

FRUIT STORAGE

Saturation of Activated Carbon Used For Air Purification

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Purification of air for fruit storage by the use of activated carbon, now in commercial use, has been studied by laboratories here and abroad. Such studies have been largely concerned with examinations of stored fruit and analyses of storage air, but no detailed attention has been given to the patterns of saturation of the carbon. This study presents qualitative and quantitative analyses of the sorbates of several carbons and their variations through a fruit storage season. Infrared spectra illustrate changes in relative prominence of several organic functionalities in the carbon sorbates as the season progresses. Analyses of brominated carbon are given. Based on these analytical results, hypotheses are made concerning functioning of activated carbon in fruit storage.

PURIFICATION OF AIR by activated carbon in fruit storage rooms is designed to accomplish three beneficial effects: control of storage odors and resulting off-flavors of fruit (8), abatement of apple scald (14, 15), and retarding of fruit maturation so that up to 2 months of additional storage life are realized (12, 19). Some workers, however, have reported no significant responses of fruit to air purification (4-6). In a recent review of the subject, Smock (12) has discussed the effect of storage and fruit conditions on the results of air purification, and the physiological roles of nonethylenic gases in the storage space. In view of the fact that the complex factors of fruit condition, air composition, and carbon saturation all profoundly affect the results of air purification, it is noteworthy that carbon saturation is the only factor which has not received detailed attention. This report therefore deals with patterns of carbon saturation under conditions of commercial fruit storage.

Air purification in Pacific Northwest fruit cold storage rooms for the 1949-50 and 1950-51 seasons was studied (20). The present study was carried out to determine qualitative and quantitative saturation of the activated coconut shell carbon used in the 1950-51 tests, to compare this with like saturation of alternative varieties of activated carbon, and to determine average organic vapor concentrations in the storage space under conditions of continuous purification.

Methods

Collection of Vapors For purification of air in the storage test room approximately 6 pounds of granular activated coconut shell carbon

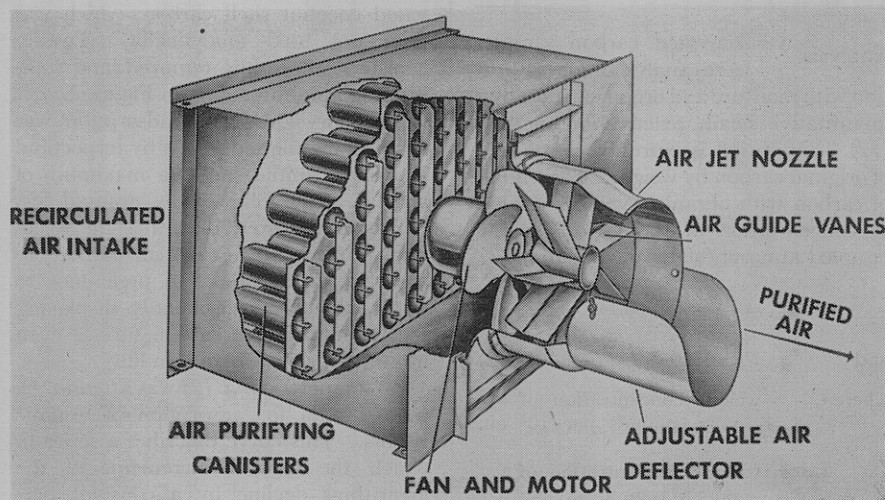
were used for each 1000 boxes of storage capacity. One of these seven identical Dorex (trade name for air purification equipment manufactured by Connor Engineering Corp., Danbury, Conn.) air purification units in this test room served as the collection equipment. This unit (Figure 1) contains 60 canisters filled with activated carbon (16), each containing about 1.7 pounds of carbon in a uniform, cylindrical bed 0.75 inch thick. These canisters are secured to a manifold plate in a pattern which ensures both equal apportionment of the intake air among the canisters and uniform air flow through each increment of carbon bed (3). It is thus valid to compare saturations of different varieties of carbon by comparing analyses of carbons from multiple canisters of one such unit. Furthermore, the linear air flow rate of

approximately 25 feet per minute through the carbon bed has been found to produce an average adsorption efficiency of 95% for vapors boiling above about 0° F., until practical saturation of the carbon with respect to any particular volatile has been reached (17). Lower boiling gases and vapors, such as ethylene, require chemisorption methods for their efficient removal.

Activated Carbon

The experimental unit contained 23 canisters of activated coconut shell carbon, 20 canisters of activated bituminous carbon, 8 canisters of activated coconut shell carbon uniformly impregnated with 15% of its weight of bromine, and 9 canisters of activated coconut shell carbon used in a previous apple storage during the 1949-50 season and then completely reacti-

Figure 1. Air purification unit



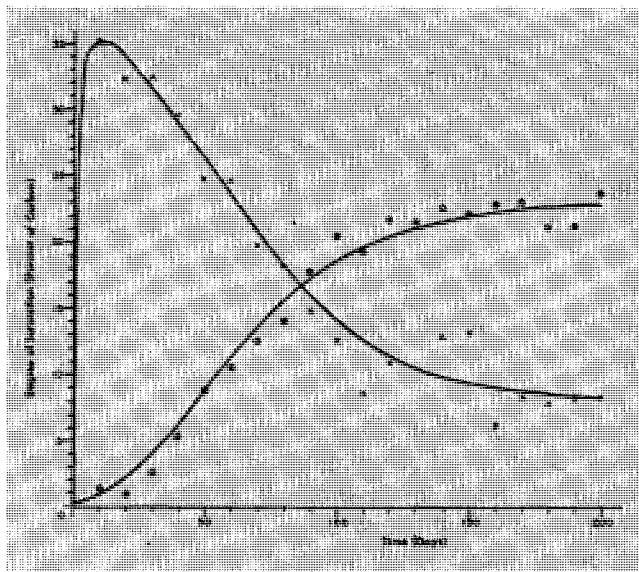


Figure 2. Saturation of coconut shell activated carbon in commercial apple storage

X Adsorbed water
O Adsorbed organics
Time origin, Sept. 27, 1950

vated. All samples of carbon conformed to the specifications listed in Table I; in the case of the bromine-impregnated carbon, these specifications describe the carbon before impregnation.

