tions. Because of the inconsistent background encountered in the development of the color, many resorted to sample splitting with treatment of half the sample with a blank reagent. These methods proved cumbersome and reduced the sensitivity of the method considerably. Nelson (*1*) used the Porter-Silber reaction with a modification which he calls an absorption factor. This factor is actually a base line measurement of the color produced by the reaction of the steroid with the phenylhydrazine hydrochloride. This measurement technique was accurate and reproducible and was adapted for the authors' method.

In his work, however, Nelson carried out the colorimetric reaction on the residue after evaporation of the solvent. Although this technique was the easiest to handle, the solvent residue contributed to the absorption at 370 mμ, resulting in apparent low recovery of the standard material. When the steroid was partitioned from the solvent into the colorimetric reagent, as in the work of Silber (*1*), this effect was not encountered, and the characteristic curve shape was obtained.

Earlier procedures (*1*, *2*) required that aliquots of the standard solution be carried through all or part of the analytical method, thus correcting the results for losses due to handling in the procedure. The method reported here utilizes a standard curve for the quantitative measurement of the samples. The standards are subjected only to the colorimetric reaction. The results presented here are absolute recoveries and not corrected for losses due to the analytical procedure.

Methylene chloride from various suppliers was investigated for use in this procedure. The concentration of large volumes yielded a yellow-colored fluorescent residue which obscured the hydrocortisone on the thin-layer chromatograms. For this reason, it was necessary to purify the solvent before use. Of the various methods of purification studied, slurrying with Nuchar C-190N activated carbon proved most rapid and efficient.

Several lots of the silica gel adsorbent were used in these studies. In only one case was a reagent blank value encountered. Since the possibility of this blank does exist, it is recommended that a reagent blank of the adsorbent be run for each set of samples analyzed.

Florisil was also examined for use in the separation of the steroid forms from the other components of the milk extract and gave approximately the same R_f for the steroid. However, the silica gel, containing a fluorescent indicator, afforded a rapid and sensitive means for locating the steroid. The yellow-green fluorescent background enhanced the contrast of the blue-absorbing spot when irradiated with a short-wave (254 mμ) UV lamp. Under these conditions, less than 1 μg. can be located on the thin-layer plates.

The solvent mixture of 7% methanol in methylene chloride employed in the development of the chromatogram gave excellent resolution in separating combinations of the forms of the steroid from other components of the milk extract. Figure 1 is a graphic representation of the thin-layer chromatogram of the milk extract.

This method can also be used as a precise semiquantitative procedure for screening milk samples for steroid content. By spotting an appropriate series of standards on the thin-layer plate, rapid estimations of steroid content can be made.

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POROSITY OF FOOD PRODUCTS

Surface Areas and Densities of Freeze-Dried Foods

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The specific surface areas and densities of a variety of freeze-dried foods were determined. The specific surface areas calculated from low temperature (−195° C.) physical adsorption data using the standard Brunauer, Emmett, Teller (BET) treatment were less than 1 square meter per gram for many vegetable, fruit, meat, and fish products. True and apparent densities determined with helium, nitrogen, or dry air as the displaced medium showed that a micropore structure curtailing rapid gas diffusion through the dried mass was restricted to those layers which formed the outer surface of some foods.

MANY PROBLEMS encountered during the production, storage, and reconstitution of dehydrated foods may relate directly to their porosity and specific surface areas. Accurate values for these properties, established by independent means are, therefore, desirable.

No thorough study of the surface characteristics of a wide variety of dried foods as determined by gas displacement and nitrogen adsorption has yet been reported. Therefore, the authors' study of the physical features of dry milk (*3*, *4*) has been extended to include representative samples of freeze-dried foods now being developed for commerce.

This paper reports the specific surface areas of various foods as derived from the isotherms for the adsorption of nitrogen at −195° C. The calculations were made in accordance with methods described by Brunauer, Emmett, and Teller (*5*), hereafter BET method.

The true and apparent densities of these foods as determined by gas displacement techniques are also presented. From these density data an estimate of the relative porosities of the foods can be obtained.

Materials and Methods

Food samples were chosen so as to represent typical vegetable, fruit, meat, and fish products, freeze-dried whole or in diced form (Freez-Dri Products Co.,

Table I. Surface Areas of Freeze-Dried Foods

Food	Surface Area, Sq. Meter/ Gram	BET C Value
Red bell peppers	0.340	5
Cut celery	0.638	21
Cooked deveined shrimp	0.305	74
Raw fish fillets	0.581	49
Small whole strawberries	0.499	102
Raw diced carrots	0.508	31
Sliced bananas	0.169	136
Orange juice	0.121	53
Canadian blueberries	0.144	...
Diced cooked white meat turkey	0.285	...
Diced cooked white meat chicken	0.085	...
Raw shrimp	0.819	29
Sliced mushrooms	3.83	...
Sliced mushrooms[a]	2.99	26

[a] Area measured without grinding sample.

