Kinetics of Thiamin and Riboflavin Loss in Pasta as a Function of Constant and Variable Storage Conditions

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ABSTRACT

The stability of thiamin and riboflavin in enriched pasta humidified to different water activities was measured at 25, 35, 45, and 55°C for periods of up to 1 yr. Riboflavin was shown to be extremely stable (dark reaction) whereas thiamin losses were significant. Thiamin loss increased with temperature (Q_{10} of 4.5) and water activity. Predictions of thiamin loss for a square wave temperature fluctuation using steady state data were compared to actual losses found in storage for pasta held at equal alternating times at 25/45 and 25/55°C. The Hicks-Schwimmer-Labuza model provided an adequate method for predicting both the amount of loss and the effective temperature from steady state data.

INTRODUCTION

THE NUTRITIONAL IMPLICATIONS of food processing and distribution in terms of nutrient destruction and loss have become very important in recent years. This is especially true in light of recent governmental recommendations regarding dietary goals and the effect of current and proposed nutritional labeling regulations. Current dietary goals for improved human nutritional status recommend that there should be an increase in the consumption of complex carbohydrates. One way to meet this recommendation would be through an increase in the consumption of pasta. In fact, pasta consumption increased over the last decade (Brown, 1977).

Thiamin and riboflavin are considered the most unstable of the water-soluble vitamins used for enrichment of flour and pasta. These nutrients can undergo degradation during processing and again when subjected to the variable conditions of time-temperature-humidity encountered in distribution and storage. Pasta and cereals can remain in distribution and on the shelf for up to 36 months following manufacture, and thus are likely to incur significant nutritional losses of these vitamins (Labuza and Kreisman, 1978).

Among the concerns of the food processor is the effect of such nutrient loss on label declarations. Nutritional labels on food products should reflect the amount of a listed nutrient at the time of purchase, although the present regulation is based on the level as measured at the time of processing. With varying modes of distribution and storage, the manufacturer must ensure that the label levels of a nutrient are met even under the most severe conditions. With the potential emergence of "open dating" regulations, some which have been tied to nutrient loss such as in the state of Massachusetts, these requirements become even more stringent (OTA Report, 1979). Thus, knowledge of the kinetics of degradation of the B-vitamins is important in assessing the amount of loss that can occur.

Labuza (1972) has demonstrated the application of chemical kinetics to the study of nutrient losses in dehydrated foods. The literature abounds with studies in which the stabilities of many different vitamins were examined over a wide range of conditions and foods. Such studies are generally of a design, which uses only endpoint analysis, i.e., measure the value after a given process/storage condition. Because of this, proper kinetic analysis is precluded. However, Farrer (1955) and later others (Feliciotti and Esselen, 1956; Goldblith et al., 1968; Mulley et al., 1975) showed that the loss of thiamin due to temperature effects could be readily predicted by a first order reaction.

$$\ell n \frac{A}{A_o} = -k\,\theta \qquad (1)$$

where: A = concentration at time θ; A_o = initial concentration; k = rate constant which depends upon temperature; and θ = time. The activation energies (E_A) derived from the Arrhenius relationship for loss of thiamin in these systems were generally about 20–30 kcal/mole (80–125 Kjoules/mole).

Even fewer studies have examined the rate of riboflavin loss. Reports on the strictly thermal loss of riboflavin (dark reaction) have generally noted greater thermostability than for thiamin (Guerrant et al., 1945; Nymon and Gortner, 1947; Brenner et al., 1948; Clifcorn, 1948; National Canners Assoc., 1955). Riboflavin data reported by Salunkhe et al. (1978) can be shown to follow first order rates of loss. This substantiates earlier observations (Farrer and MacEwan, 1954; Surrey and Nachod, 1951). There are few studies which examined the effect of the water activity (a_w) of food systems on the stability of thiamin and riboflavin. Kapsalis (1973) and Dennison et al. (1977) have demonstrated significant interaction between a_w and thiamin or riboflavin stability. However, not enough data were collected for a thorough kinetic analysis. The kinetics studies were also limited in design by restriction to steady state conditions of temperature.

