PIXE Elemental Analysis of White Soil Clarifier in Traditional Grape Syrup Production

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ABSTRACT: *The white soil is used as a clarifier, in the traditional preparation process of grape syrup, to reduce the acidity and deposit the suspended colloidal substances. Besides increasing the nutrients in grape syrup, the substances in white soil may also have side effects on the final product. In grape syrup production, heating the grape juice and soil mixture to the boiling point makes more soil absorption. Determining the chemical composition and the concentration of the used white soil is vital for producing a healthy product. In this study, white soil samples were collected from 10 areas commonly known as white soil excavation sources in Malayer City, Hamadan, Iran. The dry white soil samples were then prepared to be analyzed by the Proton-Induced X-ray Emission (PIXE) technique. Ca had the highest and Mg had the lowest value of concentration among the detected elements of Mg, Al, Si, S, K, Ca, Ti, Mn, and Fe in the collected samples. From the statistical analysis, it was revealed that the Ca content of the soil is significantly incompletely correlated with other detected elements. In addition, Ca, Si, and Al had a significant difference ($p < 0.001$) with other identified elements. The higher amount of Mn and Fe makes the darker color of the syrup while the higher content of Ca increases the transparency of the syrup color. The grape syrup made from the soil containing the highest level of Ca was tasty, more transparent, and light brown in color.*

KEYWORDS: *Elemental concentration; PIXE; White soil assessment; Grape syrup ingredients.*

INTRODUCTION

Dooshab in Persian or Pekmez in Turkish, which is translated into grape syrup, and is widely served as an individual food product or food complement in Iran, Turkey, and other neighboring countries. Flavored dairy dessert has been obtained with an optimum amount of grape syrup as a suitable source of vitamins, soluble fiber, antioxidants, amino acids, and a good source of natural sweets [1, 2]. The grape syrup could also be used as an appropriate replacement for sugar on the chemical and sensory properties of different types of cookies [3]. Due to the high average amount of energy (293 kcal/100 g), grape syrup is the source of a large amount of energy for different age groups, especially children and athletes [4]. Grape syrup, a concentrated and shelf-life-extended form of grape juice, is one of the most popular traditional food products in Eastern culture, is formed by boiling without

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the addition of sugar or other food additives after the acids are removed [5].

The grape syrup contains high amounts of glucose and fructose, besides valuable levels of minerals including Ca, Mg, K and Fe as well as organic acids such as tartaric and malic acids [13]. Due to high levels of carbohydrates mostly in the form of monosaccharides like glucose and fructose of grape syrup, it could easily pass into the blood without digestion which is nutritionally essential [14]. The mineral elements Ca, Mg, K, and Fe play an important role in the human body's metabolism [6]. Ca is the most abundant mineral in the body [7]. About 99% of the body Ca is found in the skeleton; the remainder is present in teeth, soft tissues and intercellular fluid [8]. Mg is one of the most important intercellular cations in the body. Approximately, all of the Mg is stored in soft tissues, muscles, bones, and just about 1% of total Mg is in serum and extracellular fluid [9]. Every organ in the body, especially the heart, muscles, and kidneys, needs Mg. Fe is an essential element for blood production. About 70% of the human body's iron is found in the red blood cells of blood called hemoglobin and in muscle cells called myoglobin [10]. Fe also is needed for proper immune function. When iron stores are exhausted, the condition is called iron depletion. Further decreases may be called iron-deficient erythropoiesis and still further decreases produce iron deficiency anemia [11]. If the body does not take these elements from diet enough, deficiency of them occurs and leads to some disorders in organs.

In the process of grape syrup production after washing and dehydration, various types of clarifiers (white soil, bentonite, and gelatin) are added to separate grape juice impurities [12-14]. In the traditional method of grape syrup production (Fig.), mostly the white soil known as soil syrup is added to the grape juice and the mixture is boiled and, after cooling, is filtered. To get the syrup, the filtered juice is boiled again and concentrated. The white soil lowers the acidity caused by naturally existing tartaric and malic acids by precipitating them as calcium tartrate and calcium malate [15].

