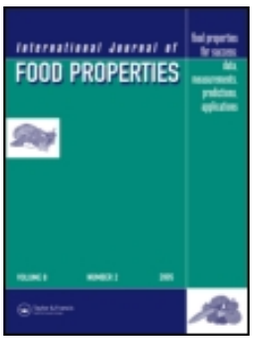

International Journal of Food Properties

ISSN: 1094-2912 (Print) 1532-2386 (Online) Journal homepage: https://www.tandfonline.com/loi/ljfp20

Effect of microwave processing on water soluble vitamins: Kinetic parameters

Zinet Aytanga Okmen & A. Levent Bayindirli

To cite this article: Zinet Aytanga Okmen & A. Levent Bayindirli (1999) Effect of microwave processing on water soluble vitamins: Kinetic parameters, International Journal of Food Properties, 2:3, 255-264, DOI: 10.1080/10942919909524609

To link to this article: https://doi.org/10.1080/10942919909524609

INTERNATIONAL JOURNAL OF FOOD PROPERTIES, 2(3), 255–264 (1999)

EFFECT OF MICROWAVE PROCESSING ON WATER SOLUBLE VITAMINS: KINETIC PARAMETERS

Zinet Aytanga Okmen, and A. Levent Bayindirli*

Middle East Technical University
Department of Food Engineering
06531 Ankara TURKEY (Tel: +90-312-210 5645, Fax: +90-312-210 1270, and E-mail: levent@metu.edu.tr, zinet@tr-net.net.tr). *Corresponding author

ABSTRACT

The effects of microwave processing on water soluble vitamins (ascorbic acid, niacin, thiamin, and riboflavin) were determined. The kinetic parameters of vitamin degradation reactions for microwave heating were determined for model vitamin systems. The degradation reactions were found to be first-order reactions. The kinetic parameters at different temperatures were also determined.

INTRODUCTION

The emphasis today is on the better retention of nutrition during food processing and preservation. New product development studies aim to preserve as much nutritional quality of a food as possible. Although it is possible to have nutritional components in processed foods as additives, the initial attempt should be to preserve health beneficial natural components present in the food. In many cases, processing has an adverse effect on certain nutrients, such as labile vitamins present in raw foods.

The vitamins are minor components of foods, which play an essential role in human health. Many of the vitamins are unstable under certain conditions of processing and storage. Some of the vitamins act as a part of co-enzyme, without which the enzyme can be ineffective as a biocatalyst. Frequently such co-enzymes are phosphorylated forms of vitamins, and play a role in the metabolism of fats, proteins and carbohydrates. The vitamins are usually divided into two main groups as: water-soluble and fat-soluble vitamins. The distribution of the vitamins in the various food groups is related to their water or fat-solubility (DeMan, 1980).

Lack of vitamins has been recognized in resulting serious deficiency diseases. It is now also recognized that overdoses of certain vitamins, especially some of the fat-soluble ones, may result in serious toxic effects. The examination of the effects of processing and storage conditions on vitamins is very important both for the optimization of the processing and storage conditions.

Vitamin C occurs in all living tissues where it influences oxidation-reduction reactions. Thiamin acts as a coenzyme in the metabolism of carbohydrates and is present in all living tissues. Riboflavin molecule consists of a d-ribitol unit attached to an isoalloxazine ring. Anything more than minor changes in the molecule results in loss of vitamin activity. The vitamin is a constituent of two coenzymes, flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD). The flavoproteins serve as electron carriers and are involved in the oxidation of glucose, fatty acids, amino acids and purines. The term niacin is used in a generic sense for both nicotinic acid and nicotinamide. Nicotinamide acts as a component of two important enzymes, NAD and NADP, which are involved in glycolysis, fat synthesis and tissue respiration. Niacin is also known as to prevent pellagra which a disease resulting from vitamin deficiency.

Microwave processing of foods causes certain changes and degradation of some of their nutritional components as is the case in any other food processing methods. From an engineering standpoint, quality of a thermal process can be defined as the maintenance of desirable food components such as color, flavor, texture, and nutrients. Efforts to adjust processing conditions to maximize the retention of quality factors while assuring microbiological safety require accurate data for mathematical modeling of the physical, chemical and biological processes involved (Datta and Hu, 1992). Processing experiments are generally performed with a multiple-regression design utilizing various times, temperatures, concentrations and other environmental factors, and there is a great need for analytical methods which are rapid, simple, precise, and accurate to accommodate modeling of these studies (Gregory, 1983).

Since the rate and distribution of heating in microwaves are different from those of conventional heating, the optimum microwave heating process is not a simple extension of the optimum conventional heating process. The modeling of degradation kinetics of food components during microwave processing by using the time-temperature-concentration data taken during the processing are the basis for the determination of optimum process conditions.

