

VITAMIN C DECOMPOSITION KINETICS IN SOLUTIONS, MODELLING CITRUS JUICES

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Fibre-rich fruit juices are playing an increasing role in healthy nutrition, and consumers are regarding them, especially citrus juices of 100% fruit content, as reliable sources of vitamin C. Nevertheless relatively few scientific data are available on vitamin C retention during the heat treatment of aseptically packed fruit juices made from fruit concentrates. Authors investigated this problem within the scope of OTKA T 014965 research project (KÖRMENDY et al., 1998, 1999a, 1999b; PÁTKAI, 1998).

Instead of separate case studies on different types of fruit juices and technologies, authors analysed the vitamin C content of model solutions with similar composition to real citrus juices as a function of temperature and duration of heat treatment and that of initial oxygen and ascorbic acid concentration. Based on the measured data, they elaborated kinetic relations and determined the reaction rate constants of vitamin C decomposition under the experimental conditions. By means of the calculated kinetic relations and reaction rate constants one can estimate the losses of vitamin C in the case of known parameters of the heat treatment, packaging material, oxygen and vitamin C concentration within the investigated domain. Results may promote technology and product development in the field of citrus fruit juices.

Keywords: vitamin C destruction, reaction rate constant, zero and first order reaction kinetics

The objective of this study was to investigate the reaction rate of vitamin C decay as a function of the temperature, initial concentration of ascorbic acid and dissolved oxygen in model solutions with similar composition to citrus juices. The authors aim was to elaborate predictive kinetic equations on the basis of the measured data, and to calculate the changes of reaction rate constants of zero and first order reactions as a function of the above mentioned independent variables.

Authors originally intended to evaluate changes of ascorbic acid concentration on the basis of empirical kinetic equations of n^{th} order, instead they developed a new kinetic description, which is based on the knowledge of the concentration of dissolved oxygen, considering simultaneous processes of aerobic and anaerobic ascorbic acid destruction as well. The role of packaging conditions was found to have primary importance in connection with the effect of dissolved oxygen.

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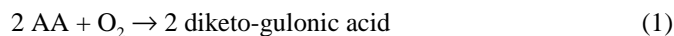
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According to the literature in low acid media ($4.0 < \text{pH} < 4.5$) all chemical forms of vitamin C, the non-dissociated ascorbic acid molecule (AA), the ascorbic acid mono-hydrogen ion (AH^-) and the dehydro-ascorbic acid (DAA) take part in the process of chemical decomposition (LEE et al., 1977). Authors distinguish two main types of the mechanism of vitamin C decomposition: by the presence (aerobic process) or the absence (anaerobic process) of oxygen.

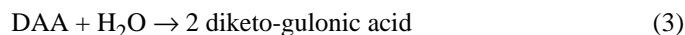
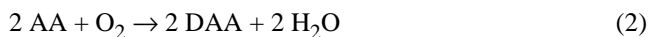
Reaction mechanism of ascorbic acid decomposition in the presence of oxygen

For the description of aerobic vitamin C decomposition kinetic equations of second order (SINGH et al., 1976, HERMANN et al., 1978), of first order (LATHROP & LEUNG, 1980, RAO et al., 1981) and of zero order (LAING et al., 1978) were used. EISON-PERCHONOK and DOWNES (1982) and KENNEDY and co-workers (1992) tried to fit the reaction curve to all three equations describing different orders of reaction. SAKAI and co-workers (1987) used a zero order equation followed by a first order one.

The ascorbic acid oxidation can proceed directly:



or indirectly through formation of dehydro-ascorbic acid (DAA):



Reactions (1) and (2) are both reactions of two components, characterised by the irreversible stoichiometric equations: $aX + bY \rightarrow \text{product}$.

According to our recent knowledge (LÖSCHER et al., 1991), the direct way of ascorbic acid oxidation is dominating in acidic media ($\text{pH} \sim 5$). Diketo-gulonic acid is decomposed to oxalic and treonic acid, and furfural will be formed, which is an interim compound of the Maillard reaction, forming brown colourings. The process is not significantly influenced by amino acids, because the Strecker-degradation, catalysed by amino acids, is launched only after splitting of the lacton-ring of the DAA, and this reaction is in acidic media partly reversible. This fact is explaining the higher stability of ascorbic acid in acid media.

In neutral media ($\text{pH} \sim 8$) the formation of DAA (2) and the reaction between amino acids and DAA are already significant, and the Strecker-degradation, following the DAA formation, overshadows direct destruction.

In amino acid containing foods the following characteristic products of ascorbic acid destruction were found: different reductons, furfural, furan-carbonic-acid and ethyl-glyoxal. These compounds can take part in the Maillard-reaction, different brown colourings can be formed, spoiling food quality.

The anaerobic way of vitamin C decomposition

The anaerobic way of vitamin C decay will be mostly treated in the literature as a reaction of first order (LEE et al., 1977; HERMANN et al., 1978). The process can be described by following equations:



According to JOHNSON and co-workers (1995) and SAWAMURA and co-workers (1994), the degradation of AA and DAA in acidic citrus juices is causing the formation of brown colourings under anaerobic conditions as well, because the products are highly reactive carbonyl compounds.

Vitamin C decay under anaerobic conditions proceeds very slowly and needs a much lower activation energy (E_a) than in the aerobic case.

1. Materials and methods

1.1. Materials

Investigations were carried out in 1996, 1997 and 1998. The independent variables (such as temperature, initial ascorbic acid concentration and nominal initial concentration of dissolved oxygen), influencing the reaction rate of vitamin C destruction were roughly constant in all three years. Values of the above mentioned independent variables are shown in paragraph 1.2.4.

Dimensions and composition of the packaging foil-bag, citric acid content of the model solution and heating time periods were partly changed in 1997 and 1998 to model different types of fruit juice packaging- and heat treatment technologies. The heat treatment in gas-permeable foil-bags with a relatively big head-space, used in 1996, is modelling the conditions in a through-flow type heat exchanger, where the dissolved oxygen can escape into the environment. Investigations carried out in non-permeable foil-bags in 1997 and 1998 are better modelling the conditions of the heat treatment in hermetically closed glass-bottles or in other non-permeable packaging without or with a very small head-space. Data on the pH values of the model solutions and packaging materials used are shown in Tables 1 and 2.

1.1.1. Composition of the model solutions used for investigations. Table 1 shows the composition of the model solutions used, which was similar to that of citrus juices.