Table I. Specifications for Activated Carbon for Air Purification

Property	Specification
Activity for CCl_4^a	At least 50%
Retentivity for CCl_4^b	At least 30%
Apparent density	At least 0.42 gram/ml.
Hardness (ball abrasion) ^c	At least 80%
Mesh distribution	6-14 range (Tyler)

^a Maximum saturation of carbon, at 20° C. and 760 mm., in air stream equilibrated with CCl_4 at 0° C.

^b Maximum weight of adsorbed CCl_4 retained by carbon on exposure to pure air at 20° C. and 760 mm.

^c Per cent of 6-8-mesh carbon which remains on 14-mesh screen after vibrating with 30 steel balls of 0.25- to 0.37-inch diameter per 50 grams of carbon, for 30 minutes.

Analysis Activated carbon samples were analyzed for saturation with moisture and organic vapors by a quantitative steam reactivation method (17). Saturation is expressed as per-cent of original carbon by weight. Saturation of carbon with organic vapors is related to concentration of the vapors in the sampled atmosphere by the equations,

$$C_w = \frac{1.67 (10)^4 SW}{tQ_r} \quad (1)$$

$$\text{and} \quad C_v = 360 C_w/M \quad (2)$$

where C_w = weight concentration of vapors, pounds per 10⁶ cu. feet of air

C_v = volume concentration of vapors, p.p.m. at 32° F.

S = proportionate nonaqueous saturation of carbon, dimensionless
 W = weight of carbon, pounds
 t = time of operation, hours
 Q_r = air flow through W pounds of carbon, cubic feet per minute
 M = average molecular weight of vapors

Qualitative determinations of various functional groups were made by applying standard tests to the aqueous and oily portions of the steam desorbate from the particular carbon sample (17).

Saturation of Activated Coconut Shell Carbon

Figure 2 illustrates the saturation pattern of activated coconut shell carbon in the 1950-51 test room. One canister of activated coconut shell carbon was removed from the test unit for analysis at 10-day intervals, and was replaced in each case by a canister with fresh activated coconut shell carbon, which was then not used analytically. Twenty canisters were thus removed and analyzed to obtain the data in Figure 2.

The curve for water adsorption was fitted to the plotted points by inspection. The sharp initial rise to a maximum of around 35%, followed by gradual loss of adsorbed water, illustrates the selective property of activated carbon to adsorb organic vapors in preference to water, the former gradually displacing the latter from the carbon surface even in atmospheres of high humidity.

A Gompertz curve (2) was fitted to the plotted data for adsorption of organic vapors. This curve describes a series in which the growth increments of the logarithms decline by a constant per-

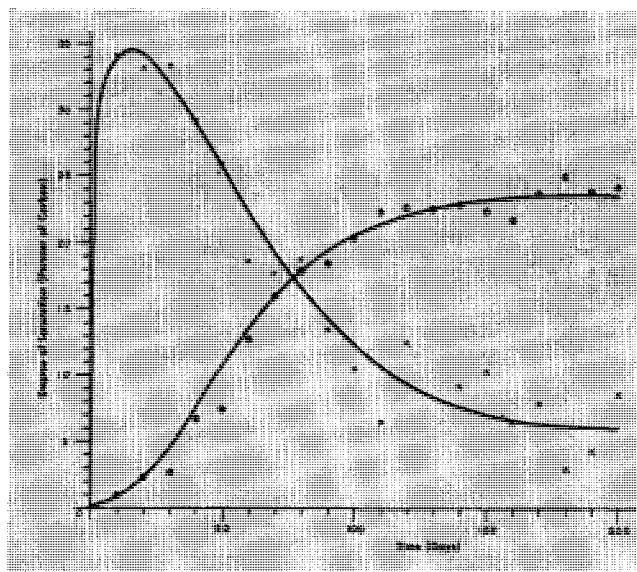


Figure 3. Saturation of bituminous activated carbon in commercial apple storage

X Adsorbed water
O Adsorbed organics
Time origin, Sept. 27, 1950

centage, and is represented by the general equation

$$\log Y = \log k + (\log a)b^X \quad (3)$$

Fitted to the "organics" saturation data of Figure 2, the values obtained for the constants are: $b = 0.742$; $\log a = -1.85$; $\log k = 1.36$. Thus:

$$\log Y = 1.36 - 1.85 (0.742)^X \quad (4)$$

where X represents time units of 10 days and Y represents saturation with organic vapors and approaches an asymptotic value of 23.05.

It is particularly worthy of note that two apparently inconsistent events take place simultaneously: The activated carbon approaches saturation around the end of January, and the beneficial results of air purification, including improved fruit firmness and odor control in the storage space, endure throughout the storage period (20). It is possible that the inhibition of maturation effected by activated carbon air purification during the preclimacteric period of storage causes a decreased rate of volatile emanation from the fruit throughout the entire storage season and independently of postclimacteric air purification. This important likelihood merits further study.

Similar saturation data obtained for the nine canisters of activated coconut shell carbon, used in a previous apple storage during the 1949-50 season and then completely reactivated, show no significant differences from the saturation of the previously unused coconut shell carbon. This is to be expected because similar surface properties of the adsorbent (Table I) were obtained in each case.

Saturation of Bituminous Carbon

Figure 3 illustrates the saturation pattern of bituminous carbon in the 1950-51

test room. Again, one canister of bituminous carbon was removed from the test unit every 10 days and replaced in each instance by a canister with fresh activated coconut shell carbon, which was not used analytically. Twenty canisters were thus removed and analyzed to obtain the data in Figure 3.

