

UNCLASSIFIED

AD NUMBER

AD020501

CLASSIFICATION CHANGES

TO: unclassified

FROM: confidential

LIMITATION CHANGES

TO:

Approved for public release, distribution unlimited

FROM:

Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; Jun 1953. Other requests shall be referred to Naval Research Laboratory, Washington, DC.

AUTHORITY

30 Jun 1965, DoDD 5200.10; NRL ltr, 25 Jun 1972

THIS PAGE IS UNCLASSIFIED

UNCLASSIFIED

AD _____

*Reproduced
by the*

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA



DOWNGRADED AT 3 YEAR INTERVALS:
DECLASSIFIED AFTER 12 YEARS
DOD DIR 5200.10

UNCLASSIFIED

Reproduced From
Best Available Copy

D

20501

NOTE: WHEN GOVERNMENT OR OTHER DRAWINGS, SPECIFICATIONS OR OTHER DATA ARE USED FOR ANY PURPOSE OTHER THAN IN CONNECTION WITH A DEFINITELY RELATED GOVERNMENT PROCUREMENT OPERATION, THE U. S. GOVERNMENT THEREBY INCURS NO RESPONSIBILITY, NOR ANY OBLIGATION WHATSOEVER; AND THE FACT THAT THE GOVERNMENT MAY HAVE FORMULATED, FURNISHED, OR IN ANY WAY SUPPLIED THE DRAWINGS, SPECIFICATIONS, OR OTHER DATA IS NOT TO BE REGARDED BY ANY PERSON OR CORPORATION, OR CONVEYING ANY RIGHTS OR PERMISSION TO MANUFACTURE, REPRODUCE, OR SELL ANY PATENTED INVENTION THAT MAY IN ANY WAY BE RELATED THERETO.

Reproduced by
DOCUMENT SERVICE CENTER
KNOTT BUILDING, DAYTON, 2, OHIO

The following **ESPIONAGE NOTICE** can be disregarded unless this document is plainly marked **RESTRICTED**, **CONFIDENTIAL**, or **SECRET**.

NOTICE: THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF THE ESPIONAGE LAWS, TITLE 18, U.S.C., SECTIONS 793 and 794. THE TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.

AD No. 225501
ASTIA FILE COPY

30

~~CONFIDENTIAL~~

NEA REPORT 4273

SECURITY INFORMATION

A SIMPLE METHOD FOR DETERMINING CARBON ACTIVITY IN TREATED TEXTILES

James H. Kettering

Protective Chemistry Branch
Chemistry Division

June 3, 1953



NAVAL RESEARCH LABORATORY

WASHINGTON, D.C.

~~CONFIDENTIAL~~

RECEIVED
JUN 10 1953
1000
4000

CONFIDENTIAL
SECURITY INFORMATION

Naval Research Laboratory. Report 4173.
A SIMPLE METHOD FOR DETERMINING CARBON
ACTIVITY IN TREATED TEXTILES, by J. H.
Kettering, 14 pp. & figs., June 3, 1953.

A simple method for measuring the gas-phase sorption of carbon tetrachloride by carbon-treated fibers, filaments, yarns, and fabrics is described. The carbon-containing sample is weighed into a glass weighing-bottle which is placed in a chamber where sorption occurs at controlled relative pressure of gaseous sorbate. The relative pressure is maintained by means of an attached cold finger in ice water. The amount of sorption is determined by difference in weight of sorbent. It is also shown that reproducible

(over)
CONFIDENTIAL

1. Textiles - Properties
2. Carbon tetrachloride - Adsorption - Measurement
3. Protective clothing - Materials - Development
1. Kettering, J. H.

CONFIDENTIAL
SECURITY INFORMATION

Naval Research Laboratory. Report 4173.
A SIMPLE METHOD FOR DETERMINING CARBON
ACTIVITY IN TREATED TEXTILES, by J. H.
Kettering, 14 pp. & figs., June 3, 1953.

A simple method for measuring the gas-phase sorption of carbon tetrachloride by carbon-treated fibers, filaments, yarns, and fabrics is described. The carbon-containing sample is weighed into a glass weighing-bottle which is placed in a chamber where sorption occurs at controlled relative pressure of gaseous sorbate. The relative pressure is maintained by means of an attached cold finger in ice water. The amount of sorption is determined by difference in weight of sorbent. It is also shown that reproducible

(over)
CONFIDENTIAL

CONFIDENTIAL
SECURITY INFORMATION

Naval Research Laboratory. Report 4173.
A SIMPLE METHOD FOR DETERMINING CARBON
ACTIVITY IN TREATED TEXTILES, by J. H.
Kettering, 14 pp. & figs., June 3, 1953.

A simple method for measuring the gas-phase sorption of carbon tetrachloride by carbon-treated fibers, filaments, yarns, and fabrics is described. The carbon-containing sample is weighed into a glass weighing-bottle which is placed in a chamber where sorption occurs at controlled relative pressure of gaseous sorbate. The relative pressure is maintained by means of an attached cold finger in ice water. The amount of sorption is determined by difference in weight of sorbent. It is also shown that reproducible

(over)
CONFIDENTIAL

1. Textiles - Properties
2. Carbon tetrachloride - Adsorption - Measurement
3. Protective clothing - Materials - Development
1. Kettering, J. H.

CONFIDENTIAL
SECURITY INFORMATION

Naval Research Laboratory. Report 4173.
A SIMPLE METHOD FOR DETERMINING CARBON
ACTIVITY IN TREATED TEXTILES, by J. H.
Kettering, 14 pp. & figs., June 3, 1953.