The most important step in the grape syrup production is the white soil addition as an acid reduction [16]. Because, the used white soil can also add various mineral salts of K, Ca, Mg and Fe to the produced syrup; this can be very harmful to the human body and may cause kidney or liver disease [17]. Furthermore, the body's need for these nutrient elements is limited, and excess amounts of some of them may cause disturbance of the body's normal functioning [18]. So, soil usage in grape syrup production may cause other problems, such as high consumption of soil, high waste production, high costs, limitation of daily production, and low performance of the production line. Indeed, interest in soil quality and health has grown with the awareness that soil is vital to life on earth both in production of food and global ecosystems function and environmental stability.

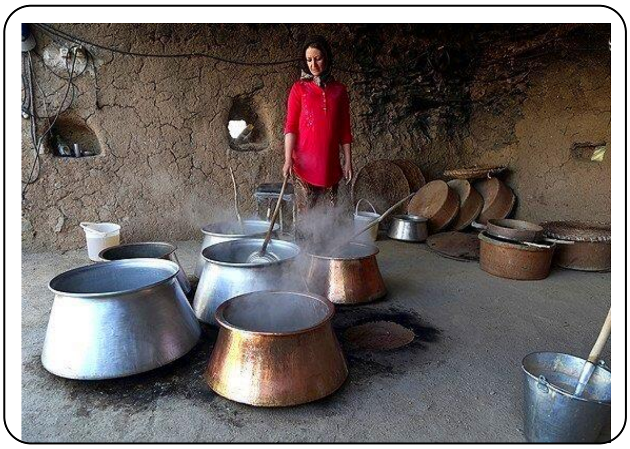

Fig. 1: A woman is preparing grape syrup, in Malayer, Iran [photo by IRNA news agency, news code: 83498082].

The effect of white soils collected from the mountains around Malayer county on the potentially toxic elements (Pb, Cd, As, Fe, Zn and Cu) content of the grape syrup is investigated [13]. Malayer is located in the vicinity of the industrial city of Arak, which the soil dust is its dominant atmospheric source pollution [19]. In this research, the composition and the amount of the elements contained in the white soil were directly determined, which is essential for producing healthy and nutritious grape syrup.

EXPERIMENTAL SECTION

Sample preparation

The white soil samples were collected from ten areas around Malayer city, Iran (Fig. 2) which people have dug previously for extraction of white soil. In order to prevent possible contamination from external sources and ensure that the sampling site is not affected by agricultural pesticides, about 15 cm of soil was removed for sampling.

The collected white soil samples were air-dried under laboratory conditions for two weeks, grounded and sieved with a 2 mm polyethylene sieve. The powdered samples were mixed with extra pure graphite (70:30 percent), and