Hicks (1944) and Schwimmer et al. (1955) presented solutions for reactions following zero order kinetics, to estimate the amount of loss or degradation that may occur under sine or square wave temperature fluctuations. Powers et al. (1965) and Wu et al. (1974; 1975a, b) tested these equations and demonstrated that when using the mean tempeature of the fluctuation, the actual amount of loss was underestimated. However, they incorrectly applied the equations to reactions that were first order and thus had a poor predictability as to extent of change. Recently,

Table 1–Stability of riboflavin in pasta under various storage conditions and a_w 0.65

Condition	Concentration (mg/100 g)
Initial	0.507
322 days at 25°C	0.510
294 days at 35°C	0.489
203 days at 45°C	0.514
147 days at 55°C	0.522

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Labuza (1979) derived equations similar to that of Hicks and Schwimmer, but for first order reactions undergoing square or sine wave fluctuations. The purpose of this research was to investigate the degradation of thiamin and riboflavin in enriched pasta as a function of temperature, water activity, and their interaction. The effect of temperature was examined under both steady and unsteady state conditions. Steady state kinetics for vitamin loss were derived from experiments at constant temperature. The Labuza (1979) prediction model was then tested for a first order reaction undergoing a square wave temperature fluctuation.

EXPERIMENTAL

Test system

Enriched pasta utilized in this study was made from durum semolina (International Multifood Corp., Minneapolis, MN). The manufacture of these noodles has been described by Kamman et al. (1980).

The dried noodles for all temperatures were preconditioned by humidification for 4–6 wk at 20°C in the absence of light to the appropriate test a_w (0.44, 0.54, 0.65) by storage over saturated salt solutions (KCO_3, $Mg(NO_3)_2$, or $NaNO_2$, respectively). After equilibration was complete, approximately 4g of the humidified noodles were vacuum packaged into 6 in x 9 in. cm retort pouches of laminated foil-Saran (Continental Can, Mt. Vernon, OH). Between 10–14 replicates of each test condition were then further packaged into resealable poly bags to insure further that there would be no moisture loss from the sample.

Water activity measurement

All water activity measurements were made at ambient temperature using the vapor pressure manometer (VPM) technique described by Labuza (1976) with modifications of Lewicki et al. (1978). Between four to five samples were measured prior to vacuum packaging and at the end of storage study to insure that the a_w had remained constant.

Thiamin and riboflavin measurement

Measurement of thiamin and riboflavin utilized an Auto-Analyzer II system (Technicon, Tarrytown, NY). This automated method uses a fluorometric determination of thiamin and riboflavin under continuous flow (AOAC, 1975). A single extraction is used for both vitamins (Kamman et al., 1980). The flow scheme of Pelletier and Madere (1975) was used for thiamin analysis and the flow scheme of Egberg and Potter (1975) was used for riboflavin. All manipulations were carried out in subdued light and/or amber glassware. Duplicate analyses of triplicate samples were analyzed to give the initial values immediately after humidification.

Storage conditions–steady/unsteady state

The samples of each test system in pouches were then stored at isothermal conditions of 25, 35, 45 and 55°C. The storage incubators were shown to vary ± 0.3°C from the set temperature. At appropriate intervals, duplicate samples were removed for vitamin analysis. During the 80–320 day storage time, between five to seven sampling times were used.

In addition to the isothermal conditions, the effects of two fluctuating square wave temperature regimes on vitamin stability were examined. The first condition was a square wave with a 14 day cycle consisting of 7 days at 45°C followed by 7 days at 25°C repeated for a total of 266 days. The second square wave condition has a 28 day cycle consisting of 14 days at 55°C and 14 days at 25°C, repeating for 112 days. Duplicate samples from these conditions were removed for vitamin analysis only upon completion of a full square wave cycle for a total of four or eight sampling times.

