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DETERMINATION OF THE MINERAL PROFILE AND PREDICTION OF THE FRUIT CONTENT IN SOUR CHERRY JUICE

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ABSTRACT: *The mineral profile of sour cherry juice was investigated to detect possible adulterations and especially to estimate fruit content in ready to drink beverages. For this purpose, sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), and phosphorus (P) content of 103 sour cherry juice samples, collected from different companies in three different years (2009, 2010, 2011), were determined. It was found that the sour cherry juice at 13.5 ^{0} brix included 8-92 mg/kg of Na, 1189- 2455 mg/kg of K, 35-198 mg/kg of Ca, 75-160 mg/kg of Mg and 124-180 mg/kg of P. Step-wise regression was applied to determine an appropriate model for estimating the fruit content in sour cherry juice. The equation with two parameters (y=5.881+0.5453 P+0.0058 K) was determined to be the best fitting model.*

KEYWORDS: Authenticity Control, Fruit Content, Mineral Profile, Sour Cherry Juice, Step-Wise Regression

INTRODUCTION

Fruit juice consumption has exhibited a significant increase from year to year, not only in Turkey but worldwide. One of the supporting factors for such an increase is undoubtedly the developing consciousness of healthy nutrition. Fruit juice is an important part of a healthy diet, due to its richness in antioxidants, moderate energy level, and high potassium and low sodium contents (Landon, 2006; Ekşi, 2006; Howlett, 2008).

The increase in fruit juice consumption contributes to healthy nutrition. However, it also attracts adulteration. The most frequently encountered adulteration types are low fruit content and the addition of foreign fruit juice. Fruit content is expressed as the percentage (% by volume) of fruit juice and/or puree in the finished product (Anonymous, 2001). While qualitative proof of foreign fruit addition is satisfactory, fruit content should also be quantitatively determined, which is not as straightforward.

Studies in the literature (Schröder, 1954; Benk, 1960; Benk, 1968; Koch & Hess, 1971; Wallrauch, 1971; Benk & Cutka, 1972; Hills, 1974) have mainly been focused on determining the fruit content or dilution ratio using a single criterion. Due to the disadvantages of fruit content estimations made using a single criterion, subsequent studies have been focused on estimating fruit content using multiple criteria. This integrated approach has been implemented in 2 different ways. The first approach is to estimate fruit content by means of multiple regression analysis, which was previously recommended by Steiner (1949). The other approach involves determining reference values for each fruit juice and then assessing fruit juice authenticity in accordance with those reference guidelines. The reference guidelines define what is considered to be an acceptable juice (AIJN, 1990) and consist of several guide values for evaluating juice identity and authenticity.

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The first study on determining guide values for sour cherry juice was published by Ekşi, Reicheneder & Kieninger (1980). According to the findings of that study, sour cherry juice contains 1830-3630 mg/L potassium (K), 139-182 mg/L calcium (Ca), 123-135 mg/L magnesium (Mg) and 153-262 mg/L phosphorus (P). Subsequently, several studies (Erbaş, 1981; Velioğlu & Yıldız, 1996) on the chemical composition of sour cherry juice produced from sour cherry varieties in Turkey have been performed. In a study conducted in Hungary (Toth-Markus, Boross & Molnar, 1993), some of the components of sour cherry juice samples produced from four different varieties were determined. In another study carried out by Bonerz, Würth, Dietrich & Will (2007), the chemical compositions of sour cherry juices were determined. According to the findings, the potassium concentration varies between 2140-3686 mg/L, while the calcium and magnesium concentrations vary between 267-368 mg/L and 148-172 mg/L, respectively.

According to the guide values compiled by the Association of the Industry of Juice and Nectars (AIJN) on the basis of research findings, sour cherry juice with a brix degree of 13.5, contains a maximum of 30 mg/kg Na, 1600-3500 mg/kg K, 80-240 mg/kg Ca, 80-120 mg/kg Mg and 150- 280 mg/kg P (AIJN, 1990). These limits are undoubtedly an important resource for assessing the existence of foreign fruit juice or detecting whether juice has been diluted with water. However, this information is not sufficient for the quantitative prediction of fruit content.

In addition to the reference guidelines, other studies (Sawyer, 1963; Lifshitz & Stepak, 1971; Lifshitz, Stepak & Brown, 1971; Goodall & Scholey, 1975; Prehn, Bosch & Nehring, 1977; Ekşi, 1981; Ooghe, 1990; Wallrauch, 1995; Ekşi & Özhamamcı, 2009;.Ekşi & Erol, 2010) on the determination of fruit content by regression analysis based on multiple components have been performed.

