

Quantitation of Water Absorption, Swelling, and Drying of Biological Materials. Soaking of Rice and Soaking and Drying of Wood

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Soaking of rice and soaking and drying of wood were studied in order to determine equilibria, rate constants, diffusion resistance constants, diffusion coefficients, activation energies, and enthalpies by simple graphical means from the time curves. The structural diffusion resistance of wood was higher than that of rice. The rate constants were higher in rice than in wood, but the diffusion coefficients were higher in wood. Brown rice had much lower rate constants and diffusion coefficients than polished rice. Activation energies and enthalpies were also determined. The determination of the kinetic constants by this method from the time curves was simple and accurate and had several advantages when compared with infinite series of the integrated Fick's equation.

Water absorption and swelling as well as drying of biological materials was studied extensively from different points of view. The rates of water absorption, swelling, and/or drying are limited by diffusion. Some investigators have studied soaking and drying of biological materials without giving any quantitative and/or predictive relationship for this process. Other investigators have based the water absorption or drying of different biological materials on simplified assumptions and approximations of the standard diffusion equations, for example, soaking and/or drying of wheat (Fan et al., 1961), of sorghum (Suarez et al., 1980), of soybeans (Hsu, 1983), of rice (Aguerre et al., 1980; Bandyopadhyay and Roy, 1978, 1980; Steffe and Singh, 1980a,b; Zhang et al., 1984; Engels et al., 1986), of woods (Sumi, 1978; Bramhall, 1978; Nikolov et al., 1979; Haishi, 1980; Schmidt, 1986), and of other similar plant materials (not shown here).

The diffusion in simple homogeneous geometric shapes can be quantitated by the integrated Fick's law of diffusion by infinite series (trigonometric, exponential, error, and Bessel functions) (Crank, 1975; Chatterjee, 1985), but the predictions of time curves and diffusion coefficients are difficult and require computer programs because the series often slowly converge. Furthermore, biological materials do not have simple regular and homogeneous geometric shapes, which makes the situation more complex, and there is a need for simple mathematical models for analysis and predictions of soaking and drying of biological materials.

The purpose of this study was to illustrate, with two example systems, application of the power exponential equation to analysis of water absorption and swelling (rice grains) and soaking and drying (wood).

EXPERIMENTAL SECTION

Materials. Short California rice grains (S-201) stored for 1 year at room temperature (25 °C) and untreated pine wood (about 2 years old) were used for experiments. The average shape of short rice grains was closer to a sphere than to a cylinder. From the average volume of the grains we have calculated the radius of the idealized average rice sphere, $r = 0.09$ cm. Small pieces of wood were cylinders about 2 cm long (1-g samples) with radius $r = 0.564$ cm. Large pieces of wood were spheres with radius $r = 1.7$ cm.

Soaking of Rice. Short rice was cleaned from foreign matter, broken into immature kernels, and dried at 110 °C to constant weight. Polished (30% polish) rice grains (10 g) were soaked at constant temperature (25, 40, 50 °C) in 100 mL of distilled water with slow mixing by a magnetic stirrer. Maximum temperature fluctuation was ± 0.5 °C. After selected time intervals the rice

was quickly decanted, placed on a filter paper, blotted on the surface, and weighed. The time curves for soaking were obtained from triplicates. The results were expressed in relative percent of dry weight. Coefficients of variation between triplicates were less than 2%.

Swelling of Rice. Polished undamaged dried rice grains were soaked at constant temperature (25 °C) in 100 mL of water with slow mixing by a magnetic stirrer. After selected time intervals the water was decanted, the wet surface of rice was quickly blotted by a filter paper, and the sample was dropped in a 200-mL volumetric flask filled with petroleum ether (specific gravity 0.639). The volume in excess of the 200-mL mark was accurately measured by pipetting, and the volume of rice was determined. The time curves of swelling were obtained from triplicate determinations. The results were expressed in relative percent of dry weight. Coefficients of variation between triplicates were less than 3%.

Soaking of Wood. Pine wood cylinders weighing approximately 1 g (10-g spheres were used for each comparison) were submerged in 100 mL of distilled water at constant temperature (25, 40, 50 °C). Maximum temperature fluctuation was ± 0.5 °C. After selected time intervals, the samples were quickly placed on a filter paper, blotted on the surface, and weighed on an automatic microbalance. The time curves for soaking were obtained from triplicate determinations. The results were expressed in relative percent of dry weight. Coefficients of variation between triplicates were less than 2%.

