SHELF-LIFE PREDICTION OF PLUM FOODS USING ANTIOXIDANT ACTIVITY INDICES

Pavel Gh.Tatarov[a]*, Raisa A. Ivanova[b], Artur V. Macari[a]

[a] *Technical University of Moldova, Chisinau, Moldova,*
[b] *Centre of Advanced Biological Technologies, Academy of Science of Moldova, Chisinau*
** e-mail: p_tatarov@yahoo.com; tel. (+37322-509958); fax. (+37322-509960)*

Abstract: The reducing activity and radical scavenging activity of hydrosoluble antioxidants in food compositions from plums during the storage were evaluated. The speeds of changing the reducing activity and radical scavenging activity were different. It was observed that the reducing activity diminished by 63.2% after 62...105 days of storage. The same modification of radical scavenging activity determined *in vitro* was discovered after 110...254 days of storage. Shelf-life of plum foods was calculated using Weibull distribution. The functional relationship of failure probabilities between the reducing and radical scavenging capacities have been detected (r^2= 0. 94-0.98).

Keywords: shelf-life, antioxidant activity, Weibull distribution, plum, chokeberry

Introduction

Vegetable food is the most important source of antioxidants in human nutrition. Fruits, berries and vegetables contain different groups of antioxidants such as polyphenolics, carotenoids, anthocyans, α, β, γ-tocopherol, ascorbic acid, etc [1-4]. Due to their activity, antioxidants play a positive role in prevention of cancer, gastrointestinal and cardio-vascular diseases [5-8].

Basic characteristics of antioxidant activity are the inhibition of oxidation processes and scavenging of free radicals. The modification of antioxidant's reducing state "*in vitro*" in food compositions is the result of security effect from oxidative degradation of food. The action of antioxidants "*in vivo*" in human organism refers to deliverance from free radical $R^{\cdot}$, $ROO^{\cdot}$, $O_2^{\cdot}$, OH excess and maintaining the equilibrium of oxido-reducing processes on cellular level.

There exists some correlation between reducing state of antioxidants and their capacities to inactivate free radicals or their radical scavenging activity [9]. This research is an attempt to identify the existence of a correlation between the described properties of antioxidants. The goal of investigation was to determine the modification of activity of hydrosoluble antioxidants in plum juice and sauce during storage.

Materials and methods

The food compositions from plums such as juice and sauce were examined. For increasing the content of antioxidants the samples of juice and sauce from plums with addition of pulp of chokeberries (*Aronia melanocarpa Elliot*) in amount of about 8.0% of total weights were prepared. Thus, juice with pulp from plums (JP), juice with pulp from plums and chokeberries (JPC), and sauce from plums and chokeberries (SPC) were pasteurized at 100^0C and stored during 12 months in nonadjustable conditions.

The reducing activity (RA) of hydrosoluble antioxidants in tested food was determined by potentiometric method [9, 10]. The mode of this method consists in carrying out to equality, or equilibrium state of redox potential between solution of tested food and solution of L-hydroascorbic acid in two separated electrochemical cells. L-hydroascorbic acid was used as etalon of reducing activity for food antioxidants. The measurement of redox potentials was effectuated at the room temperatures (20±2^{0}C) by multi-parameter analyzer Consort C-835 with combination of silver and platinum electrodes. The differences between redox potential values of food solution and etalon solution were equalized by dosing of L- hydroascorbic acid concentration in etalon solution. Index *K* expressed the reducing activity of antioxidants in tested food in equivalent of L- hydroascorbic acid. Index K is the ratio of concentration of L- hydroascorbic acid (AA) to concentration of hydrosoluble substance in food determined by refractive index (mgAA/gRI).

Index K is calculated by equation:

$$K = \frac{C_1 \times V_1 \times m_1}{m_2 \times C_2 \times m_3}$$

where: C_1 – concentration of L- hydroascorbic acid, etalon solution, mg/cm^3;
C_2 – mass fraction of hydrosoluble substance in food, g/cm^3;
V_1 – used volume of L- hydroascorbic acid solution, cm^3;
m_1 – weight of food probe after dilution, g;
m_2 - weight of etalon solution, g;
m_3 - weight of tested food sample, g.

The calculations of reducing activity index (K) in tested food were made with confidence factor P=0.05. The coefficient of correlation between concentration of L- hydroascorbic acid and concentration of hydrosoluble reducing substance in tested food in state of equilibrium was r^2= 0.90-0.98.

