MOISTURE-STABILITY RELATIONSHIPS IN WALNUTS

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Total annual production of edible tree nuts in the United States, including walnuts, pecans, almonds, and filberts, is in excess of 125,000 tons on an in-shell basis with a farm value of more than $50,000,000. Production is normally in excess of the per capita consumption of about 1.5 pounds. Sizeable imports of these nuts plus Brazil, cashew, and pistachio nuts have added to the over-abundant supply in this country. When new plantings come into bearing it is estimated that the annual crop of walnuts alone may approach 100,000 tons with an estimated farm value of $40,000,000. With a per capita consumption of walnuts below 1 pound (in-shell basis), disposition of the crop would appear to be dependent upon their utilization in the shelled form.

The present day consumer prefers food items that require a minimum effort to prepare and whose quality and stability they can recognize and depend upon. This has brought into focus a major problem, that is, the rapid development of rancidity and darkening in shelled nuts under ambient conditions. Low quality inhibits the expansion of markets and contributes to consumer sales resistance, burdensome surpluses, and depreciated prices. Recognizing these problems, Diamond Walnut Growers, Inc., in 1952, entered into a cooperative agreement with this laboratory to support jointly research investigations on the chemistry and technology of walnuts. These investigations were directed toward: basic studies on the chemical composition of kernels; elucidation of the physical and chemical factors responsible for darkening of the pellicle and the concurrent development of rancidity; and elaboration of a practical, commercial process for the stabilization of kernels. Although primary objectives have been realized, a number of important problems remained to be solved. Diamond Walnut Growers, Inc., is continuing to support basic investigations at this laboratory directed toward: the development of new information on the chemistry of kernels; objective methods for the estimation of kernel quality; and improvements in the process for kernel stabilization.

During the nine years these investigations have been underway, many new problems have been uncovered as some of the more apparent ones were solved. Solution of these new problems, perhaps more than the apparent problems, have pointed the way toward the accomplishment of the primary objectives. It has been demonstrated that kernel quality depends on a large number of biological, physical and chemical variables. Variety, climatic conditions, skin color, abrasion, heat, light, oxygen, metal ions, and moisture are among the important factors which affect quality and stability. Several of these variables exert their influences synergistically in an unpredictable manner. However, because of the complexity of the problem as well as the major importance of moisture, the present discussion will be limited largely to a brief review of the role of water in the maintenance of kernel quality.

COLOR-STABILITY RELATIONSHIP

Organoleptic evaluation of kernel quality is slow, tedious, subject to the availability of a large number of panel members, and requires relatively large samples. Fortuitously, it was observed that the development of rancidity was paralleled generally by darkening of the pellicle (skin) of the kernel. Therefore, an early objective was the elaboration of a method for estimating changes in pellicle color. This was accomplished by measuring, photometrically, the absorbance of light by an aqueous, 65% methanolic extract of kernels (9). It was concluded that the amber to brown color extracted from kernels could be related to the color grade designations of commercial kernels (Table 1). In addition, a nearly linear relationship was observed between the color and the percentage of light and dark kernels in an ad hoc mixture (Table 2).

The color values obtained for uniform lots of kernels adjusted to different moisture levels and stored for two months at 38° or 95° F. are shown in Fig. 1. This graph illustrates some interesting and unanticipated results. First, after storage at 95° F., apparent skin color changes appeared as a function of moisture content of the kernels. Second, kernels stored at 38° F. showed minimum skin color changes, with the exception of a slight tendency to darken at the lowest moisture levels. Third, only small differences in color were apparent for kernels maintained at 3% moisture, independent of storage temperature. Lastly, there appeared to be an optimum moisture level, above and below which the skin color darkened significantly at the higher temperature. It became important, therefore, to determine if these results could be repeated and if the color changes could be related directly to general quality and flavor characteristics.

A series of similar, but more comprehensive, experiments were performed encompassing: smaller moisture level increments; various storage temperatures ranging from 38° to 140° F.; and extended storage periods ranging up to two years. These studies demonstrated unequivocally that color changes in the pellicle could be related to changes in flavor and general quality, and therefore, could provide a convenient and objective procedure for estimating rates of kernel deterioration (5, 9). Perhaps of even greater importance was the confirmation of the optimum moisture phenomenon. It was shown that the optimum moisture range was temperature dependent, decreasing with increasing storage temperature. At ambient temperatures of about 75° F., the optimum moisture range was estimated as 3.5 + 0.5%.

ESTIMATION OF MOISTURE

The delicate relationship between kernel stability and moisture content necessitated an evaluation of methods and procedures for rapid and precise estimations of moisture in kernels and whole in-shell walnuts (4, 10). A modified Moisture Balance[1] procedure, which required only a 5-gram sample and which could be completed within 25 minutes, yielded essentially the same moisture values as the generally accepted xylene distillation procedure (Table 3). A further comparison of the Moisture Balance, Moisture Register and vacuum oven procedures with the Karl Fischer method confirmed the efficacy of the Moisture Balance method (Table 4). The vacuum oven procedure also gave precise and reproducible results. However, this procedure was inconvenient and subject to a 3-day time lag. The Moisture Register method, useful for either kernels or ground, whole, in-shell nuts, lacked the fine precision of other procedures. However, satisfactory analyses could be obtained within 1 minute and this technique was extremely useful for rapid estimations of moisture in large numbers of similar samples. Addition of an automatic pumping unit (Fig. 2) increased the utility of the Moisture Register by effecting more reproducible pumping rates and a more exact pressure cutoff.

1/ Mention of special instruments or materials throughout this paper does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over others of a similar nature not mentioned.