In any case, the analytical parameters selected for fruit content prediction by multiple regression analysis should naturally vary within a very narrow range, be stable during processing and storage, and the addition of fruit into fruit juice should be out of the question under normal conditions. According to different studies, magnesium and potassium are the two fruit juice components having the lowest coefficients of variation (Ekşi, 1980; Erbaş, 1981; Doğan, 1985). It is also known that these two components are stable during food processing and storage (Skorski, 1997).

The aim of this research was to reveal the mineral profile of sour cherry juice, which is widely consumed in Turkey, and to develop a model for estimating fruit content in ready-to-drink sour cherry juice and similar beverages by means of multivariate regression analysis based on mineral components.

MATERIALS AND METHODS

MATERIAL

The research material consisted of sour cherry juice concentrate (SCJC) samples used for the production of sour cherry juice and similar beverages.

SCJC samples were provided from 5 different companies in Turkey, namely Aroma, Dimes, Etap, Limkon and Penkon in three different years (2009, 2010 and 2011). The number of samples analysed was 22 in 2009, 43 in 2010 and 38 in 2011, for a total of 103 samples. The processing periods for the samples were 2^{nd} June – 1^{st} September in 2009, 9^{th} June – 18^{th} August in 2010 and 13^{th} June – 28^{th} August in 2011.

Because the minimum brix degree is defined as 13.5 for sour cherry juice obtained from concentrate in the reference guideline for sour cherry juice (AIJN, 1990), SCJC samples were diluted to 13.5^{o} Bx for analysis, and the results are expressed on the basis of 13.5^{o}Bx.

Methods

The total soluble solids (Brix degree) and sodium, potassium, calcium, magnesium and phosphorus contents of sour cherry juices were determined. Analyses were performed in triplicate and the applied methods are described below.

Determination of The Total Soluble Solids (Brix Degree)

The total soluble solids content was determined by means of the refractometric method recommended by the International Fruit Juice Union (IFU, 1991).

Determination of Mineral Compounds

Analyses of sodium, potassium, calcium and magnesium in fruit juice samples were performed using an atomic-absorption spectrophotometric method (IFU, 1984). For this purpose, samples diluted with ultra-pure water were filtered through ashless filter paper. Prior to analysis, the appropriate dilution factors for each fruit juice sample and each element were determined. Lanthanum (0.2-0.5%) was added to the last dilution for the analyses of Ca and Mg, and 0.1-0.4% caesium chloride was added to the last dilution for the analyses of K and Na.

A Shimadzu AA-7000 atomic absorption spectrophotometer (AAS) (Shimadzu, Kyoto, Japan) was used for measurements. Absorbance measurements were performed at a wavelength of 422.7 nm for Ca, 285.2 nm for Mg, 589.0 nm for Na and 766.5 nm for K. The amounts of minerals in fruit juice samples were calculated based on the absorbance values, calibration graphs for each element and dilution factors.

For the analysis of phosphorus, a spectrophotometric method based on measurement of the absorbance of the yellow colour formed by the reaction of this element with a molybdate-vanadate solution was applied (IFU, 1965). A Unicam UV2/UV Vis spectrophotometer was used for the absorbance measurements. The concentration of phosphorus in fruit juice samples was calculated based on the standard curve and dilution factor.

Statistical Analysis

The mineral content results of sour cherry juice were first corrected according to 13.5^{0} brix as mentioned in the AIJN reference guidelines, and then descriptive values such as the variation range, mean, standard deviation, coefficient of variation (CV) and confidence interval (CI) for each mineral, as well as the coefficients of correlation (R) for assessing the possible relationships between mineral materials were calculated.

For the most accurate estimation of fruit contents, the results were examined to derive multiple regression equations relating the mineral contents by step-wise regression analysis and coefficients of determination (Kesici & Kocabaş, 1998).

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RESULTS AND DISCUSSION

Mineral Profile of Sour Cherry Juice

Descriptive values for the mineral components of 103 different sour cherry juice samples from 3 different years are given in Table 1.