The curve for water adsorption (fitted by inspection) shows that activated bituminous carbon will relinquish its moisture to make room for adsorption of organic vapors even more easily than activated coconut shell carbon. The moisture content of the bituminous carbon leveled off at about 6% compared to about 8% by weight for the coconut shell carbon.

The Gompertz curve fitted to the plotted data for adsorption of organic vapors has the following values: $b = 0.708$; $\log a = -1.94$; $\log k = 1.38$. Thus:

$$\log Y = 1.38 - 1.94 (0.708)^X \quad (5)$$

where X represents time units of 10 days and Y represents saturation with organic vapors and approaches an asymptotic value of 23.75.

The comparative data on adsorption of vapors by coconut and bituminous carbon, each corresponding to the specifications of Table I, show very similar patterns, with slight advantages of moisture release and organic vapor adsorptive capacity in favor of bituminous carbon. In a number of experiments comparing the effects of coconut shell and bituminous carbon in retarding the softening of Wealthy, Duchess, and McIntosh apples, Smock and Gross (73) have shown that the coconut shell carbon is the more effective. This is presumably related to a greater area of small pores in the coconut shell carbon available for adsorption of the volatiles of lower

Table II. Concentration and Generation of Organic Vapors in Commercial Apple Storage

Time, Days	Saturation Period, Hours	Average Carbon Satn., 100S, %	$C_w = 0.0243S$ lb./10 ⁶ Cu. Ft.	$C_v = 4.5 C_w$ P.P.M.	$G = 5.43 C_w$ lb./Hour
20	480	2.7	0.066	0.30	0.36
40	480	4.5	0.11	0.50	0.60
60	480	7.1	0.17	0.77	0.92
80	480	8.7	0.21	0.95	1.1
100	480	10.4	0.25	1.1	
120	480	12.6	0.31	1.4	
140	480	12.6	0.31	1.4	
160	480	13.0	0.32	1.4	
180	480	14.7	0.36	1.6	
200	480	13.3	0.32	1.4	

molecular weight, which are specific maturation stimulants, such as ethylene and acetaldehyde.

Volatile Levels

Figure 4 illustrates the changes in average concentration of organic vapors in the 1950-51 test room as the storage season progressed. These data were obtained as follows:

Three canisters of activated coconut shell carbon were removed from the test unit for analysis after 20 days (480 hours), and were replaced with three similar fresh canisters. Saturation analyses of the carbon in the three removed canisters gave an average value for S (Equation 1) for the first 20-day test period. This value of S was used to calculate C_w (Equation 1), and, with an appropriate average molecular weight, gave a value for the volume concentration, C_v , by Equation 2. An approximate average molecular weight of 80 was assumed, based on mass spectrographic data for apple volatiles (78). The three fresh replacement canisters then served for a similar determination of "volatiles" concentration during the second 20-day period; this schedule was continued throughout the 200 days of the testing program. By this

procedure, determination of volatiles was based, in each case, on analysis of relatively fresh, efficient carbon, rather than on analysis of carbon which had served continuously through a large portion of the storage season. To calculate the results for C_w and C_v in Table II, the following values were used: $W = 1.75$ pounds of carbon per canister; $Q_r = 25$ cu. feet per minute per canister; $t = 480$ hours; $M = 80$. Then, from Equations 1 and 2, $C_w = 0.0243 S$, and $C_v = 4.5 C_w$.

The graph in Figure 4 shows that organic vapor or volatiles concentration approached a maximum of only 1.5 p.p.m. near the end of the season, indicating good control of "apple aromas" and of transfer of flavors by vapor diffusion. The leveling off of the curve is probably related to increased rate of removal of fruit from storage during the latter part of the season.

The data for average concentration of organic vapors may also be used to calculate the total weight of vapors emanated from the fruit, as follows (77):

$$C_w = 1.67 (10)^4 G / Q_d \quad (6)$$

or $G = 6 (10)^{-3} Q_d C_w$ where G = rate of generation of volatiles, pounds per hour

Q_d = total contaminant-free air supplied to storage, cubic feet per minute = $Q_r + Q_i$

Q_r = rate of contaminant-free air supplied by Dorex units = 6 units (Figure 1) \times 60 canisters per unit \times 25 cu. feet per minute per canister = 90,000 cu. feet per minute

Q_i = rate of contaminant-free air supplied by infiltration. This is a variable depending on leakage rates, frequency of door opening, etc. It is estimated to be 0.1 air change per hour for a space of 270,000 cu. feet, or 450 cu. feet per minute

$$\text{Then, } G = 6 (10)^{-3} (90,000 + 450) C_w = 5.43 C_w$$

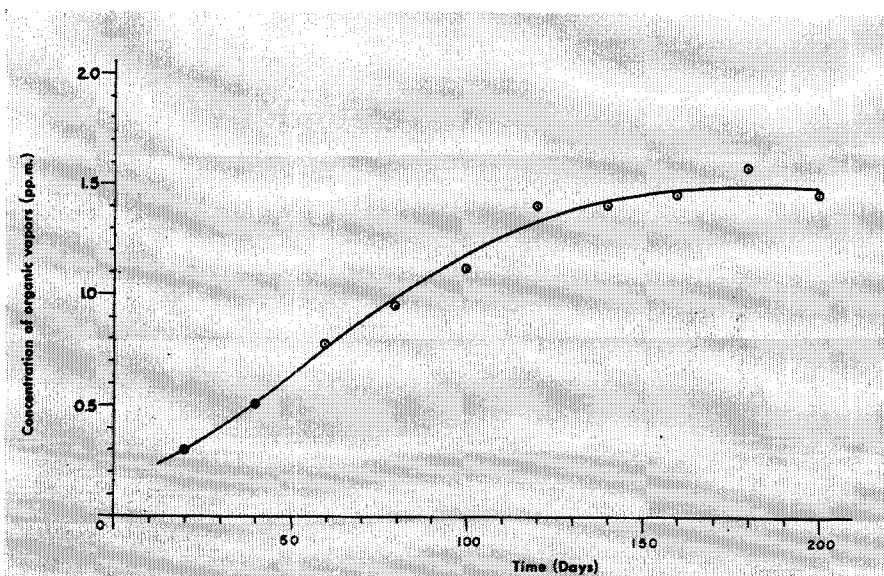
The values for G during the storage season are given in Table II.

