MATHEMATICAL ASPECTS REGARDING THE POSSIBILITY OF ASSESSING THE REDUCING CAPACITY OF SOME VEGETAL PRODUCTS

ASPECTE MATEMATICE PRIVIND POSIBILITATEA EVALUĂRII CAPACITĂȚII REDUCĂTOARE A UNOR PRODUSE VEGETALE

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Abstract: *In some studies regarding protection properties of some vegetal products, significant linking relations (correlations) have been observed between the position of one stability point and the series of some primary indicators of reducing capacity of vegetal sample. The measured variable is decolouration time in some redox reactions that lead to the colour change of some substances with oxidant character in the presence of analyzed vegetal samples. These aspects lead to new hypotheses regarding the possibility of promoting some numerical indicators of reducing character of different substances which, also, have antioxidant potential.*

Rezumat: *Au fost remarcate relaţii semnificative de legătură între poziţia unui punct de stabilitate şi indicatori primari ai puterii reducătoare a unor probe vegetale analizate. Variabila măsurată este timpul de decolorare în cadrul unor reacţii ce conduc la modificarea culorii unor substanţe cu caracter oxidant în prezenţa probelor vegetale analizate (în cantităţi iniţial fixate), propus astfel ca un indicator primar al puterii reducătoare a acestora. Utilizarea acestuia nu mai este de actualitate datorită interpretărilor subiective pe care le oferă. Totuşi, corelaţiile amintite conduc la noi ipoteze privind posibilitatea promovării unor indicatori numerici ai activităţii antioxidante totale a diverse substanţe.*

Key words: *mathematical model, reducing substances, antioxidant substance, vegetal produce*
Cuvinte cheie: *model matematic, capacitate reducătoare, substanţe antioxidante, produse vegetale*

INTRODUCTION

The vegetable products are characterized by a substantial content of reductive substances, representing an important supply source for the organism. Most of the reactions in which the ascorbic acid is involved are oxidoreduction processes which provide a complete protection process. In this paper there has been studied the reductive power of some sorts of natural fruit juices correlated with an ascorbic acid standard solution (vitamin C). [1, 2, 3]. The aim is to observe the bleaching time of a $KMnO_4$ 0,1N solution in an acid environment, within a redox reaction and in the presence of some vegetal samples to be analyzed. The statistic interpretation of the experimental data is based on a mathematic model which permits the determination of a “stability point” [13], that is a point in the vicinity of which a "cause” change produces an “effect” change of the same dimensions. There have been reported results regarding the reductive power analysis for some vegetal samples induced by the bleaching power of a $KMnO_4$ solution, by using as parameter the time of bleaching. This permits the initialization of the use of a new indicator, the RPBT (reductive power – bleaching point).This indicator represents the proportion of the reverted bleaching time averages (x/y) and gives information about the redox character of the active substances to be found in the vegetal material, substances which in most of the cases have a high antioxidant capacity.

The statistic interpretation of the experimental data is based on a mathematic model which permits the determination of a „stability point”, that is a point in the vicinity of which a

„cause" change produces an „effect" change of the same dimensions. For this purpose there has been used the Wilcoxon test and the Pearson correlation coefficient.

Most of the reactions in which the ascorbic acid is involved are oxidoreduction processes which provide a complex protection process. By taking into account the role of some reductive substances as bioantioxidants in sanogenesis and in the prophylaxis of many diseases and the fact that they are to be found mainly in vegetal materials, for the present paper there has been chosen the study of some natural fruit juices: pear, apple, orange and kiwi. There has been studied the reductive power of some sorts of natural fruit juices correlated with an ascorbic acid standard solution (vitamin C).

MATERIALS AND METHODS

The study of the reductive power some natural fruit juices have has been done by means of a analysis method which permits a qualitative characterization of the alimentary products having different contents of substances with reductive character. The method consists in determining the bleaching rate of a $KMnO_4$ 0,01N solution in an acid environment which also contains the vegetal sample, by following the below described procedure:

- Into an Erlenmeyer glass are introduced 10 ml $KMnO_4$ 0,01N solution (fresh prepared), 8 ml distilled water, 1 ml H_2SO_4 20% solution and 1 ml fruit juice. There has been followed the bleaching time of the violet $KMnO_4$ solution at 20°C.