MOISTURE-RELATIVE HUMIDITY RELATIONSHIPS

The critical relationship between stability and moisture content of walnuts, as well as diverse other materials, led to the consideration of the basic process through which water exerts its influence; and to an attempt to elucidate the mechanism through which an intermediate moisture content lends greater stability to kernels than either higher or lower moisture levels. It soon became clear that the stability of kernels and other natural products is more directly related to the equilibrium relative humidity than to the water content. The relationship between the equilibrium relative humidity and total moisture content is frequently called a moisture sorption isotherm. Most moisture sorption isotherms are characteristically sigmoid or S-shaped curves which vary in contour with the temperature and other variables not pertinent in the present discussion. The moisture sorption isotherms for walnut kernels at two temperatures are presented in Fig. 3.

The data necessary for the construction of moisture sorption isotherms consist basically of a series of corresponding values of the moisture content and equilibrium relative humidity of a number of samples held at a constant temperature in sealed containers. The data may be obtained by equilibrating a series of samples for extended periods over systems maintained at different relative humidities and finally estimating the total moisture content of each sample. This procedure takes many months because of the long equilibration period required and has several other disadvantages. A more rapid and convenient procedure entails the adjustment of a series of uniform samples to different known moisture levels followed by the estimation of the equilibrium relative humidity of each sample held at a constant temperature in a sealed container. An effective apparatus for estimating the equilibrium relative humidity of a sample in sealed container is shown in Fig. 4. An electronic humidity-sensing head is sealed within a jar and suspended directly above a mass of kernels. A magnetically-coupled fan stirs the moist air within the jar to effect a rapid equilibration of the kernels with the free air space. The relative humidity is read directly from the electric hygrometer connected to the sensing head by a wire connected through the top of the container.

Kernels having an equilibrium relative humidity above about 65% may be expected to darken and develop off-flavors and -odors within a few weeks. At relative humidities below 20%, autoxidative processes proceed rapidly and cause the development of the familiar rancid odor and copper-colored darkening of the pellicle. If kernels having an equilibrium relative humidity of above 65% at 7° C. are placed in a sealed container and raised to a temperature of 22.5° C. or greater, the equilibrium relative humidity of the kernels would exceed 70% and the kernels would become susceptible to mold growth and other types of deteriorative processes. The same principles may be expected to apply to other food products and particularly to other nut species.

Further consideration of the basic mechanism regulating the effects of moisture on kernel stability led to the construction of a new type of isotherm (4). This isotherm (Fig. 5) represents the first derivative of the moisture sorption isotherm with respect to moisture, or a plot of the reciprocal of the rate of change of relative humidity with moisture content ($\Delta M/\Delta R.H.$) vs. moisture. A close analogy is apparent between this isotherm and color, flavor, and odor data observed after storage of kernels for 7 months at 35° C. It is possible that this approach could be employed for estimating the optimum moisture content of other nuts.

MOISTURE ADJUSTMENT IN WALNUTS

The need for a practical process for the critical adjustment of moisture in kernels to within the optimum moisture range led to studies on the utility of the belt-trough dryer for the dehydration of both in-shell (2) and shelled walnuts (8). The pilot-plant model belt-trough dryer, designed and engineered by Lowe et al. (1), was employed. A diagramatic representation of the cross section of this efficient dryer is shown in Fig. 6. In continuous operation, a tilted rotating stainless steel wire mesh screen gently rotates a bed of product, gradually displacing it toward the discharge port while a heated dry air stream is percolated through the bed. This process exposes kernels alternately to the direct hot-air stream and to the surface where moisture escapes freely and lowers the temperature of the kernel. It has been accepted generally for the past 35 years that the drying temperature of in-shell walnuts should not exceed a temperature of 110° F. during the 24 to 48 hour period normally required for the dehydration of nuts in common bin-type dryers. Experiments performed with the belt-trough dryer on both in-shell and shelled walnuts indicate that temperatures considerably higher than 110° F. can be tolerated for short periods without any detectable adverse effects on initial or storage quality (2, 8). It was concluded that air temperatures as high as 210° F. could be employed in the final stages of drying on the belt-trough dryer as long as the kernel temperature was not permitted to exceed 145° F.

Results of a series of studies on the drying of shelled walnuts with the belt-trough dryer are presented in Table 5. The most rapid drying of kernels, containing initially about 20% moisture, was accomplished using a two-stage drying process. It is of interest that the design of the two-stage drying process and the use of a final drying temperature as high as 210° F. was predicated upon previous observations that kernels become more heat-stable as their moisture content is reduced. Using an initial air temperature of 180° F. and a final air temperature of 210° F., drying to 3.5% moisture was accomplished within 50 minutes. It should be noted that, with the exception of the experiment in which the air temperature was held at 255° F., kernel temperatures did not exceed 145° F. At a constant air temperature of 255° F., kernel temperatures reached 178° F. within 30 minutes and kernel flavor was altered significantly. Under these conditions, kernels were literally "roasted in their own oil" and developed a toasted, although not necessarily objectionable, flavor.

PACKAGING

Supplementary investigations demonstrated that the stability of kernels could be enhanced by: adjustment of kernel moisture to within the optimum moisture range; application of an antioxidant coating; and restriction of exposure to light, particularly in the ultra-violet region. Therefore, attention was focused upon the relative effectiveness of various types of plastic films and laminations and particularly on several types of material that could be employed as a replacement for rigid and/or opaque containers. Specifications for the choice packaging material included: low permeability to moisture and oxygen; transparency to visible and opaqueness to ultra-violet light; chemical inertness and resistance to oil; and simplicity in effecting reliable hermetic seals.

In order to make critical comparisons of available types of plastic and other film materials, it was necessary to design and construct a laboratory model, universal sealing machine.