Saturation of Brominated Carbon

One of the canisters filled with brominated coconut shell carbon was removed

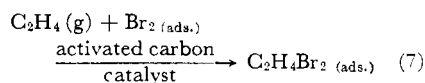
Figure 4. Concentration of organic vapors in commercial apple storage

Time origin, Sept. 27, 1950



from the test unit for analysis at 20-day intervals, and was replaced in each case by a canister with fresh unimpregnated coconut shell carbon, which was then not used analytically.

Because the purpose of bromine impregnation is to serve as a specific method for chemisorption of atmospheric ethylene according to the equation,



a meaningful analysis of brominated carbon must reveal the residue of adsorbed free bromine which is available for reaction with ethylene at the carbon surface. As no such analytical scheme has previously been reported, the details of the method are presented here.

An adaptation of the standard method for bromine determination, whereby brominated carbon was ground in a mortar under an excess of potassium iodide solution, and the liberated iodine was then titrated with sodium thiosulfate, was found inapplicable. Under all the conditions used, a substantial portion of the liberated iodine was quickly reabsorbed by the carbon and rendered unavailable for analytical indication. A variant of the method was tried, in which the brominated carbon was ground with an excess of sodium thiosulfate solution, and the unused thiosulfate was then leached from the carbon with hot water and titrated with standard iodine solution. Analysis by this method of 1 gram of carbon impregnated with 0.070 gram of bromine revealed only 0.0526 gram of bromine, or about 75% of the actual amount present. This low value is probably related to the difficulty of quantitative removal of the adsorbed excess thiosulfate.

The method finally adopted used ethylene itself, in excess, as the analytical reagent for adsorbed bromine (Equation

7); the difference between the amount of ethylene streamed through a sample of the brominated carbon and the unused ethylene recovered on the "downstream" side was taken to represent the quantity of ethylene consumed in reaction with adsorbed free bromine. Preliminary tests showed that it is possible to recover about 99% of a sample of ethylene, diluted 1 to 100 with air, which has been streamed through a bed of unimpregnated activated carbon held at 70° C. If the activated carbon has previously adsorbed organic material such as apple volatiles, it is necessary to insert an absorber containing cold 95% sulfuric acid in the apparatus train after the carbon. The sulfuric acid will absorb miscellaneous organic volatiles, displaced from the carbon, which would otherwise give a high value for recovered ethylene, but it will not absorb any ethylene.

Figure 5 illustrates the equipment set up for bromine analysis. The bromine bubbler, *H*, was used only to check the method of analysis and is otherwise omitted from the apparatus. To avoid ethylene losses in the apparatus, all connections were ground glass with a carbohydrate lubricant (Nonaq, Fisher Scientific Co.) or were short sleeves of Butyl rubber.

Impregnation The carbon sample tube, *J*, was charged with 0.515 gram of unimpregnated activated coconut shell carbon; a small quantity of bromine was placed in the bromine bubbler and stopcock *G* was turned to position *T*. The sulfuric acid bubbler, *K*, and mercuric perchlorate absorber, *L*, were not connected to the carbon sample tube. The compressed air was turned on and the leak, *A*, was constricted until about 70 ml. per minute of air streamed through the carbon. A small auxiliary stream of air introduced into the bromine bubbler

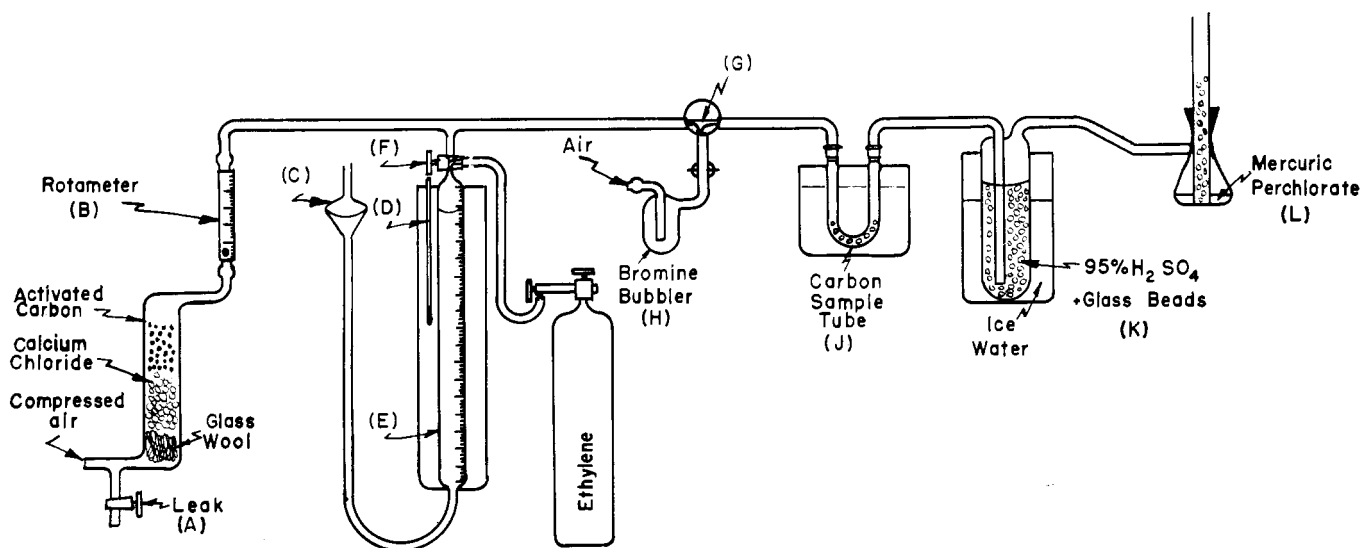
then forced some bromine vapor into the main air stream, by which it was carried to the carbon sample for adsorption. Stopcock *G* was then turned to position \perp and air flow was continued until the carbon sample tube reached constant weight (0.598 gram of impregnated carbon; 0.083 gram of bromine, 16.1% impregnation based on carbon).