A simple method for measuring the gas-phase sorption of carbon tetrachloride by carbon-treated fibers, filaments, yarns, and fabrics is described. The carbon-containing sample is weighed into a glass weighing-bottle which is placed in a chamber where sorption occurs at controlled relative pressure of gaseous sorbate. The relative pressure is maintained by means of an attached cold finger in ice water. The amount of sorption is determined by difference in weight of sorbent. It is also shown that reproducible

(over)
CONFIDENTIAL

1. Textiles - Properties
2. Carbon tetrachloride - Adsorption - Measurement
3. Protective clothing - Materials - Development
1. Kettering, J. H.

CONFIDENTIAL
SECURITY INFORMATION

oven-dry moisture contents of carbon-containing textiles may be determined without degradation of the material by heating four hours at 105° C.

CONFIDENTIAL

CONFIDENTIAL
SECURITY INFORMATION

oven-dry moisture contents of carbon-containing textiles may be determined without degradation of the material by heating four hours at 105° C.

CONFIDENTIAL

CONFIDENTIAL
SECURITY INFORMATION

oven-dry moisture contents of carbon-containing textiles may be determined without degradation of the material by heating four hours at 105° C.

CONFIDENTIAL

CONFIDENTIAL
SECURITY INFORMATION

oven-dry moisture contents of carbon-containing textiles may be determined without degradation of the material by heating four hours at 105° C.

CONFIDENTIAL

CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
BACKGROUND	1
INTRODUCTION	1
LITERATURE REVIEW	2
MATERIALS	2
Carbons	2
Fabrics	2
Carbon Tetrachloride	3
Stopcock Lubricant	3
APPARATUS	3
METHOD	4
RESULTS AND DISCUSSION	6
SUMMARY	9
APPENDIX A -- Moisture or Regain Determinations in Carbon- Containing Textiles	10
INTRODUCTION	10
MATERIALS AND METHODS	11
RESULTS AND DISCUSSION	11
CONCLUSIONS	13
REFERENCES	14

ABSTRACT

A simple method for measuring the gas-phase sorption of carbon tetrachloride by carbon-treated fibers, filaments, yarns, and fabrics is described. The carbon-containing sample is weighed into a glass weighing-bottle which is placed in a chamber where sorption occurs at controlled relative pressure of gaseous sorbate. The relative pressure is maintained by means of an attached cold finger in ice water. The amount of sorption is determined by difference in weight of sorbent. It is also shown that reproducible oven-dry moisture contents of carbon-containing textiles may be determined without degradation of the material by heating four hours at 105°C.

PROBLEM STATUS

This is an interim report; work on the problem is continuing.

AUTHORIZATION

NRL Problem C04-24
RDB Project NS 181-002

Manuscript submitted May 1, 1953

A SIMPLE METHOD FOR DETERMINING CARBON ACTIVITY IN TREATED TEXTILES

BACKGROUND

The general utility of activated carbon as a gas adsorbent for protective clothing has been established (15). Carbon-treated protective clothing has been manufactured but manufacture has been difficult (19) and the products have been generally unsatisfactory. In general two types of carbon treatments have been used: (a) the fabric surface was coated with a carbon-containing adhesive material and (b) the carbon was placed in the viscose bath and extruded in the rayon filaments. Both types of carbon treatments have been unsatisfactory for one or more of the following reasons: poor adhesion, poisoning of the carbon, low strength, short wear life, or poor "hand" of the yarn and fabric.

A program has been in progress at the Naval Research Laboratory, the purpose of which is to produce an improved fabric meeting acceptable standards of strength, flexibility, "hand" and "drape," and at the same time afford adequate protection against chemical warfare agents. Instead of putting the carbon on the fabric surface or within the filaments, the carbon is coated on the filament surfaces. By improving the desirable properties of filaments and yarns, coating them with activated carbon, spinning and weaving them, the resulting fabrics should be satisfactory.

INTRODUCTION

The development of a carbon-coated or impregnated yarn has been hampered by the complexity of the analytical techniques for determining carbon activity. The two analytical methods thus far employed (4, 5, 7, 16) are designed to provide reproducible results which are related to service performance. Both of them require regulation and control of air-flow rates, H-Vapor concentration, humidity, temperature, and pressure differentials across the fabric. They differ in that in one case air is driven through the fabric whereas in the other there is zero pressure differential across the fabric. Both of the analytical methods, although used in measuring carbon activity, were designed for testing clothing which had been impregnated with chloroamides under conditions approaching those that exist when a garment is worn in combat. Neither method provides a means of determining the activity of carbon-coated or impregnated yarns and neither method is suited for the granular or micronized carbon.

Sheffer (21) describes the use of isopiestic measurements to obtain, among other data, charcoal activity and adsorption isotherms. The present report gives the adaptation of the desiccator technique of Sheffer, Waldock, and Ferguson (20) for the measurement of comparative activity of carbon coated or impregnated filaments, yarns, and fabrics as well as of granular and micronized carbon. The adapted method, when carbon contents (14) are known, provides data for computing loss of carbon activity or poisoning of the carbon.

The application here reported consists of comparing two or more sorbents by placing them in gaseous sorbate in a vacuum desiccator at controlled temperature. The concentration of gaseous sorbate is maintained constant by keeping it in contact with its liquid phase maintained at 0°C by means of a connected cold finger in an ice bath. The relative activity of sorbents is found by comparing weights before and after sorption.