This prototype machine was employed for preparing vacuum or inert gas packages with materials requiring either heat or high frequency electronic seals (6, 7). The development of this apparatus facilitated the evaluation of numerous types of packaging materials (3). An example of some of the results observed for the permeability to moisture of various plastic and foil bags containing kernels is presented in Fig. 7. In terms of moisture permeability as well as other important specifications, polyvinyl chloride-polyvinylidene chloride (saran) film proved to be the material of choice.

Integrating the available information on factors affecting stability, a practical process was devised for the stabilization of kernels. A commercially acceptable transparent package was produced in which kernel stability was increased by a factor of more than 12, or from a stability of less than 6 weeks for ordinary bulk kernels to more than 18 months in the plastic package under similar conditions.

CURRENT INVESTIGATIONS

One of the prime objectives of the walnut stabilization investigations has been accomplished. Important secondary objectives remain to be realized. Foremost among these is the development of a rapid, convenient, and objective method for the absolute estimation of kernel quality. It is important for the processor to be able to determine the initial quality and potential stability of kernels and to have an accurate and reliable measure of the quality of a sample chosen at random. A reliable measure of kernel quality will permit quality standards to be enforced so that a standard product may be prepared and marketed.

Methods which have been suggested for kernel evaluation, such as estimation of peroxide numbers, have limited, if any real value, in estimating kernel quality. Organoleptic measurements by experienced judges of taste quality remain the only acceptable method. However, this type of evaluation is inconvenient, not adaptable to the evaluation of large numbers of samples, and has other practical disadvantages.

A reasonable solution to problems of quality control may be found through a systematic study of the chemistry of kernels. The establishment of kernel composition and the measurement of chemical changes associated with the development of rancidity and darkening should permit the elaboration of practical objective chemical methods for quality control. Compositional studies have progressed to a point where specific qualitative and quantitative changes have been observed during the development of rancidity. Investigations of the chemical process involved in deterioration are in progress. Preliminary work has been initiated on the development of a practical procedure for estimating kernel quality.

SUMMARY

Methods have been developed for rapid and precise estimation of moisture and pellicle color in shelled walnuts. These methods have facilitated studies on a critical relationship between walnut stability and moisture content.

Kernels are most stable within a limited moisture range, above and below which darkening and development of rancidity progress at an accelerated rate. The optimum moisture range is $3.5 \pm 0.5\%$ for kernels maintained at near ambient temperature. At their optimum

moisture content, kernels are more resistant to the effects of light, heat, and oxygen.

Critical adjustment of moisture can be accomplished rapidly and continuously in commercial operation using the belt-trough dryer.

Supplemental protection afforded by the application of antioxidants, elimination of oxygen, and protection from ultra-violet light synergistically enhance the stability of kernels.

Various packaging materials have been evaluated for their efficacy in supplementing the benefits derived from critical moisture adjustment and other processing procedures.

CONCLUSION

A series of chemical and technological studies on walnut kernels have resulted in the development of a practical commercial process for their stabilization. Incidental to the development of the process, improvements were made in methodology and some new principles were uncovered. It is proposed that some of the methods and principles could be applied to the stabilization of other nuts and possibly to other dehydrated food products.

Further improvements in the processing and the development of objective methods for evaluating quality would appear to be dependent upon basic chemical studies and the development of new information on the composition of kernels and the chemical processes that attend the deterioration processes.

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Table 1.

Color variations in samples of three commercial grades of four varieties of shelled walnuts[1]

Commercial Grade	Variety				
	Franquette	Payne	Eureka		Placentia Perfection (budded)
			Lot 1	Lot 2	
Light	20.8	16.0	20.0	34.4	40.0
Medium	36.8	38.8	52.4	68.0	49.2
Dark	64.0	66.0	82.0	120.0	110.4

1 Expressed as color units/100 g. of shelled walnut halves and pieces.

Rockland, Slowdoski and Luchsinger (9)

Table 2.

Estimation of color in *ad hoc* test mixtures of light and dark walnut kernels

Light Kernels	Dark Kernels	Color, found
%	%	Units/100 g.
100	0	36.8
90	10	46.4
75	25	60.4
70	30	66.4
50	50	84.0
25	75	98.4
0	100	110.0

Rockland, Slowdowski and Luchsinger (9).

Table 3.

Comparison of procedures for estimation of moisture

Sample No.	% of Moisture Found			Moisture Balance % deviation from	
	Vacuum oven	Xylene distillation	Moisture balance	Vacuum oven	Xylene distillation
1	2.87	3.13	3.13	0.26	0.00
2	3.05	3.13	3.25	0.20	0.12
3	3.74	4.17	4.25	0.51	0.08
4	3.92	4.27	4.28	0.36	0.01
5	3.69	4.07	4.17	0.48	0.10
6	3.88	4.27	4.33	0.45	0.06
			Avg.	0.38	0.06

Rockland, Swarthout and Johnson (10).

Table 4.

Comparison of procedures for estimation of moisture in shelled walnuts

Sample	Procedure			
	Vacuum oven	Moisture balance	Moisture Register	Karl Fischer
	%	%	%	%
A	2.35	2.55	2.00	2.45
B	3.35	3.52	3.21	3.45
C	4.20	4.30	4.19	4.25

Rockland (4).

Table 5.

Dehydration rates at various temperatures on belt-trough dryer, expressed as time required to reach optimum (3.5%) moisture

Drying temperature	Kernel bed depth	Final kernel temperature	Total time to reach 3.5% moisture[2]
°F	inches	°F	minutes
180	4	135 est.	100
190	7	138	80
190	4	138	65
200	4	143	60
160 (15)/200[1]	4	144	70
180 (25)/210[1]	4	144	50
255	4	178	30

[1]Two-stage drying. The first number indicates the first stage drying temperature followed by time in minutes at this temperature given in parentheses.

