

OXIDO-REDUCTIVE STATE OF JAM WITH REDUCED SACCHAROSE CONTENT

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Summary: Currently, a major trend in the food industry presents the production of food with sweet taste with reduced saccharose added. Jams low in sucrose differ from traditional jams by an increased content of biologically active compounds, in particular, compounds from the family of polyphenols. The validity of the quality of jam with low sucrose content depends on the oxido-reductive state of antioxidants. The study of stability duration of active antioxidants in those jams composition was examined using Weibull distribution. It has been shown that changing the oxido-reductive state of jam takes place involving chemical compounds of flavonoids class. The stability duration of flavonoids and validity of jam quality is 90 – 160 days depending on the content of antioxidants in fruits.

Keywords: jam validity, oxido-reductive state, antioxidants, Weibull distribution.

Stability and validity of finite products after manufacture, during storage, are of major importance. Therefore, investigations had been carried out concerning physico-chemical changes of chemical compounds that affect the quality of products. Jams and comfitures low in saccharose are characterized by an increased content of biologically active substances in fruits and, particularly, by the complex of phenolic substances. Following our research it was found that during jam storage, the physico-chemical indices provided in the standard SM 162-1997 [1] (solid substances, pH value, total acidity) practically have not changed. The deviation of these characteristics from baseline values did not exceed $\pm 5\%$. Therefore, the physico-chemical indices mentioned above can be used to assess the change in the quality of jam during storage.

At the same time, significant changes in substances with oxido-reductive properties had been found. The index of oxido-reductive state of cherry and plums jam decreased over storage by $90 \pm 5\%$. The phenolic substances of cherries and plums represent the most valuable natural labile antioxidants, being involved in oxido-reductive reactions and directly reflect the change in biological value of jam. The oxido-reductive state of jam depends on the content and activity of polyphenols, anthocyanins, L-hydro and L-dehydroascorbic acids etc. The highest reductive activities have the antioxidants of cherries (table 1). The oxido-reductive state index was used as a criterion for assessing biological changes in the biological value of cherry and plums jam.

Table 1. The content of antioxidants and the average values of oxido-reductive state of cherries and plums

Nr.	Name	The content of soluble solid substances, SU, %	pH value	Total polyphenols, mg/100 g	Anthocyanins mg/100 g	Ascorbic acid, mg/100 g	Oxido-reductive state, mg AA/ g SU
1	Cherry	15.3 – 17.8	2.8 – 3.5	380 - 525	36.0 – 56.2	10 - 16	0.70 ± 0.15
2	Plums	16.2 – 22.0	3.6 – 4.0	220 - 280	24.3 – 32.0	4.0 – 6.2	0.16 ± 0.02

The change of oxido-reductive state had a decreasing character among variable fluctuations during jam storage. The appreciation of the biological value change in time for such complex foods represents a difficult problem. It was determined that the reduction of the biological value of jam can be estimated using the probability theory.

The Weibull distribution [2, 3] was used for estimating the validity and storage duration of products depending on their biological value. The parameters of Weibull distribution allowed determining the decay probability by time of the oxido-reductive state of jam and appreciating the change of biological value of the product during storage. Weibull distribution is shown as follows [3]:

$$f(\tau) = \frac{\beta}{\eta} \left(\frac{\tau - \gamma}{\eta} \right)^{\beta-1} e^{-\left(\frac{\tau - \gamma}{\eta} \right)^\beta}, \quad (1)$$

where: γ – Weibull distribution parameter, expressing the minimum storage duration with no oxido-reductive state change;

β – Weibull distribution parameter, which reflects the dynamics of the decrease process of oxido-reductive state;

η – Weibull distribution parameter, which shows the characteristic value of the oxido-reductive state, estimated time units (number of days, months, etc.);

τ – storage duration.

Function of Weibull distribution [2, 3]:

$$F(\tau) = \begin{cases} 1 - e^{-\left(\frac{\tau - \gamma}{\eta} \right)^\beta}, & \tau \geq 0, \\ 0, & \tau < 0 \end{cases} \quad (2)$$

The probability of decay time of the oxido-reductive state of jam during storage was calculated using the relation (3) with two Weibull parameters, β and η :

$$F(\tau) = 1 - e^{-\left(\frac{\tau}{\eta} \right)^\beta}, \quad (3)$$

The parameter η is determined using equation (4). When the storage time τ will be equal to η ($\tau = \eta$ days), the function $F(\eta)$ is calculated using the expression (4):

$$F(\eta) = 1 - e^{-\left(\frac{\eta}{\eta} \right)^\beta} = 1 - e^{-1} = 1 - 0.367 = 0.632 \text{ or } 63.2\%. \quad (4)$$

Therefore, the parameter η characterizes the probable decrease time of the oxido-reductive activity of jam by 63.2% of the original activity of 100%.