Drying of Wood. Water-saturated wood cylinders from the soaking experiments were dried freely in a hanging position (without air flow or fan) at constant temperature (25, 40, 50 °C). At selected time intervals the samples were quickly weighed on an automatic microbalance. The time curves of drying were obtained from triplicate determinations. The results were expressed in relative percent of the total water content at time zero. Coefficients of variation between triplicates were less than 2%.

THEORY

The kinetic behavior of diffusion limited systems can be explained by an exponential binomial power equation (Chrastil, 1987, 1988a; Chrastil and Parish, 1987).

We have found that this exponential binomial equation can be successfully used for absorption, swelling, or drying of biological materials, such as seeds, beans, woods, and other similar tissues. For water absorption the equation can be written in the form

$$W = W_{\infty}[1 - \exp(-kt)]^n \quad (1)$$

where W is the water absorption in time t , W_{∞} is the equilibrium absorption (at $t \rightarrow \infty$), k is the rate constant related to diffusion coefficients, and n ($n < 1$) is the diffusion resistance constant that depends on the structure of the studied material. The rate constants k and the water absorption equilibria W_{∞} are related to absolute temperature T by the Arrhenius equation

$$k = \exp(-\Delta E^*/RT + e) \quad (2)$$

and

$$W_{\infty} = \exp(-\Delta H/RT + h) \quad (3)$$

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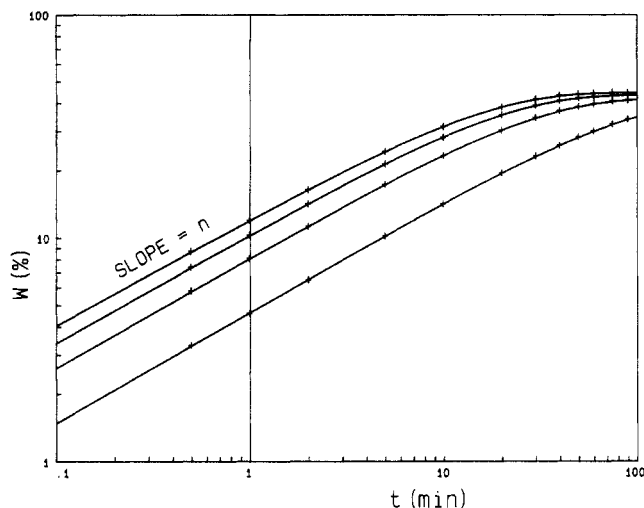


Figure 1. Water absorption by rice. From base to top: brown rice, 25 °C; polished rice, 25, 40, and 50 °C. Experimental points are averages from triplicate determinations. Curves were calculated from experimental values by mathematical computer regression analysis of eq 1 (D is the diffusion coefficient and r is the correlation coefficient of mathematical regression). The vertical line shows the intercepts at $t = 1$. Brown rice, 25 °C: W_{∞} (%) = 41.0; $n = 0.498$; k (min^{-1}) = 0.0127; D ($\text{cm}^2 \text{s}^{-1}$) = 1.55×10^{-7} . Polished rice, 25 °C: W_{∞} (%) = 42.0; $n = 0.495$; k (min^{-1}) = 0.0366; D ($\text{cm}^2 \text{s}^{-1}$) = 4.64×10^{-7} . Polished rice, 40 °C: W_{∞} (%) = 43.6; $n = 0.488$; k (min^{-1}) = 0.0531; D ($\text{cm}^2 \text{s}^{-1}$) = 7.41×10^{-7} . Polished rice, 50 °C: W_{∞} (%) = 44.6; $n = 0.478$; k (min^{-1}) = 0.0662; D ($\text{cm}^2 \text{s}^{-1}$) = 1.05×10^{-6} . All r 's were better than 0.99.

where ΔE^* is the activation energy and ΔH is the enthalpy of soaking or drying.

Although the molecular interpretation of the observed activation energy can only be made in terms of a specific reaction mechanism, by means of eq 2 and 3 we may often make important thermodynamic conclusions.