LITERATURE REVIEW

Ferguson and co-workers (20) point out that isopiestic ("equal pressure") sorption is a general method applicable to all equilibria involving the "taking up (sorbing) of a substance (sorbate) by another phase (sorbent)" and that "sorption capacities of activated charcoals toward vapors may be tested simply and rapidly using the isopiestic method." Sheffer, Waldock and Ferguson (20) used the isopiestic method to test activated charcoals and found that ratios of vapor sorbed at saturation agreed very well with ratios of activities obtained by a flow method (18,p333). They compared sorptive capacities of nine different activated charcoals for carbon tetrachloride, water, amyl chloride, benzene, methyl alcohol, n-hexane, mustard gas, and phosgene. Barnartt and Ferguson used "isopiestic charges (milligrams of sorbate per gram of sorbent at equilibrium)" to plot isotherms, to discover errors in isotherms, to show structural regularities in activated charcoals (2), and to study various stages of steam activation of charcoals (3).

Ferguson and his co-workers (2, 3, 20) used carbon tetrachloride in many of their isopiestic measurements. Lauer (17), using a quartz-spring-balance apparatus described by Kanamaru and Chao (12), showed that carbon tetrachloride is only slightly sorbed by cotton. That rather unexpected result has been confirmed in this Laboratory and extended to include viscose rayon. Carbon tetrachloride isotherms are now available for some twenty different carbons (9). All those isotherms are type I of Van der Waal's adsorption isotherms (18,p22) which become flat, or nearly so, at sorbate partial pressures (P/P_0) of 0.150 to 0.200.

MATERIALS

Carbons

Five activated carbons were used in this investigation:

1. Pittsburgh Coke and Chemical Co. (P.C.I.) "hard char" prepared from coal, 12 - 30 mesh carbon.
2. National Carbon Co. (N3A), extruded wood, 12 - 30 mesh carbon.
3. National Carbon Co. (Type G), coconut base, 12 - 30 mesh carbon.
4. National Carbon Co. (CWS N44), wood base, micronized carbon.
5. National Carbon Co. (CWS N182), wood base, micronized carbon.

Fabrics

The fabrics used were chosen from those on hand in this Laboratory. They represent a range of materials adequate to test the method. A brief description of the fabrics follows:

1. Carbon-in-rayon twill (nylon plied in the filling). Resembles sample No. 176 (9, Appendix I).
2. Carbon-impregnated rayon knitted fabric. Source unknown.
3. Carbon-coated herringbone twill. Source unknown.
4. Carbon-coated herringbone twill, CWS Lot S-42.
5. Carbon-coated cotton sheeting. Source unknown.

6. Carbon-coated 9-oz sateen. "Darex" resin emulsion, N-182 micronized carbon with "Hycar" topping.
7. Unbleached cotton twill, 10-1/2 oz/sq.yd.
8. Bleached cotton twill, 10-1/2 oz/sq.yd.
9. Sheeting extensively degraded in service.

Carbon Tetrachloride

The carbon tetrachloride used was C. P. grade, further purified by the method of Gunther, Von der Horst and Cronheim outlined by Weissberger and Proskauer (23). The method briefly is as follows: Shake one liter of carbon tetrachloride with three successive 100-ml portions of alcoholic potassium hydroxide, separate, discard the potassium hydroxide layer, wash with plenty of water, discard the washings, dry over CaCl_2 and distil from paraffin using the part that distills at 76.8°C . Approximately 30 percent of the carbon tetrachloride distills within 0.61°C of this temperature.

Stopcock Lubricant

Sheffer, Waldock and Ferguson (20) found that a grease made by partially saponifying linseed oil was satisfactory for the retention of carbon tetrachloride vapor and used this "soap" on the inner half of the desiccator flange with "ordinary stopcock grease" on the outer half when the desiccator was placed in a thermostatically controlled water bath. The Herrington and Starr ether-insoluble stopcock lubricant (10) is also satisfactory for retention of carbon tetrachloride vapors. However, even though Apiezon M^{*} and silicone High Vacuum Grease (Dow-Corning) are soluble in carbon tetrachloride, the solvent action is not great enough in the isopiestic measurements here described to preclude their use.

APPARATUS

The apparatus (Figures 1 and 2) consists of a 250-ml vacuum-type desiccator (A), with the lid opening ground down and fitted with the female portion of a $\text{F} 45/50$ joint (B), to the side of which is attached a 10-mm, 2-way stopcock (C), leading to a $\text{F} 28/15$ ball joint (D), a mercury manometer (E), and a 3-way, 10-mm stopcock (K). The upper end of the female portion of the $\text{F} 45/50$ joint is drawn down and attached to a second $\text{F} 28/15$ ball joint (F). The tube from this joint runs through the top of an insulated box where its enlarged end (G) rests in an ice bath (H). The stopcock (I) is 2 mm in size with one side sealed into the enlarged end of the tube (G) and the other side flared to a funnel shape with the top 20 mm in diameter. To one tube from the stopcock (K) is attached the drying tower (L) containing anhydrous calcium chloride or calcium sulfate ("Drierite") drying agent and having a capillary opening (M) which has been drawn down to a still smaller opening. The tube from the remaining end of the stopcock (K) leads into a liquid trap (N), which is connected to the side-arm vapor trap (O) resting in a vacuum bottle (P) containing "dry ice." The outlet tube from the vapor trap, (O) leads to a Cenco Hyvac pump (U). A joints are carefully ground and fitted for high vacua.

The box (Figures 1 and 2) surrounding the desiccator (A) with its attached joints (B), (C), (D), and (F), and manometer (E) is constructed of plywood covered with "Celotex." It is 28 inches wide, 22 inches deep, 22 inches high and has approximately 1-1/2 inch wall thickness. The front is closed by two 11-3/4 by 19-3/4 inch glass doors. Each door has a double glass with an air space between. A fan (Q) mounted in the top of the

*Apiezon lubricants for high vacuum work are marketed by James Biddle Co., Philadelphia, Pa.

