Evaluation of Extraction Rate Measurements

ALLEN S. SMITH, University of Notre Dame, Notre Dame, Indiana

THE extraction of vegetable oils from solid materials by solvents has been investigated in the laboratory to determine the effects of variables on residual oil in the material as a function of time. Although much of this work has been erroneously described as rate measurements, the objective of the work has been accomplished; i.e., the economic design of extraction equipment. Extraction rate data have not been reported because there has been no satisfactory theoretical or practical basis on which to formulate a rate equation. This has been no obstacle in evaluating the general effects of material thickness, moisture content, temperature, and solvent on the extraction time required to reach an arbitrary residual oil content; it has led to erroneous conclusions in comparing the extraction of different materials.

Extraction rate, defined as the rate of change of oil content with time (—dx/dt), has the same significance as chemical reaction rate: if a rate equation can be established, the extent of change can be determined at a given time by integration of the equation. The effect of variables will appear as parameters in the equation relating concentration to time and will be included in a proportionality or rate constant. This rate constant will be equivalent to the resistance term in the general equation for material and heat transfer: rate = driving force/resistance. The driving force will be the difference in oil concentration between solid and solution at a given time.

Absolute values of rate constants are of significance in equipment design when determined with materials and by extraction methods which are the same as those encountered in commercial practice. Rate constants obtained by a percolation procedure are applicable only to percolation equipment on the basis of dynamical similarity because the concentration gradient cannot be defined. In general, plant equipment will be operated in a manner different from laboratory apparatus used to obtain extraction rates, and rate constants will then be most useful for correlation of the effect of variables.

If the mechanism of extraction were known to be controlled by diffusion within the solid, rate constants would permit an apparent diffusion coefficient to be calculated. This coefficient, including the value of the true diffusivity of solvent in oil and a pore shape factor characteristic of a particular solid, could be used for the solution of countercurrent extraction problems in the manner suggested for heterogeneous catalytic processes (8). Neither the true diffusivity nor the effect of the solid on diffusion is known at the present time.

The purposes of this paper are to present an empirical method of evaluating rate constants from residual oil content-time data; to determine the mechanism of vegetable seed extraction by comparison of data with those of porous plates in which the process is one of molecular diffusion; and to re-examine the effect of variables on extraction rate. The published and personal experimental data used have been determined by batch, semi-batch, and percolation methods. Inasmuch as solution concentration has not been determined in the course of percolation experiments, a rate equation has been established in which the driving force is expressed as a function of time, and only the initial oil concentration of the material is required.

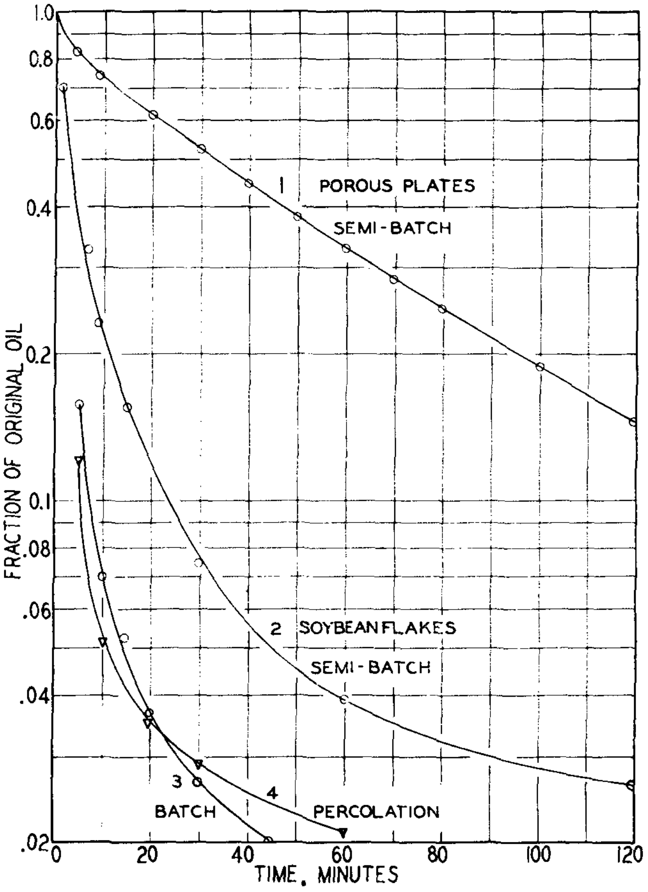

FIG. 1.