It has been shown (Steffe and Singh, 1980b) that the volume changes (swelling) of biological materials are often proportional to water absorption and, thus, by replacing W by V (volume of swollen material) eq 1–3 also represent the kinetics of swelling.

When compared to the Fick's integrated diffusion infinite series, eq 1 has several advantages. The greatest advantage is that the kinetic constants can be easily determined from the time curve by simple graphical or statistical methods.

For example, if the time curve is plotted in log–log scale, all constants can be read from the graph. Constant W_{∞} is apparent from W at longer reaction times, constant n is a slope of the log–log curve at short reaction times (as apparent from eq 1 expressed by Taylor's series), and constant k is read from an intercept at $t = 1$ (at $t = 1$, $k = -\ln(1 - (W_1/W_{\infty})^{1/n})$ (see Figure 1). The determination of kinetic constants of eq 1, n and k , directly from experimental results requires more complex statistical computer analysis [see, for example, Chrastil (1988b)]. This determination is more accurate, but in most cases the graphical determination from the slope and intercept is sufficient. Equation 1 agreed well with water absorption and/or drying of different biological materials, like corn, wheat, coffee beans, peanuts, soybeans, and woods or gels (not shown here).

In this work two typical examples are shown: water absorption and swelling of rice grains and soaking and drying of wood.

RESULTS AND DISCUSSION

Soaking of Rice. Water absorption of rice is shown in Figure 1. The water absorption equilibrium constants, W_{∞} , were read from time curves at long reaction times. Diffusion resistance constants, n , were read from the slopes of the log–log plots, and rate constants, k , were read from the y intercepts at 1-min reaction times. The diffusion resistance constants, n , did not change with temperature and remained close to 0.5. The rate constants, k , and the water absorption equilibria, W_{∞} , increased with tempera-

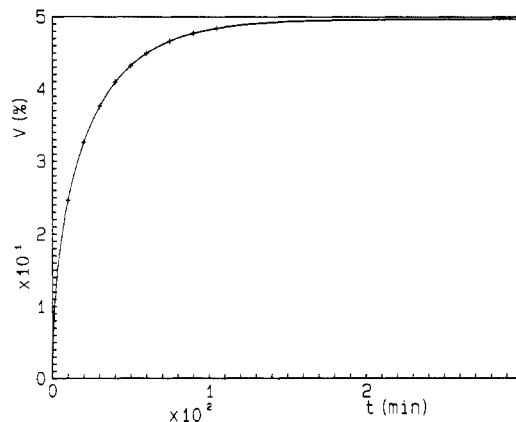


Figure 2. Swelling of polished rice. Experimental values are averages from triplicate determinations. Curve was calculated from experimental values by mathematical computer regression analysis of eq 1 (r is the correlation coefficient of mathematical regression). W_{∞} (%) = 49.7; $n = 0.500$; k (min^{-1}) = 0.0282; $r = 0.999$.

ture by Arrhenius eq 2 and 3. The absorption equilibria, W_{∞} , were 42.0, 43.6, and 44.6% at 25, 40, and 50 °C, respectively. The average slope for all samples was, $n = 0.49$. The intercepts at $t = 1$ were 8.1, 10.2, and 11.6, respectively. The rate constants, k , determined from the y intercepts (W_1) at $t = 1$ ($k = -\ln(1 - (W_1/W_{\infty})^{1/n})$) were 0.035, 0.054, and 0.066 min^{-1} , respectively. The rate constants were also calculated by computer regression analysis. These constants and the regression coefficients are shown in Figure 1. The rate constants increased with temperature, and the activation energy of soaking was 4574 cal/mol ($k = \exp(-4574.2/RT + 4.364)$) with a correlation coefficient of $r = 1.000$. The water absorption equilibria also increased with temperature, and the enthalpy of soaking was 463 cal/mol ($W_{\infty} = \exp(-463.2/RT + 4.515)$) with a correlation coefficient of $r = 1.000$.

Soaking of brown rice was slower than soaking of polished rice with $W_{\infty} = 41.0\%$, $n = 0.49$, and $k = 0.012$ (from intercept) at 25 °C.

Diffusion resistance during swelling of polished rice was similar to that for water absorption ($n = 0.500$), but the equilibrium V_{∞} (volume at equilibrium) when expressed in relative percent was higher (49.7%). The rate constant, k , for swelling was smaller ($k = 0.0282$) than for water absorption at the same temperature (Figure 2).