Kinetics of Vitamin Degradation during Microwave Processing

Thermal processing and storage conditions of food materials cause a considerable amount of nutrient degradation. Since nutrient retention is of primary concern in food systems subjected to deleterious conditions, a special attention has to be given in studying vitamin degradation. The water soluble vitamins are very easily degraded upon thermal processing, oxidation or contact with light. Other factors that play role in the degradation of these vitamins are the water activity, humidity, pH, and the presence of metal trace elements like iron and copper (DeMan, 1980).

The degradation reaction of water soluble vitamins generally follow first-order reaction kinetics. On the other hand, the vitamin degradation rates are changed due to the presence of different degradation products, which are caused by the different

degradation pathways. Although the reaction kinetics is affected by the pH of the medium, the presence of metal catalysts and the reaction being aerobic or anaerobic, at most of the times an increase in the temperature results in an increase in the vitamin degradation rate.

The kinetic study in food systems is important due to primarily optimization or at least to maintain the quality of food products during processing and storage. Moreover, a good understanding of the reaction kinetics can provide a better idea to formulate or fortify food products to preserve the existing nutrients or components in a food system or to minimize the appearance of undesirable breakdown products (Heldman and Lund, 1992). At present limited kinetic information is available for food systems or ingredients to facilitate the stability or to select optimum processing conditions. When the discussion comes regarding the microwave processing of foods, the kinetic data present for the microwave processed food systems is much more limited. While examining the quality of a thermal process the maintenance of desirable food components, such as the nutrients should be one of the major concerns. In this study, a basic approach is used to determine the reaction kinetics of vitamins during the microwave oven processing. Initially applicability of the basic kinetic principles to microwave processed compounds was examined, and then the kinetic data for the specified process conditions was generated.

Kinetic Equations

Reaction Rate Constant

A mathematical expression for the first-order reaction kinetics is:

$$-\frac{d(C)}{dt} = k.(C) \tag{1}$$

where C is the vitamin concentration at any time t (g/ml), k is the reaction rate constant (min^{-1}), and t is reaction time (min). When Equation 1 is integrated and $log(C/C_0)$ versus t is plotted, then slope of the straight line is defined as reaction rate constant (k) where C_0 is the initial concentration of vitamin.

Effect of Temperature on Reaction Rate Constant

Arrhenius Equation

Reaction rate constant depends on temperature. The classical method of correlating the effect of temperature on reaction rate constant is the Arrhenius equation as:

$$k = A.e^{-\frac{E_a}{RT}} \tag{2}$$

where A is pre-exponent factor, E_a is the activation energy (J/mole), R is gas constant (8.314 J/mole K), and T is absolute temperature (K). The reaction rate constants and the activation energies at different temperatures can be calculated for a food component by using the Arrhenius equation (Merson, 1986).

z-Value

Another relation between the reaction rate (k) and temperature is the z-value. Thermal Death Time (TDT) curve can be generated by plotting *log D* versus *T*, where $D=1/k$. The slope of this curve reflects the temperature dependency of *D* and is used to derive the temperature dependency factor z. The z-value is expressed as the temperature difference required for the curve to traverse one log cycle, or the temperature difference required for a tenfold change in the *D* value (Heldman and Lund, 1992).

Q_{10}

A third quantity used to characterize the effect of temperature on reaction rates is the Q_{10}. The ratio of rate constants at temperatures which differ by 10°C is known as Q_{10} (Merson, 1986).

$$Q_{10} = \frac{k_{T+10}}{k_T} \tag{3}$$

F-Value of a Thermal Process

An *F* value expresses the thermal destruction which has taken place in a process in terms of the initial and final concentrations of the nutrient or the time and temperature of the process. F-value for each nutrient can be determined by using the z-value corresponding to the thermal degradation rate. When the equation relating the *F* value to the initial and final concentrations of the nutrient is used the amount of nutrient that is retained can be found as percent (Merson and Leonard, 1986).

$$F^{z}_{T_{ref}} = D_{T_{ref}} .(\log a - \log b) \tag{4}$$

where a is the initial concentration of vitamin, e. g. 100%, and b is the final concentration in percent, and T_{ref} is the reference temperature of processing.

MATERIALS

Apparatus

A conventional microwave oven (700 W) equipped with a built-in temperature sensor (max. 92°C±1) was used in this study. The oven could be controlled at constant temperature in the sample. The HPLC configuration used for the vitamin analysis was LKB Model with LKB 2150 solvent delivery system and Rheodyne injector.