Analysis The bromine bubbler was removed, stopcock *G* was kept in position \perp , and the sulfuric acid bubbler and mercuric perchlorate absorption flask were connected as shown in Figure 5. The water temperature in the bath surrounding the carbon sample tube was held at about 70° C. An air flow of 105 to 115 ml. per minute was maintained through the system. Ethylene was introduced into the buret, *E*, liquid levels in *C* and *E* were equalized, and buret, barometer, and thermometer *D* readings were recorded. Bulb *C* was then raised and stopcock *F* opened slightly, so that ethylene was slowly introduced into the main air stream and thus into the brominated carbon. Ethylene introduction was thus continued until 16.00 ml. (corrected to standard conditions) were introduced; *F* was then closed and air flow continued for 15 minutes to sweep all residual ethylene through the carbon. The residual gas above the buret stopcock, *F*, was swept into the main stream by a small jet of air introduced through the side opening of the stopcock.

Analysis for ethylene absorption by the mercuric perchlorate solution was now made by the method of Gross (7):

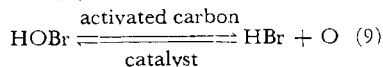
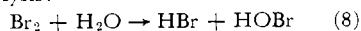
Ethylene titration = 19.7 ml. of 0.1 *N* perchloratocerate solution (1 ml. = 0.0003506 gram of ethylene)
Ethylene passed through brominated carbon = 0.0069 gram

Figure 5. Apparatus for bromine analysis



Ethylene introduced from buret = 16.00 ml. = 0.020 gram
 Ethylene retained by brominated carbon = 0.020 - 0.0069 = 0.0131 gram
 This is stoichiometrically equivalent to 0.075 gram of bromine.
 Result for carbon impregnation = 0.075/0.515 = 14.5%
 Actual impregnation = 0.083/0.515 = 16.1%
 Efficiency of bromine detection = 14.5/16.1 = 90.4%

A number of similar succeeding trials gave values of 90% or higher for efficiency of bromine detection by this method. Possibly the residual moisture in the original carbon sample (less than 2% by weight of the carbon) renders some of the free bromine unavailable by hydrolysis:



No check runs, however, were made under rigorously anhydrous conditions, which would require high vacuum, high temperature "out-gassing" of the carbon.

Table III. Saturation of Brominated Activated Coconut Shell Carbon in Commercial Apple Storage

Time, Days	Satn. with Nonaqueous Matter, % of Carbon	Satn. with Free Bromine, % of Carbon
0	15.	15.
20	14.9	1.6
40	16.8	0.7
60	14.6	0.1
80	16.8	Positive ^a
100	17.8	0.1
120	17.1	0.3
140	16.4	Positive ^a
160	16.5	Positive ^a

^a Qualitative test only.

Table III presents the saturation data for the brominated carbon canisters. It is noteworthy that all but a small fraction of the bromine was quickly consumed, but that some bromine remained available throughout the duration of the test. A large fraction of the consumed bromine is apparently lost by hydrolysis (Equation 8) in the humid atmosphere of the commercial apple storage, rather than by reaction with ethylene from the fruit. In fact, samples of freshly brominated carbon, when placed in a moist air stream, showed extensive hydrolysis within one day. The values for total nonaqueous saturation given in Table III show that brominated carbon, aside from its action in specifically removing ethylene, is an ineffective agent for reducing the total "volatile level" of a space.

Immediately after analysis, the carbon samples showed negative qualitative tests for bromine (carbon shaken with potassium iodide-starch solution), but, on further standing, free bromine again became available and positive tests were