Table 1. Composition of the model solutions

Year of investigation	Component	Concentration (g dm ⁻³)
1996-1997	Saccharose	30
	Glucose	30
	Fructose	40
	Citric acid	15
	Vitamin C	0.25; 0.5; 1
	Soluble solids	116
	pH	2.05
1998	Saccharose	30
	Glucose	30
	Fructose	40
	Citric acid	5
	Vitamin C	0.25; 0.5; 1
	Soluble solids	106
	pH	2.45

1.1.2. Data of the foil-bags used for investigations. Table 2 shows the composition and size of the foil-bags used in 1996, 1997 and 1998.

Table 2. Composition and size of the foil-bags used for investigations

Year of investigation	Composition of foil-bag	Dimensions of foil-bag (cm)	Volume of model solution (cm ³)	Foil-bag property	
1996	80 µm polyamide + 100 µm polyethylene	Inside	8 × 8	15	Gas-permeable
		Outside	10 × 10		
1997	50 µm polyethylene + 10 µm Al	Inside	8 × 8	15	Non-permeable for gases
		Outside	10 × 10		
1998	12 µm polyester	Inside	6 × 11.5	15	
		Outside	5 × 10.5		

1.2. Methods

The following analytical methods were used:

1.2.1. Measuring the concentration of dissolved oxygen. An instrument of type Oxi 320 with a sensor Cellox 325 from the company WTW Wilhelm was used for measurements. The concentration of dissolved oxygen was measured in 1996 and 1997 in the model solution before filling it into the foil-bags. This measurement was repeated in 1998 after each heat-treatment period, immediately after cooling and opening of the foil-bags.

1.2.2. Measuring the pH value. The pH value of the model solution was measured by a precision pH meter Type RADELKIS OP-205/1.

1.2.3. Measuring the concentration of vitamin C. The quantitative determination of vitamin C was done at 20 °C by the 2,6-indophenole-dichlorophenole method according to the HUNGARIAN STANDARD (1992).

1.2.4. Parameters of the heat treatment of the model solutions

- *Temperature of the heat treatment.* Heat treatment of the model solutions was carried out uniformly at 80 °C, 90 °C and 100 °C in a water bath with controlled temperature.
- *Nominal initial concentration of vitamin C.* The initial concentration of vitamin C was set to 0.25; 0.5 and 1.0 g dm⁻³ by adding of ascorbic acid to the model solutions before filling in foil-bags.
- *Concentration of dissolved oxygen.* The concentration of dissolved oxygen was set at three different levels (nominal values): 2.5; 7.5 and 25 mg dm⁻³ by the following special treatments:
 - 2 min bubbling of N₂ gas through the model solution
 - no treatment used (spontaneous concentration)
 - 2 min bubbling of O₂ gas through the model solution.
- *Duration of the heat treatment.* Five heat treatment time periods were applied: 0, 10, 20, 30 and 40 min in 1996; 0, 20, 40, 60 and 80 min in 1997 and 1998.

The vitamin C concentration was measured in three replicate treated bags at the end of each heating time period, and 2 replicate measurements were made from each bag.

Number of treatment variations was $5 \times 3 \times 3 \times 3 = 135$ in each year. (5 heating time periods, 3 temperatures, 3 oxygen- and 3 initial vitamin C concentrations.)

Number of replicate measurements: $3 \times 2 = 6$

Number of concentration data per year: $135 \times 6 = 810$

1.2.5. Determination of the concentration of dissolved oxygen during the heat treatment. The actual concentration of dissolved oxygen during the heat treatment depends on the initial oxygen concentration of the solution, on the partial pressure of O₂ in the sealed foil-bag, oxygen permeability of the foil and on the oxygen transport between solution and gas-space in the foil-bag. Its lower limit could be calculated by applying Henry's law (KÖRMENDY, 1982). The partial pressure of oxygen inside the bag depends on the temperature, the gas and solution volumes and on the total oxygen content of the bag.

1.2.6. Methods of data evaluation. The decrease of vitamin C concentration as a function of time was evaluated by regression analysis with two variables.

Reaction rate constants of zero order (k_0) were determined in 1996 by fitting the equation

$$c = c_0 - k_0 t \quad (6)$$

and reaction rate constants of first order (k_1) by fitting the equation

$$\ln c = \ln c_0 - k_1 t \quad (7)$$

In 1997 and 1998 reaction rate constants were calculated in a similar way, but instead of the fitted initial vitamin C concentration (c_0) the mean value of the measured initial concentration was used as a fixed value of the curve, because the standard deviation of the initial vitamin C concentration was negligible compared to the mean standard deviation of concentrations measured in other periods of the heat treatment.

Equations of the fitted functions are the following in this case:

$$c = c_{0m} - k_0 t \quad (8)$$

and

$$\ln c = c_{0m} - k_1 t \quad (9)$$

First order reaction rate constants (k_1) and the maximum concentration decrease, data $\Delta c_{\max} = (c_0 - c_5)$ were evaluated by three factorial analysis of variance.

Factors of the analysis of variance were the following:

- Temperature (T)
- Nominal concentration of dissolved oxygen (O)
- Nominal initial concentration of vitamin C (c_{nom})

The effect of the temperature and the initial concentration of vitamin C on time dependent vitamin C concentration were determined by multivariate regression analyses. As a result 12 equations of zero order and 12 equations of first order were formed in each year. The above mentioned effects were analysed under the following suppositions regarding reaction rate constants versus temperature or versus temperature and initial vitamin C concentration relations:

$$k = A + BT + CT^2 \quad (10)$$

$$k = A + BT + CT^2 + D c_{0m} \quad (11)$$

Equation (10) is valid at a fixed level of oxygen concentration and constant initial vitamin C concentration as independent variable.

Equation (11) includes the initial vitamin C concentration, and is valid in a wider range: $250 < c_{0m} < 1000 \text{ mg dm}^{-3}$.

The constants A, B, C and D in equations (10) and (11) were calculated by fitting the following multiple regression equations:

$$c = c_0 - k_0 t = c_0 - A_0 t - B_0 (Tt) - C_0 (T^2 t) \quad (12)$$

$$\ln c = \ln c_0 - k_1 t = \ln c_0 - A_1 t - B_1 (Tt) - C_1 (T^2 t) \quad (13)$$

$$c - c_{0m} = -k_0 t = -A_0 t - B_0 (Tt) - C_0 (T^2 t) - D_0 (c_{0m} t) \quad (14)$$

$$\ln c - \ln c_{0m} = -k_1 t = -A_1 t - B_1 (Tt) - C_1 (T^2 t) - D_1 (c_{0m} t) \quad (15)$$

Data evaluation had to be carried out for 1996, 1997 and 1998 separately because of differences in the packaging conditions and pH value of the samples.