Reagents

(a) Mobile Phase: methanol: 4.3 mM hexane sulfonate w/ 0.1 % triethylamine (pH = 2.8 w/ phosphoric acid) 15:85, where hexane sulfonate source was

Sigma No. H-5269 and triethylamine was HPLC grade Carlo Erba No. 489556.

(b) Ascorbic acid stock solution: 0.5 gm/100 ml solution was prepared by L-ascorbic acid standard (Sigma No. A-1417) in the solution of metaphosphoric acid in glacial acetic acid. Working standards were prepared by diluting this stock solution.

(c) Thiamin stock solution: 0.5 gm/100 ml solution was prepared by thiamin standard (Sigma T-4625) in 0.01 N H_2SO_4. Working standards were prepared by diluting this stock solution.

(d) Riboflavin stock solution: 0.5 gm/100 ml solution was prepared by riboflavin standard (Sigma R-4500) in 0.01 N H_2SO_4. Working standards were prepared by diluting this stock solution.

(e) Niacin stock solution: 0.5 gm/100 ml solution is prepared by Nicotinic acid standard (Sigma N-4126) in 0.01 N H_2SO_4. Working standards were prepared by diluting this stock solution.

METHODS

Since it was not possible to have uniform initial vitamin content in foods and uniform temperature distribution in foods during microwave heating, the kinetic parameters were determined for model systems. The prepared vitamin solutions were kept at constant temperature for predetermined time intervals. The sample temperature was maintained at constant (±1°C) during processing by automatic on/off control of the oven. It was operated at full power until the sample temperature reached the preset temperature.

Thermal Processing of Water Soluble Vitamins by Microwaves

Initial vitamin solutions (0.02 gm/100 ml) were prepared from stock solutions. 100 ml of vitamin solutions were placed into glass dishes with a depth of 1.5 cm (less than the predicted penetration depth of 3.0 cm). The sample solutions were heated at constant temperatures of 60, 70, 80 and 90°C in the microwave oven. One ml samples were taken from the heat treated solutions after 20, 40, 60 and 80 minutes intervals. These solutions were filtered and analyzed in HPLC for vitamin concentration.

Operating Conditions of UV Detector

The operating conditions for detection of vitamins were: the flow rate of the mobile phase was set at 1 ml/min, UV detector was set to detection at 240 nm, and the sample injection port, the column and the detector were kept at ambient temperature (25°C).

Chromatography

10 µl of standard solution of a vitamin was injected into chromatograph. The retention times and the peak heights were recorded and standard curves were prepared as

concentration versus peak height for each vitamin. Linear regression equation of each standard curve was determined. After filtration the heat treated samples were injected as 10 µl and the peak height of each sample was recorded. The concentration of each vitamin sample was calculated by using the regression equation for that vitamin.

RESULTS AND DISCUSSION

A large number of reactions occurring in food systems appear to follow a first-order reaction. The mathematical expression of the first-order reaction kinetics indicates that the reaction is independent of the initial concentration. However, in food systems, the initial composition changes and the reaction appears to follow first-order reaction kinetics, but the initial vitamin concentration could influence its rate of degradation (Heldman and Lund, 1992). In order to overcome this, studies were carried in a model system with constant initial vitamin concentration.

Vitamin C was the least stable of all vitamins and was easily destroyed during processing and storage conditions. Ascorbic acid was oxidized in the presence of air under neutral and alkaline conditions. Factors that affect the vitamin C destruction during processing are heat treatment and leaching.

Niacin was probably the most stable of the B vitamins. It was unaffected by heat, light, oxygen, acid and alkali (DeMan, 1980). The main loss resulting from processing involved leaching into process water. In many foods the amount of niacin was increased by application of heat such as in roasting or baking which would be due to the change of bound niacin to the free form.

Thiamin was one of the more unstable vitamins. Various food processing operations might considerably reduce thiamin levels. Heat, oxygen, sulfur dioxide, leaching, and neutral or alkaline pH might all result in the destruction of thiamin. Light had no effect. A number of factors would be highly influential on the stability of thiamin, including water activity, pH, temperature, ionic strength, and the presence of other compounds (Heldman and Lund, 1992).

Riboflavin was relatively stable in foods under ordinary conditions. Its stability was pH dependent, being more stable under acidic conditions. Its photochemical cleavage under alkaline conditions resulted in the formation of the highly reactive compound lumiflavin, which mediated the destruction of other vitamins. Very small changes in the vitamin molecule caused the loss of vitamin activity. Riboflavin was stable to oxygen and acid pH but was stable in alkaline medium and was very sensitive to light. Under conditions of light exposure the rate of destruction increased as pH and temperature increased. Heating under neutral or acidic conditions does not destroy the vitamin. The wavelengths of light responsible for the riboflavin destruction were in the visible spectrum with in 500-520 nm. Ultraviolet light had been reported to have no destructive effect on riboflavin (DeMan, 1980). Microwave uses radiation between the radio waves and the ultraviolet wavelengths (0.025-0.75 m in air).