The assay for measurement peroxyl radical scavenging activity (RSA) is based on the degree of inhibition of potassium iodide oxidation by antioxidants that scavenge peroxyl radicals, generated from thermal degradation of 2,2'-azobis(2-amidinopropane)-dihydrochloride (AAPH). Peroxyl radical scavenging activity of extracts was assayed in vitro by method Sano M. et al. [11] in our modification [12]. Namely, 0.7 ml of sample solution was added to 2 ml acetonitrile-phosphate buffer (1:1), followed by addition of 100µl of saturated KI solution. After preincubation of the mixture at 39±1^{0}C for 2min. radical-induced oxidation was started by the addition of 200µl of 0.5M AAPH. After 60min of incubation at 39±1^{0}C in the dark, the reaction vessel was chilled immediately in an ace bath to stop the radical production from AAPH and was allowed to stand for 5min in an ace bath. Subsequently, the volume of the reaction mixture was adjusted to 30ml with water. The concentration of molecular iodine in the mixture was determined by potentiometric titration with 0.25mM $Na_2S_2O_3$. The minimum titration amount of $Na_2S_2O_3$ was fixed at 0.01ml and the maximum potential difference was determined as the end point of the titration. The RSA of tested food is expressed as the percentage inhibition for iodine release of blank reagent without sample (control). The RSA was calculated from the following equation:

$$\text{RSA}\ (\%) = \left(1 - \frac{V_S(\text{sample})}{V_C(\text{control})}\right) \times 100$$

where V_S - amount of $Na_2S_2O_3$ expended for sample titration, ml;
V_C - amount of $Na_2S_2O_3$ expended for blank reagent titration (control), ml.

The reproducibility of RSA assay is good. The coefficients of variance were less than 4.78% and mean relative errors were within ±7.01% [13].

Results and discussions

The end of shelf-life of food is ultimately assessed by activity failure of antioxidants. The curves of antioxidants activity modification in tested food are presented in fig 1, 2. The activity indices of antioxidants in food have undergone permanent changing practically during all time of storage. The modification of reducing activity (fig.1) and radical scavenging activity (fig.2) had a nonadjustable character, but in general, tended to decreasing of both the reducing and the radical scavenging activities. The most profound fluctuations of antioxidants activity were observed at the primary stage of storage, in first 50…100 days.

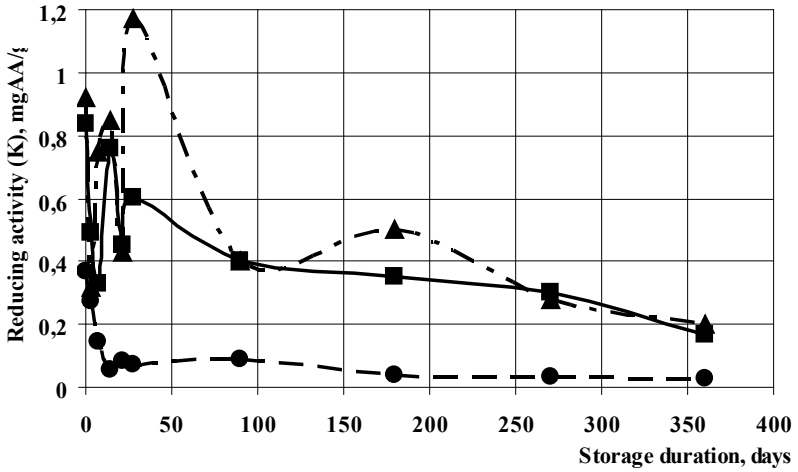

Fig. 1. Modification of reducing activity of antioxidants in food:
● – JP; ■ -JPC ▲- SPC during the storage

Perhaps the fluctuation of antioxidants activity appeared as results of different processes that were developed simultaneously in nonadjustable conditions. During the storage the diffusion processes of anthocyans and polyphenolics from solid phase (pulp of plums and chokeberries, their skins) to liquid phase took place. That has been led to increasing of concentration and activity of antioxidants in liquid phase. At the same time the speeds of oxidation and degradation reactions of antioxidants were accelerated concurrently because of symbiosis and antagonism effects between antioxidants and prooxidants in conditions when the temperature and viscosity of food were variable.