1. Results and discussion

2.1. Results of the quantitative determination of vitamin C

Measured data of vitamin C concentrations were arranged in tables according to the year of measurement, temperature, oxygen concentration level, nominal initial vitamin C concentration and heat treatment time (KÖRMENDY et al., 1999a).

In the frame of the present work it was only possible to publish a part of the kinetic parameters, calculated on the basis of vitamin C concentration measurements, carried out at 5 terms of the heat treatment, such as reaction rate constants (Tables 3, 4 and 5), regression equations, describing the vitamin C destruction (Table 6), and results of the analysis of variance, showing the effect of the investigated variables (T), (O) and (c_{nom}) on the reaction rate (Table 8).

Table 3. Zero and first order reaction rate constants in 1996

Temperature (°C)	Nominal O ₂ conc. (mg dm ⁻³)	Initial vitamin C conc. (mg dm ⁻³)	k_0 (mgdm ⁻³ min ⁻¹)	r_0	$k_1 \times 10^{-3}$ (min ⁻¹)	r_1	
80	2.5	250	0.3557	-0.9465	1.4520	-0.9455	
		500	0.7727	-0.9839	1.6434	-0.9853	
		1000	0.5290	-0.9795	0.5564	-0.9792	
	7.5	25	250	1.3157	-0.9947	5.7940	-0.9948
			500	1.3428	-0.9862	2.8068	-0.9844
			1000	1.6858	-0.9702	1.7523	-0.9708
		25	250	1.499	-0.9929	6.7473	-0.9897
			500	3.0965	-0.9959	6.9885	-0.9966
			1000	3.7433	-0.9789	4.0912	-0.9824
	90	2.5	250	0.5760	-0.9889	2.3777	-0.9894
			500	0.9620	-0.9911	2.0602	-0.9923
			1000	0.7440	-0.9426	0.7874	-0.9412
7.5		25	250	1.2177	-0.9963	5.3277	-0.9967
			500	1.5730	-0.9853	3.3984	-0.9879
			1000	1.7030	-0.9346	1.7806	-0.9382
		25	250	2.2090	-0.9993	10.6667	-0.9978
			500	2.6497	-0.9924	6.0297	-0.9955
			1000	2.2877	-0.9893	2.4191	-0.9902
100		2.5	250	0.3988	-0.9343	1.6253	-0.9375
			500	0.5600	-0.9388	1.1806	-0.9407
			1000	0.7042	-0.9591	0.7444	-0.9590
	7.5	25	250	1.1443	-0.9967	4.9573	-0.9974
			500	0.7793	-0.9571	1.6424	-0.9592
			1000	1.2082	-0.9193	1.2497	-0.9217
		25	250	0.9710	-0.9332	4.1928	-0.9422
			500	1.3579	-0.8128	2.9662	-0.8177
			1000	1.9470	-0.8787	2.0528	-0.8836

2.2. Results of the regression analyses

On the basis of the above mentioned vitamin C concentration data, regression analyses with two variables were carried out according to equations (6), (7), (8) and (9). Using the above mentioned equations reaction rate constants of zero (k_0) and first order (k_1), correlation coefficients for the regressions were calculated for each level of (T), (O) and (c_{nom}) separately for each year because of the differences in packaging material and pH value. Results are shown in Tables 3, 4 and 5.

Table 4. Zero and first order reaction rate constants in 1997

Temperature (°C)	Nominal O ₂ conc. (mg dm ⁻³)	Initial vitamin C conc. (mg dm ⁻³)	k_0 (mgdm ⁻³ min ⁻¹)	r_0	$k_1 \times 10^{-3}$ (min ⁻¹)	r_1	
80	2.5	250	0.4787	-0.9970	2.0620	-0.9970	
		500	0.6076	-0.9908	1.2670	-0.9917	
		1000	0.7556	-0.9686	0.7810	-0.9693	
	7.5	250	0.6452	-0.9898	2.7550	-0.9918	
		500	0.7077	-0.9882	1.4800	-0.9888	
		1000	1.0812	-0.9909	1.1270	-0.9907	
	25	250	500	1.3929	-0.9943	6.8250	-0.9968
			500	1.4421	-0.9960	3.1890	-0.9976
			1000	2.0424	-0.9942	2.2080	-0.9956
		2.5	250	0.5656	-0.9813	2.3040	-0.9829
			500	0.5652	-0.9783	1.1720	-0.9794
			1000	0.8283	-0.9941	0.8420	-0.9943
90	7.5	250	0.9590	-0.9822	4.1070	-0.9858	
		500	1.1416	-0.9546	2.4300	-0.9568	
		1000	1.3112	-0.9793	1.3440	-0.9747	
	25	250	1.3813	-0.9812	6.7210	-0.9873	
		500	1.4386	-0.9869	3.1930	-0.9896	
		1000	2.0289	-0.9815	2.1810	-0.9837	
	2.5	250	0.5107	-0.9780	2.1340	-0.9802	
		500	0.5744	-0.9817	1.1960	-0.9829	
		1000	0.9297	-0.9877	0.9470	-0.9885	
	100	7.5	250	0.7292	-0.9858	3.1860	-0.9885
			500	0.8563	-0.9577	1.7770	-0.9595
			1000	0.7572	-0.9794	0.7820	-0.9802
25		250	1.1207	-0.9703	5.2060	-0.9746	
		500	1.5091	-0.9607	3.3550	-0.9641	
		1000	1.6954	-0.9721	1.8000	-0.9738	

Table 5. Zero and first order reaction rate constants in 1998

Temperature (°C)	Nominal O ₂ conc. (mg dm ⁻³)	Initial vitamin C conc. (mg dm ⁻³)	k ₀ (mgdm ⁻³ min ⁻¹)	r ₀	k ₁ × 10 ⁻³ (min ⁻¹)	r ₁	
80	2.5	250	0.5544	-0.9922	2.5630	-0.9931	
		500	0.0645	-0.9725	1.4390	-0.9739	
		1000	0.5504	-0.9838	0.6090	-0.9840	
	7.5	250	0.8045	-0.9817	4.2510	-0.9831	
		500	1.0711	-0.9817	2.3480	-0.9853	
		1000	1.1328	-0.9734	1.4130	-0.9725	
	25	250	250	1.3430	-0.9953	7.2100	-0.9963
			500	2.1149	-0.9799	5.3180	-0.9833
			1000	2.4476	-0.9712	2.9000	-0.9721
		7.5	250	0.5432	-0.9902	2.5150	-0.9899
			500	0.7662	-0.9546	1.7300	-0.9558
			1000	0.7729	-0.9306	0.8940	-0.9303
90	2.5	250	0.6166	-0.9774	3.2300	-0.9778	
		500	0.7432	-0.9565	1.6760	-0.9572	
		1000	0.8217	-0.8972	1.7230	-0.9746	
	7.5	250	1.5219	-0.9871	8.9840	-0.9924	
		500	2.0744	-0.9648	5.4550	-0.9668	
		1000	2.6523	-0.9590	3.3100	-0.9616	
	25	250	250	0.5850	-0.9732	2.5280	-0.9759
			500	0.6143	-0.9567	1.3070	-0.9574
			1000	0.5341	-0.9569	0.5570	-0.9577
		7.5	250	0.4926	-0.9369	2.2430	-0.9387
			500	0.7759	-0.9575	1.8590	-0.9571
			1000	1.0369	-0.9079	1.5560	-0.9727
100	2.5	250	1.2770	-0.9690	6.1540	-0.9565	
		500	1.6048	-0.9374	3.6570	-0.9399	
		1000	2.5893	-0.9919	2.8440	-0.9928	