[2]Interpolated from smoothed dehydration rate curves.

Rockland, Lowe, Swarthout and Johnson (8).

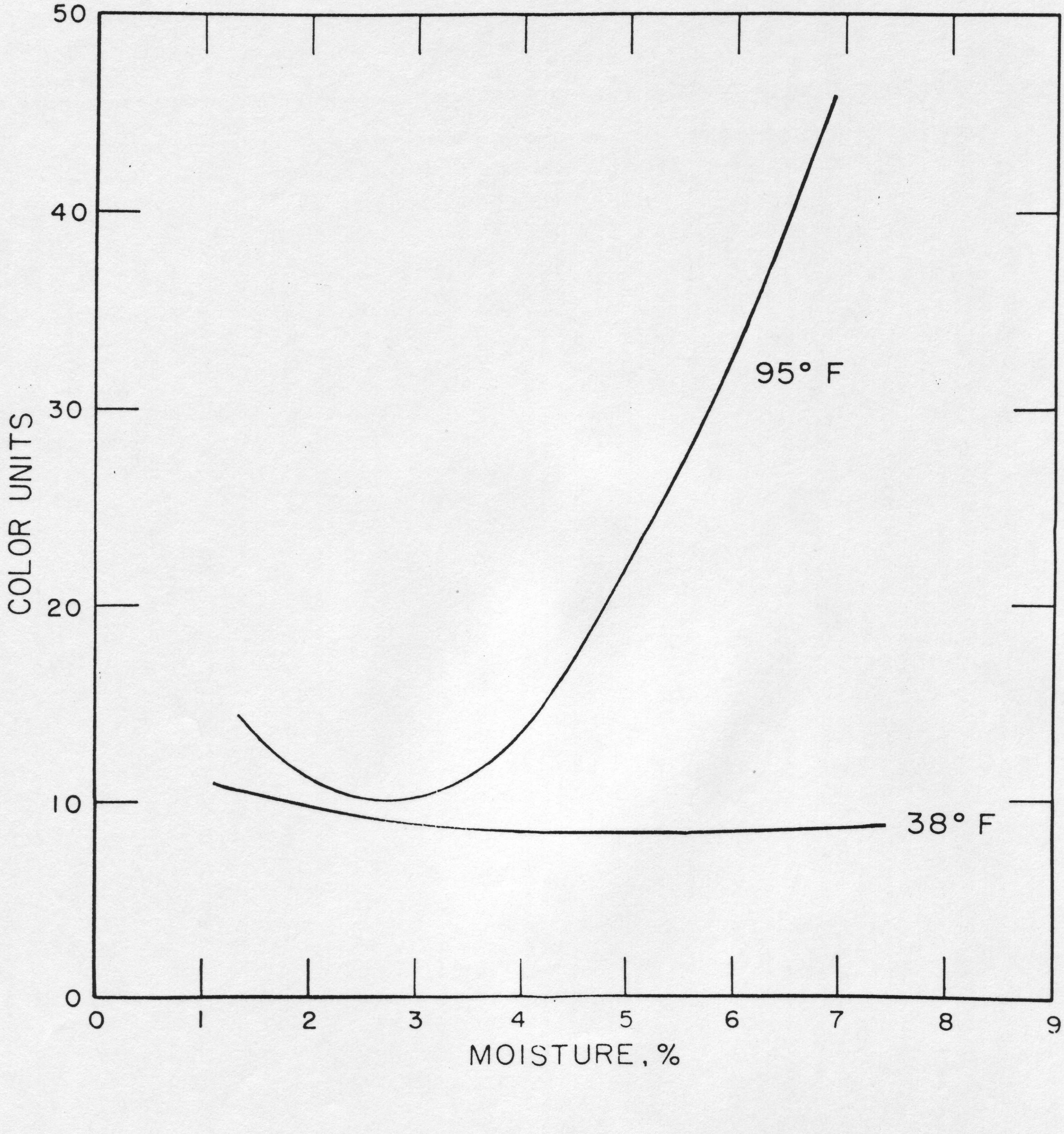


Fig. 1
Color-moisture relationship after 2 months storage of walnut kernels at 38° and 95° F.