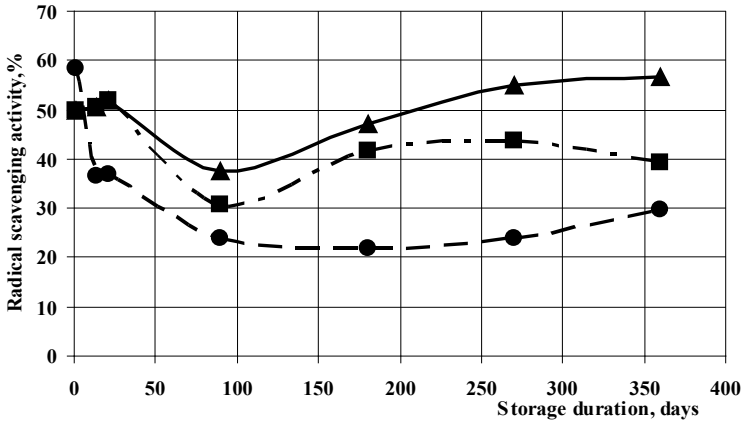

Fig. 2. Modification of radical scavenging activity of antioxidants in food:
● – JP; ■ -JPC ▲- SPC during the storage

In these complicated compositions and nonadjustable conditions the decreasing degree of antioxidants activity by time can be valued by determining the probability of modification appearances [14-18]. The probability of antioxidants activity evolution in tested food was analyzed by Weibull distribution (1):

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

*where: **γ** - localization parameter expresses the minimal duration to time when the antioxidants activity does not manifest the modification;*
***β** - shape parameter reflects the dynamics of decreasing process of antioxidants activity;*
***η** - scale parameter reflects "the characteristically activity" of antioxidants, named Weibull's parameter;*
***τ** - time of food storage.*

Experimental results were analyzed by application of Weibull distribution; the dynamics of decreasing process (parameter β) and the characteristic value of antioxidants activity (parameter η) were calculated (table 1). The third parameter of Weibull distribution, parameter of localization (γ) was equal to 0, that means there have not observed any minimal periods of storage time when the activity of antioxidants was stable.

The decreasing probability of reducing activity degree and radical scavenging activity of antioxidants during the food storage was calculated by two parameters Weibull (Weibull++) distribution. The probability of product failure ***F(τ)*** is related to days of storage ***(τ)*** as follows:

$$F(\tau)=1-e^{-\left(\frac{\tau}{\eta}\right)^{\beta}} \quad (2)$$

*where: **η** and **β** are the scale and shape parameters of Weibull distribution, respectively.*

Whereas that the meaning of parameter η "characteristically activity" of antioxidants is the storage time during $\tau=\eta$ days, from equation (2) we obtaine:

$$F(\tau)=1-e^{-\left(\frac{\eta}{\eta}\right)^{\beta}}=1-e^{-(1)}=1-0.368=0.632 \quad (3)$$

Parameter η characterized the duration of storage when the antioxidants activity has been decreased by 63.2% from initial activity 100%. Results presented in table 1 show that antioxidants in juice from plums and chokeberries were the most stable according to reducing activity. The loss of reducing activity by 63.2% was fixed after 105 days of storage, but the same decreasing index of radical scavenging activity was obtained just only after 184 days.

The antioxidants in sauce from plums and chokeberries demonstrated the sufficient stability of radical scavenging activity. Activity loss by 63.2% was determined after 254 storage days, at the same time the reducing activity decreased during 86 days. There was observed that the diminution of reducing activity and loss of radical scavenging activity of food antioxidants had different kinetics.

To mention, that the speed of decreasing the reducing activity was bigger than the radical scavenging activity. Using the parameters from table1 the relationship between reducing activity and radical scavenging activity was calculated.

Table 1

Weibull distribution parameters of antioxidants activity

Food	Parameters of Weibull distribution			
	Reducing activity (K) of antioxidants		Radical scavenging activity (RSA) of antioxidants	
	β	η	β	η
Juice from plums (JP)	0.65	61.59	0.91	109.9
Juice from plums and chokeberries (JPC)	0.78	105.5	1.0	184.36
Sauce from plums and chokeberries (SPC)	0.82	86.72	2.45	254.58

Figures 3, 4 and 5 show the relationship between reducing activity and radical scavenging activity of antioxidants in tested food during the storage. In juice from plums the relationship between reducing activity and radical scavenging activity had the exponential correlation with coefficient equal to 0.98. The function of this correlation is (4):