Correlation coefficients of zero and first order regressions (r_0 and r_1) were compared by the “ t -test” of paired comparison (“ $r_1 - r_0$ ” difference method; SVÁB, 1981). The one sided t -test verified that r_1 values are significantly greater than values for r_0 , i.e. first order equations (7) and (9) describe vitamin C decay more exactly than those of zero order (6) and (8). (Probability level: 1%, D.F. = 35, number of r_0 and r_1 compared = 36).

Analyses of pH and packaging material effect will be performed similarly by the above mentioned “ t -test” of paired comparison of the corresponding data, measured in different years, and will be published in the near future.

Table 6. First order predictive equations
Nominal initial oxygen concentration
7.5 mg dm⁻³, 80 ≤ T ≤ 100 °C

Year	Fitting equation	Nominal initial conc. vitamin C (mg dm ⁻³)	Predictive equations c _{om} : initial vitamin C concentration (mg dm ⁻³), 250 ≤ c _{om} ≤ 1000 mg dm ⁻³	Number of groups of measured data
1996 t ≤ 40 min. pH=2.05	(13)	250	$\ln c = 5.5384 + 0.579 \times 10^{-2} t - 0.31 \times 10^{-4} (T) + 0.3891 \times 10^{-6} (T^2)$	(16)
		500	$\ln c = 6.2070 - 12.2440 \times 10^{-2} t - 27.92 \times 10^{-4} (T) + 15.0000 \times 10^{-6} (T^2)$	(17)
		1000	$\ln c = 6.8957 - 4.0908 \times 10^{-2} t - 9.59 \times 10^{-4} (T) + 5.3604 \times 10^{-6} (T^2)$	(18)
1997 t ≤ 80 min. pH=2.05	(15)	250-1000	$\ln c = \ln c_{om} + 4.9708 \times 10^{-2} t - 12.71 \times 10^{-4} (T) + 7.198 \times 10^{-6} (T^2) + 4.4 \times 10^{-6} (c_{om} t)$	(19)
		250	$\ln c = 5.5260 + 3.5051 \times 10^{-2} t - 8.20 \times 10^{-4} (T) + 4.388 \times 10^{-6} (T^2)$	(20)
		500	$\ln c = 6.1998 + 6.1830 \times 10^{-2} t - 14.16 \times 10^{-4} (T) + 7.848 \times 10^{-6} (T^2)$	(21)
1998 t ≤ 80 min. pH=2.45	(15)	250-1000	$\ln c = \ln c_{om} + 6.1737 \times 10^{-2} t - 0.0306 \times 10^{-4} (T) + 0.096 \times 10^{-6} (T^2)$	(22)
		250	$\ln c = 6.9004 - 0.1450 \times 10^{-2} t - 14.62 \times 10^{-4} (T) + 8.084 \times 10^{-6} (T^2) + 2.8 \times 10^{-6} (c_{om} t)$	(23)
		500	$\ln c = 5.4595 + 1.8481 \times 10^{-2} t - 6.16 \times 10^{-4} (T) + 4.204 \times 10^{-6} (T^2)$	(24)
1998 t ≤ 80 min. pH=2.45	(13)	250	$\ln c = 6.1398 - 0.5531 \times 10^{-2} t + 0.12 \times 10^{-4} (T) + 0.3539 \times 10^{-6} (T^2)$	(25)
		500	$\ln c = 6.8504 + 6.2633 \times 10^{-2} t - 14.93 \times 10^{-4} (T) + 8.615 \times 10^{-6} (T^2)$	(26)
		1000	$\ln c = \ln c_{om} - 1.5228 \times 10^{-2} t - 2.2900 \times 10^{-4} (T) - 1.0755 \times 10^{-6} (T^2) + 2.1 \times 10^{-6} (c_{om} t)$	(27)

Table 7. Constants of the predictive equations in Table 6 (T)°C

$$\ln c = \ln c_0 - k_1(T) = \ln c_0 - A_1 t - B_1(T) - C_1(T^2) - D_1(C_0)$$

$$\ln c - \ln c_0 = -k_1(T)t = -A_1 t - B_1(T) - C_1(T^2) - D_1(C_0)$$

Year	Measured conc. of O ₂ (mg dm ⁻³)	Nominal initial conc. of vitamin C (mg dm ⁻³)	ln c ₀	s _e (ln c ₀) × 10 ⁻³	A ₁ × 10 ⁻²	s _e (A ₁) × 10 ⁻³	B ₁ × 10 ⁻⁴	s _e (B ₁) × 10 ⁻⁴	C ₁ × 10 ⁻⁶	s _e (C ₁) × 10 ⁻⁷	korr. koef. (total)	D ₁ × 10 ⁻⁶	s _e (D ₁) × 10 ⁻⁷
			(min ⁻¹)				(°C ⁻¹ min ⁻¹)				(mg ⁻¹ dm ⁻³ min ⁻¹)		
1996	7-8	250	5.538429	1.253	0.579	5.046	0.31	1.13	-0.3891	6.2673	0.9961	-	-
		500	6.207033	2.309	-12.2440	9.295	27.92	2.08	-15.0000	11.5462	0.9576	-	-
		1000	6.895660	1.577	-4.0908	6.347	9.59	1.42	-5.3604	7.8838	0.9407	-	-
1997	6.98-7.54	250-1000	-	-	-4.9708	0.8833	12.71	1.98	-7.1980	10.9723	0.9736	-4.4	1.68
		250	5.525954	4.309	-3.5051	8.671	8.20	1.94	-4.3884	10.7713	0.9648	-	-
		500	6.199767	4.031	-6.1830	8.113	14.16	1.81	-7.8480	10.0779	0.9043	-	-
		1000	6.900352	1.805	0.1450	3.632	0.0306	0.81	-0.09600	4.5117	0.9424	-	-
		250-1000	-	-	-0.6137	0.6200	14.62	1.39	-8.0840	7.7027	0.9688	-2.8	1.17
1998	8.20-9.61	250	5.459460	6.185	-1.8481	12.448	6.16	2.78	-4.2040	15.4618	0.9425	-	-
		500	6.139819	4.528	0.5531	9.114	-0.12	2.04	-0.3539	11.3205	0.9110	-	-
		1000	6.850403	5.891	-6.2633	11.857	14.93	2.65	-8.6154	14.7282	0.8445	-	-
	8.20-9.61	250-1000	-	-	1.5228	0.8164	-2.29	1.83	1.0755	10.1392	0.9496	-2.1	1.61