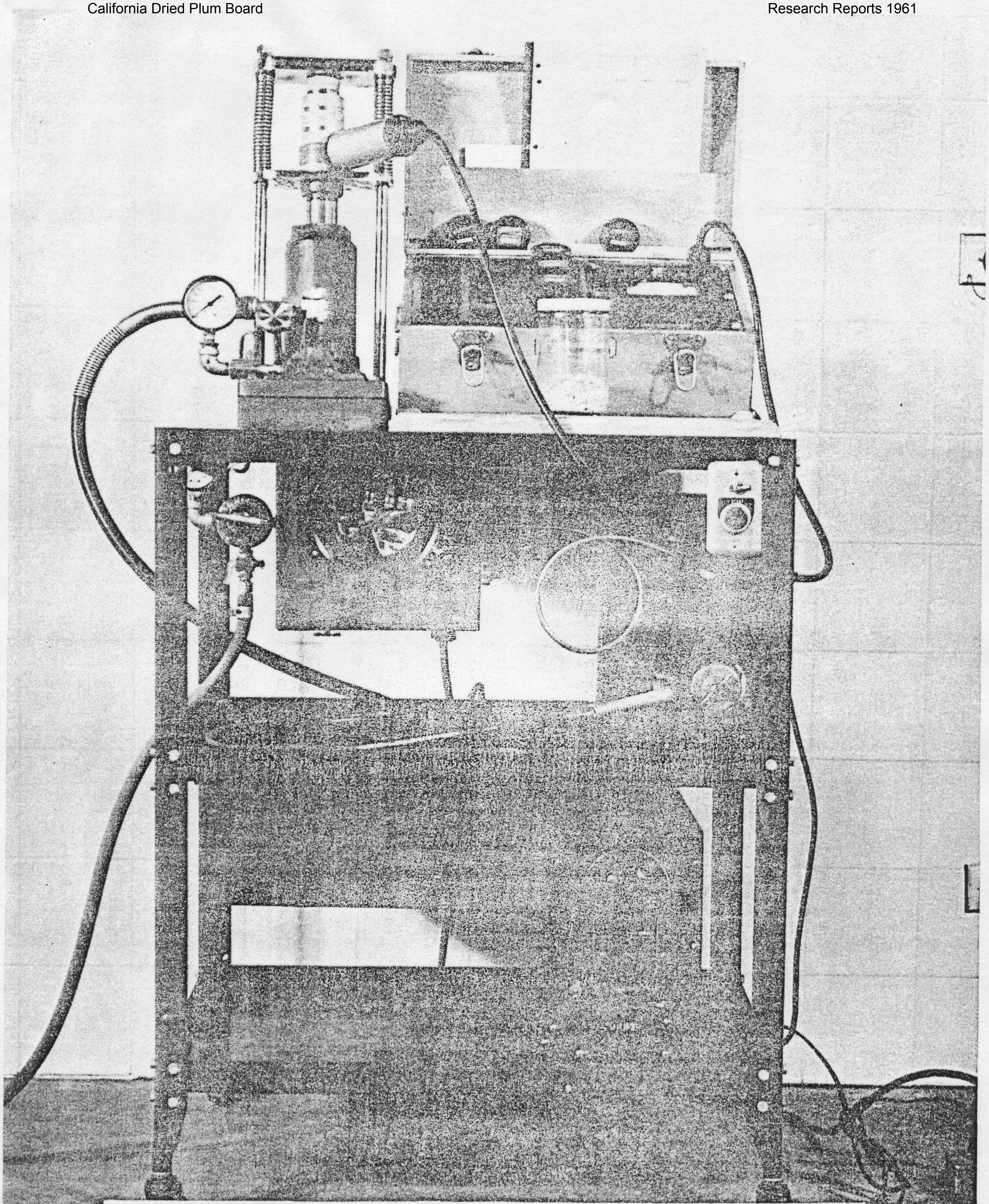


Fig. 2
Electronic moisture meter equipped with automatic pumping unit (4).