Table 1. Descriptive values for the mineral components of sour cherry juice (13.5° brix) (2009-2011)

Mineral (mg/kg)	Variation Range	Mean ($\bar{x}$)	Standard Deviation (±SD)	Coefficient of Variation (CV) (%)
Na	8-92	21	10	48
K	1189-2455	1724	302	18
Ca	35-198	107	36	34
Mg	75-160	106	18	17
P	124-180	151	14	9

According to the findings in Table 1, sour cherry juice contains 1189- 2455 mg/kg K, 35- 198 mg/kg Ca, 75- 160 mg/kg Mg, 124- 180 mg/kg P and 8- 92 mg/kg Na. When these ranges are compared with the AIJN reference guidelines (Table 2), it is clear that the amounts of Na and Mg exceed the maximum limit and that the amounts of K, Ca and P exceed the minimum limit. According to the findings of Ekşi et al. (1980), the amounts of K, Ca and Mg exceed the minimum limit and the amounts of Ca and P exceed the maximum limit.

P has the lowest natural variability of 9% in sour cherry juice, followed by Mg and K, with 17% and 18% variability, respectively according to the coefficients of variation (CV) (Table 1). On the other hand, the natural variabilities of Na (48%) and Ca (34%) are considerably higher.

The 99% confidence intervals (CI) for the mineral contents of sour cherry juice samples were also calculated. They are displayed in comparison with the reference guidelines (AIJN, 1990) in Table 2.

Table 2. Variation range (VR) and confidence interval (CI) for the mineral components of sour cherry juice

Mineral (mg/kg)	VR	CI (99%)	Reference guideline (AIJN 1990)
Na	8- 92	18-23	< 30
K	1189- 2455	1646-1803	1600-3500
Ca	35 - 198	97-116	80- 240
Mg	75 - 160	101-111	80- 120
P	124 - 180	148-155	150- 280

As seen in Table 2, based on the 99% confidence interval, all of the mineral components of sour cherry juice are in compliance with the reference guidelines (AIJN, 1990).

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Predictive Model For Fruit Content

Suitable calculation models for the prediction of fruit content including mineral components were researched using multiple regression analysis (Kesici & Kocabaş, 1998). For this purpose, the natural mineral components of fruit juice were assumed to be independent variables, and a step-wise regression analysis was applied to the findings.

The applied general-purpose regression equation is given below (1):

$$y= a+ b_1x_1 + b_2x_2+\ldots\ldots+b_nx_n \qquad (1)$$

In the above equation, y corresponds to the predicted value, x_1, x_2, etc. are independent variables, a is the regression constant and b_1, b_2, etc. are the coefficients of regression for each independent variable.

Na, which is one of the mineral components of fruit juice, was not taken into consideration as a prediction criterion due to its high relative variability. Therefore, the prediction of fruit content was carried out using 4 independent variables (P, K, Ca and Mg). When those variables are applied to equation (1), the following equation (2) is obtained:

$$y= a+ b_1P + b_2K + b_3Ca + b_4Mg \qquad (2)$$

By substituting fruit content (FC) with y in the above equation, a regression equation with 4 criteria (3) for fruit content prediction can be derived:

$$FC\ (\%)= a+ b_1P + b_2K + b_3Ca + b_4Mg \qquad (3)$$

In the above equation, FC corresponds to the fruit content (%); while P, K, Ca and Mg are the amounts of phosphorus, potassium, calcium and magnesium in fruit juice (as mg/kg), respectively, a is the regression constant and b_1, b_2, b_3 and b_4 are coefficients of regression for P, K, Ca and Mg, respectively.

A step-wise regression method was applied to estimate the fruit content in sour cherry juice by means of not only a regression equation with 4 criteria but also regression equations with 3, 2 and a single criterion to determine the most appropriate model. According to this method, a regression equation containing the 4 criteria is first determined for the prediction of fruit content prediction followed by the derivation of regression equations containing 3, 2 and a single criterion by excluding and including variables one at a time. The most appropriate model for each combination was chosen based on coefficients of determination (R^2).

R^2 reflects the correlation between the actual fruit content and the calculated value. Therefore, a higher R^2 and statistical significance level (p) for a model means that the prediction has a higher accuracy level. The applied method indicates the combination with the highest R^2 and eliminates the other combinations. Additionally, if an equation containing less variables has a higher R^2 than that of an equation with more variables and the difference is significant, the method prefers the equation with less variables.

Using this approach, fruit juice calculation models obtained by applying step-wise regression analysis to the mineral content of sour cherry juice (excluding Na) are given in Table 3.