Los Angeles, Calif.), in a fashion designed to assure maximum retention of the color and form of the original product.

Surface Area Measurement. Nitrogen adsorption was measured volumetrically, using an all-glass, custom-made adsorption apparatus. The apparatus was of the conventional type, the construction and operation of which have been described in the literature (*1*, *7*).

The helium (Southern Oxygen Co.) used for the free space measurements was purified by passing it through a charcoal trap maintained at −195° C. with a liquid nitrogen bath. The charcoal was degassed at 250° to 300° C. for several hours to remove any adsorbed impurities. Prepurified nitrogen (Southern Oxygen Co.) was passed through a liquid nitrogen–cooled trap to remove any traces of moisture before use. Mercury float values were installed between the gas reservoirs and the manifold to ensure the purity of the gases after they were admitted to the apparatus.

Prior to measuring N_2 adsorption, the foods were degassed under high vacuum maintained by a mercury diffusion pump in series with a mechanical oil pump. All samples were degassed at room temperature until the pressure in the system remained constant in the range of 10^{-5} to 10^{-6} torr. This usually was accomplished by degassing overnight.

Table II. Densities of Freeze-Dried Foods Exhibiting Molecular Sieve Properties

Food	Displaced Gas, Grams/Cc. He	N_2	Air
Whole large strawberries	1.336	1.221	1.126
Strawberry halves	1.452	1.381	1.325
Diced raw carrots	1.349	1.299	1.299
Fresh cut celery	1.314	1.263	1.244
Sliced mushrooms	1.473	1.039	1.053

Initially, several attempts were made to measure the areas of freeze-dried foods maintaining their gross dimensions intact—e.g., whole strawberries, blueberries, large pieces of meat or fish. This however, posed serious limitations on the size of the sample which could be utilized. For whole foods, the mass-to-bulk volume ratio is quite small. This necessitates the use of sample tubes of relatively large volumes, thereby increasing what is commonly referred to as dead space error. It was, therefore, found necessary to crush or grind the food prior to the adsorption measurements. This was done by placing the sample in a 1-gallon Waring Blendor and grinding at low speed for six consecutive 30-second periods. Powder thrown on the side walls during the grinding was pushed back in contact with the blender blades between grinding periods.

The surface areas were calculated from the N_2 adsorption data using the unlimited multilayer formulation of the BET equation (*5*):

$$\frac{X}{V(1-X)} = \frac{1}{V_m C} + \frac{(C-1)X}{V_m C}$$

where X is the relative pressure, P/P_0, for the adsorbate; V is the volume of gas adsorbed at relative pressure X; V_m is the volume (STP) of adsorbate required to form a monolayer on the surface of the adsorbent; and C is a constant exponentially related to the difference between the energy of adsorption in the first adsorbed layer and the energy of liquefaction of the adsorbate. A plot of the left-hand side of this equation against the relative pressure, P/P_0 yields values for V_m and the constant C.

Density Measurement. The true and apparent densities of the food samples were determined with a Beckman air comparison pycnometer equipped with a purge attachment to permit evacuation of the sample as well as measuring the displacement of gases other than air.

The pycnometer was evacuated with an oil diffusion pump backed by a mechanical oil pump. A thermocouple-type vacuum gage was inserted in the line for pressure measurements. Helium and prepurified nitrogen were used as supplied (Southern Oxygen Co.) without further purification. When air was used as the displaced medium, it was admitted to the pycnometer through a column of indicating Drierite.

The food samples were prepared for density measurements by drying to constant weight at room temperature in a vacuum oven equipped with a mechanical oil pump. Densities of both intact foods and ground samples were measured.

Densities based on compositional data were calculated by the method of Verhoog (*8*) using his values for the average densities of fats, proteins, and minerals. The calculated densities are based on average values for protein, fat, carbohydrate, and mineral content reported for these foods in a United States Department of Agriculture publication (*9*) which tabulates the composition of an extremely wide variety of foods in terms of various nutrients as reported in numerous scientific journals.

Results

The surface areas and C values obtained from the BET plots are listed in Table I. Nearly all the food samples exhibited low areas in the range 0.1 to 0.8 square meter per gram. A surface area greater than 1 square meter per gram was observed only with samples of freeze-dried mushrooms. All the BET plots for freeze-dried foods were linear in the expected relative pressure range, $0.05 < P/P_0 < 0.35$.