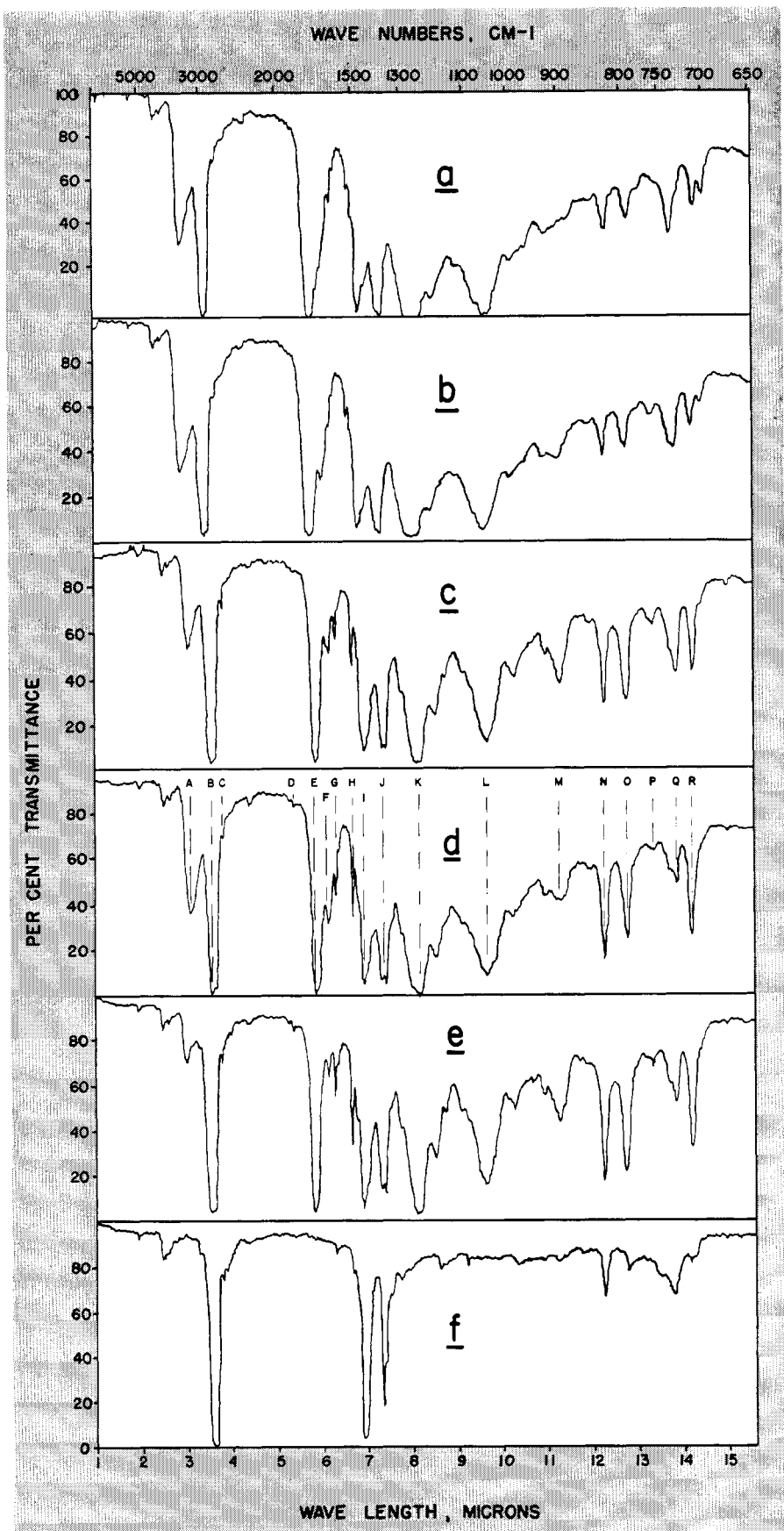


Figure 6. Infrared spectra of desorbates from coconut carbon

- a. Exposed 50 days
- b. Exposed 90 days
- c. Exposed 140 days
- d. Exposed 170 days
- e. Exposed 200 days
- f. Sulfuric acid-washed desorbate from carbon exposed 200 days

obtained. Even when a brominated carbon sample was allowed to stand overnight in an atmosphere of pure ethylene, free bromine again became available on further standing. These results indicate that Reactions 8 and 9 take place reversibly on the carbon surface.

Qualitative Saturation Analyses

Samples of adsorbed organic material may be obtained for qualitative analysis by either of two methods: (1) displacement of the adsorbate with superheated steam and condensation of the effluent gases, and (2) high-vacuum desorption and low temperature trapping of the released volatiles (17). The superheated steam method offers more complete removal of adsorbed material and greater convenience, because the steaming is a necessary part of the quantitative saturation analysis and thus requires little additional effort for collecting the condensed effluent. One serious disadvantage, however, is the likelihood that the steam will hydrolyze some of the adsorbed organic material, such as esters, and thus change its chemical composition. The vacuum method, on the other hand, avoids excessively high temperatures which would promote hydrolysis or decomposition, and is, therefore, preferred for yielding a sample for analysis which is more truly representative of the atmosphere from which the collection was made.

In this study, samples were collected by both the steam and vacuum methods. The steamed samples were used for qualitative chemical tests for various functional groups; the samples obtained by evacuation were used for analysis by infrared spectra.

Vacuum Desorption. A 40-gram sample of carbon to be analyzed is placed in a 250-ml. flask connected to a train of three traps cooled, respectively, in ice-salt, dry ice-methyl Cellosolve, and liquid nitrogen. A second dry ice trap may be substituted for the liquid nitrogen trap. The system, which also includes a mercury U-tube manometer and a McLeod gage, is then arranged so that it can be evacuated either with a water aspirator or with an oil diffusion pump and mechanical forepump.

For analysis, the flask containing the carbon sample is placed in a sand bath held at 120 to 150° C. and the system is evacuated with the water aspirator (10 to 15 mm.) for 1 hour. The carbon is thus substantially dried and the desorbed moisture is collected in the ice-salt trap. The water aspirator is then shut off and the mechanical forepump is switched on and allowed to evacuate the system; the traps need not be emptied at this juncture. When the pressure drops to about 0.2 mm., the diffusion pump is started, and the sand bath temperature is raised to about 250° C. Pumping is continued about 1.5 hours at a pressure of 2 to 3 microns. The vacuum is then gently released, and the material in the traps is thawed and removed. The ice-salt trap contains substantially all the