Extraction Rate Equation

Figure 1 shows typical data obtained in the extraction of soybean oil from porous plates and from soybean flakes by laboratory batch, semi-batch, and percolation methods. The curve relating the fraction of original oil to time in the extraction of porous plates approximates a straight line after about 20 minutes. Boucher (2, 3) considered the latter portion of the curve to be linear. He obtained the following equations, based (1) on the two-film theory of mass transfer and (2) on Fick's law of diffusion, to express extraction rate.

$$\frac{dW}{dt} = K\,A\,(X - Y)\ (2) \qquad (1)$$

$$\frac{dW}{dt} = \frac{\pi^2 \rho D A}{2L^2}\,(X - X^*)\ (3) \qquad (2)$$

King *et al.* (7) obtained a non-linear relation between the fraction of original oil and time in semi-batch extractions of soybean flakes with trichloroethylene. They used the following equation to represent extraction rate:

$$\frac{dX}{dt} = f\,(X - X^{*}) \qquad (3)$$

X = oil concentration in solid
X^{*} = oil concentration in solid at equilibrium
Y = oil concentration in liquid
W = weight of oil
t = extraction time
A = surface area
K = rate constant
ρ = density of solid
L = thickness of solid
D = diffusion coefficient

Equation (3) was satisfactorily used to compare continuous extraction with results predicted from data obtained by a semi-batch experimental method (3). Although data indicated that molecular diffusion controlled the removal of at least part of the oil in soybean flakes, it has been concluded that the use of diffusion coefficients, as in equation (2), is not applicable to practical extraction problems (7). Individual extraction experiments are necessary for every solid. Batch and semi-batch experimental methods, in which concentration can be determined, give data which can be handled by equation (3) to predict commercial extraction results.

Most of the experimental data available on extraction has been obtained by percolation methods. None of the rate equations can be applied to this process because the variation of the concentration of oil in solid and liquid with time has not been evaluated in percolation. However equation (1) does express the rate at a particular point in a column of material being extracted by percolation. In equation (1) X varies from a maximum to zero; Y varies from zero to a maximum, and then diminishes to zero. Both X and Y are functions of time and consequently Y is a function of X. X is related to X_0, the initial oil concentration in the solid. A rate equation representing this is:

$$dW/dt = K\,[X - f'(X)] \qquad (4)$$

In this equation the rate constant, K, includes the area term of equation (1) and varies with temperature, material thickness, and other characteristics of the material which affect extraction rate. In batch measurements, where X diminishes to an equilibrium value, K will vary with the initial liquid concentration. K will also vary with concentration in semi-batch work where Y is fixed; and when solution, rather than pure solvent, is used in percolation measurements. It would be expected that K would also vary with Reynold's number, but it has been shown to be invariant in semi-batch extraction of porous plates (2). There is no indication that flow rate is controlling in percolation experiments which confirms the conclusion (3) that the liquid film resistance is negligible compared to internal resistance to diffusion.

To obtain a rate equation according to equation (4), an equation is fitted to residual oil-time curves. A single type equation has been found to hold for batch, semi-batch, and percolation experiments; and for the work on porous plates by a semi-batch method after an initial extraction period of about 20 minutes. The similarity of experimental extraction data obtained by these methods is evident in Figure 1. The equation is:

$$(X + b)\,(t + a) = c \qquad (5)$$

in which a, b, and c, are constants. To evaluate these constants, experimental data are used to plot the quantity $t/(X - X_0)$ against time. X_0 is the oil concentration in the solid at zero time, and X is the residual oil concentration at time t. Plots of the data for the four examples in Figure 1 are shown in Figure 2. The equation of the straight lines in Fig. 2 is:

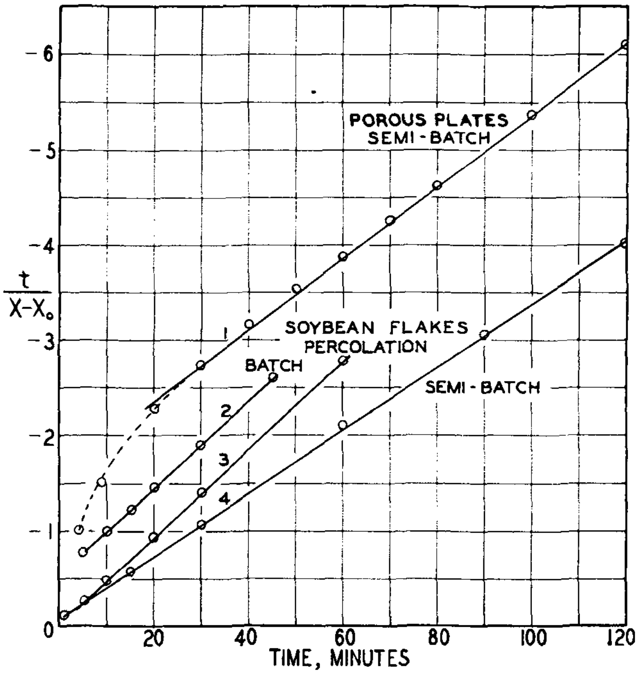

FIG. 2

$$\frac{t}{X - X_0} = -\left(\frac{1}{X_0 + b}\right) t - \left(\frac{a}{X_0 + b}\right) \qquad (6)$$

The slope and intercept in equation (6) are computed from two points on a straight line, from which a and b are evaluated; c can be evaluated from equation (5). Equation (5) has been tested on all published experimental data and is applicable to these data including those on porous plates. It has been observed to be valid over the practical range of extraction: to a concentration of residual oil as low as 0.1% and to a time of 180 minutes. The equation cannot be extrapolated to 0% oil as t does not become infinite when $X = 0$. Much experimental work is observed, by tests of the equation, to be incomplete or uncertain. This equation serves to check the reliability of work which otherwise appears satisfactory when results are plotted in the usual ways.

A rate equation is derived from equations (5) or (6) by differentiation. It is:

$$-\frac{dX}{dt} = K\,(X + b)^2 \qquad (7)$$

On integration between the limits of X and X_0 this becomes:

$$t = \frac{1}{K}\left(\frac{1}{X + b} - \frac{1}{X_0 + b}\right) \qquad (8)$$

which reduces to equation (5) where $a = 1/(X_o + b)$ and $c = 1/K$.

To evaluate the rate constant K, experimental data must be plotted according to equation (6) and a and b evaluated. Although experimental data can be graphically differentiated to obtain $-dX/dt$ at a series of time values, which divided by $(X + b)^2$ at the time will give K, this is not usually necessary. Since $-dX/dt$ also equals $(X + b)/(t + a)$, the experimental data serve for direct determination of the rate. The value at X_o when $t = 0$, $(X_o + b)/a$, is usually as reliable as any value at times greater than zero. For scattered data K should be calculated at all measured times and averaged. No trend in K has been observed in any data; K is a constant dependent only on temperature, solvent, and on the properties of the material extracted by percolation. In semi-batch or batch work, K depends also on the initial solution concentration used for the extraction experiment.

Effect of Material Thickness on Extraction Rate

The rate constant K is proportional to the term $(\pi^2 \rho D/2L^2)$ in equation (2) which is based on Fick's law of diffusion. The rate of extraction, and K, should therefore vary inversely with the square of material thickness if a diffusional process controls extraction. It is shown in the subsequent discussion on the effect of temperature that K is directly proportional to D. This is in agreement with the conclusion (3) that the liquid film resistance is negligible compared to the internal resistance to diffusion.

K is related to thickness in all consistent data by the equation:

$$K = m/L^n \qquad (9)$$

in which m and n are constants. Some typical data are shown in Figure 3; n varies from 2 to 3, but most materials give values of $n = 3$. The limited data (two thicknesses) on porous plates give a value of 1.5 for n. It can be concluded that there is a definite agreement with diffusion theory, considering the variations between flaked material unavoidable in sampling and the fact that some curves can be drawn with either a slope of 2 or 3. The value of n is the same in the extraction of both soybean flakes and grits. Some typical data are given in Table I.