Depending on the storage temperature of experimental samples, the decrease probability of the oxido-reductive state of cherry jam at 6°C is 90 storage days. The decrease probability of the oxido-reductive state is 45 days at high temperatures of 40°C (Figure 1).

Following our research it was found that the biological value of cherry jam, expressed in oxido-reductive state, decreases definitely over 60-90 days after manufacture, depending on the storage temperature.

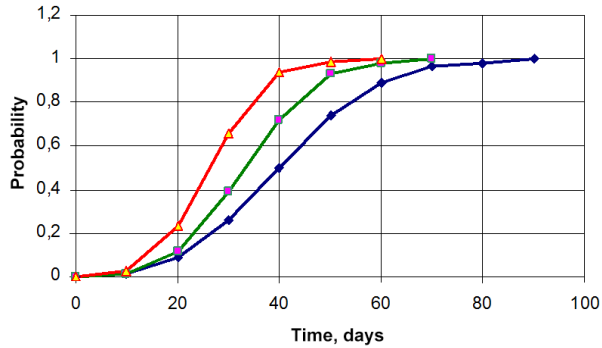


Fig. 1. The decrease probability of oxido-reductive state of cherry jam depending on the temperature and storage time,

▲ - $t = 40^{\circ}\text{C}$; ■ - $t = 30^{\circ}\text{C}$; ◆ - $t = 6^{\circ}\text{C}$.

Following our research it was found that the biological value of plums jam definitely decreases over 120-160 days after manufacture, depending on the temperature storage.

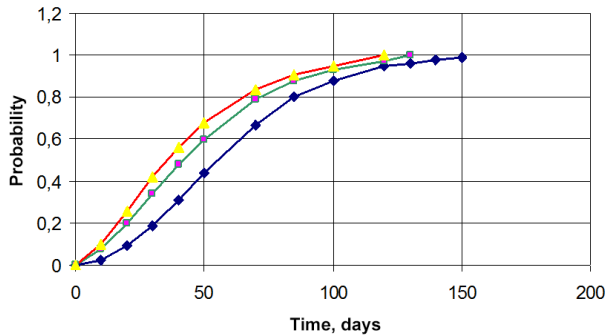


Fig. 2. The decrease probability of oxido-reductive state of plums jams depending on the temperature and storage time,

▲ - $t = 40^{\circ}\text{C}$; ■ - $t = 30^{\circ}\text{C}$; ◆ - $t = 6^{\circ}\text{C}$.

The analysis of spectral characteristics of experimental samples was performed to obtain additional information about the change of the biological value of plums jam during storage.

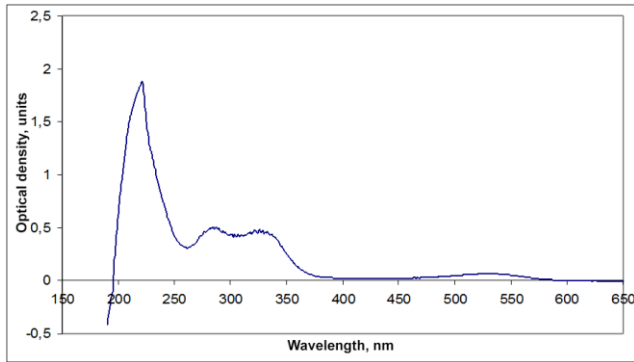
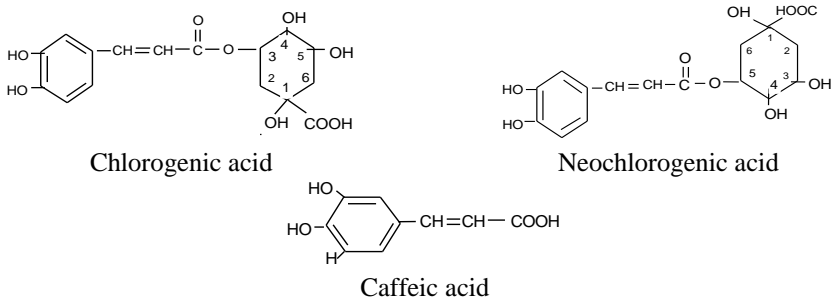


Fig. 3. Spectral characteristics of the optic density of plums jam. The storage temperature of plums jam was $+6^{\circ}\text{C} - +80^{\circ}\text{C}$.

Three peaks of optical density had been identified at the examined samples in the UV area, in particular, wavelengths in the range $\lambda = 220 - 225$, for $\lambda = 270\text{nm}$ and $\lambda = 340\text{nm}$. The insignificant peak of the optical density in the visible spectrum, $\lambda = 530 - 540\text{nm}$, belongs to anthocyanins [4]. The most significant peak of the optical density of plums jam has been identified in the wavelength range $\lambda = 220 - 225$. According to chinese researchers Chun OK, Kim DO., Moon HY, this peak belongs to phenolic monomer compounds, especially to caffeic, chlorogenic, and neochlorogenic acids [5].