When densities of whole pieces of freeze-dried foods were measured with the gas displacement technique, in some cases lower values were obtained for the density with N_2 displacement than with He displacement. These lower values can be ascribed to the restricted passage

Table III. Densities of Freeze-Dried Foods Exhibiting No Molecular Sieve Properties

Food	Displaced Gas, Grams/Cc. He	N_2	Air
Cooked white meat turkey	1.268	1.270	1.265
Strawberry quarters	0.636	0.643	0.653
Honey dew melon	1.035	1.042	1.044
Sliced bananas	1.349	1.341	1.330
Dover fillet	1.351	1.352	1.344
Whole cherry tomatoes	1.072	1.062	1.124
Italian parsley	0.134	0.152	0.146
Diced cooked chicken (white and dark meat)	1.222	1.255	1.247
Cooked cocktail shrimp	1.293	1.335	1.358
Tangerine sections	1.357	1.479	...
Delicious apples	0.913	1.047	...
Red bell peppers	1.204	1.292	...
Raw shrimp	1.335	1.389	...
Sliced salmon fish	1.189	1.255	...

of the larger N_2 molecule through the pore structure of the dried material. The foods containing such a pore structure which could select between He and N_2 on a molecular size basis are listed in Table II.

Density values for foods which did not exhibit any molecular sieve behavior are listed in Table III. In these cases, the densities as determined with He or N_2 were identical or slightly higher for N_2.

Table IV presents data obtained for the density of several forms of freeze-dried strawberries where the measurements were made both on whole pieces and on ground samples.

The true chemical densities measured with helium displacement on ground samples are listed in Table V, together with calculated values based upon composition.

Table IV. Densities of Freeze-Dried Strawberries, Grams/Cc.

	Intact Samples		Ground Samples	
	Displaced Gas			
Initial Physical Form	He	N_2	He	N_2
Halves	1.452	1.381	1.499	1.504
Quarters	0.636	0.643	1.478	1.527
Small whole	0.842	0.852	1.497	1.502
Large whole	1.336	1.221	1.521	1.534

Table V. True Densities, Grams/Cc.

Food	Observed Values	Calculated Values
Cooked white meat turkey	1.283	1.219
Sliced bananas	1.507	1.517
Whole cherry tomatoes	1.438	1.539
Fresh cut celery	1.584	1.623
Canadian blueberries	1.511	1.510
Raw diced carrots	1.534	1.552
Diced cooked white chicken meat	1.275	1.399
Diced ripe green peppers	1.510	1.523
Delicious apples	1.520	1.523
Diced honey dew melon	1.525	1.535
Tangerine sections	1.518	1.531
Sliced salmon fish	1.203	1.326
Raw shrimp	1.331	1.471
Red bell peppers	1.499	...
Mushrooms	1.497	...

Discussion

The surface area values listed in Table I correspond to the true surface areas of the solid mass of dried foods as they were measured by the nonspecific low temperature adsorption of N_2. The BET equation was originally derived (*5*) for such cases where physical adsorption is the only type of adsorption present, and the nature of interaction between adsorbate and adsorbent involves nothing stronger than van der Waals forces without localized adsorption on specific sites on the adsorbent surface.

The *C* values, obtained from the BET plots and reported in Table I, are for the most part in the range 5 to 50 for the various nitrogen adsorption isotherms. Since the *C* values are related to the heats of adsorption, the results suggest that nitrogen is not so strongly adsorbed on such materials as it is on the numerous miscellaneous inorganic substances on which BET isotherms have been determined. Similar low *C* values have been reported for nitrogen adsorption on such polymeric materials as dried milk powders (*3*), dried bacterial spores (*2*), and polyolefins (*6*).

The density data reported in this paper give some insight into the nature of the porosity of freeze-dried foods. The data in Table II illustrate that the micropores in some foods are of such dimensions that they can discriminate between helium and nitrogen molecules having diameters of 3.0 and 4.0 A, respectively. Comparison of the helium values given in Tables II and III with those in Table V reveals the presence of completely sealed-off internal cavities which are even inaccessible to helium. The volume of these internal spaces may be estimated from the relation:

$$\frac{1}{\rho_a} - \frac{1}{\rho_t} = V_{ic}$$

where ρ_a and ρ_t are the apparent and true densities, respectively, and V_{ic} is the volume of the internal cavities.

These structures disappear on mechanical grinding as shown in Table IV. The data shown here indicate that the physical form of the food prior to drying may determine the porosity of the dried material. It is difficult to decide whether the observed differences between whole and cut strawberries arose from a "case hardening" of intact fruit or a difference in ice crystal structure induced in the material prior to drying by the different freezing obtained with the cut material.

The general validity of the data obtained by use of techniques described in this paper is further established by consideration of the data in Table V. Here are listed the true densities determined by helium displacement of a number of the freeze-dried foods as well as values calculated from the composition of the food materials. These foods were all ground before measuring their densities to eliminate any internal cavities which may have been completely sealed off.

Although chemical differences in some of these materials, particularly the meat and fish products, preclude accurate density evaluation by calculation alone, there was remarkably good agreement between the observed and calculated values for all the fruits and vegetables listed.

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