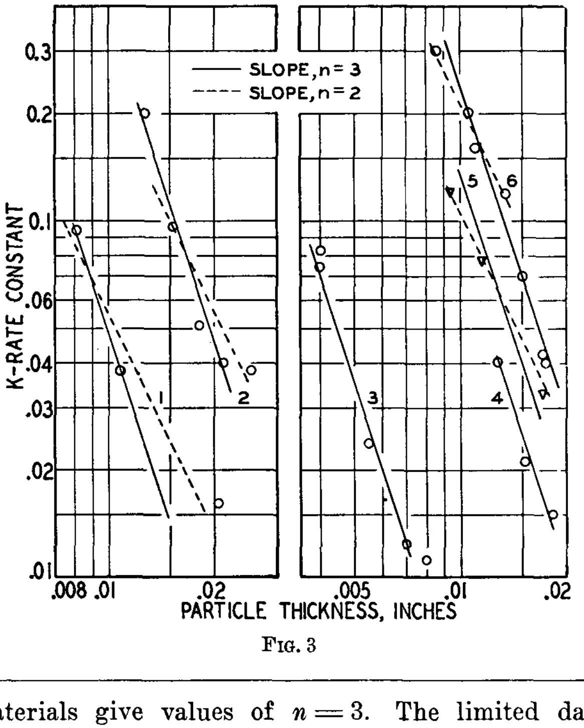

FIG. 3

TABLE I

Effect of Variables on Extraction Rate by Percolation

Thickness			
	L, inches	K	Initial Rate[a]
Soybean Grits—Hexane (4)	0.0128	0.20	18.6
	0.0152	0.10	9.4
	0.0181	0.05	6.3
Soybean Flakes—Hexane (4)	0.0085	0.30	146.0
	0.0110	0.16	84.0
	0.0150	0.07	35.0
	0.0175	0.04	20.0
Temperature			
	°F.	K	Initial Rate[a]
Soybean Grits—Hexane (10)	84	0.05	21.0
	114	0.10	45.0
	192	0.17	82.0
Soybean Grits—Hexane (10)	68	0.05	21.0
	110	0.06	26.0
	150	0.12	56.0
Soybean Flakes—Hexane (10)	75	0.05	22.0
	95	0.06	28.0
	150	0.10	48.0
Moisture			
	%	K	Rate at 100 min.[b]
Peanut Slices—Hexane (5)	10	0.0028	0.17
	13	0.0032	0.15
	22	0.0035	0.12

[a] Basis is oil in whole material.
[b] Basis is oil in oil-free solid.

The Effect of Temperature

Liquid diffusion is related to viscosity by the Stokes-Einstein equation $D\mu = kT$. Each property varies with temperature according to the rate equations $\mu = k'e^{E_{vis.}/RT}$ and $D = k''e^{-E_{diff.}/RT}$. The quantities $E_{vis.}$ and $E_{diff.}$ are the energies of activation for viscosity and diffusion. Because of the similarity in the mechanism of the two processes the relation $E_{vis.} = E_{diff.}$ can be derived (9). This relation was found to be valid within 10% for dibutyl phthalate diffusing into n-butyl alcohol when $E_{vis.}$ was computed for the solvent (9). It is not valid for diffusion in soybean oil-solvent solutions when $E_{vis.}$ is that of the solvent, the common assumption in mixtures of large and small molecules. In the extraction of soybean oil from flakes and porous plates by hexane, perchlorethylene, and a mixture of carbon tetrachloride and trichloroethylene $E_{diff.} = 2\,E_{vis.}$ where $E_{vis.}$ is that of the solvent, and the experimental rate constant K is taken as proportional to D. A difference in activation energies calculated from viscosity and from diffusion has been reported also in recent work on the extraction of various oils with solvents (1).

It is apparent that the viscosity of both oil and solvent influence diffusion and $D = f(\mu_o, \mu_s)$ at constant temperature. An empirical equation of this form has been used by Boucher (3) to correlate diffusion data on the extraction of soybean oil from porous plates by perchlorethylene, and by a carbon tetrachloride-trichloroethylene mixture.

The extraction rate constant K has been plotted against the product of oil and solvent viscosities in Figure 4. Although the limited data for each run