The come-up and come-down times during the cycles were measured by inserting an internal pouch thermocouple (Model 5.1 brass receptacle; O. F. Ecklund Inc., Cape Coral, FL) into representative samples and recording the temperature profile on a Leeds and Northrup Speedomax Model W recorder (Leeds and Northrup, North Wales, PA). The come-up and come-down times for both fluctuating conditions were shown to be less than 35 min in each case. Test samples removed for analysis were stored for not more than 3 days at 4°C. The pouches remained sealed until the time of analysis.

RESULTS & DISCUSSION

Riboflavin stability

Riboflavin, in the absence of light, proved to be quite stable throughout the study as shown in Table 1 based on endpoint analysis. In each case, there was essentially no change in riboflavin concentration from the initial condition, including a rather severe condition of 147 days at 55°C.

The stability of riboflavin noted in this study was comparable to the stability observed by Rice et al. (1944) for pork loaves, Guerrant et al. (1945) for canned meats and Salunkhe et al. (1978) in which no loss was found at 35–45°C for up to one year in canned vegetable and meat foods. Thus, riboflavin loss is not accelerated in reduced water activity systems.

Thiamin stability-steady state

Significant losses of thiamin in the enriched system were observed at constant storage temperature. Figure 1 shows a representative semilog plot of thiamin retention for the

Table 2—Effect of temperature and water activity on rate constant and half life ($\theta_{1/2}$) for thiamin loss in enriched pasta during steady state storage conditions

					Activation energy		Q_{10}	
a_w	(°C)	Measured rate constant k (days)$^{-1}$ x 10^4[a]	r^2	$\theta_{1/2}$ (days)	kcal/mole	(r^2)	35°C	45°C
0.44	25	1.99 ± 0.0	0.875	3,480	30.8	(0.98)	4.9	4.6
	35	6.5 ± 2.5	0.931	1,070				
	45	22.2 ± 2.5	0.982	313				
	55	156.5 ± 12.7	0.992	44				
0.54	25	2.2 ± 0.0	0.828	3,120	29.8	(0.996)	4.6	4.4
	35	9.5 ± 0.0	0.979	730				
	45	38.5 ± 2.5	0.994	180				
	55	202.4 ± 12.7	0.995	34				
0.65	25	6.1 ± 0.0	0.941	1,130	26.6	(0.999)	3.9	3.8
	35	18.3 ± 2.5	0.983	380				
	45	62.6 ± 3.5	0.997	110				
	55	260.5 ± 16.0	0.995	27				

[a] ± 95% confidence limits

pasta at an a_w of 0.54 showing good linearity, and thus indicating first order as per Equation 1. The rate constants calculated from the slopes of the best regression lines (see Freund, 1967) are shown in Table 2. As the a_w of the test system is increased, as shown in Table 2, the rate of loss of thiamin increases as evidenced by the higher rate constant and the decreasing $\theta_{1/2}$. For example, at 45°C the half life of thiamin at an a_w of 0.44 was 313 days compared to a value of 111 days at an a_w of 0.65. The results become more obvious by using the calculated time to reach 25% loss of thiamin as an endpoint for nutrient based shelf life, as has been suggested in the OTA report. Figure 2 indicates that storage at as low an a_w as possible can significantly extend the shelf life, particularly at lower temperatures. In addition as a_w increases, the slope of the shelf life plot decreases, indicating a change in activation energy with a reduced temperature sensitivity at higher a_w. Caution should be exercised in extrapolating shelf life data to lower temperatures due to the nonlinearity of these plots over wide temperature ranges. However, the lines curve upwards at lower temperature Since pasta normally has an a_w of between 0.44–0.5 and is stored for about 12–18 months, thiamin loss should be insignificant if it is kept below 30°C and 50% RH.