By comparison of eq 1 with integrated Fick's law at short reaction times (assuming that rice was a sphere and ignoring the volume changes), we got an apparent relationship between the rate constants, k , and the diffusion coefficients, D , for rice: $D = k^{2n} \pi r^2 / 36$, where r was the average radius of the rice grain spheres (0.09 cm). From that we obtained the apparent diffusion coefficients for analyzed rice samples: $D = 4.6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (25 °C), $7.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (40 °C), and $1.05 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (50 °C) for polished rice; $D = 1.6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (25 °C) for brown rice, respectively. This is in good agreement with values from the literature obtained by other methods (Steffe and Singh, 1980a; Engels et al., 1986).

Soaking of Wood. Water absorption by wood is shown in Figure 3. The water absorption equilibria, W , were 63, 82, and 96% at 25, 40, and 50 °C, respectively. The structural diffusion resistance constants, n , for all samples were $n = 0.30$. Intercepts, W_1 ($k = -\ln(1 - (W_1/W_{\infty})^{1/n})$), at $t = 1$ were 9.1, 10.1, and 10.6, respectively. The structural diffusion resistance constant, n , for water absorption in wood was smaller (larger resistance) than for water absorption in rice (0.3 and 0.5, respectively). The

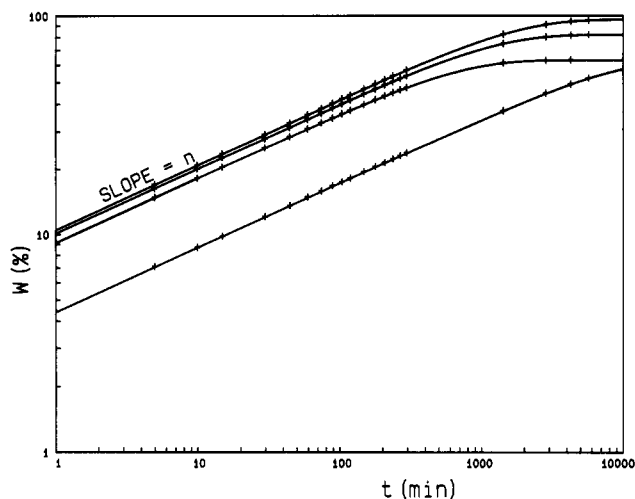


Figure 3. Water absorption by wood. From base to top: large spheres (10 g) of wood at 25 °C; small cylinders (1 g) of wood at 25, 40, and 50 °C. Experimental values are averages from triplicate determinations. Curves were calculated from experimental values by mathematical computer regression analysis of eq 1 (D is the diffusion coefficient and r is the correlation coefficient of mathematical regression). Wood (10 g), 25 °C: W_{∞} (%) = 63; $n = 0.298$; k (min^{-1}) = 0.000131; D ($\text{cm}^2 \text{s}^{-1}$) = 1.07×10^{-4} . Wood (1 g), 25 °C: W_{∞} (%) = 63; $n = 0.302$; k (min^{-1}) = 0.00165; D ($\text{cm}^2 \text{s}^{-1}$) = 1.10×10^{-4} . Wood (1 g), 40 °C: W_{∞} (%) = 82; $n = 0.300$; k (min^{-1}) = 0.000926; D ($\text{cm}^2 \text{s}^{-1}$) = 8.10×10^{-5} . Wood (1 g), 50 °C: W_{∞} (%) = 96; $n = 0.302$; k (min^{-1}) = 0.000646; D ($\text{cm}^2 \text{s}^{-1}$) = 6.24×10^{-5} . All r 's were better than 0.99.

water absorption equilibria, W_{∞} , increased with temperature, but in contrast to rice, the rate constants, k , for wood decreased with temperature. Activation energy was -7225 cal/mol ($k = \exp(7225/RT - 18.523)$) with a correlation coefficient of $r = 1.000$. The enthalpy was 3250 cal/mol ($W_{\infty} = \exp(-3250/RT + 9.594)$) with a correlation coefficient of $r = 1.000$. The kinetic constants, n and k , for wood were determined by graphic means ($n = 0.30$; $k = 0.0016$, 0.00093 , 0.00065) and/or by computer regression analysis (Figure 3).