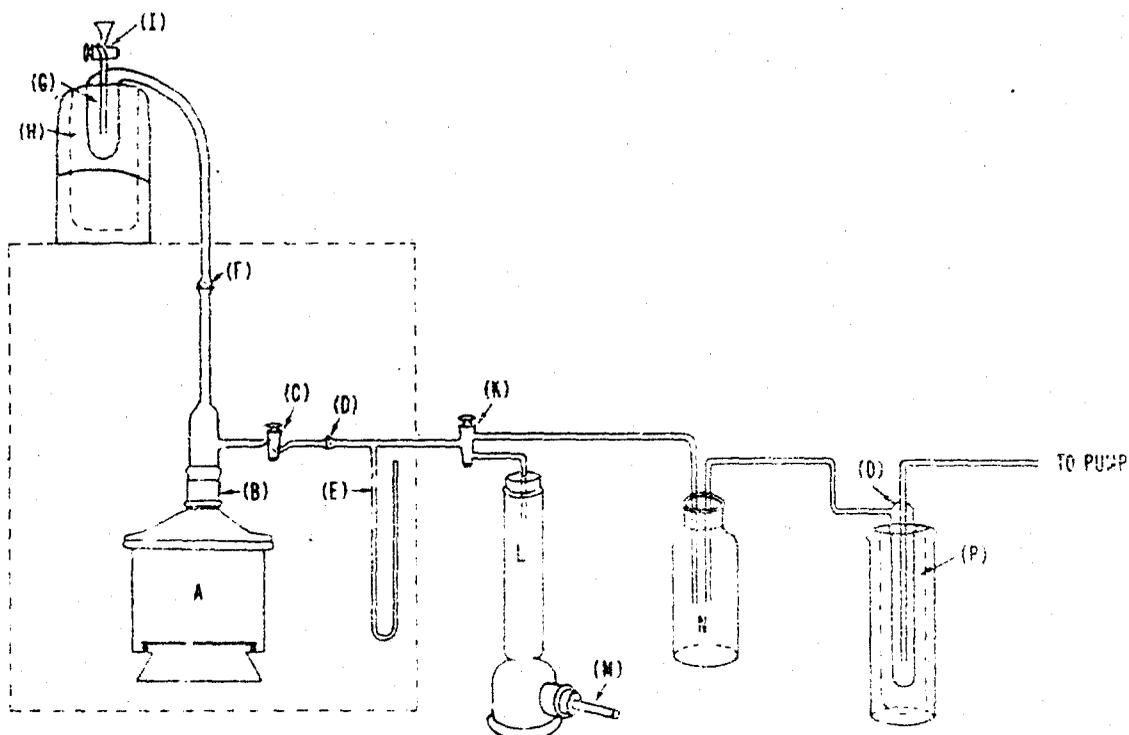


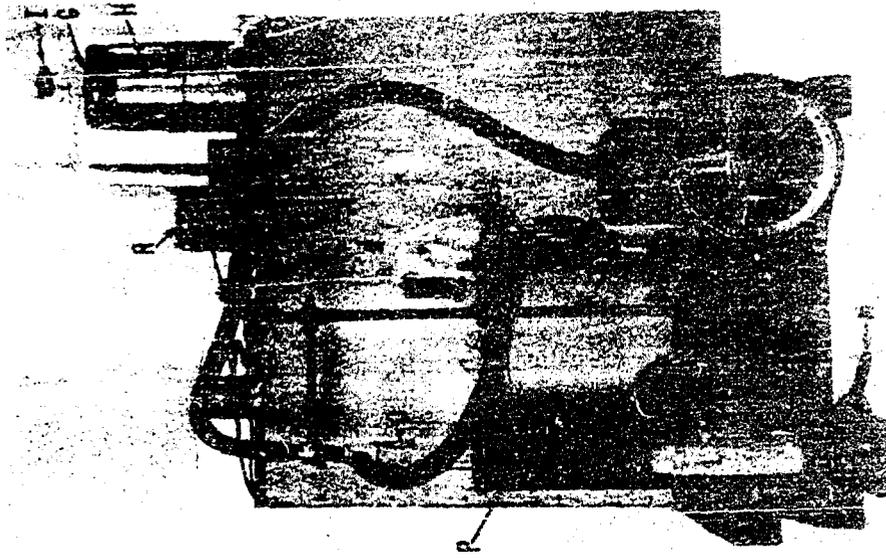
Figure 1 - Assembly for isopiestic sorption measurement

box (with motor (R) outside) maintains rapid air circulation, thereby reducing temperature variations within the box to a minimum. The box is heated by two 250-watt, 115-volt "Aminco Lo-Lag Oven Heaters" (S) connected in series. Temperature is controlled by a thyatron electronic relay (not shown) and sensitive mercury thermoregulator (T) set at 40°C.