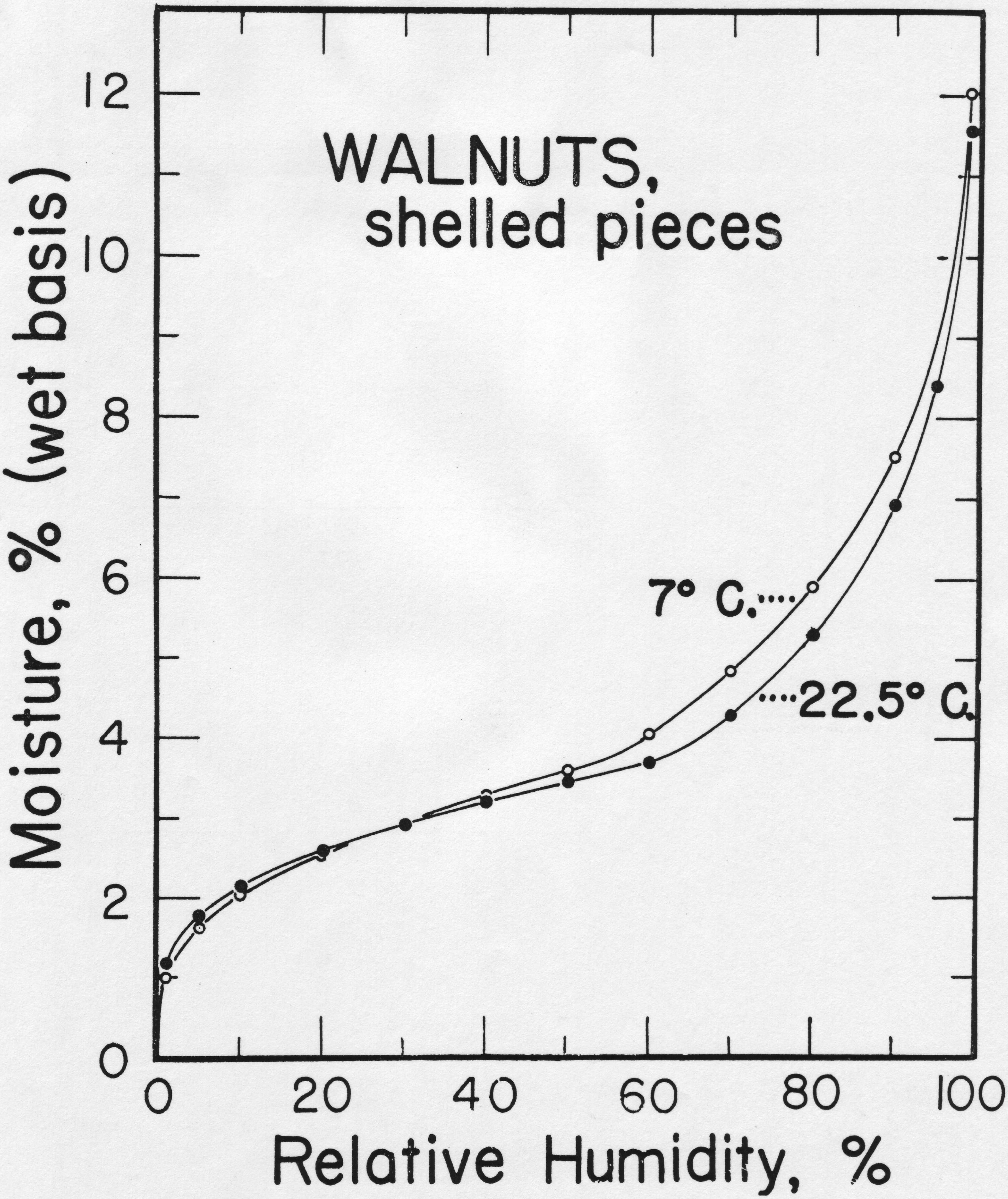


Fig. 3
Moisture sorption isotherms for shelled walnuts of 7° and 22.5° C.

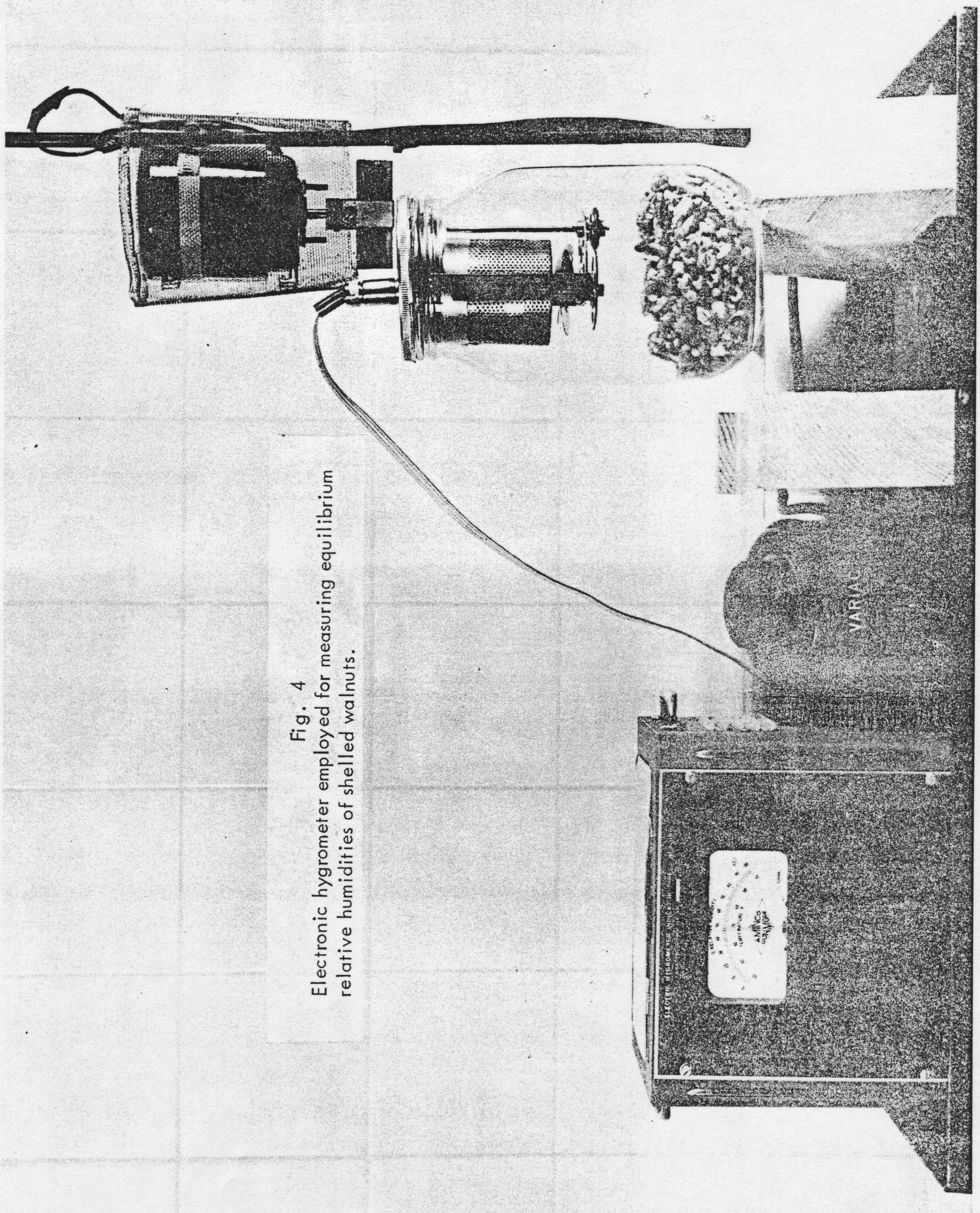


Fig. 4
Electronic hygrometer employed for measuring equilibrium relative humidities of shelled walnuts.