By comparison of eq 1 with the integrated Fick's law at short reaction times for the wood cylinders we got an apparent relationship between the rate constants, k , and the diffusion coefficients, D , for wood: $D = k^{2n} \pi r^2 / 16$, where r was the average radius of the wood cylinders (0.564 cm). From that we calculated the apparent diffusion coefficients for analyzed wood samples: $D = 1.10 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$ (25 °C); $8.10 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (40 °C); and $6.24 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ (50 °C), respectively.

When larger pieces of wood with a different shape (spheres) were tested, the water absorption equilibria ($W_{\infty} = 63\%$) and the diffusion resistance constants ($n = 0.298$) remained the same as with the smaller pieces (cylinders) but, as expected, the rate constants were much smaller ($k = 1.31 \times 10^{-4} \text{ min}^{-1}$) than with the small pieces of wood at the same soaking temperature, 25 °C. For the wood spheres the diffusion coefficients should be $D = k^{2n} \pi r^2 / 36$, and at 25 °C we obtained $D = 1.07 \times 10^{-4}$ (same as for the cylinders at 25 °C).

Drying of Wood. The kinetics for the drying of wood were different from that for soaking (Figure 4). Average slope (diffusion resistance) was $n = 0.90$. The absorption equilibrium (samples dried from saturation to zero water content) was chosen as $W_{\infty} = 100\%$. Intercepts at $t = 1$ were 0.45, 1.4, and 2.8, and thus the rate constants k ($-\ln(1 - (W_1/100)^{1/n})$) were 2.5×10^{-3} , 9×10^{-3} , and $1.9 \times 10^{-2} \text{ min}^{-1}$, for 25, 40, and 50 °C, respectively. The reaction was close to first order ($n = 0.9$); the rate constants, k , were

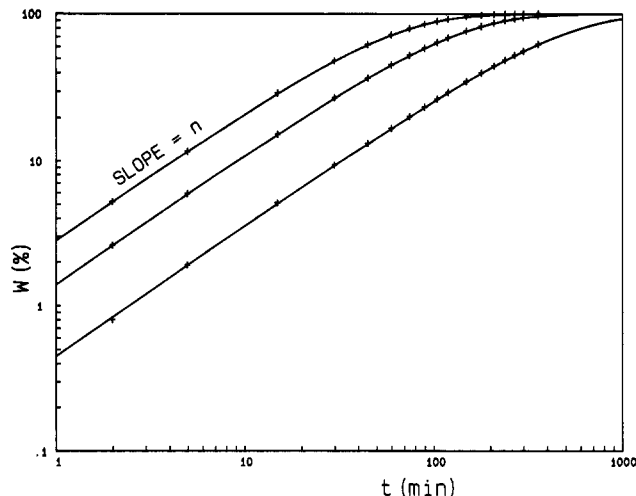


Figure 4. Drying of wood. From base to top: wood cylinders dried at 25, 40, and 50 °C. Experimental values are averages from triplicate determinations. Curves were calculated from experimental values by mathematical computer regression analysis of eq 1 (r is the correlation coefficient of mathematical regression). Wood (1 g), 25 °C: W_{∞} (%) = 100; $n = 0.900$; k (min^{-1}) = 0.00247. Wood (1 g), 40 °C: W_{∞} (%) = 100; $n = 0.904$; k (min^{-1}) = 0.00891. Wood (1 g), 50 °C: W_{∞} (%) = 100; $n = 0.907$; k (min^{-1}) = 0.0196. All r 's were better than 0.99.

much larger than that for soaking of the same wood and increased quickly with temperature. The activation energy was high, 15955 cal/mol, and the reaction was highly endothermic ($k = \exp(-15955/RT + 20.754)$). This was expected because during drying the water escapes in a vapor phase and the heat of evaporation is a part of the enthalpy and activation energy.

From this and other studies (not shown here) it was apparent that the kinetic constants for water absorption or desorption in biological materials could be accurately determined from the time curves by means of eq 1. The method is simple, and all kinetic constants can be read graphically from the time curves. The absorption equilibria and the rate constants of eq 1 are related in a simple way to activation energies, reaction enthalpies, and diffusion coefficients. The structural diffusion resistance constants, n , are related mainly to the structure of the absorbent, and not to other kinetic factors.