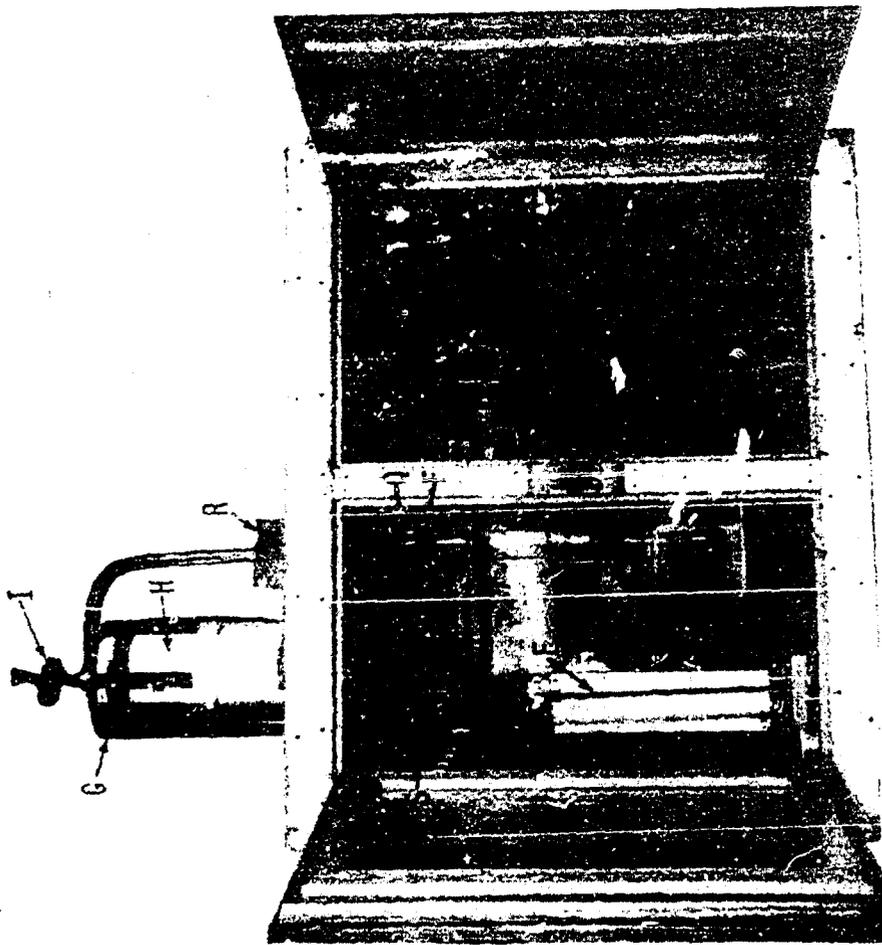
METHOD

Experience has shown that the following procedure is satisfactory:

Weigh samples directly in weighing bottles and dry for 4 hours at 105°C (Appendix A) in an electrically controlled air oven, cool 30 minutes in a desiccator over anhydrous calcium chloride or calcium sulfate "Drierite," and weigh. This gives the dry weights of samples and sufficient data for calculating moisture contents. Place the dry samples in the desiccator (A) of the apparatus with the lids of weighing bottles turned to leave the samples exposed. Close the apparatus and evacuate to a pressure of less than a millimeter of mercury and then continue pumping for 30 minutes. Stop the pump and allow dry air to enter the apparatus through the capillary (M) and drying tower (L) by manipulating the stopcock (K). Without opening the apparatus, again evacuate to less than a millimeter pressure, pump for an additional 30 minutes and then close the stopcock (K). Wait long enough to be sure there are no leaks and then pour the required amount of carbon tetrachloride into the chamber (G) through the stopcock (I), being careful to admit no air to the evacuated chamber. Be sure there is an excess of carbon tetrachloride in the chamber. Let the sorption continue for 4 hours. Admit dry air as



(b) Rear view



(a) Front view

Figure 2 - Apparatus for isopiestic measurements

before and open the apparatus. Wait 5 minutes to allow the carbon tetrachloride to evaporate from the inner surfaces of the weighing bottles, then close and weigh them. (An alternate procedure would be to omit this step and apply a correction.) Determine the carbon tetrachloride sorbed by difference and report as grams or milligrams per gram of sample or per gram of carbon in the sample.

RESULTS AND DISCUSSION

The time, 4 hours, for samples to remain in the evacuated apparatus is somewhat longer than the 2 to 3 hours used by Sheffer, Waldock, and Ferguson (20), but is still short enough to permit completion of the analyses within a working day. Four hours has given reproducible results, and Table I shows that nothing is gained by prolonging adsorption beyond that time. Moreover, the results are in the order expected from previous knowledge of the samples.

TABLE I
Isopiestic Sorption of Carbon Tetrachloride
Vapors for Periods of 2 to 24 hours

Carbon No.	Grams of Carbon Tetrachloride Absorbed per Gram of Sample			
	2 hr	3 hr	4 hr	24 hr
1	0.4137	0.4166	0.5329	0.5700
2	.7904	.8782	.8866	.8795
3	.7149	.7378	.7359	.7660
5	.9168	1.0870	1.1191	1.1180
Fabric 1	0.0438	0.0428	0.0560	0.0567

The precision of the method is evident from the following analyses run at different times. Each reported figure is the average of two determinations.

TABLE II
Isopiestic Sorption of Carbon Tetrachloride by Carbon

Carbon Tetrachloride Sorbed per Gram of Activated Carbon		
Date	Carbon No. 2	Carbon No. 3
April 4	0.904	0.789
April 7	.889	.780
April 15	.895	.769
May 4	.879	—
April 19	—	.787
July 20	.910	—
	Av. 0.895 ± .011	Av. 0.781 ± 0.008

To determine whether size of sample, or bed depth, had any effect on the results, various quantities of carbon No. 2 were weighed into tallform weighing bottles, which were of the same diameter and the sorption was determined. The results, Table III,

show that considerable variation in sample size, or bed depth, has very little effect on the analytical results.

TABLE III
Isopiestic Sorptions of Carbon
Tetrachloride at Different Bed Depths

Dry Sample	CCl ₄ Sorbed per Gram of Carbon (gm)	Av. of Duplicate Samples
0.9713	0.879	0.875
1.0042	.871	
1.9405	.870	.874
1.9529	.878	
2.9734	.879	.878
2.9031	.878	
3.8871	.876	.878
3.8469	.879	
4.9431	.879	.878
4.8308	.876	
6.8545	.876	.878
6.7419	.879	

To ascertain the sorption of carbon tetrachloride on cotton, three cotton fabrics (Nos. 7, 8, and 9) that contained no activated carbon, were sampled and analyzed. The sorptions of all these samples were measured at the same time. Activated carbon used as a check showed normal sorption. The results are shown in Table IV. Cotton fabric sorbs from 0.2 to 0.3 percent carbon tetrachloride by weight. Considerable variation in size of sample does not alter this percentage. A correction factor of 0.2 to 0.3 percent is within the precision of the method.