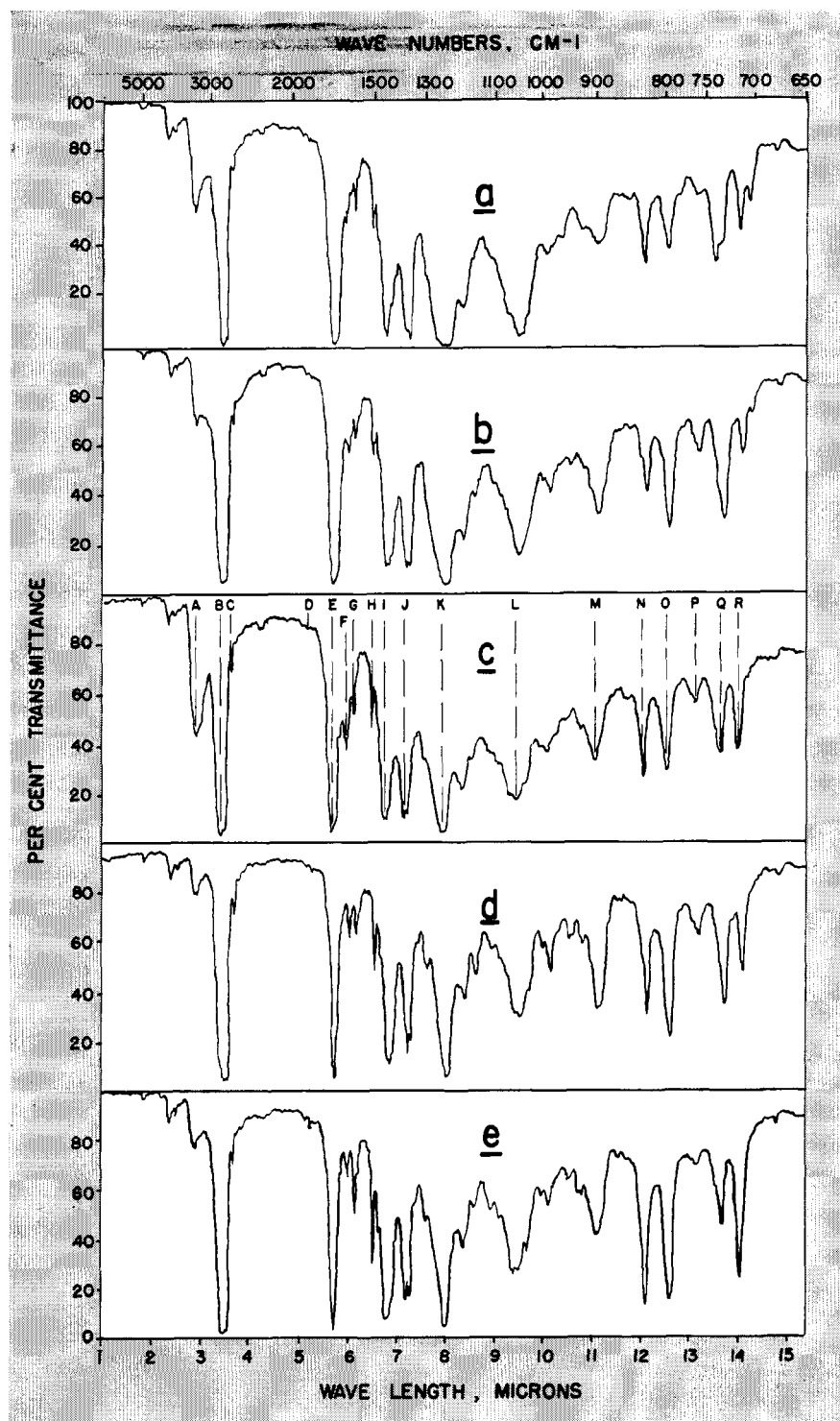


Figure 7. Infrared spectra of desorbates from bituminous carbon

- a. Exposed 50 days
- b. Exposed 90 days
- c. Exposed 140 days
- d. Exposed 170 days
- e. Exposed 200 days

water; the dry ice trap contains substantially all the organic material plus traces of water; the nitrogen or second dry ice trap contains traces of organic material. The organic material thus obtained is available for qualitative analysis.

Comparative steam and vacuum desorptions of identical carbon samples show that the vacuum method releases only about three-quarters of the amount of organic material which is removable

by superheated steam, but avoids decomposition or hydrolysis. It may be possible to obtain a greater yield of desorbed material by molecular distillation from the saturated carbon, but this step was not undertaken in the present study.

Analysis of Steam Desorbate Chemical tests for various functional groups revealed on qualitative differences between the materials desorbed from coco-

nut or bituminous carbon. After 20 days of exposure of carbon in the apple storage, positive tests for aldehydes (fuchsin reagent) were obtained in the steam desorbate; after 40 days, positive tests were obtained for nitrogen compounds as ammonium (Nessler's reagent) and amines (Sanchez reagent, 9); after 60 days, positive tests were obtained for esters (Takahashi reagent, 10) and for carbon unsaturation (bromine). All these tests then remained positive through the remainder of the 200-day period.

Infrared Analysis of Vacuum Desorbate Figures 6 to 8 show the infrared spectra of vacuum desorbates from coconut and bituminous carbon after several different periods of exposure in apple storage. The instrument used was a double-beam infrared spectrophotometer (Model 21, Perkin-Elmer Corp., Norwalk, Conn.); the thickness of the liquid film in the absorbing cell was 0.03 mm. The labeled absorption peaks correspond to functional groups and molecular patterns as follows (1):

- A. Hydroxyl
- B. C—H stretching (organic compounds generally)
- C. C=O (aldehyde)
- D, G, H, N, O, Q, and R. Aromatic structures
- E. C=O (esters or aldehydes)
- F. C=C (unsaturation, such as ethylene)
- I. C—H bending (organic compounds generally)
- J. Methyl groups
- K. —C—O (esters)
- L. —C—O (alcohol, ether, or aldehyde)
- M, P. Unsaturation at terminal portion of molecule

The following interpretations may be made:

Alcohols of lower molecular weight, aldehydes, and unsaturates are strongly adsorbed by coconut shell carbon early in the season. The relative prominence of these materials, however, decreases markedly, but with some irregularities, as the season progresses (peaks A, E, and F in Figure 6, a to e). Among these substances, the unsaturates and aldehydes are most likely to act as the specific maturation stimulants for apples. As the season progresses, a relatively larger portion of the adsorbed material consists of vapors of higher molecular weight, resulting in relatively lower prominence of functional peaks A, E, and F.

A relative increase in adsorption of aromatics in both coconut and bituminous carbon occurs as the season progresses (peaks D, G, H, N, O, Q, and R, in Figures 6 and 7, a to e). Their source is not known.

