adsorbate would have if the entire filled volume of the charcoal were pure adsorbate.

Breakthrough times can be sufficiently estimated for engineering purposes by assuming step functions for the shape of the front and applying the simultaneous solution of the mass balance equations.

Reactions of compounds on charcoal can lead to error in calculation. However, if the concentration of a component (s) can be controlled within reasonable limits, breakthrough calculations can accurately be predicted.

The use of a short column and a flame ionization detector produces experimental results that compare favorably with those obtained by much more sophisticated methods. Error from this data appear to be on the side that would be more likely to produce a safety factor if critical capacities were to be calculated from this method. i. e. predicted breakthrough slightly lower than true capacity. Use of such a simple system would allow economical determination of the many isotherms of interest in a closed environmental study.

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