$$RSA = 7{,}94 \; (\exp 0{,}027 \; K) \qquad (4)$$

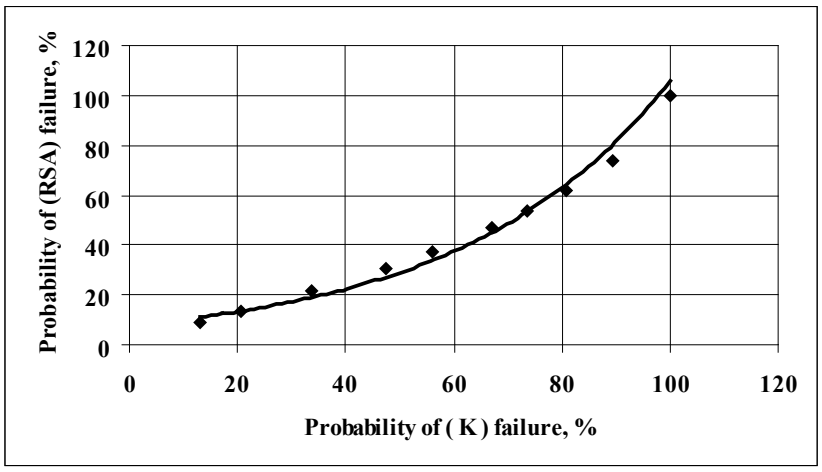

Fig. 3. Correlation (r^2=0.98) between probabilities of reducing activity (K) and radical scavenging activity (RSA) failure of antioxidants in juice from plums

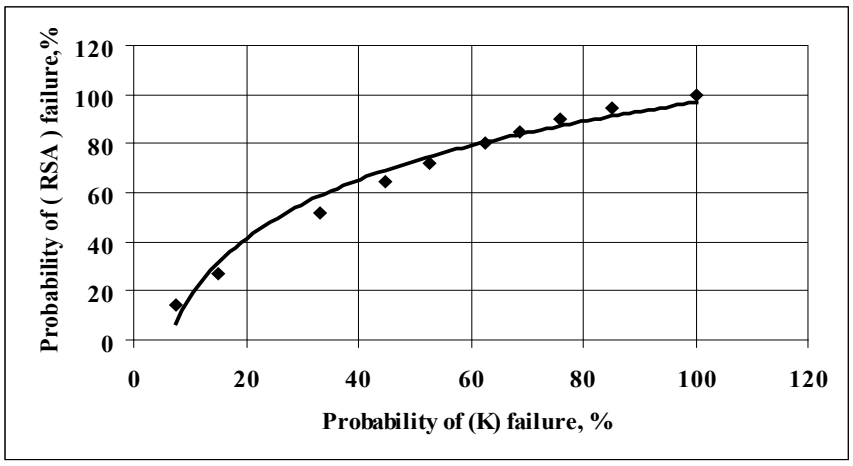

Fig. 4. Correlation (r^2=0.97) between probabilities of reducing activity (K) and radical scavenging activity (RSA) failures of antioxidants in juice from plums and chokeberries

The decreasing of antioxidants activities in juice from plums and chokeberries and sauce from plums and chokeberries carried the character of logarithmic dependence of reducing activity on radical scavenging activity with correlation coefficients 0.94-0.97.

In composition of juice from plums and chokeberries RSA = 34.4 Ln (K) – 61.8 (5)

In composition of sauce from plums and chokeberries RSA = 30.2 Ln (K) – 27.4 (6)

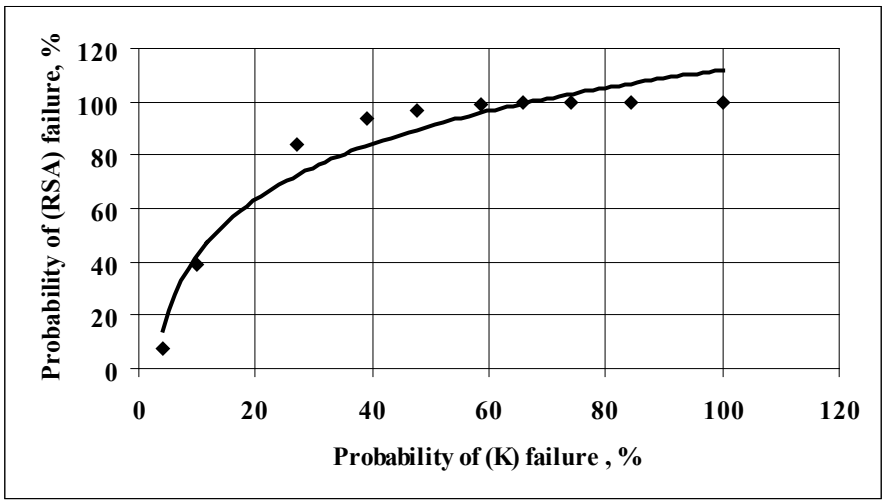

Fig. 5. Correlation (r^2=0.94) between probabilities of reducing activity (K) and radical scavenging activity (RSA) failures of antioxidants in sauce from plums and chokeberries

Conclusion

Thus, the reducing and radical scavenging capacities of antioxidants in plum food have a functional relationship with high coefficients of correlation r^2= 0.94-0.98. The differences of speed of reducing activity and radical scavenging activity degradation reflect the diverse mechanisms of oxido-reduction processes and reactions of free radical inactivation *in vitro*, which depend on antioxidants composition in food.

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