Table 2 also lists the activation energies (E_A) calculated from the slope of the plot of $\ln k$ vs $1/T$. It can be seen that excellent regressions were obtained. The E_A values are within the range reported by Farrer (1955) and Feliciotti and Esselen (1965). It should be noted that E_A fell with increasing a_w which agrees with earlier studies on vitamin deterioration in food (Lee and Labuza, 1975; Laing et al., 1978; Labuza, 1980a) and may be attributable to the enthalpy/entropy compensation phenomenon (Labuza, 1980b). This may be evidence of possible solvation effects by water on the reactants in the system in which the reaction is more likely to proceed at higher a_w due to the availablity of more free water. Table 2 also lists the calculated Q_{10} based on the method of Labuza (1979).

Thiamin stability—unsteady state

Hicks (1944) and Schwimmer et al. (1955) theorized that the mean or average temperature of periodic temperature fluctuations was inappropriate in predicting the amount of degradation of a food subjected to fluctuating temperatures. The constant temperature that gave a degradation rate equivalent to the fluctuating regime was called the effective temperature (T_e) and could be calculated from constant temperature data as shown in Equation 2.

$$T_e = T_m + \frac{1}{b} \ln \Gamma_{sq} \qquad (2)$$

where: T_m = fluctuation mean (35°C or 40°C in this present study); $b = \ln Q_{10}/10$ or slope of shelf life plot; Γ_{sq} = square wave function based on steady state data and presented in a table in Powers et al. (1965). The original Γ_{sq} function of Hicks (1944) and Schwimmer et al. (1955), however, did not take the temperature dependence of Q_{10} into account and was only derived for zero order reactions. The table of Γ_{sq} in Powers et al. (1965) has similar limitations. More recently, Labuza (1979) showed that by taking the temperature dependence of reactions into account and applying the kinetic analysis to a first order reaction, Γ_{sq} can be found from Equation 3.

$$\Gamma_{square} = \frac{1}{2}\left[Q_{10}^{+\frac{a_o}{10}\left[\frac{T_m+10}{T_m+a_o}\right]} + Q_{10}^{-\frac{a_o}{10}\left[\frac{T_m+10}{T_m-a_o}\right]} \right] \qquad (3)$$

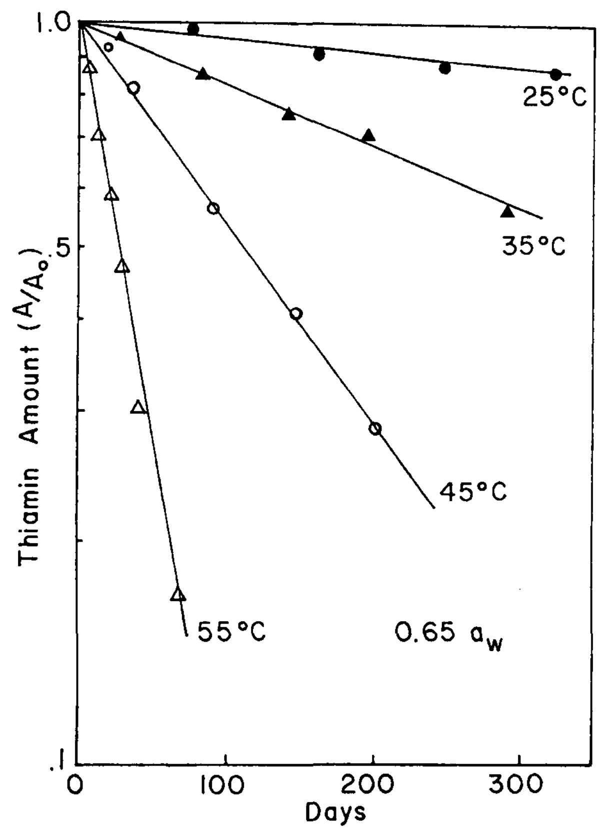

Fig. 1—Fractional retention of thiamin in enriched pasta stored at 25, 35, 45 and 55°C and a water activity of 0.54.