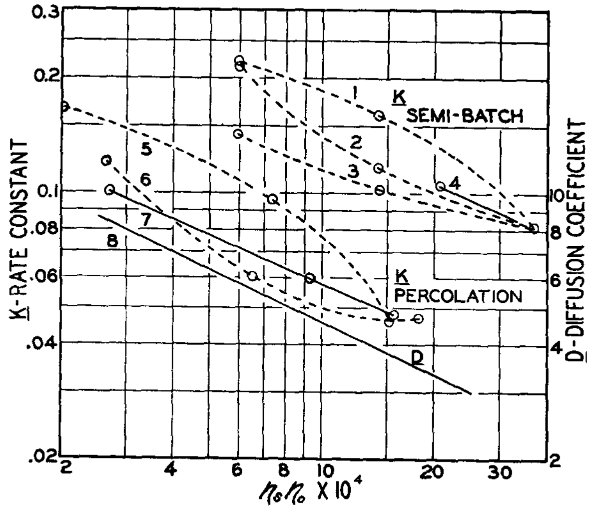

FIG. 4

do not lie on straight lines, it is evident that the points can be smoothed to give lines having a common slope. The smoothed lines would have a slope essentially the same as the line representing the variation of diffusion with the viscosity product as given by Boucher (3). This line included data for both perchlorethylene and the constant boiling mixture of carbon tetrachloride and trichloroethylene. The assumption that K is proportional to D is therefore justified.

The effect of temperature on extraction is identical for soybean flakes and grits, and for soybean oil from porous plates. The effect of temperature is consistent with diffusion theory but not consistent with the assumption that, in a mixture of large solute and small solvent molecules, the properties of the solvent predominate. Some typical values of rates and rate constants are given in Table I.

Effect of Solvent

The effect of solvent on extraction rate cannot be predicated because of inherent differences in the solubility characteristics of different solvents. Two solvents which are mutually soluble in an oil are not necessarily equal in solvent power for the oil. The activity of the oil-solvent mixture is a measure of solubility, and it is known that solvents, such as hydrocarbons, have activity coefficients which vary with molecular weight of the solvent. No correlation is to be expected, then, in the rate of extraction with hexane and heptane. The correlation shown by Boucher (3) is fortuitous and obtained probably because of the similarity in the two chlorinated solvents compared. A decrease in viscosity due to temperature increases extraction rate, but it does not follow that the rates with two solvents will be proportional to their viscosities.

Effect of Moisture

No satisfactory data are available on the effect of moisture in the extraction of commercial materials. Either the results are erratic or variables other than moisture content are present. The extraction of peanut slices with hexane (5) shows that extraction rate diminishes with increase in moisture content between 10 and 22%. The rate constant however increases. This indicates that moisture may not alter diffusion but only the ability of the solvent to wet the solid. The concentration gradient, or driving force, in extraction is thus reduced at high moisture content. Data are given in Table I for the extraction of peanut slices with hexane by percolation.

Effect of Material

No comparison can be made of the relative rate of extraction for different oil-bearing materials. No experimental work has been reported in which all variables were held constant. Since the oil content of different materials, such as soybean and cottonseed flakes, will necessarily be different, a comparison can be made with other variables the same only by batch or semi-batch methods. A percolation method would not be suitable because there can be no control over the concentration gradient.

Comparisons of the extraction of different materials which have been made are based on the time for extraction to a given residual oil content. Such comparisons do not give relative rates of extraction as they ignore the effect of concentration gradient. Relative rates must be expressed in terms of a rate constant.

Summary

An empirical equation has been presented which can be used to correlate published data on the extraction of soybean, corn, cottonseed, flaxseed, wheat germ, and peanut flakes and grits by solvents. The equation is also satisfactorily applied to the extraction of oil from porous clay plates and peanut slices after an initial period of time.

The difference between commercial flakes and grits compared to porous plates and peanut slices indicates that the manner in which oil is extracted initially is different for the actual and simulated materials. The extraction process must therefore be studied with actual materials to obtain data for design.

The empirical equation enables the rate of extraction by batch, semi-batch, and percolation methods to be calculated, and a rate constant obtained. The rate of extraction of actual materials is proportional to a constant during the entire course of extraction. This is true for simulated materials only after an initial period of extraction.

The rate constant is proportional to the diffusivity of oil and solvent under the conditions found in a material. It varies with the reciprocal of the temperature, directly with the product of oil and solvent viscosities, and approximately with the reciprocal of the square of the material thickness.

An increase in moisture content decreases the rate of extraction but does not necessarily reduce the coefficient of diffusion. Results showing such a decrease in diffusion with increase in moisture have been erroneously interpreted because there is no variable to include the condition of the material.

The effect of different solvents on the rate of extraction cannot be predicted. The rate with different solvents is not only a function of viscosity but also of solvent power.

The relative rates of extraction of different materials have never been evaluated.