Monomeric phenolic compounds with the carbon skeleton of molecules **C₆-C₃** represent 98-99% of the total content of phenolic compounds from plum. According to their properties, these are antioxidants with increased *in vivo* activity. *In vitro*, phenolic compounds are stable monomers and are kept well in food compositions. Chlorogenic and neochlorogenic acids are leading compounds to the formation of specific taste sensations of plums [6]. As a result of our research it has been found that, during the storage of plums jam for 100 - 150 days at a temperature of $+6 - +40^{\circ}\text{C}$, the optical density at 220 nm wavelength was constant.

Spectra with absorption maximum at $\lambda = 270 - 340\text{nm}$ reflect the presence of flavonoid compounds in the analyzed media. Oxidative degradation of flavanols upon storage leads to variable decrease of optical density. The decrease probability of the optical density of flavonoids was determined using the Weibull distribution (Figure 4).

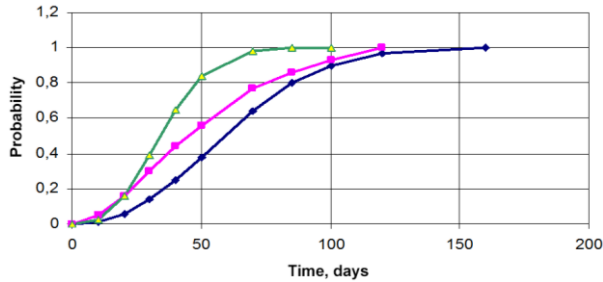


Fig. 4. The decrease probability of the optical density ($\lambda = 270\text{-}340\text{nm}$) of plums jam depending on temperature and storage time.

▲ - $t = 40^\circ\text{C}$; ■ - $t = 30^\circ\text{C}$; ◆ - $t = 6^\circ\text{C}$.

The slowest changes of the optical density were observed at low temperatures of 6°C . The native flavonoids had been practically modified with the probability $F(\tau) = 1.0$ or 100% after 160 days of storage of the plums jam.

We conducted a comparative analysis of the decrease probability of oxido-reductive state and optical density of flavonoids expressed by the Weibull distribution parameters (table 2), for usage purposes [2, 3].

Table 2. Weibull distribution parameters of the oxido-reductive state and optical density ($\lambda = 270 - 340 \text{ nm}$) of plums jam

Thermal storage conditions	Oxido-reductive state, Weibull distribution parameters		Optical density of flavonoids, Weibull distribution parameters	
	β	η	β	η
$t = 6^\circ\text{C}$	1.9	65.9	2.26	68.15
$t = 30^\circ\text{C}$	1,54	52.0	1.66	55,51
$t = 40^\circ\text{C}$	1.42	45.4	2.56	39.14

The values of β and η parameters, which characterize the change probability of oxido-reductive state and the optical density of flavonoids of the plums jam stored at of 6°C and 30°C temperatures, were practically identical.

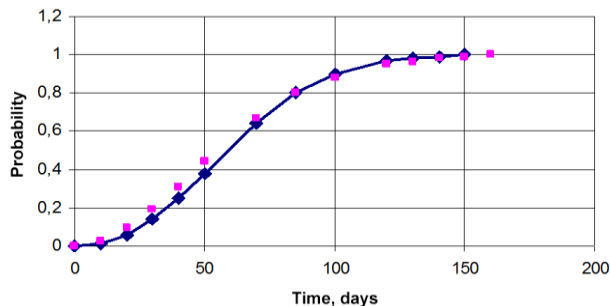


Fig. 5. The decrease probability of the oxido-reductive state and optical density of plums jam stored at $+6^\circ\text{C}$.

◆ – oxido-reductive state; ■ – optical density.

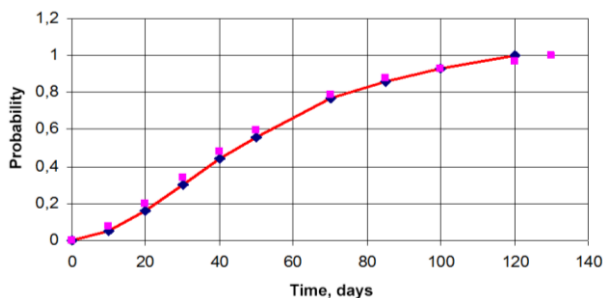


Fig. 6. The decrease probability of the oxido-reductive state and optical density of plums jam stored at 30°C

■ – oxido-reductive state; ◆ – optical density.

The obtained data have shown that the phenolic compounds from the natural antioxidants class are the most valuable biologically active substances in plum and cherry jam. In particular, flavonoids determine the oxido-reductive state of antioxidants in jam. The decrease of the reducing state and optical density of plums jam during storage with identical probability shows that one and the same chemical compounds of flavonoids' class are involved in these changes [7].

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