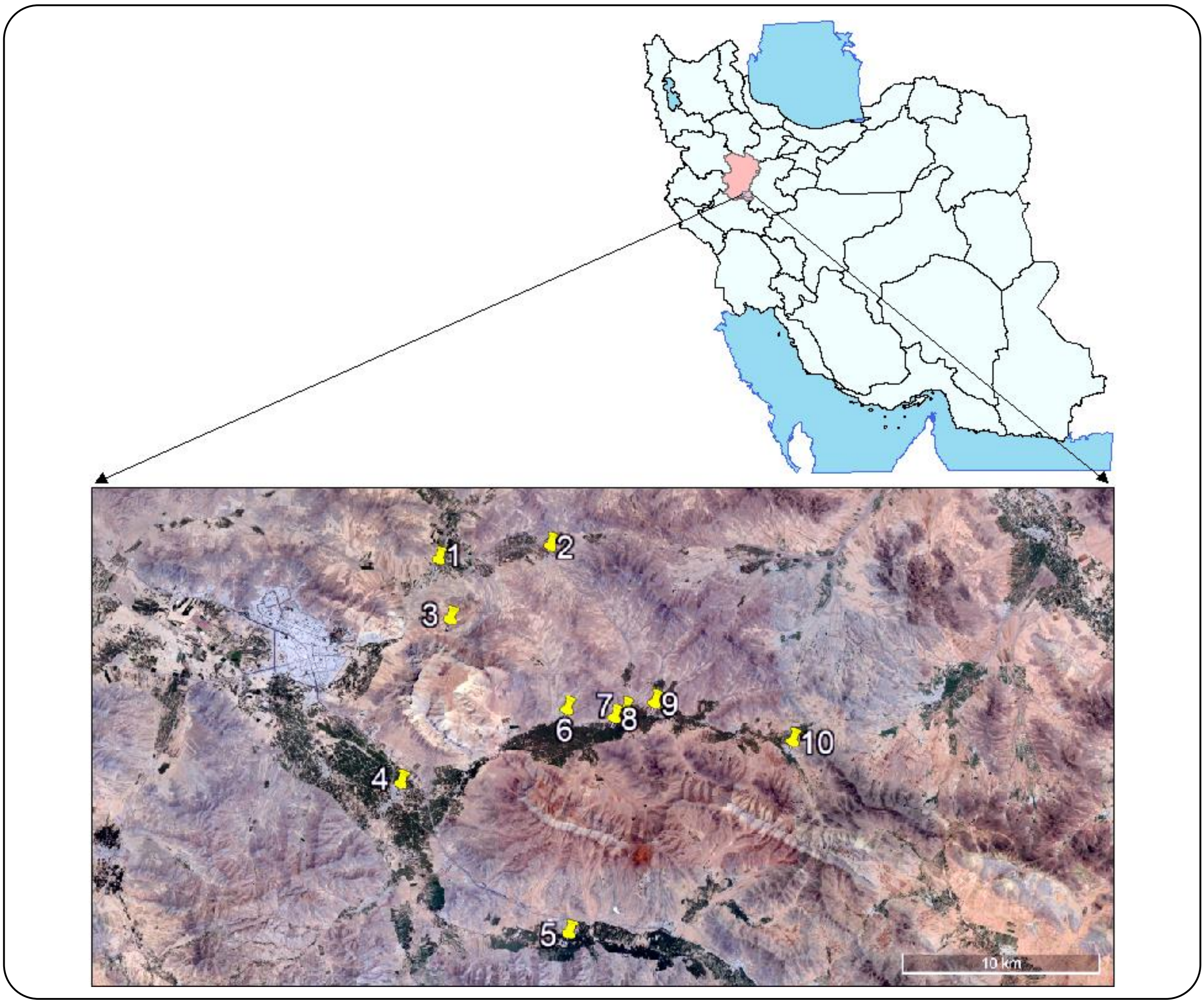

Fig. 1: Geographical locations of the collected white soil samples in Malayer, Iran.

then using a tabletop pelletizer (pressure 100–110 kg/cm^2), pellets with 1 mm in thickness and 10 mm in diameter were made. For investigating the effect of the addition of white soil on the quality of the grape syrup, the preparation process and the ingredients were the same in all prepared grape syrup except the addition of soil. The pH of each syrup was measured with HORIBA M-12 pH meter for pH determination.

PIXE measurement

The Particle Induced X-ray Emission (PIXE) technique has been successfully applied for thick and semi-thick soil sample analysis [20-22]. The PIXE technique has several advantages when a rapid and accurate elemental analysis of soil samples, mostly occurring for heavy metals in the soil matrix, with the detection limit in the ppm (µg/g). The PIXE analysis of the samples was performed by 2 MeV proton beams at the Van de Graaff accelerator in Tehran, Iran. All the measurements were carried out in vacuum (around 10^{-5} Torr) and the beam current was 1.5 nA. The characteristic X-Ray s emitted from the samples were detected by Si(Li) detector at an angle of 135° with respect to the beam direction. The resolution of the detector was 145 eV at the energy of 5.9 keV for Mn Kα. The beam size at the target position was 2 mm in diameter. The PIXE spectra were fitted by GUPIX software to extract the elemental concentrations [23]. The GUPIX software utilizes the fundamental parameter method for the quantitative elemental concentration. For a known experimental geometry, the sample composition can be

Table 1: Concentration and standard error of detected elements from collected samples at ten areas (μg/g).