TABLE IV
Isopiestic Sorption of Carbon Tetrachloride by Cotton Fabrics

Sample (No.)	Fabric (No.)	Dry Sample Weight (gm)	Carbon Tetrachloride Sorbed per Gram of Dry Sample (gm)
1	7	1.1046	0.0021
2	7	1.1391	.0019
3	7	7.5521	.0022
4	7	7.5759	.0022
5	8	3.9652	.0021
6	8	4.0242	.0025
7	9	3.7952	.0030
8	9	3.7962	.0028

Sheffer, Waldock, and Ferguson (20), in their experiments, noticed droplets of carbon tetrachloride condensed on the weighing bottles after sorption, which they allowed to evaporate by exposing the open bottles to the air for 5 minutes before placing the lids on them. In order to ascertain the magnitude of error from this source, 12 carbon

samples were weighed in weighing bottles, and, with four weighing bottles containing no samples, were tested for sorption by the method here outlined except that the bottles were closed in the apparatus, were weighed without being open to the air, were then opened to the air for 5 minutes and were again weighed. The differences between the weighings (or the error) averaged 5.3 milligrams. See Table V. The data show no evidence of evaporation or desorption from the carbon itself.

TABLE V
Condensation of Carbon Tetrachloride
on the Walls of Weighing Bottles
During Isopiestic Sorptions

Sample (No.)	Dry Sample (gm)	CCl ₄ Condensed (mg)	Sample (No.)	Dry Sample (gm)	CCl ₄ Condensed (mg)
1	1.8855	4.1	11	1.3927	5.3
2	2.2157	5.7	12	1.3006	4.4
3	1.6012	6.4	13	—	6.6
4	1.2383	7.4	14	—	3.5
5	1.8120	7.0	15	—	5.5
6	1.4037	4.9	16	—	3.5
7	1.0501	6.1	Average	All carbon-containing bottles	5.3
8	1.4515	2.7	Average	All empty bottles	4.8
9	1.6254	5.5	Average	All bottles	5.2
10	1.5118	4.0			

Typical data for isopiestic sorptions of carbon tetrachloride by fabrics coated or impregnated with activated carbon are shown in Table VI. The data were taken from weighings made on an analytical balance or computed therefrom by standard methods. Carbon No. 4, for which values were already available, was used as a check for errors in technique.

TABLE VI
Isopiestic Sorption of Carbon Tetrachloride
by Six Different Fabrics

Sample (No.)	Dry Sample (gm)	CCl ₄ Sorbed (gm)	CCl ₄ /gm Dry Sample (gm)
Carbon 4	1.4794	1.2388	0.837
	1.0419	0.8742	.838
Fabric 1	3.8466	.2579	.069
	3.9713	.3071	.077
2	4.2041	.1325	.032
	3.8097	.1421	.037
3	5.0468	.3625	.072
	4.4022	.3213	.073
4	4.6761	.4865	.104
	5.2784	.5548	.105
5	3.4914	.1225	.035
	3.2049	.1230	.038
6	4.5186	.4244	.094
	4.6767	.4560	.098

SUMMARY

A simple procedure has been devised for the determination of carbon tetrachloride sorbed on activated carbons, and on fibers, filaments, and fabrics coated with activated carbons. The necessary apparatus has been described. The method gives reproducible results and may be used in exploratory investigations of the sorptions of carbon coated and/or impregnated fabrics in place of the more complex flow methods. The method has the added advantage that it applies to granular or micronized carbon and to fibers and filaments as well as to fabrics. Although recommended for carbon tetrachloride as sorbate, a variety of sorbates may be used.

* * *

APPENDIX A
Moisture or Regain Determinations in Carbon-Containing Textiles

INTRODUCTION

Both activated carbon and cellulosic materials absorb water and hold it tenaciously. "Bone dry" carbon is extremely hard to obtain and "bone dry" cotton or rayon is rare. Indeed, Houtz and McLean (11) state that "paper cannot be obtained in the dry state without degradation" and Haas (8) found signs of degradation in cotton heated from 30° to 100°C for a few hours. Moreover, Stamm's summary (22) shows that the hysteresis effects and other anomalous behavior of cellulosic materials in moisture determinations are well known. Deitz and Gleysteen (8) failed to bring activated carbon samples to constant weight by heating them in an air oven at temperatures ranging from 105° to 150°C for periods of from a day to a week. Fortunately, adequate analytical procedures for carbon-containing fibers, filaments, yarns, and fabrics depend more on measurements of moisture contents that are precise and reproducible than on absolute accuracy. The purpose of this appendix is to present a procedure for moisture determinations which has been found adequate for general use in the analyses of carbon-containing fibrous materials and the theoretical, experimental and practical considerations supporting it.

Four methods are available for the determination of moisture in the textile materials: (a) distillation from an organic liquid such as xylene or benzene, (b) titration of water after cold extraction with methanol using Karl Fischer reagent, (c) drying in a vacuum desiccator at room temperature over a drying agent, and (d) oven drying at elevated temperatures.

The first of these methods depends upon distilling from a flask containing a large volume of xylene or benzene. The moisture distills over with the xylene or benzene and is collected in a graduated cylinder or graduated arm of the apparatus. This method requires large samples, bulky apparatus, and a recovery of the xylene or benzene used.