The reductive power of the analyzed sample is reversed proportional with the bleaching time of the $KMnO_4$ solution.

In the same time, the reductive power of the analyzed fruit juices has been referred to a ascorbic acid reference, 1% solution, the last being an important antioxidant.

In this way there has been analyzed the reductive power of some vegetal samples and of an ascorbic acid reference solution reported to the bleaching power of a KMnO4 solution by using as parameter the bleaching time, which permits to initialize the use of a new indicator, the RPBT (reductive power – bleaching time). This indicator represents the average of the bleaching times reversed value ration $\bar{x}/\bar{y}$ (vegetal and reference sample).

The experimental data statistic studies consist in:

1. Determining a "stability point" [13] in the vicinity of which a „cause" change produces an „effect" change of the same dimensions.

2. There will be analyzed the reductive power of a vegetal sample, which will be evaluated according to a reference substance (1% ascorbic acid solution, 1:5 dilution) about which clear information are known. Taking into consideration the reverse proportion relations between the bleaching times and the reductive power of the samples to be analyzed, there will be proposed as reductive power value indicator the reverse ratio *1/t* of the bleaching time. [11,12]. The procedure will be as follows: there will be determined the bleaching times for a sample to be analyzed according to the used dilutions, and the results will be compared with the similar values of the reference solution. For this purpose there will be used the statistic Wilcoxon test. If the differences are significant, we will mark with x_i and y_i the reductive power of the analyzed samples respectively of the reference sample (where „i" represents the index corresponding to the used dilution) and then calculate the average ratio for the two series, $\bar{x}/\bar{y}$. This ratio may become an indicator we name RPBT and gives information about the redox character of the active substances to be found in the vegetal material, substances which most of the time have a high antioxidant capacity.

If the result of Wilcoxon test indicates insignificant differences, we can not express strict conclusions regarding to values comparison for the analyzed interval. However, in this case we can use the x/y ratio described above.

The study continues with interpretations regarding the values obtained for different analyzed samples (apple juice, pear juice, orange juice, kiwi juice, lemon juice).

RESULTS AND DISCUSSIONS

The working will be presented in detail only for the sample of pear juice, the other experiments being similar and in the end all the results will be presented.

The experiment results are given in the table below.

Table 1

Experimental data corresponding to the bleaching time variation for the $KMnO_4$ 0,01 N solution according to the volume of the analyzed sample (pear juice)

Added juice volume (ml)	Bleaching time at 20^o C (s)
1	160
2	71
3	21
5	8

In the given situation there have been obtained the coefficients a = 189,059 and b= 1,913 of the regression function and the stability point A (7.55 , 3.94) (figure 1).

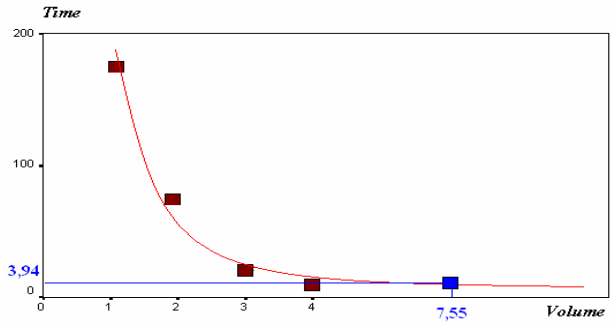

Figure 1. Graphic representation of the experimental data (pear juice)

There has been generated the following table, which contains the images through the regression function (theoretical) for a number of 19 values of the analyzed pear juice sample volumes.

Table 2

Generated results (by means of the regression function) corresponding to the bleaching time variation for the $KMnO_4$ 0,01 N solution according to the volume of the analyzed sample (pear juice)

Sample volume (mL)	**Time (s)**	**Sample volume (mL)**	**Time (s)**
1	189.059	6	6.137535
1.5	87.04319	6.5	5.266161
2	50.20269	7	4.570091
2.5	32.75956	7.5	4.005024
3	23.11343	8	3.539861
3.5	17.21057	8.5	3.152238
4	13.33081	9	2.825735
4.5	10.64147	9.5	2.548074
5	8.698968	10	2.309922
5.5	7.249091		

The same procedure has been also used for a 1% ascorbic acid reference solution, dilution 1:6.