The alcohols of lower molecular weight aldehydes, and unsaturates are also adsorbed on bituminous carbon, but, in the early part of the season, less strongly so than on coconut carbon (peaks A, E, and F in Figure 7, a to e). The relative prominence of these peaks also decreases, although irregularly, as the season pro-

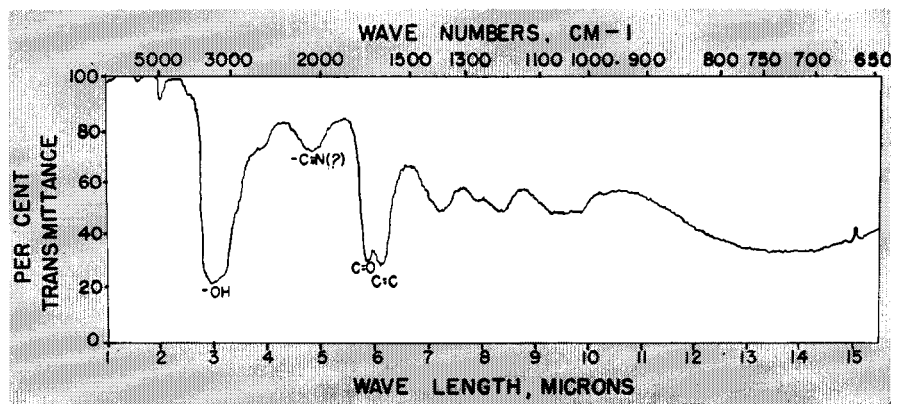


Figure 8. Infrared spectrum of vacuum distillate of pine dust

gresses. By the end of the season, the two types of carbon are equivalent with respect to adsorption of these substances (peaks A, E, and F in Figures 6, e, and 7, e).

Analysis of Pine Dust In an attempt to determine whether or not the volatile emanations from the storage structure contribute materially to carbon saturation, a sample of new pine dust from the test room at Entiat, Wash., was vacuum distilled by the procedure described for vacuum desorption. The infrared spectrum of the distillate is shown in Figure 8. The strong alcohol prominence is to be expected as a major component of wood essence. The possible presence of nitrogen compounds shown in Figure 8 is not reflected in the spectra of the apple vapors (Figures 6 and 7), but does appear in the chemical analyses of the steam desorbates previously described. Possibly these materials are not desorbed from the carbon by the vacuum method. In any case, volatile emanations from the wood structure, especially when new, probably contribute to saturation of the carbon.

Saturated Compounds In an effort to clarify the structural significance of the nonhydrolyzable oils obtained by steaming, about 100 ml. of the oily layer of the steam desorbate of coconut shell carbon exposed for the full storage period was washed repeatedly with concentrated sulfuric acid to remove unsaturated and oxygenated compounds. The resulting clear, colorless liquid (about 15 ml.) was washed twice with dilute aqueous sodium bicarbonate and then several times with water, and finally dried over calcium chloride. This material did not produce a crystalline nitration product. It had a characteristic naphthenic odor. Its infrared spectrum (Figure 6, f) is made up only of hydrocarbon peaks and shows that the material is a light mineral oil. Peaks N, O, Q, and R of Figure 6, f, are not as prominent as the corresponding peaks in Figure 6, a to e, indicating that only a small portion of the aromatics were hydrocarbons. The source of this hydrocarbon vapor is probably the oiled paper wraps used on stored fruits.

Thus volatilization of oils on such paper wraps contributes appreciably to carbon saturation.

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Better Wine and Bread by Scientific Fermentation

Fermentation practices and advances in the food industry were surveyed in a symposium presented by the Fermentation Subdivision of the Division of Agricultural and Food Chemistry at 123rd Meeting of the American Chemical Society in Los Angeles. Two of the papers are presented in this issue. Others will appear in future issues.

FERMENTATION

Present Practices in the California Wine Industry

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The current fermentation practices of the California wine industry are reviewed and evaluated, and suggestions for their improvement are offered.

A NUMBER OF FACTORS are involved in the selection of grapes to be used in the production of the various types of wine. The suitability of the variety for the type of wine to be made, the yield of the wine, the ease with which it can be aged, clarified, and prepared for the market, and the economic and engineering factors involved must be considered.

The more important factors influencing quality and suitability are: the amount of sugar and acid present, the ratio of acid to sugar, the response of the grape to the climatic conditions of the region where grown, and the physical and chemical characteristics, other than sugar and acid, of the variety of grape. A high total acid with moderate sugar content is desired for table wines, and a moderate acid with high sugar content for dessert wines.

The varieties of grapes differ markedly in the amount of sugar and acid present at full maturity. Amerine and Winkler (3) have shown that the climatic conditions, particularly temperature, of the region where the grapes are grown have a decisive effect on the ratio of sugar to acid; increasing temperature causes a corresponding increase in this ratio. On this basis they have classified the varieties according to the region to which they are best adapted. Amerine and Joslyn (7) have listed the varieties according to their desirability for the production of the various types of table wines. It has long been known that the acid decreases as the grape becomes riper. Amerine and Winkler (2) showed that the stage of maturity at which the grapes were harvested had a decided bearing on the suitability of that grape for producing a

given type of wine. Resistance to disease, intensity of varietal flavor, level of production, and ease of training, picking, and crushing are other factors which need to be considered in selecting a variety.

The producer of premium-quality wines usually considers all these factors in his selection of grapes. The producer of standard wines, because of the price he receives for his product, is more limited in his choice of varieties, as he cannot compete on a price basis with the premium wine producer. However, of the large number of varieties remaining to him, he too often fails to make an intelligent choice. One of the greatest improvements which could be made in the quality of California wines would be

the utilization by all producers of the available knowledge in making their selections of grapes. This could be accomplished by selecting from the available grapes those best suited for each type of wine, and then harvesting them at the optimum stage of maturity.

Harvesting and Transporting

Three methods of harvesting and transporting grapes are in general use. In one the grapes are picked into wooden boxes, placed on a flat bed truck, and hauled to the winery, and each box is individually emptied into the crusher-conveyor. This method is the most costly, but it permits the least damage to

Figure 1. Gondola truck and unloading crane