Keating and Scott (13) found that moisture of cotton textiles can be determined with Karl Fischer reagent as efficiently and more accurately than by oven drying and "saves an appreciable amount of time" when it is necessary to make "a large number of moisture determinations daily." The Fischer technique is applicable to a large number of organic compounds but the reagents are unstable and require daily standardization. Moreover, the wide variety of resins, rubbers, and other adhesives required for the investigation of carbon-coated or impregnated fibrous materials would require elaborate constant evaluation to establish the accuracy and precision of this technique. No evidence has been found which justifies the use of Karl Fischer reagent on noncellulosic fibers or filaments.

The third method, using phosphorus pentoxide in the desiccator was used by Urquhart (24) in extensive investigations of moisture relations in cotton. It is very accurate and precise, but each determination requires from 1 to 3 weeks, which precludes its use for most investigations of carbon-coated or impregnated materials.

The fourth method, oven drying at elevated temperatures, appeared best for general use when time and temperature were considered in connection with accuracy, precision, and the nature of the carbon-containing materials. This method was, therefore, investigated and standardized for use.

MATERIALS AND METHODS

The three fabrics used in this investigation were: (a) unbleached cotton twill, approx. 10.5 oz/sq. yd; (b) carbon-rayon twill with undyed rayon warp and carbon-rayon filling and; (c) a carbon-rayon fabric having a rayon warp and carbon-rayon plied with nylon in the filling. All samples were weighed in an air-conditioned laboratory after conditioning overnight at 25°C and 50 percent relative humidity. Approximately one-gram samples were dried to constant weight in tall glass weighing bottles in an electrically controlled air oven at temperatures of 105° ± 0.5°C, 115° ± 0.5°C, 125° ± 1°C, 135° ± 1°C, 140° ± 1°C, and 150° ± 1°C. Breaking strengths were determined by the raveled-strip method (1). Strips were cut 6 inches long (warpwise) by 1.25 inches wide (fillingwise), raveled to one inch and broken on a pendulum-type Scott Tester between jaws set 3 inches apart, the lower jaw travelling downward at the rate of 12 inches per minute. The Scott Tester was not in an air-conditioned laboratory. The breaks, however, were made under conditions that remained reasonably constant throughout the test. The breaking strengths are, therefore, believed to be comparable. Previous to breaking, the strips were suspended by clips in the oven for the time found to be required to reach constant weight at each of the temperatures used in obtaining oven-dry weight. For each temperature used, samples from each of the three fabrics were heated in the same oven at the same time.

RESULTS AND DISCUSSION

TABLE VII
Time Required for Three Different
Fabrics to Reach Constant Weight
When Heated at Different Temperatures

Temperature of Heating (°C)	Fabric 1 Unbleached Cotton Twill (hrs)	Fabric 2 Rayon Twill (hrs)	Fabric 3 Rayon-Nylon Twill (hrs)
105	4	4	4
115	3	3	3
125	2	2	2
135	2	2	2
140	2	2	2
150	2	2	2

At temperatures above 125°C, the unbleached cotton twill was yellowed and at 150°C showed definite evidence of scorch. Owing to the original color of the material, such color changes could not be observed in Fabrics 2 and 3. However, increases in "moisture contents" (loss in weight on heating) (Table VIII) and lowering of breaking strengths (Table IX) leave little doubt that some changes also occurred in these fabrics.

TABLE VIII
Moisture Determinations in Three Fabrics
Found by Drying at Different Temperatures

Temperature of Heating (°C)	Fabric 1 Unbleached Cotton Twill* (%)	Fabric 2 Rayon Twill* (%)	Fabric 3 Rayon-Nylon Twill* (%)
105	5.09	9.77	7.15
115	5.62	10.42	7.69
125	5.43	10.04	8.16
135	5.50	10.24	8.29
140	5.48	10.05	7.74
150	5.55	10.10	7.92

*Each recorded figure is the average of ten determinations.

Because of the appearance of the samples, and changes in breaking strength (Table IX), the increased moisture contents found at temperatures above 105°C may represent some distillation of fabric impurities rather than true moisture content. However, Dietz and Gleysteen's observations on the reluctance of carbon to part with absorbed or adsorbed moisture (6) make it plausible to assume that, at least, part of this increase is due to moisture driven from the carbon. The apparent increase in oven-dry moisture content due to prolonged heating was in the order of 0.5 percent for Fabrics 1 and 2 and became considerably larger with Fabric 3, where the strength loss was greatest (Figure 3).

TABLE IX
Breaking Strengths of Fabrics Heated
to Oven-Dryness at Different Temperatures

Temperature (°C)	Time Heating (hrs)	Fabric 1 Cotton Twill		Fabric 2 Rayon Twill		Fabric 3 Rayon-Nylon Twill	
		Break (lbs)	STD. Dev.*	Break (lbs)	STD. Dev.	Break (lbs)	STD. Dev.
Control	0	180	5	76	3	113	6
105	4	178	4	76	4	113	3
115	3	181	8	74	6	108	7
125	2	180	5	71	3	100	6
135	2	182	5	55	3	78	7
140	2	177	10	59	2	70	8
150	2	174	5	41	3	29	2

*Standard Deviation is the square root of the mean square deviation.

$$\text{Standard Deviation} = \sqrt{\frac{\sum d^2}{n}}$$

Each recorded figure in Table IX is the average of ten determinations. The relatively large changes in breaking strength of Fabrics 2 and 3 leave little doubt that at all temperatures measured above 105°C some degradation of these samples occurred. The yellowing and scorch appearing in Fabric 1, are evidence that, here also, some degradation occurred even though breaking strengths do not show it conclusively. The loss in breaking strength is more clearly demonstrated in Figure 3.