s_e: standard error

2.3. Predictive equations

Regression equations in Table 6 can be used to predict vitamin C destruction, since equations (16), (17), (18), (20), (21), (22), (24), (25) and (26) describe vitamin C destruction as a function of temperature and time at 7.5 mg dm^{-3} nominal dissolved oxygen content and fixed nominal initial vitamin C concentrations. Equations (19), (23) and (27) include the nominal initial vitamin C concentration (c_{nom}) as independent variable, too.

The constants of the predictive equations, describing the joint effect of time, temperature and initial vitamin C concentration, were calculated by equations (14) and (15) for each level of oxygen concentration. Table 6 contains 12 of the 72 predictive equations (3 years x 2 reaction orders x 12 equations).

Authors published in the frame of the present work only the regression equations of first order reactions related to nominal oxygen concentration of 7.5 mg dm^{-3} , because this oxygen concentration corresponds approximately to the oxygen concentration of fruit juices in factory production. First order kinetics proved to describe more exactly the vitamin C destruction than zero order equations (see paragraph 2.2.).

On the basis of the equations in Table 6, the retained quantity of vitamin C can be predicted in the range of the described research conditions. Independent variables are temperature, initial concentration of vitamin C and heat treatment time. Predictive equations for oxygen levels of 2.5 and 25 mg dm^{-3} were formed in a similar way, and will be published in the near future as well.

The equations give new information on the vitamin C retention during fruit juice preservation, but they are valid only in the range of the parameters used for the present investigations.

Equations (16)–(19) were formed on the basis of the results in 1996. They might be used in the case of pasteurization by flow-through type heat exchanger, if the pressure is not significantly higher than 1 bar. In this case the dissolved oxygen content of the solution might be about the same as in the case of gas-permeable foil, used in 1996. Results of the heat treatment investigations, carried out in 1997 and 1998 in non-permeable foil-bags, are better modelling the heat treatment of juices in hermetically closed, non-permeable glass-bottles or other non-permeable packages. Laboratory conditions, used in 1998, are reflecting more exactly the real conditions of juice preservation praxis because of the very small free head-space in the package.

The absolute values and standard deviations for the constants A_0 , A_1 , B_0 , B_1 , C_0 , C_1 , D_0 and D_1 are shown in Table 7 to demonstrate the verification of the “predictive equations”.

Table 8 contains the measured initial oxygen concentrations and values calculated for the heat treatment temperature, applying Henry’s law.

Table 8. Oxygen concentrations measured in the model solution before heat treatment and values calculated on the basis of Henry's law for 7.5 mg dm^{-3} initial oxygen concentration and different heat treatment temperatures

Year of investigations	Temperature (°C)	Values of initial O ₂ concentration (mg dm ⁻³)		
		Nominal values	Measured values	Calculated values
1996 (Gas-permeable packaging-foil was used)	80	2.5	1.5–3.5	–
		7.5	7–8	1.20
		25	20–25	–
	90	2.5	1.5–3.5	–
		7.5	7–8	0.57
		25	20–25	–
	100	2.5	1.5–3.5	–
		7.5	7–8	0
		25	20–25	–
1997 (Non-permeable packaging-foil was used)	80	2.5	2.32	–
		7.5	7.14	2.28
		25	22.9	–
	90	2.5	1.16	–
		7.5	7.52	0.69
		25	24.1	–
	100	2.5	3.38	–
		7.5	7.84	0.402
		25	29.5	–
1998 (Non-permeable packaging-foil was used)	80	2.5	3.52–5.20	–
		7.5	9.21–9.61	1.70
		25	22.00–28.70	–
	90	2.5	2.06–3.16	–
		7.5	8.20–9.23	1.52
		25	21.60–30.00	–
	100	2.5	2.28–2.82	–
		7.5	8.41–8.70	0.86
		25	21.20–28.30	–

2.4. Analysis of variance

First order reaction rate constants (k_1) and maximum vitamin C losses during the heat treatment (Δc_{\max}) were examined according to paragraph 1.2.6. by three factorial analysis of variance to verify the effect of the investigated variables (T),(O) and (c_{nom}) on the vitamin C destruction. Mean squares were related to the residual variance: $F_2 = MS/MS_R$ and to the variance of the three factorial interaction: $F_3 = MS/MS_{\text{HOB}}$. Results are available in the research report of KÖRMENDY and co-workers (1999a).

Table 9. Significance of major effects and interactions

Year of investigation	Investigated variable	Major effect interaction	Order of importance	F ₂	Test	F ₃
1996	Δc_m	O	1	**		**
		C _{nom}	2	**		*
		T	3	**		*
		TxO	1	**		-
		Oxc _{nom}	2	**		-
		Txc _{nom}	3	**		-
		TxOxc _{nom}	-	**		---
	k ₁	O	1	**		**
		C _{nom}	2	**		**
		T	3	**		*
		TxO	2	**		-
		Ox C _{nom}	1	**		-
		Tx C _{nom}	3	**		-
		TxOxc _{nom}	-	**		---
1997	Δc_m	O	1	**		**
		C _{nom}	2	**		**
		T	3	**		*
		TxO	1	**		*
		Oxc _{nom}	2	**		-
		Txc _{nom}	3	**		-
		TxOxc _{nom}	-	**		---
	k ₁	O	2	**		**
		C _{nom}	1	**		**
		T	3	**		-
		TxO	2	**		-
		Oxc _{nom}	1	**		*
		Txc _{nom}	3	**		-
		TxOxc _{nom}	-	**		---
1998	Δc_m	O	1	**		**
		C _{nom}	2	**		**
		T	3	**		-
		TxO	3	**		-
		Oxc _{nom}	1	**		*
		Txc _{nom}	2	**		-
		TxOxc _{nom}	-	**		---
	k ₁	O	1	**		**
		C _{nom}	2	**		**
		T	3	**		*
		TxO	2	**		-
		Oxc _{nom}	1	**		*
		Txc _{nom}	3	**		-
		TxOxc _{nom}	-	**		---

** P≤1%

* P≤5%

Levels of significance were determined by the comparison of tabulated and calculated F-values. The intensity of the effects of the major factors and their interactions were ranked on the basis of the calculated F_2 and F_3 values, using an "intensity scale". The intensities of the effects of major factors and those of interactions are given in Table 9.