Table 3

Experimental data corresponding to the bleaching time variation for the $KMnO_4$ 0,01 N solution according to the 1% ascorbic acid reference solution volume, dilution 1:6

Sample volume (mL)	**Time (s)**
2	410
3	219
5	5

The equation of the regression curve (power) is: $y = 20243{,}9 \cdot x^{-4{,}9195}$ and the generated table is the following.

Table 4

The generated results (through the regression function) corresponding to the bleaching time variation of the $KMnO_4$ 0.01 N solution according to the volume of the 1% ascorbic acid reference solution, dilution 1:6

Vitamin C volume C (mL)	**Time (s)**	**Vitamin C volume (mL)**	**Time (s)**
1	20243.9	6	3
1.5	2754.3	6.5	2
2	668.9	7	1.4
2.5	223.1	7.5	1
3	91	8	0.7
3.5	42.6	8.5	0.5
4	22.1	9	0.4
4.5	12.3	9.5	0.3
5	7.3	10	0.2
5.5	4.6		

The **Wilcoxon** test will continue to be used in order to make a statistic decision regarding the existence or non-existence of some significant differences between the bleaching time values of the 1% ascorbic acid reference solution and the analyzed sample (pear juice). The following table is obtained:

Table 5

Bleaching time variation for the $KMnO_4$ 0,01 N solution according to the volumes of the analyzed sample (pear juice) and the 1% ascorbic acid reference sample, dilution 1:6

No.	T_{sample}	$t_{vitamin\ C}$
1	189.059	20243.9
2	87.04319	2754.3
3	50.20269	668.9
4	32.75956	223.1
5	23.11343	91
6	17.21057	42.6
7	13.33081	22.1
8	10.64147	12.3
9	8.698968	7.3
10	7.249091	4.6
11	6.137535	3
12	5.266161	2
13	4.570091	1.4
14	4.005024	1
15	3.539861	0.7
16	3.152238	0.5
17	2.825735	0.4
18	2.548074	0.3
19	2.309922	0.2

The values corresponding to the Wilcoxon test have been calculated, and the processed data are presented in the table below.

Table 6

Experimental data processing given in Table 5, by using the Wilcoxon statistic test

Ctr. No.	**Evaluation 1** x_i	**Evaluation 2** y_i	**Differences** $x_i - y_i$	**Difference module** $\lvert x_i - y_i \rvert$	**Difference rang**	**Difference sign**
1	189.059	20243.9	-20054.8	20054.8	1	-
2	87.04319	2754.3	-2667.26	2667.26	2	-
…	…	…	…	…	…	…
18	2.548074	0.3	2.248074	2.248074	18	+
19	2.309922	0.2	2.109922	2.109922	19	+
				T (-) = 36 T (+) = 154 Tc = 46		

After using the Wilcon test we notice the following situation:

T (-) = 36, T (+) = 154, Tc = 46 for N = 19 *(α = 5%)*

We notice that the lowest value between *T (+)* and *T (-)* is *T(-) = 36*, this representing the result of the Wilcoxon test, and its signification level is determined by comparing this value to a critical value obtained from the special table corresponding to the test. For *N=19* the critical value is *Tc = 46*.

But *T (-) <Tc*, so that we can reject the null hypothesis which means that there are significant differences between the times corresponding to the reference sample and the times corresponding to the analyzed sample, the bleaching time values corresponding to the pear juice being higher than those of the 1% ascorbic acid reference solution, dilution 1:6. In conclusion, the reductive power of the sample to be analyzed is inferior to that of the reference solution.

Table 7

The reversed values of the bleaching times (reductive power) and their ratio

Ctr. No.	Reductive power (sample to be analyzed) x_i	Reductive power (reference sample) y_i	x_i / y_i
1	0.005289	4.93976E-05	107.0772
2	0.011489	0.000363069	31.64291
…	…	…	…
18	0.392453	3.333333333	0.117736
19	0.432915	5	0.086583

In order to compare we can use the graphic below.