Table 3—Comparison of measured and predicted rate constant and amount of loss and effective temperature for thiamin in enriched pasta subjected to square wave temperature fluctuations

a_w	T_{fluc}	Measured rate constant k $(days)^{-1} \times 10^{4a}$	(r^2)	Predicted rate constant k_{eff} $(days)^{-1} \times 10^4$	Fraction retention after 112 days or 196 days[b] Actual	Predicted	Effective temp Actual	Predicted
0.44	25/45°C	11.62 ± 2.36	(0.973)	16.06	0.84	0.73	39.0°C	40.7
	25/55°C	66.68 ± 20.41	(0.930)	55.24	0.50	0.54	50.4°C	49.1
0.54	25/45°C	18.99 ± 3.35	(0.960)	22.49	0.75	0.64	39.4°C	40.6
	25/55°C	84.76 ± 21.36	(0.954)	78.74	0.32	0.41	49.4°C	48.9
0.65	25/45°C	27.86 ± 2.36	(0.989)	36.52	0.51	0.49	39.0°C	40.1
	25/55°C	127.74 ± 15.46	(0.989)	97.29	0.20	0.34	50.5°C	48.4

[a] ± 95% confidence limits
[b] 112 days for 25/55°C; 196 days for 25/45°C

where: a_o = amplitude of fluctuation in °C; T_m = mean temperature of fluctuation in °K. Applying this then to Equation 1, the extent of change for a first order reaction undergoing a square wave temperature fluctuation is:

$$A = A_o e^{-k_{T_m} \Gamma \text{ square } \theta} \qquad (4)$$

where: k_{T_m} = rate constant at mean temperature T_m. The effective rate constant for any given square wave fluctuation condition can be related to the rate constant conditions of T_m by:

$$k_{eff} = k_{T_m} \Gamma \text{ square} \qquad (5)$$

This aspect of the study examined the rates of loss of thiamin under square wave temperature fluctuations and compared the rates of loss under such conditions to rates of loss predicted by the above equations using the data generated in the steady state study.

The data from each square wave storage condition were plotted by linear regression. Figure 3, for example, shows the relationship between the data from the square wave condition in relation to the steady state data (dashed lines) at the same water activity of 0.44. This verifies what Hicks (1944) had originally theorized, that the fluctuation condition proceeds at a faster rate that the mean temperature of the fluctuation. Table 3 lists the calculated kinetic constants for the fluctuating storage conditions in comparison to the predicted k_{eff} for the square wave fluctuations. The predicted percent retention was calculated using the effective rate constant for each case from Equation 4 at either 112 or 196 days. It is apparent from Table 3 that the predictive equations are fairly accurate in estimating the rate constant and amount of loss after storage during temperature fluctuations.

Table 3 compares the predicted effective temperature of fluctuation to the measured effective fluctuation temperature as determined by the rate constant from the Arrhenius plot for similar a_w. Both values are greater than the mean temperature of fluctuation and are within 1–2°C of each other. It is interesting to note that Equation 2 tended to overpredict the temperature for the 25/45°C square wave and underpredict for the 25/55°C square wave. This means that, for example, the rate of loss of thiamin is greater at the 25/55°C condition that would be predicted by Equation 2. This underprediction may be explained by a possible history effect in which there is an acceleration in the rate of loss at the lower temperature (25°C) due to a possible nonadditive effect occuring during storage at the higher temperature (55°C) during the 25/55°C square wave. At the higher temperature, other reactions such as nonenzymatic browning of thiamin may be induced. The degradation products of this reaction may catalyze the loss of thiamin by similar reactions at 25°C. The result is a faster rate of loss during the 25°C temperature part of the cycle that would normally be observed at a constant temperature of 25°C. Van der Poel (1956) has reported on the participation of thiamin in a Maillard-type reaction. The fact that such a reaction occurred may be substantiated by the appearance of the pasta when stored at a constant temperature of 55°C. The enriched pasta stored at 55°C was observed to brown and discolor significantly during storage, whereas this was not seen with the pasta stored at lower temperatures. This browning at 55°C may have affected the rate constant and conceivably affected the fit of the Arrhenius data.