Degradation Reaction Constants for Microwave Processing of Water Soluble Vitamins

Linear regression analysis was performed to the first set of data to obtain the standard

curves of the vitamins as concentration of each vitamin in mg/100 ml of solution against the peak height obtained from HPLC analysis.

The model systems consisted of 20 gm vitamin/100 ml distilled water and these solutions were kept at constant temperature for predetermined periods of time. The temperature of the solutions was controlled by the use of the needle type build-in probe of the microwave oven. Samples were taken at different time intervals and they were analyzed with HPLC, and by using the standard curves the concentrations were determined.

Since the penetration depth of microwaves for water was about 3.0 cm for the temperature range of consideration (Mudgett, 1986), the samples were placed into the oven in plastic dishes in which the solutions were 1.5 cm deep. By this method uniform heating within the solution would be possible.

The slope of the log (vitamin retained) versus time graph represented the reaction rate constant at that temperature. The rate kinetics followed first order reaction in the temperature range studied. A typical *log (C/Co)* versus *t* graph is given in Figure 1 for vitamin C. Similar plots were obtained for the other vitamins. The first-order reaction rate constants obtained for each vitamin at four different temperatures are tabulated in Table 1. It could easily be observed that as the temperature is increased the reaction rate constants are increased for all vitamins which indicates that the degradation reactions occur faster at higher temperatures.

The activation energies for degradation of vitamins were determined from *ln k* versus *1/T* plots. The temperature sensitivity of degradation reactions of vitamins followed the sequence as: ascorbic acid, thiamin, riboflavin, and niacin in the order of most sensitive to least sensitive.

Again by using the degradation reaction rate constants, z-values for each vitamin were determined. When *log D* versus temperature curves were plotted, where D=1/k, the slope of each curve gave the z-value of vitamins. It should be noted that z-value represents the change in temperature required for the thermal death time curve to traverse one logarithmic cycle and measured the change in thermal death times or death rates with change in temperature. When the z-values for vitamins are tabulated in Table. 2, the highest z-value was observed for ascorbic acid followed by thiamin, riboflavin and niacin in descending order.

The Q_{10} values gave the effect of temperature on reaction rates directly. When Q_{10} values tabulated in Table 2, the sensitivities of vitamins to temperature decreased in the order of vitamin C, thiamin, riboflavin and niacin.

The above results can be generalized as: the effect of temperature was greatest on the rates of degradation reactions when large activation energies or large Q_{10} values or small z values were observed.

Order of magnitude estimates of E_a, z and Q_{10} for destruction of vitamins by conventional thermal processing were found to be $8x10^4$ J/mole for E_a, 45-60°C for z and 2-3 for Q_{10} (Merson and Leonard, 1986). When the kinetic parameters obtained for microwave heating were compared with the order of magnitude, the microwave heating caused less degradation in water soluble vitamins. In order to be able to compare two methods of processing for vitamin degradation the processing conditions should be identical for both processes. Since such a detailed information on vitamin destruction by conventional heating methods is difficult to find, order of magnitude is taken as a reference for comparison.

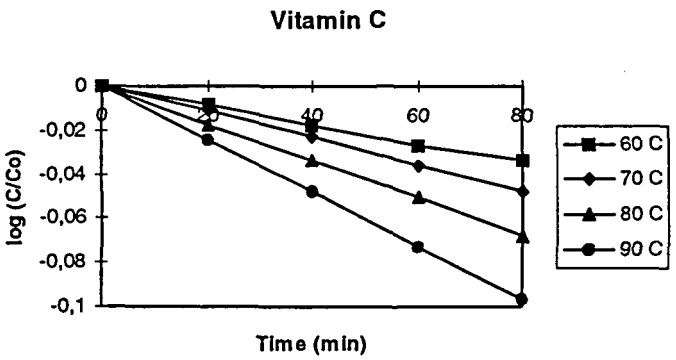

Figure 1. A typical graph of *log (C/Co)* versus time for vitamin C

Table 1. Degradation reaction rate constants of water soluble vitamins

	VitaminC		Niacin		Riboflavin		Thiamin	
T (K)	k (min^{-1})	r^2	k (min^{-1})	r^2	k (min^{-1})	r^2	k (min^{-1})	r^2
333	9.79E-04	0.998	1.15E-04	0.900	5.76E-04	0.975	3.17E-04	0.989
343	1.41E-03	0.999	1.15E-04	0.750	7.20E-04	0.990	3.74E-04	0.993
353	1.99E-03	0.999	2.01E-04	0.941	1.04E-03	0.998	5.18E-04	1.000
363	2.80E-03	0.999	2.01E-04	0.950	1.32E-03	0.991	6.33E-04	0.999