According to the F_2 values the effects of all factors and of all interactions are highly significant. F_3 values validate a highly significant effect of the oxygen concentration and the initial vitamin C concentration on first order reaction rate constants (k_1) and on the maximum concentration change of vitamin C (Δc_{\max}). The effect of temperature proved to be significant in 4 of 6 cases, and was not significant in 2 of 6 cases. (see Table 9). Having summarised the results of investigations of three years, the following sequence of the major effects on both investigated variables could be established:

- Oxygen concentration (O)
- Nominal initial vitamin C concentration (c_{nom})
- Temperature (T)

Only in one single case was the above mentioned sequence changed, in 1997. In this year the nominal initial vitamin C concentration had a stronger effect on the first order reaction rate constants than the concentration of oxygen.

According to the intensities of the effects of interactions on the first order reaction rate constant, the following sequence was observed in all three years:

- Oxygen concentration x Nominal initial vitamin C concentration ($O \cdot c_{\text{nom}}$)
- Temperature x Oxygen concentration (T·O)
- Temperature x Nominal initial vitamin C concentration ($T \cdot c_{\text{nom}}$)

The sequence of the interactions, according to the effect on the maximum change of vitamin C concentration (Δc_{\max}), was different. This sequence was the following in 1996 and 1997:

- Temperature x Oxygen concentration (T·O)
- Oxygen concentration x Nominal initial vitamin C concentration ($O \cdot c_{\text{nom}}$)
- Temperature x Nominal initial vitamin C concentration ($T \cdot c_{\text{nom}}$).

The sequence of interactions according to the effect on (Δc_{\max}) in 1998 was:

- Oxygen concentration x Nominal initial vitamin C concentration ($O \cdot c_{\text{nom}}$)
- Temperature x Nominal initial vitamin C concentration ($T \cdot c_{\text{nom}}$)
- Temperature x Oxygen concentration (T·O).

According to the results the concentration of oxygen dissolved in the solution, thus available for the reaction, is of decisive importance for vitamin C destruction. The initial concentration of vitamin C has more influence on variables (k_1) and (Δc_{\max}) too, than the temperature of the heat treatment in the range of 80–100 °C.

2.5. The influence of the temperature on the reaction rate constants

The influence of the temperature on the zero and first order reaction rate constants (k_0 and k_1) was investigated according paragraph 1.2.6, postulating the validity of equation (10). The constants A; B and C were determined by linear multivariate regression

analysis. Zero order reaction rate constants (k_0) were described as a function of the temperature by altogether 27 equations 9 equations according to the results of each year. Other 27 predictive equations were elaborated to determine first order reaction rate constants (k_1) as a function of the temperature in a similar way. Nine of them, related to the oxygen concentration of 7.5 mg dm^{-3} are presented in Table 6. Though equations in Table 6 [(16), (17), (18), (20), (21), (22), (24), (25), (26)] are explicit for $\ln c$, it is easy to deduce the proper formula for (k_1) by eliminating the time (t) as independent variable. Between 80–90 °C a slight increase of the reaction rate constant was noticed in most cases, but the increase of the reaction rate was still far from the values calculated according to literature sources. Moreover, the temperature increase from 90 °C to 100 °C was followed by a decrease of the reaction rate constants. This statement is valid for the results of all three years with following details: in 1996 a significantly higher decrease of the reaction rate constant was found than in 1997 and 1998. The reason for this surprising result is probably the use of gas-permeable packaging-foil in 1996, a free diffusion of the escaping oxygen into the environment and the decrease of the dissolved oxygen concentration due to the temperature increase. By using impermeable packaging-foil in 1997 and 1998 the escaping oxygen remained inside the package, consequently a higher equilibrium concentration was present at the same temperature. This equilibrium concentration is influenced by the extent of the free head-space in the package as well.

2.6. The influence of the temperature and the average initial concentration of vitamin C on the reaction rate constant

The effect of the initial vitamin C concentration was considered by applying equation (11). In this way the constants A_1 , B_1 , C_1 , D_1 in the range of $250 \leq c_{\text{nom}} \leq 1000 \text{ mg dm}^{-3}$ nominal initial vitamin C concentration were calculated. For each year and for each oxygen concentration two predictive equations were determined, one for (k_0) and the other for (k_1). Three of altogether 9 predictive equations concerning k_1 values at the nominal oxygen concentration of 7.5 mg dm^{-3} are presented in Table 6. The conversion of equations (19), (23) and (27) can be executed in the same way as in paragraph 2.5. The other 12 equations for k_0 and k_1 at the lower oxygen concentration (bubbling N_2 through the solution) and at the higher one (bubbling O_2 through the solution) were formed by a similar method. Results were published in the research report of KÖRMENDY and co-workers (1999a).

Equations for k_0 and k_1 , taking both the effect of temperature and initial vitamin C concentration into consideration, are demonstrated in Figs 1, 2, 3, 4, 5 and 6. These curves, however, were calculated by neglecting D_1 in equations (14) and (15). Slow increase of both k_0 and k_1 in the temperature range between 80–90 °C and a similarly slow decrease of the reaction rate constants in the temperature range of 90–100 °C could be often found. However, monotonous slow decrease and increase also occurred.