Conversely, the rate of loss of thiamin during the 25/45°C was less than would be predicted due possibly to the fact that the E_A used in predicting effective parameters includes

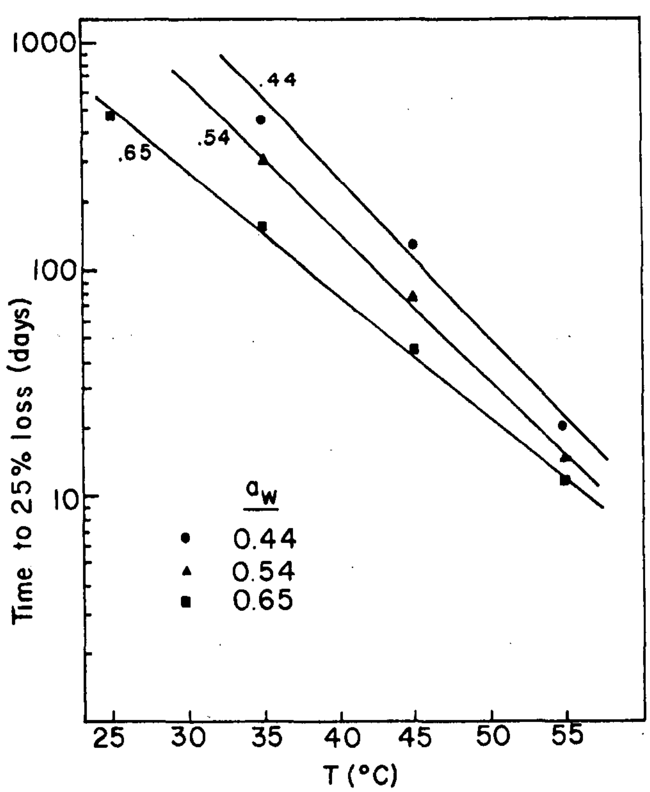

Fig. 2—Shelf life plot of enriched pasta for 25% thiamin loss in days as a function of storage temperature and water activity.

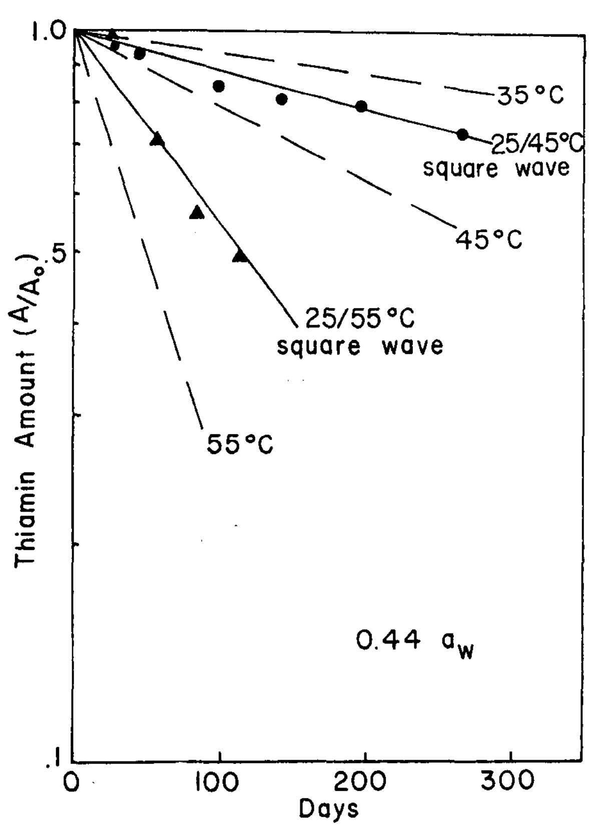

Fig. 3—Fractional retention of thiamin in enriched pasta stored under at 25/45°C and 25/55°C square wave condition as compared to steady state storage (a_w = 0.44).

rate constants at 55°C although the test samples were not stored above 45°C.