The difficulty in extraction of residual oil, in the region of 5 to 0.5%, is due to a low concentration gradient at the end of extraction.

The fact that extraction data with porous plates could be represented by Fourier equations of heat

conduction applicable to the drying of solids where internal diffusion controls led Boucher (3) to the conclusion that the extraction process was one of pure molecular diffusion. Since the importance of the process of diffusion in the extraction of actual materials has been questioned (6), a comparison was made between the extraction data on porous plates and on other materials. It is apparent that the results are comparable, and the effect of variables are the same. Diffusion, apparently, controls the entire process in the solvent extraction of the commercial oil-bearing materials.

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The Determination of Moisture in Tung Fruit[1]

RAIFORD L. HOLMES, JACOB C. MINOR, and R. S. McKINNEY, U. S. Tung Oil Laboratory,[2] Bogalusa, Louisiana

THE determination of moisture on materials containing tung oil is particularly difficult because of the tendency of tung oil to oxidize and increase in weight when heated. In this laboratory it has been standard practice to determine the moisture content of tung products by heating them in a vacuum oven for 2.5 hours at 101°C. under a vacuum of 12 mm. pressure. Such a procedure was used to minimize the error from the oxidation of the oil.

In 1948 the Subcommittee on the Analysis of Tung Fruit and Meal of the American Oil Chemists' Society adopted the procedure of drying the ground sample to constant weight at 101°C. in a forced draft oven as its tentative method for determining moisture in whole fruit (1). In collaborative work of this subcommittee no significant differences were found for the oil content of tung fruit when determined by different analysts, but significant differences in moisture content were found, indicating that the conditions specified for moisture determination were inadequate.

A comparison of the different methods for determining moisture was made on samples of fruit and seeds to determine their relative reliability and practicality.

All samples were ground through a Wiley[3] mill equipped with a 0.25-inch screen. For the finely ground samples the material which had been ground through the Wiley mill was reground through the Bauer[3] attrition mill with plates set at .008 inch. In the coarse grinding through the Wiley mill since the system is closed there is no appreciable loss of moisture, and the moisture content of the ground sample is considered to be the same as that of the original sample. Moisture is lost from the sample on fine grinding, and when oil is determined on the finely ground sample it is necessary to correct for this loss of moisture if the oil content of the original sample is required.

Methods Investigated

The methods studied were:

1. Drying in a forced draft oven to constant weight at 101-103°C. (1).
2. Drying in a vacuum oven under not more than 12-mm. pressure for 2.5 hours at 101-103°C. with no bleeding of air into oven.
3. Distilling with toluene (2).
4. Drying by hot air blower (Dietert Teller[3]) in which a large volume of heated air is blown through the sample held in a pan with a finely screened bottom (3). Air was blown through the sample for 15 minutes at 126.7°C.
5. Measurement of radio frequency impedance and correlation with moisture content (Steinlite Moisture Meter[3]) as determined by vacuum oven.
6. Titration with Karl Fischer reagent (6). Titrations were made in 40 x 120 mm. weighing bottles with standard ground outside tops using a magnetic stirrer. Electrodes were sealed into a top with a hole drilled through it to closely fit the burette tip.

Experimental Data

The results of moisture determinations on tung fruit and kernels, using the six different methods, are given in Table I. Comparisons were made between the first five methods on 34 samples. Subsequently comparisons were made between the vacuum oven and Karl Fischer methods for moisture determinations on 15 samples of fruit. All the data are shown in the same table.

Using the data in Table I, it cannot be shown that there are any differences in the comparative behavior of the different methods when used on the different materials (statistically, there is not a significant interaction between methods used and materials analyzed). Hence the results on all three materials can be averaged without obscuring any significant results, and only the means compared, provided for the means to be compared the same samples are averaged.

A statistical analysis of the data shows that the difference between the means for the vacuum oven and Karl Fischer methods is not significant. This is also true for the difference between the means for the distillation and forced draft methods. The mean of the values for the vacuum oven method is significantly higher than those for the distillation and forced draft oven methods, which in turn are significantly higher than the mean for the method using the hot air blower. The mean for the radio frequency meter was slightly but significantly lower than that for the vacuum oven method.

To study the effect of oxidation on apparent moisture content, percentages of moisture were determined

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[2] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[3] Mention of equipment by trade name does not constitute endorsement by the Department of Agriculture.