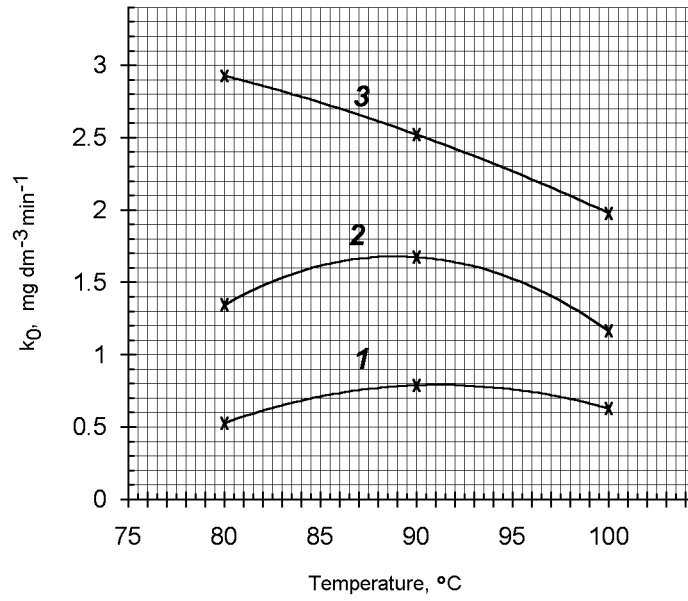


Fig. 1. Zero order reaction rate constants as a function of temperature (1996)

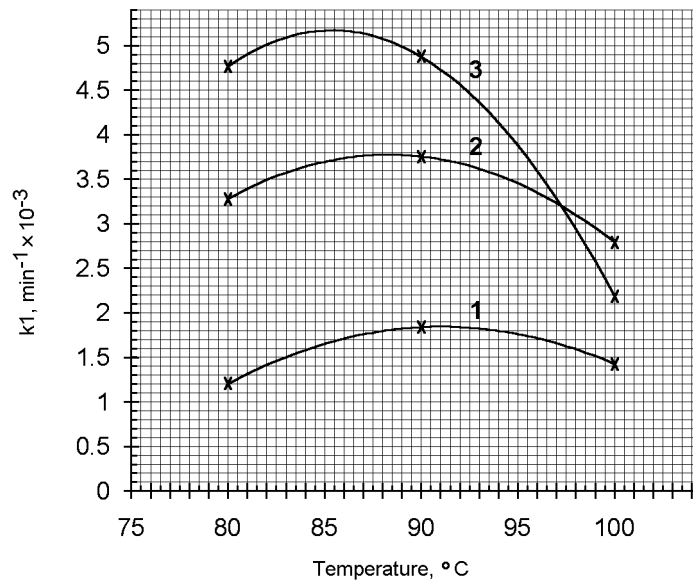


Fig. 2. First order reaction rate constants as a function of temperature (1996)

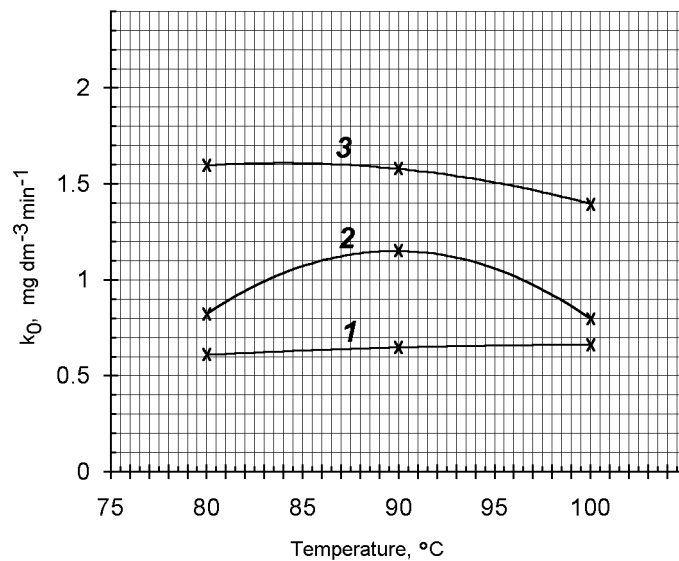


Fig. 3. Zero order reaction rate constants as a function of temperature (1997)

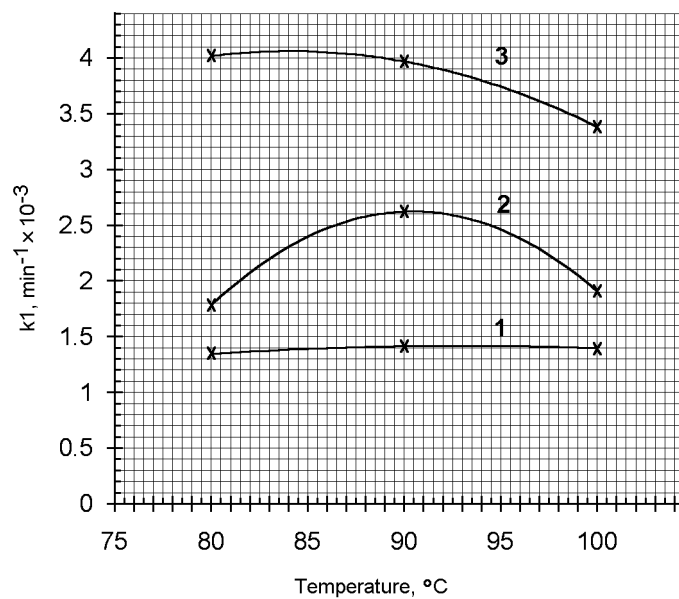


Fig. 4. First order reaction rate constants as a function of temperature (1997)

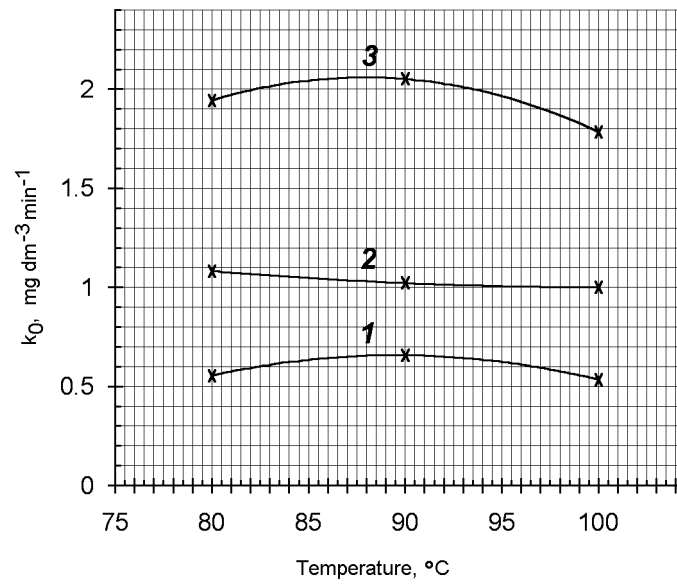


Fig. 5. Zero order reaction rate constants as a function of temperature (1998)