The effective temperatures were nonetheless close, especially in those systems with the larger fluctuation amplitude (25/55°C). It would appear that as the amplitude of fluctuation becomes larger, the efficacy of the predictive equations is better.

CONCLUSIONS

THE PREDICTIVE EQUATIONS that were presented for square wave fluctuations proved to be reasonably accurate when compared to actual rates of loss. The mean temperature of the fluctuation was shown to be an inadequate measure of anticipated loss, especially with larger temperature amplitudes. The equations are useful in predicting the amount of loss that may occur in foods subjected to conditions of variable temperature without the need to gather data on the rates of loss during those conditions of variable temperature. The Hicks-Schwimmer-Labuza model enables the prediction of these losses based on steady state data generated in the laboratory. As demonstrated here, the critical factors of such experiments are sufficient degradative loss or change to confidently determine the steady state rate constants and sufficient number of data points to accurately determine the E_A (from which the Q_{10} is estimated) with normal experimental variability.

From a practical standpoint, thiamin and riboflavin (dark reaction) can be expected to experience little or no loss during distribution and storage of pasta for periods of up to 1 yr under moderate conditions and in the dark. The retention of these vitamins during moderate conditions of temperature and humidity suggests little change in the nutritional value of finished pasta on the retail level. Extreme conditions of high temperature and high humidity, such as those of southern climates, or just high temperature, such as the Middle East where desert warehousing of food is anticipated and significant diurnal temperature fluctuations occur, may adversely affect the thiamin content of warehoused pasta and contribute to a shortened shelf life.

REFERENCES

AOAC. 1975. "Official Methods of Analysis," 12th ed. Association of Official Analytical Chemists, Washington, DC.

Brenner, S., Wodicka, V.O., and Dunlop, S.G. 1948. Effect of high temperature storage on the retention of nutrients in canned foods. Food Technol. 2: 207.

Brown, R. 1977. How high the pasta barrier? Staff and Welfare Caterer, Feb. 24: 27.

Clifcorn, L.E. 1948. Factors influencing vitamin content of canned foods. Adv. Food Res. 1: 39. Academic Press Inc., New York.

Dennison, D., Kirk, J., Bach, J., Kokoczka, P., and Heldman, D. 1977. Storage stability of thiamin and riboflavin in a dehydrated food system. J. Food Proc. & Preserv. 1: 43.

Egbert, D.C. and Potter, R.H. 1975. An improved automated determination of riboflavin in food products. J. Agric. Food Chem. 23(4): 815.

Farrer, K.T.H. 1955. The thermal destruction of vitamin B_1 in foods. Adv. Food Res. 6: 257. Academic Press Inc., New York.

Farrer, K.T.H. and MacEwan, J.L. 1954. The thermal destruction of riboflavin. Austral. J. Biol. Sci. 7: 73.

Feliciotti, E. and Esselen, W.B. 1956. Thermal destruction rates of thiamin in pureed meats and vegetables. Food Technol. 10: 77.

Freund, J. 1967. "Modern Elementary Statistics," 3rd ed. Prentice Hall, NY.

Goldblith, S.A., Tannenbaum, S.R., and Wang, D. 1968. Thermal and 2450 MHz microwave energy effect on the destruction of thiamin. Food Technol. 22: 1266.

Guerrant, N.B., Vavich, M.G., and Dutcher, R.A. 1945. Nutritive value of canned food. Ind. Eng. Chem. 37: 1240.

Hicks, E.W. 1944. Note on the estimation of the effect of diurnal temperature fluctuation on reaction rates in stored foodstuff and other materials. J. Counc. Sci. Ind. Res. (Australia) 17: 111.

Kamman, J.F., Labuza, T.P., and Warthesen, J.J. 1980. Thiamin and riboflavin analysis by high performance liquid chromatography. J. Food Sci. 45: 1497.

Kapsalis, J.G. 1973. Moisture and food characteristics. Activities Report R&D Assoc. Military Food & Packaging Systems, Inc.) 25(1): 60.

Labuza, T.P. 1972. Nutrient losses during drying and storage of dehydrated foods. CRC Crit. Rev. Food Technol. 3: 217.