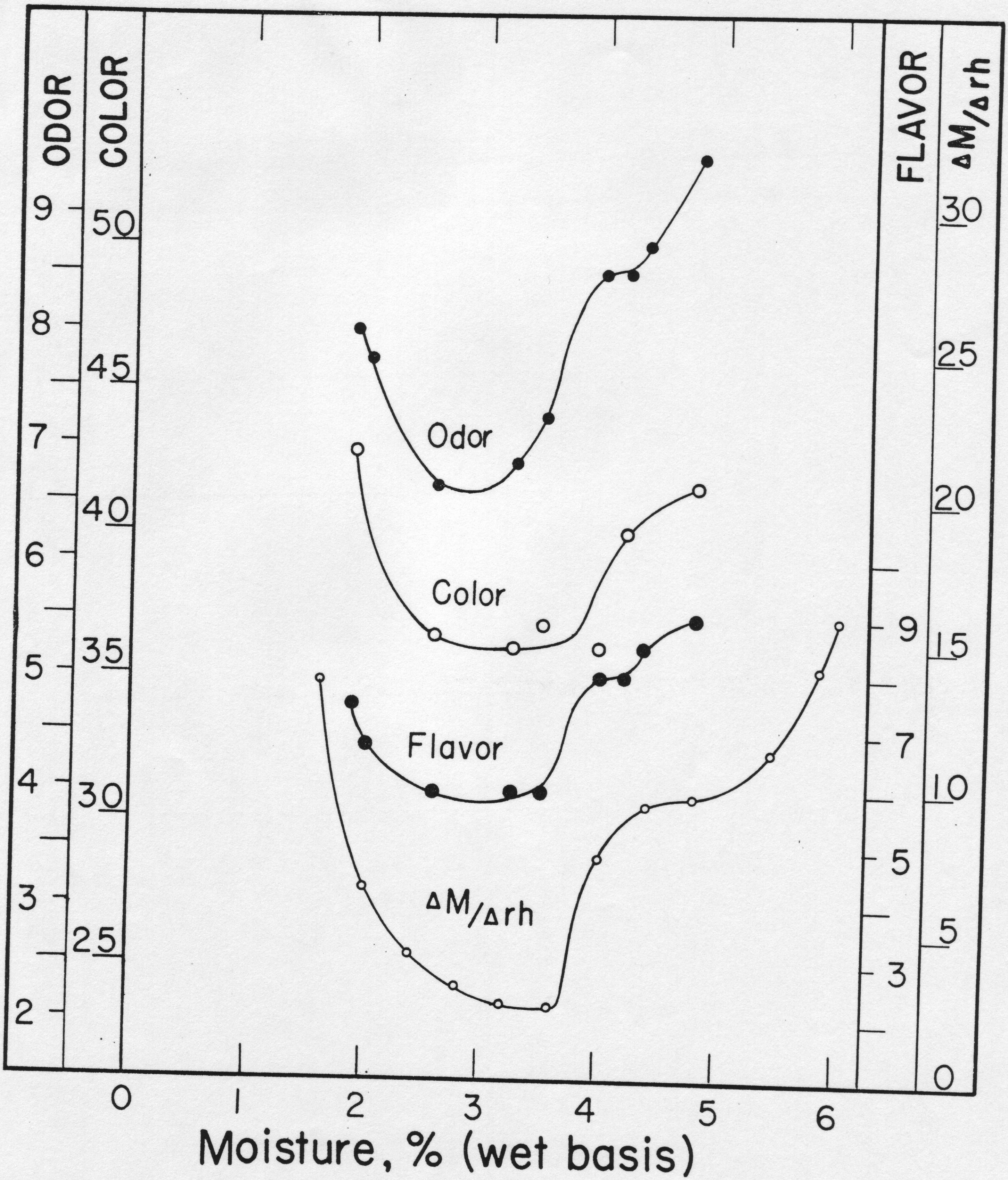
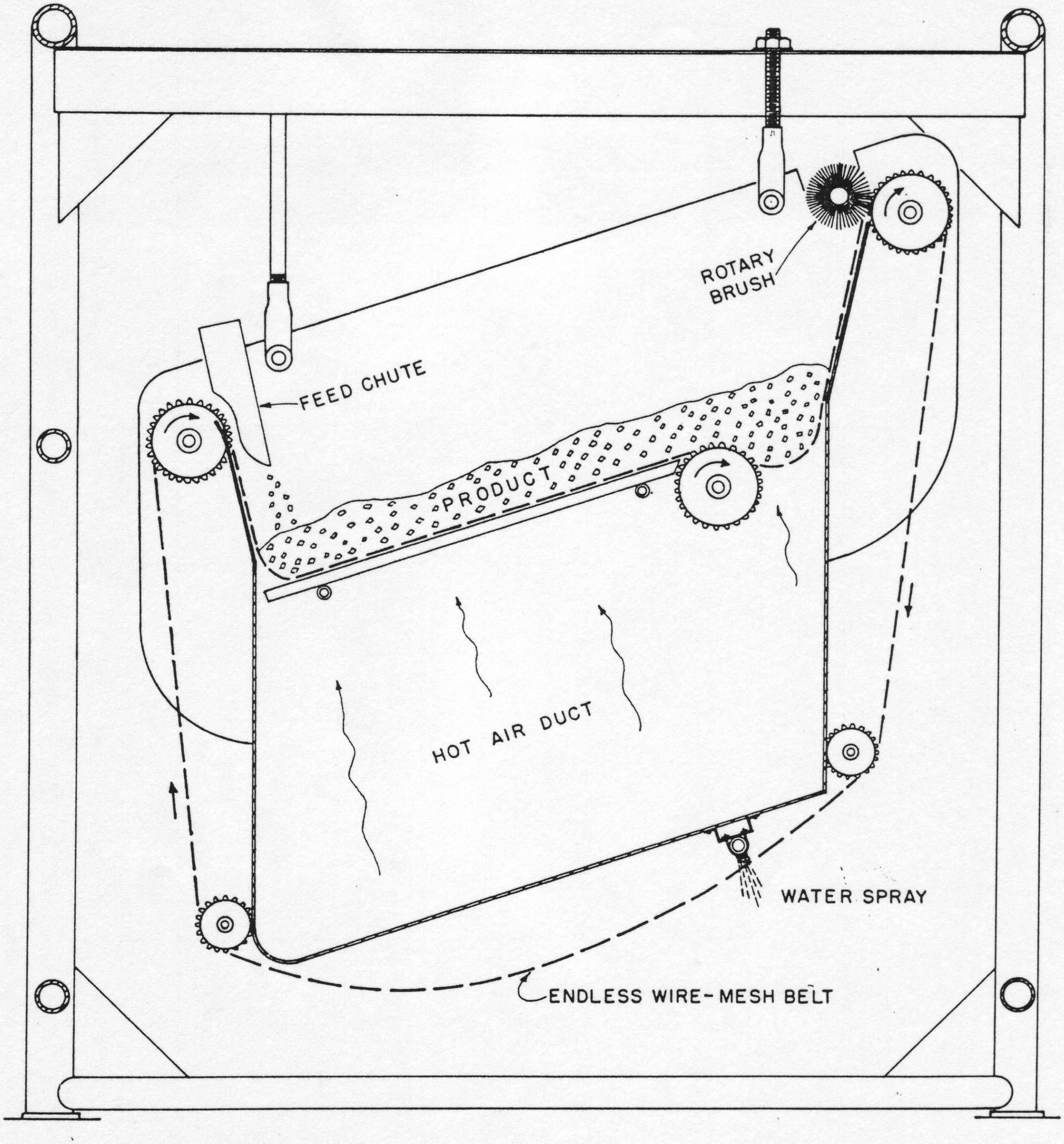