The average values are:

$$\bar{x} = 0{,}1678\ ,\ \bar{y} = 0{,}9121$$

and the ratio between them:

$$\frac{\bar{x}}{\bar{y}} = 0.184106 \Leftrightarrow \frac{\bar{y}}{\bar{x}} = 5{,}4326$$

So, the average reductive power of the 1% ascorbic acid solution, dilution 1:6. is of 5,4326 or higher than that of the pear juice sample.

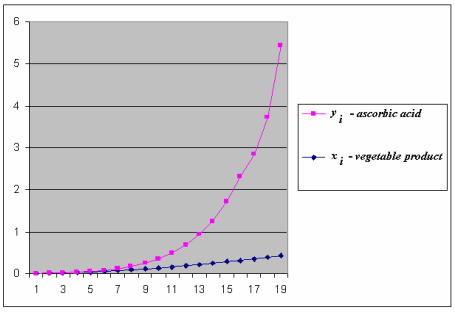

Figure 2. The variation of the reductive power (bleaching time inverse values for the $KMnO_4$ 0.01 N solution) when using different dilutions for the analyzed sample (pear juice), respectively the reference solution

The intensity of the relation between the bleaching time of the $KMnO_4$ 0.01 N solution in the case of the analyzed sample and of the reference solution is to be determined by using the correlation coefficient (Pearson). Its value is ***0.872***. So the bleaching time decrease concurrently with the increase in volume of the analyzed sample is strongly correlated with the similar results obtained for the reference solution (figure 3). Evidently the same samples (pear juice and 1% ascorbic acid reference solution) action similar from the point of view of the reductive character variation and from the Wilcoxon test there can be noticed that, in the case of the analyzed sample, the bleaching time is higher.

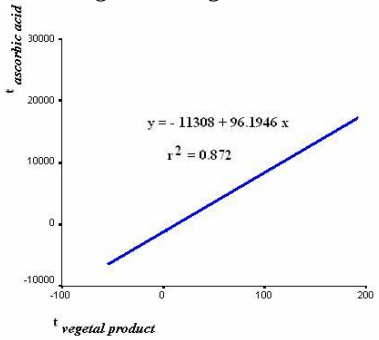

Figure 3. The correlation of the data series corresponding to the bleaching time of the $KMnO_4$ 0.01 N solution for the analyzed sample and for the 1% ascorbic acid reference solution

The final results for all the other analyzed vegetal samples are given in the table below.

Table 8

The final results for all analyzed vegetal samples

Analyzed sample	$f(x)=a\cdot x^{-b};a,b>0$		Stability point	$\bar{x}$	$\bar{y}$	$\bar{x}/\bar{y}$
	a	**b**				
Kiwi	56.729	2.7868	A(3.80.1.36)	3.2895	0.9121	**3.60**
Apples	233.967	2.9778	A(5.18. 1.7)	1.3802	0.9121	**1.52**
Oranges (fresh)	167.376	2.3623	A(5.92.2.50)	0.47	0.9121	**0.51***
Oranges (4 days refrigeration)	165.571	2.2381	A(6.21.2.77)	0.37	0.9121	**0.40***
Oranges (8 days refrigeration)	164.929	2.1371	A(6.48.3.03)	0.30	0.9121	**0.33***
Oranges (16 days refrigeration)	170.448	2.0523	A(6.81.3.32)	0.24	0.9121	**0.26***
Pears	189.059	1.913	A(7.55.3.94)	0.1678	0.9121	**0.1841**

*Insignificant differences after applying the Wilcoxon test.

CONCLUSIONS

1. There can be defined a RPBT (reductive power – bleaching time) indicator which represents the average of the bleaching times reversed values ration $\bar{x}/\bar{y}$ (vegetal sample and reference sample). The reductive power is higher is the bleaching time of the $KMnO_4$ 0,01N solution is shorter.

2. Taking into consideration the close to maximum values of the correlation coefficient between the bleaching times corresponding to the analyzed vegetal samples and those of the 1% ascorbic acid reference solution, there can be concluded that both sample categories (that to be analyzed and the reference one) have a similar action way when it comes to the reductive character.

3. From the analyzed vegetal samples the kiwi juice has a 3,6 times higher reductive power than the 1% ascorbic acid reference solution, being followed by the apple juice, which has a 1.52 reductive power value. These are followed by the orange and pear juice, which are inferior in terms of reductive power, as compared to the 1% ascorbic acid reference solution.

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