Area #	Mg	Al	Si	S	K	Ca	Ti	Mn	Fe
1	15014 ± 633	51832 ± 642	122931 ± 676	705 ± 146	6514 ± 128	405736 ± 811	3008 ± 161	224 ± 67	17783 ± 304
2	18545 ± 673	44253 ± 623	140322 ± 729	830 ± 154	4542 ± 122	390343 ± 819	1174 ± 141	-	14371 ± 275
3	7547 ± 638	33821 ± 639	68167 ± 593	502 ± 150	2202 ± 118	534364 ± 1068	1873 ± 169	258 ± 81	13300 ± 340
4	23359 ± 890	53526 ± 770	111004 ± 688	1273 ± 169	3358 ± 131	415708 ± 956	1921 ± 139	-	13195 ± 300
5	26754 ± 850	63382 ± 773	169555 ± 813	825 ± 129	8853 ± 163	288618 ± 750	2965 ± 131	552 ± 77	29297 ± 386
6	24140 ± 794	51390 ± 693	124315 ± 658	727 ± 132	4727 ± 126	396776 ± 833	1847 ± 125	270 ± 65	16693 ± 300
7	17071 ± 679	57446 ± 660	114655 ± 584	732 ± 121	5538 ± 125	412363 ± 783	2099 ± 122	208 ± 72	17366 ± 283
8	13117 ± 699	45345 ± 657	93752 ± 628	822 ± 155	3947 ± 126	469556 ± 1079	1494 ± 137	221 ± 80	14745 ± 312
9	10108 ± 627	53429 ± 662	124351 ± 634	1229 ± 139	5630 ± 130	409129 ± 818	1534 ± 116	1198 ± 103	16543 ± 297
10	8240 ± 570	53352 ± 634	106897 ± 566	878 ± 96	4852 ± 122	436532 ± 829	1866 ± 120	1254 ± 106	20060 ± 316

-Element was not found in the sample or it was near to the detection limit.

calculated from the measured intensities of the X-Ray lines by using known physical parameters like X-Ray ionization cross-section, mass attenuation coefficient and fluorescent yields. To validate the accuracy of the PIXE method for soil sample measuring, 150 mg from each of the reference materials powder of IAEA-SOIL7 and IAEA-SL1 were measured. The powdered references material were oven-dried at 60 °C, mixed with extra pure graphite (70:30 percent), and then using a tabletop pelletizer (pressure 100–110 kg/cm2) pellets with 1mm in thickness and 10 mm in diameter were made and accuracy of the method was obtained better than 5%.

RESULTS AND DISCUSSION

The major elements of Mg, Al, Si, S, K, Ca, Ti, Mn, and Fe were found (Table) in the collected sample from the most used ten areas for soil collecting in the process of grape syrup production. The mean concentration of the detected elements was decreased in the order of Ca > Si > Al > Fe > Mg > K > Ti > S > Mn although Mn was not found in the samples collected from the regions 2 and 4 in Fig. 1. The white soil collected at region # 3 has the highest amount of Ca. The average abundances of white soil elements collected in the Malayer county were Ca (66%), Si (18%) and, Al (8%), and the other elements (8%). From the chemical analysis of the samples, it was found that these oxide elements appear in the compound form of MgO, Al_2O_3, SiO_2, SO_3, K_2O, $CaCO_3$, TiO_2, Fe_2O_3 respectively.

Pearson's correlation coefficient (Table 1) was used to understand whether there is a direct relationship between the soil elements collected at different regions. The elements with significant correlation have an asterisk label. Pearson's product-moment correlation coefficient, ρ, measures the linear relations between the two variables [24], the value of correlation coefficients lies between -1 and +1 values. The value close to 1 means the correlation of two elements is complete while the value close to -1 means the correlation of two elements is incomplete. Accordingly, the correlation value near to 0 indicates that there is no linear correlation between the two elements. Ca had a significant incomplete correlation with most of the detected elements while had a moderate incomplete with Ti and Mn. The negative relationship indicates that as Ca content increases, the other element values decrease. In other words, collecting the white soil in a region with the high level of Ca is associated with the low level of other identified elements. The element of Si had a significant complete correlation with K, and Fe and had a moderate complete correlation with other elements (except Ca). The element of Al also had a significant complete correlation with elements of Si, K and, Fe.

Mean concentration values, standard deviation, and p-value were used to express statistically meaningful differences between the identified elements using OriginPro software (version 200. 8.9). The values of $p < 0.001$, $p < 0.01$ and $p < 0.05$ indicate respectively a significant, moderate and weak difference between elemental content.