Fig. 5
Moisture-stability relationships compared with the first derivative of the moisture sorption isotherm with respect to moisture for shelled walnuts.



DIAGRAMMATIC CROSS-SECTIONAL VIEW OF BELT-TROUGH DRYER

Fig. 6
Diagramatic cross-sectional view of belt-trough dryer (1).

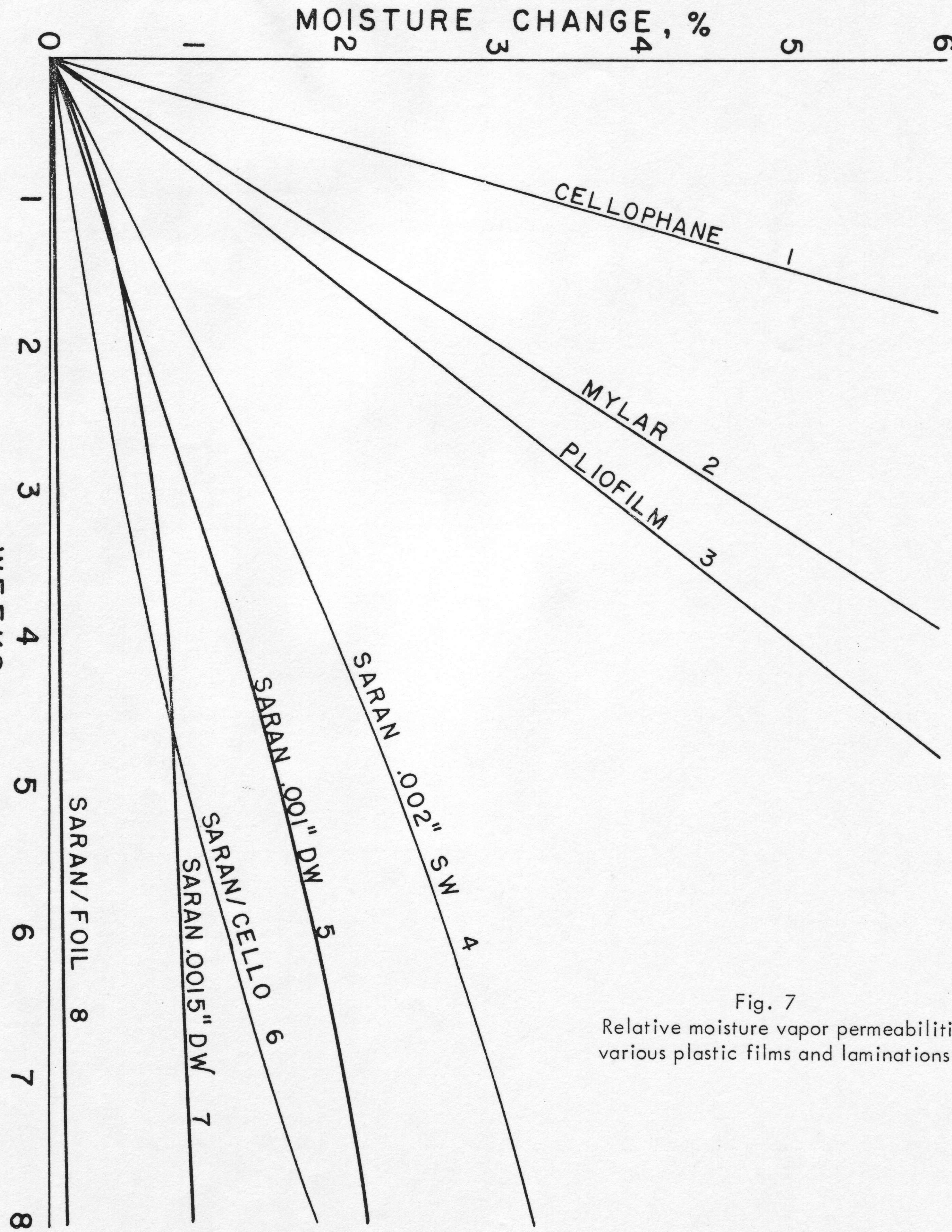


Fig. 7
Relative moisture vapor permeabilities of various plastic films and laminations (3).