Table 2. E_a, z, and Q_{10} values of water soluble vitamins for microwave processing within a temperature range of 333-363 K

VITAMIN	E_a (J/mol)	r^2	z (°C)	r^2	Q_{10}
Vitamin C	4.58E+04	0.999	65.8	0.999	1.41
Thiamin	5.47E+03	0.985	83.3	0.991	1.32
Riboflavin	4.59E+03	0.991	99.7	0.985	1.26
Niacin	3.65E+03	0.800	125.0	0.800	0.86

Table 3. Percent vitamin retained at the end of 80 minutes of thermal processing for different process temperatures

	% Vitamin Retained			
T (°C)	Vitamin C	Niacin	Riboflavin	Thiamin
60	83.40	97.95	94.40	89.90
70	77.10	97.95	93.30	87.50
80	69.20	96.40	90.80	82.60
90	59.70	96.40	88.90	78.34

CONCLUSIONS

The degradation reactions of water soluble vitamins by microwave heating followed first order kinetics. The kinetic parameters obtained for the water soluble vitamins when heat treated by microwave showed that the most sensitive vitamin was ascorbic acid, followed by thiamin, riboflavin and niacin. Riboflavin loss was not expected during this process but a small amount of degradation was observed which could be related to the presence of light bulb in the oven which turned on during the operation of the microwave oven. Microwave heating caused considerably less degradation in water soluble vitamins when compared to the conventional thermal heating.

ACKNOWLEDGMENTS

The authors would like to thank the National Planning Organization (DPT) and the Scientific and Technical Research Council of Turkey, Agriculture and Forestry Research Grant Committee (TUBITAK, TOGTAG) for the financial support.

REFERENCES

Ang, C. Y. W., and Moseley, F. A. 1980. Determination of thiamin and riboflavin in meat and meat products by high-pressure liquid chromatography. *Journal of Agricultural and Food Chemistry.* 28(3): 45-48.

Bushway, R. J., King, J. M., Perkins, B., and Krishnan, M. 1988. High-performance liquid chromatographic determination of ascorbic acid in fruits, vegetables and juices. *Journal of Liquid Chromatography.* 11(16): 3415-3422.

Cross, G. A., and Fung, D. Y. C. 1982. The effect of microwaves on nutrient value of foods. *CRC Critical Reviews in Food Science and Nutrition.* April: 355-381.

Datta, A. K., and Hu, W. 1992. Optimization of quality in microwave heating. *Food Technology.* vol. December: 53-56.

DeMan, J. 1980. *Principles of Food Chemistry.* The AVI Publishing Company, Westport, Connecticut.

Fallom, A., Booth, R. F. G., and Bell, L. D. 1987. *Laboratory Techniques in Biochemistry and Molecular Biology.* Elsevier Science Publishers, Netherlands.

Gregory, J. F. 1983. Methods of vitamin assay for nutritional evaluation of food processing. *Food Technology.* January: 75-80.

Heldman, D. R., Lund, D. B. 1992. In: *Handbook of Food Engineering,* Marcel Dekker, Inc., New York.

Kamman, J. F., Labuza, T. P., and Warthesen, J. J. 1980. Thiamin and riboflavin analysis by high performance liquid chromatography. *Journal of Food Science.* 45: 1497-1499.

Merson, R. L., Leonard, S. J. 1986. *Notes on Thermal Processing,* Department of Food Science and Technology, University of California, Davis, California.

Mudgett, R. E. 1986. Microwave Properties and Heating Characteristics of Foods. *Food Technology.* June: 84-93.

Rodriguez, M. A. R., Oderiz, M. L. V., Herriandez, J. L., and Lozano, J. S. 1992. Determination of vitamin C and organic acids in various fruits by HPLC. *Journal of Chromatographic Science*. 30: 433-437.

Toma, R. B., and Tabekhia, M. M. 1979. High performance liquid chromatographic analysis of B-vitamins in rice and rice products. *Journal of Food Science*. 44(1): 263-265.

Tweeten, T. N., and Euston, C. B. 1980. Application of high performance liquid chromatography in the food industry. *Food Technology*. December: 29-37.

(Received October 23, 1998; revised February 15, 1999; accepted March 9, 1999)