Table 3. Appropriate calculation models for the fruit content of sour cherry juice

	Regression equation	R^2
(1)	FC% = 5.87+ 0.553 P + 0.0075 K -0.0023 Ca - 0.0367 Mg	92.3 ***
(2)	FC% = 5.881 + 0.5453 P + 0.0058 K	92.3***
(3)	FC% = 6.105 + 0.6090 P	92.0***

**** significant at p<0.001*

As seen above (Table 3), the coefficient of determination (R^2) for the regression equation using 4 criteria applied to the estimation of fruit content in sour cherry juice is 92.30 and it is statistically significant ($p<0.001$). The most accurate prediction with a single criterion can be made using the regression equation based on the amount of P (R^2=92.00, $p<0.001$). It was determined that the most relevant (R^2= 92.30, $p<0.001$) regression equation containing 2 criteria is the one based on the amounts of P and K.

As mentioned above, the possibility of misleading results from the model is higher in predictions based on a single variable. In addition because the difference between the coefficients of determination of regression equations with 4 and 2 criteria were insignificant, the most appropriate equation for the prediction of fruit content (FC) in sour cherry juice is the equation based on 2 criteria (P and K concentrations in mg/kg):

$$FC(\%)= 5.881 + 0.5453P + 0.0058\ K \qquad (4)$$

Likewise, the regression equation with 4 criteria based on the amounts of P, K, Ca and Mg Table 3) is also appropriate for this purpose.

Correlations Between Mineral Components

Correlations between the mineral components (except sodium) in sour cherry juice were calculated and are given in Table 4. Na was not taken into consideration in calculations because it is not used as a fruit content prediction criterion due to its high variability.

Table 4. Coefficients of correlation between the mineral components of sour cherry juice (R)

Mineral	K	Ca	Mg	P
K	1.000	0.410***	0.829***	0.327***
Ca		1.000	0.316***	0.199*
Mg			1.000	0.417***
P				1.000

**significant at p≤0.05, **significant at p≤0.01, ***significant at p≤0.001*

As seen in Table 4, all of the correlations between K, Ca, Mg and P are statistically significant. Only the coefficient of correlation (r) between Ca and P was significant at the level of $p\leq0.05$; whereas the coefficients of correlation between K and Ca, K and Mg, K and P, Ca and Mg, Ca and P, and Mg and P were significant at the level of $p\leq0.001$.

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The ratios between mineral components were also calculated, and their descriptive values are given in Table 5.

Table 5. Ratios between the mineral components of sour cherry juice (N=103)

Ratio	Variation Range	Mean(x-)	Standard Deviation (±SD)	Coefficient of Variation (CV) (%)
K/Ca	10.4- 65.8	18.3	8.5	46.7
K/Mg	11.5- 20.5	16.3	1.5	9.2
K/P	7.9- 17.1	11.5	2.0	17.4
Ca/Mg	0.2 - 1.5	1.0	0.3	30.7
P/Ca	0.7 - 4.2	1.6	0.6	40.1
P/Mg	0.9 - 1.9	1.5	0.2	14.5

The function of above-mentioned ratios are to indicate whether any variation in the natural mineral profile used for fruit content prediction occurs. In case of any decrease or increase in the natural amount of any element for any reason, the ratio between that element and the others will also vary and exceed the natural limits. Such variation may occur intentionally or unintentionally. If such variation occurs, the fruit content prediction results will be misleading. Therefore, prior to fruit content prediction, it should be determined if the ratios between mineral components are within the natural variation range.

It can be observed from the coefficients of variation in Table 5 that variations in the K/Mg, P/Mg and K/P ratios are lower in comparison with the others. Thus, it is easier to reveal a deviation from natural variation in the amounts of such minerals.

CONCLUSIONS

The natural mineral profile of sour cherry juice was investigated for the first time through a comprehensive sample analysis. The natural variation ranges of K, Ca, Mg and P were not in compliance with the reference guidelines for sour cherry juice published by AIJN (1990). These incompliances should be taken into consideration while updating the reference guidelines.

A model is recommended for fruit content prediction in ready-to-drink sour cherry juice and similar beverages. For this purpose, it is sufficient to determine the amounts of P and K (mg/kg) in the beverage in question and to apply these values to the recommended regression equation (FC% = 5.881 + 0.5453 P + 0.0058 K).

Prior to calculations, it should be determined if any manipulation in the natural amounts of these minerals exists by comparing the determined mineral amount and the natural variation range with the ratios between these minerals.

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