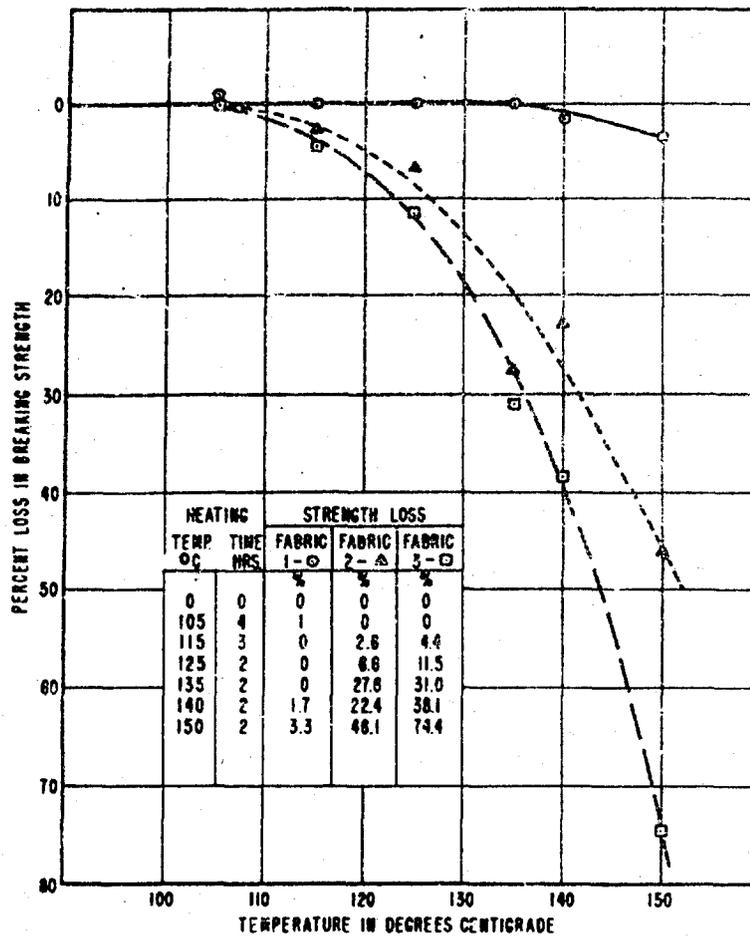


Figure 3 - Losses in the breaking strengths of three fabrics, caused by heating them to dryness

CONCLUSIONS

In view of the foregoing considerations, the following conclusions appear justified:

1. Prolonged heating of carbon-containing textile materials should be avoided since it causes some degradation of the materials.
2. "Oven-dry" moisture contents are satisfactory for investigations of carbon containing fibers, filaments, yarns or fabrics.
3. All quantities required should be weighed at one time and moisture determined on one of the samples.
4. Four hours at 105°C using glass moisture bottles in an electrically heated and controlled oven are satisfactory conditions for determination of "oven-dry" moisture contents of carbon-containing textiles.

REFERENCES

1. American Society for Testing Materials. ASTM Standards on Textile Materials D 39-39 (1946)
2. Barnartt, S., and Ferguson, J. B., Can J Research, 27B, 87-100 (1949)
3. Barnartt, S., and Ferguson, J. B., Can J Research, 27B, 101-115 (1949)
4. Cooke, A. A., TDMR No. 940 Army Chemical Center (Restricted), January 17, 1945
5. Cooke, A. A., and Little, G. A., TDMR No. 1247 Army Chemical Center (Restricted), April 30, 1946
6. Deitz, V. R., and Gleysteen, L. F., J Research, Nat Bur Standards, 28, 795-805 (1942)
7. Guss, W. I., and Adkins, H., OSRD Report No. 6084 (Confidential), October 17, 1945
8. Haas, H., Kunstseide u Zellwolle, 21, 88-90 (1939)
9. Heise, G. W., Sylh, J. A., Janes, M., Winslow, N. M., Taylor, S. A., and Sullivan, J. B., NDRC Informal Report No. 10.5-34 (Confidential), May 1944
10. Herrington, B. L., and Starr, M. P., Ind Eng Chem, Anal Ed, 14, 62 (1942)
11. Houtz, C. C., and McLean, D. A., J Phys Chem, 43, 309-321 (1939); 45, 111-127 (1941)
12. Kanamaru, K., and Chao, J., Kolloid-Z, 84, 85-99 (1938)
13. Keating, J. F., and Scott, W. M., Amer Dyestuff Repr, 31, P306-P310 (1942)
14. Kettering, J. H., NRL Report No. 3722 (Confidential), August 7, 1950
15. Lanning, W. C., NRL Report No. P2719 (Confidential), December 17, 1945
16. Lanning, W. C., Gantz, G. M., and Taylor, W. H., NRL Report No. P1831 (Confidential), January 6, 1942
17. Lauer, K., Kolloid-Z, 107, 86-88 (1944)
18. Mantell, C. L., "Adsorption," p. 333, McGraw-Hill Book Company, Inc., New York and London (1945)
19. Moss, S. A., Jr., OSRD Report No. 6287 (Confidential), November 19, 1945
20. Sheffer, H., Waldock, K. T., and Ferguson, J. B., Can J Research, 27B, 25-34 (1949)
21. Sheffer, H., "Physico-Chemical Measurements Using Isopiestic Methods," DRCL Report No. 54 (1950)
22. Stamm, A. J., U. S. Dept of Agriculture, Miscellaneous Publication No. 240, p. 90, June 1936
23. Weissberger, A., and Proskauer, E., "Organic Solvents; Physical Constants and Methods of Purification," New York, Oxford University Press (1935)
24. Urquhart, A. R., and Williams, A. M., J Textile Inst, 15, 138T-148T (1924)

* * *

UNCLASSIFIED

UNCLASSIFIED