Labuza, T.P. 1976. Storage stability and improvement of intermediate moisture foods. Phase 4. Contract NAS 9-12560, National Aeronautics and Space Administration, Food & Nutrition Office, Houston, TX.

Labuza, T.P. 1979. A theoretical comparison of losses in foods under fluctuating temperature sequences. J. Food Sci. 44: 1162.

Labuza, T.P. 1980a. The effect of water activity on reaction kinetics of food deterioration. Food Technol. 34(4): 36.

Labuza, T.P. 1980b. Temperature/entropy/ehthalpy compensation in food reactions. Food Technol. 34(2): 67.

Labuza, T.P. and Kreisman, L. 1978. Open shelf life dating of foods. Office of Technology Assessment Contract OTA-C-78-001. Washington, DC.

Laing, B., Schlueter, D., and Labuza, T.P. 1978. Degradation kinetics of ascorbic acid at high temperature and water activity. J. Food Sci. 43: 1440.

Lee, S. and Labuza, T.P. 1975. Destruction of ascrobic acid as a function of water activity. J. Food Sci. 40: 370.

Lewicki, P.P., Busk, G.C., Peterson, P.L., and Labuza, T.P. 1978. Determination of factors controlling accurate measurement of a_w by the vapor pressure manometric technique. J. Food Sci. 43: 244.

Mulley, E.A., Stumbo, C.R., and Hunting, W.M. 1975. Kinetics of thiamin degradation by heat. J. Food Sci. 40: 985.

National Canner's Association. 1955. Retention of nutrients during canning. National Canner's Assoc., Washington, DC.

Nymon, M.C. and Gortner, W.A. 1947. Niacin, riboflavin and thiamin studies on dehydrated pork loaves. Food Res. 12: 77.

Office of Technological Assessment. 1979. Open Shelf Life Dating of Foods. Supt. of Doc. #052-003-00694-4.

Pelletier, O. and Madere, R. 1975. Comparison of automated and manual procedures for determining thiamin and riboflavin in foods. J. Food Sci. 40: 374.

Powers, J.J., Lukaszewicz, W., Wheeler, R., and Dornsetter, T.P. 1965. Chemical and microbial activity ratio under square wave and sinusoidal temperature fluctuation. J. Food Sci. 30: 520.

Rice, E.E., Beuk, J.F., Kauffman, F.L., Schultz, H.W., and Robinson, H.E. 1944. Preliminary studies on stabilization of thiamin in dehydrated foods. Food Res. 9: 49.

Salunkhe, D.K., Wu, M.T., Do, J.Y., and Giffee, J.W. 1978. Effects of long-term storage on quality of processed foods. 1. Meal, ready-to-eat, individual ration items packed in flexible retortable pouches. J. Food Quality. 2: 75.

Schwimmer, S., Ingraham, L.L., and Hughes, H.M. 1955. Temperature tolerance for frozen food processing. Effective temperature in thermally fluctuating systems. Ind. Eng. Chem. 27(6): 1149.

Surrey, A.R. and Nachod, F.C. 1951. Alkaline hydrolysis of riboflavin. J. Amer. Chem. Soc. 73: 2336.

Van der Poel, G.H. 1956. Participation of B-vitamins in nonenzymatic browning reactions. Voeding. 14: 452.

Wu, A.C.M., Eitenmiller, R.R., and Powers, J.J. 1974. Effect of Fluctuating temperature on the stability and activity of invertase. J. Food Sci. 39: 1179.

Wu, A.C.M., Eitenmiller, R.R., and Powers, J.J. 1975a. Responses of chymotrypsin and lysozyme under fluctuating temperature treatments. J. Food Sci. 40: 840.

Wu, A.C.M., Eitenmiller, R.R. and Powers, J.J. 1975b. Effect of fluctuating temperature treatment on milk coagulation and inactivation of soybean trypsin inhibitors. J. Food Sci. 40: 1171.

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