The elements of Ca, Si and Al, the constituents of $CaCO_3$ (Calcium carbonate), SiO_2 (Silica) and Al_2O_3

Table 1. Pearson correlation between the detected elements in white soil samples.

	Mg	Al	Si	S	K	Ca	Ti	Mn	Fe
Mg	1.00								
Al	0.55	1.00							
Si	0.69*	0.73*	1.00						
S	0.16	0.41	0.25	1.00					
K	0.44	0.80*	0.85*	0.05	1.00				
Ca	-0.75*	-0.83*	-0.98*	-0.28	-0.87*	1.00			
Ti	0.32	0.51	0.36	-0.24	0.66*	-0.45	1.00		
Mn	-0.37	0.27	0.17	0.75*	0.15	-0.14	-0.26	1.00	
Fe	0.38	0.71*	0.70*	-0.07	0.88*	-0.75*	0.66*	0.23	1.00

** Correlation is significant at the 0.05 level.*

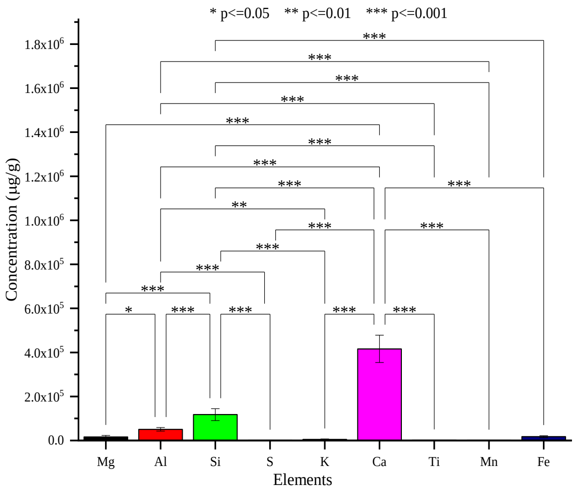

Fig. 3: Mean value, standard deviation and p-value of white soil constituent elements concentration.

(Alumina), had the most significant differences ($p < 0.001$) with other detected elements; except Al had a weak difference with Mg (Fig.). Calcium carbonate combines with tartaric acid and malic acid to form calcium tartrate crystals and calcium malate [25]. Silica is one of the most important adsorbents and apparently is more efficient for the adsorption of cations relative to anions [26]. Alumina is highly resistant to various chemical environments and can withstand extreme stress and maintain its properties [27].

From the experience, a ratio of 3% (30 g/kg) white soil is used to produce a high-quality grape syrup. In the process of grape syrup production, if the food ingredients are filtered then only a small amount of the soil is absorbed in the soluble, but if the mixture of grape juice and soil is heated to boiling point then more soil is absorbed. The food safety, nutritional quality, color and taste are important factors for producing a high-quality of the grape syrup. The heavy metal except Fe was not found in the samples. The excess amount of the Mn and Fe makes the color of the syrup darker while the excess content of Ca in the white soil makes the syrup transparent and bright brown in color. The transparency of the syrup after the mud boil-up process may be attributed to the fact that the colloidal substances are adsorbed by the ions, in particular iron, in the soil during juice boiling with soil which results in the precipitation of those particles as sludge. The prepared syrup with the white soil collected from region 3 was tasty and had a lower acidity with pH value of 3.20. This is because the white soil collected from this region had the highest amount of the Ca and the calcium compounds are acid-neutralizer.

CONCLUSIONS

In this study, the composition and concentration of ten soil samples, mostly used in the grape syrup production chain in Malayer, Iran, were investigated. The type of the added soil to grape juice causes differences in the quality, taste, and color of the grape syrup. The acidity of grape juice was decreased by alkaline salt especially in the white soils with a large amount of Ca. There was no noticeable heavy metal element in the used soil for grape syrup production. The higher levels of Ca within the white soil clarifier make the grape syrup tastier, more transparent, and lighter brown in color. Although, only about 30 g of white soil is used for 1 kg grape syrup processing. Nevertheless, strategies for sustainable management in the region by the department of environment and natural resources should be employed to undertake the conserving soil organic matter, minimizing erosion, and balancing excavation with commercial needs.

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