Registry No. H₂O, 7732-18-5.

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Received for review September 30, 1988. Accepted February 15, 1989.

Urea Analysis for Wines

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An analysis for urea in wine was developed in which urea is isolated by ion exchange and then derivatized with 1-phenyl-1,2-propanedione 2-oxime. Measurements of the derivative are made by colorimetry. The analysis gave good linear response to additions of 0-50 mg/L of urea to either red or white wine. Blank experiments in which either urea or 1-phenyl-1,2-propanedione 2-oxime was withheld with either red or white wine samples or model solutions gave less than 1.0 mg/L of urea in all cases. Good agreement was obtained for wine samples that were submitted to the present method and one to HPLC.

Wines and other fermented beverages can occasionally have relatively high levels of ethyl carbamate (a carcinogen). Studies by Ough et al. (1988a) have determined that urea reacting with ethanol is the major cause of formation of ethyl carbamate in wines. This has been verified by tracer work (Bisson, personal communication). Citrulline present in wines can also contribute to ethyl carbamate formation by reacting with ethanol. Ough et al. (1988b) reported the Arrhenius data for both urea and citrulline for their reaction with ethanol. Both urea and citrulline are found in wines at about the same amount, but urea reacts to a much greater extent than does citrulline. Ough et al. (1989) and Caputi (personal communication) found that heavily fertilized vineyards were probably the major cause of high urea remaining in the wine because of high nitrogen nutrients in the juice. The yeast strain and fermentation temperature can also cause increased urea accumulation, resulting in high-potential ethyl carbamate formation (Ough, unpublished work). The need for a quick and reasonably accurate urea method to screen wines for high urea content was enhanced by the report of Yoshizawa and Takahashi (1988), which indicated that an acid urease, active in sake and in wine, was being developed commercially. In addition, the Food and Drug Administration has indicated a need to maintain low levels of ethyl carbamate in wines.

Wine contains ammonia in concentrations high enough to interfere with the enzymatic method of urea determi-

nation. Wine also contains sugars that would interfere with colorimetric methods unless they were first removed. For these reasons, we sought to develop a simple method for wine that would measure urea at the 1-50 mg/L range.

EXPERIMENTAL SECTION

Reagents. Urea (Sigma, St. Louis, MO), 1-phenyl-1,2-propanedione 2-oxime (Aldrich, Milwaukee, WI—also known as α -isonitrosopropiophenone), and other reagents were purchased and used without further purification. Deionized water was used as solvent unless otherwise specified.

Ion-exchange columns were prepared by loading 0.90 g of Dowex 50W-X8, 50-100 mesh, onto 5 mm (i.d.) \times 90 mm glass columns with frits (Bio-Rad, Richmond, CA, Catalog No. 737-0510); these columns were prewashed and regenerated after use with 7 mL each of water, ethanol, water, 2 M HCl (14 mL), water, 1.5 M NaOH (14 mL), water, and 0.1 M HCl (21 mL).

Chromatography, Derivatization, and Measurement. A mixture of 2.0 mL of the wine or calibration sample and 0.32 mL of 1.0 M aqueous HCl was placed onto the column. Two 1.5-mL portions of 0.1 M HCl and then 1.5 mL of 4 M NaCl in 0.1 M HCl were added. The receiver was then changed, and the urea-containing fraction was eluted with 3.7 mL of 4 M NaCl in 0.1 M HCl. Two 1.75-mL portions of this fraction were placed in separate 16 mm (o.d.) \times 150 mm culture tubes. To one tube was added 0.100 mL of a solution of 0.200 g of 1-phenyl-1,2-propanedione 2-oxime in 5.0 mL of ethanol, and to the other (the blank) was added 0.100 mL of ethanol. Each tube was vortexed, and 1.25 mL of a 1:3:1.25 (by volume) mixture of 18 M H₂SO₄-14 M H₃PO₄-H₂O was added. The tubes were vortexed again, sealed with PTFE-lined screw caps, placed in boiling water for 2 h without light, and then brought to room temperature over 30 min in the dark.

Colorimetric measurements of optical density to the nearest thousandth of an absorbance unit at 540 nm were made on a Bausch and Lomb Spectronic 710 instrument equipped with a micro flow-through system, a microcell, and a digital readout. In

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