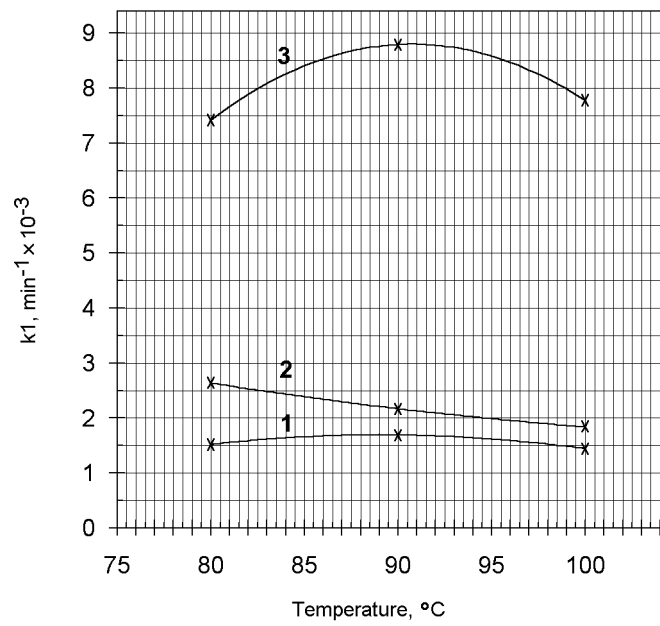


Fig. 6. First order reaction rate constants as a function of temperature (1998)

2. Conclusions

Regression analysis with two variables was used to describe changes of the vitamin C concentration as a function of time, and reaction rate constants of zero order (k_0) and first order (k_1) were determined for all investigated variations of the temperature, nominal oxygen concentration and nominal initial concentration of vitamin C.

The absolute value of the correlation coefficients varied between 0.8177 and 0.9978, when first order regression analysis was used. Paired comparison of zero order and first order correlation coefficients (r_0 and r_1) by the *t*-test showed that first order relation is better correlated. It describes the destruction of vitamin C in a more adequate way. Consequently, vitamin C decomposition can be more exactly modelled by first order kinetic equations.

The *sequence* of the investigated variables [nominal concentration of dissolved oxygen (O), nominal initial concentration of vitamin C (c_{nom}) and temperature (T)] according to the intensity of their effect on the vitamin C decomposition was the following:

- in 1996: O > c_{nom} > T (in the case of effect on k_1 and Δc_{max} as well);
- in 1997: c_{nom} > O > T (effect on k_1);
- and O > c_{nom} > T (effect on Δc_{max});
- in 1998: O > c_{nom} > T (in the case of effect on k_1 and Δc_{max} as well).

The concentration of dissolved oxygen has a primary effect on the rate of vitamin C decomposition, therefore the choice of adequate packaging material and packaging method is the key issue of vitamin C retention. As a consequence of heating, the major part of dissolved oxygen turns into gaseous state and tends to the head-space of the package, or it tends in the case of gas-permeable packaging material or under special conditions of flow-through type heat treatment to the environment. A low equilibrium oxygen concentration in the solution, as a result of adequate heat treatment technology and packaging method, is the most important condition of a satisfactory vitamin C retention.

The initial vitamin C concentration proved to be the second important factor regarding its effect on vitamin C destruction.

The concentration of dissolved oxygen, according to the Henry's law, is inversely proportional to temperature. The increase of temperature reduces the concentration of dissolved oxygen, consequently it decreases the reaction rate. On the other hand, it is well known, that temperature increases the reaction rate. The actual shape of the rate constant versus temperature relation is the result of these reverse effects. The initial vitamin C concentration proved to be also an important factor regarding rate constants.

On the basis of the predictive equations the amount of retained vitamin C can be estimated in the investigated range of the variables (pH 2.05–2.45; initial concentration of vitamin C: 250–1000 mg dm⁻³; initial oxygen concentration: 2.5–25 mg dm⁻³ and temperature: 80–100 °C).

After studying the literature and analysing the evaluated kinetic parameters, authors thought it appropriate to describe vitamin C decomposition as a result of simultaneous aerobic and anaerobic chemical reactions. According to the relevant literature the anaerobic process is treated by first order kinetics (reaction rate constant = k_1), and is considerably slower than the aerobic one. The aerobic process can be modelled by the following reaction: $2 AA + O_2 \rightarrow 2$ -diketo-gulonic acid. This relation leads to a mixed third order reaction. A mathematical model and computer program were also elaborated for this type of reaction (KÖRMENDY et al., 1999b). Results help to promote the development of more reasonable processes in the field of heat treatment and packaging of fruit juices.

Symbols

a, b: Number of molecules of component X and Y resp. in a stoichiometric relation

A; A_0 ; A_1 : Temperature independent constants in the equations describing reaction rate constant as a function of temperature ($[A]=[k]$, $[A_0]=[k_0]$, $[A_1]=[k_1]$)

B; B_0 ; B_1 : Constants of the members which contain T in the equations, describing the reaction rate constants as a function of the temperature ($[B]=[k].^\circ C^{-1}$, $[B_0]=[k_0].^\circ C^{-1}$, $[B_1]=[k_1].^\circ C^{-1}$)

c: Vitamin C concentration ($mg\ dm^{-3}$)

c_0 : Initial concentration, calculated by fitting of the equation describing the concentration of vitamin C as a function of time and temperature ($mg\ dm^{-3}$)

c_{nom} : Nominal initial concentration of vitamin C, nominal value of vitamin C concentration, added before the heat treatment of the model solutions ($mg\ dm^{-3}$)

c_{om} : Average value of the measured initial vitamin C concentrations ($mg\ dm^{-3}$)

C; C_0 ; C_1 : Constants of the members which contain T^2 in the equations, describing the reaction rate constants as a function of temperature ($[C]=[k].^\circ C^{-2}$, $[C_0]=[k_0].^\circ C^{-2}$, $[C_1]=[k_1].^\circ C^{-2}$)

D; D_0 ; D_1 : Constants of the members which contain c_{om} in the equations, describing the reaction rate constants as a function of temperature and of initial vitamin C concentration (D: generally; D_0 : zero order rate constant; D_1 : first order rate constant ($[D]=[k]$) ($mg^{-1}\ dm^3$))

F; F_1 ; F_2 ; F_3 : Quotient of the variances calculated for the *t*-tests

k_0 : Reaction rate constant of zero order ($mg\ dm^{-3}\ min^{-1}$)

k_1 : Reaction rate constant of first order (min^{-1})

MS; MS_{HOB} ; MS_R : Estimated variances (mean squares), their dimension is equal to the square of the analysed variable's dimension

r ; r_0 ; r_1 : Correlation coefficients, subindex indicates the reaction order in the fitted equation

t : Time (min)

T : Temperature ($^{\circ}\text{C}$)

Δc_{max} : Maximum change of vitamin C concentration on the basis of measured values (mg dm^{-3})

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