

Qualitative and Quantitative Analysis of the White Soil: Implication for Production of Grape Syrup

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Abstract: Grape syrup (like honey) is widely used in Iran. In the traditional method of producing grape syrup, white soil is added to the grape juice and the mixture is boiled. After cooling, it is filtered. To get syrup, the filtered juice is boiled again and concentrated. In this research, the soil used in the syrup production was studied experimentally for identifying its useful and possible harmful elements (such as heavy metals) and measuring their amounts. To this end, after randomly sampling, the laboratory samples of the soil were dissolved. A number of experiments were performed to identify the anions and cations of each solution separately. The results showed that the soil is free of any contaminant ion. In contrast, calcium, aluminium, magnesium and iron cations are present in the soil sample. The iron and aluminium were measured using absorption spectrophotometry. Also, calcium and magnesium were determined using volumetric titration. The calcium, magnesium, aluminium and iron quantity in 2.0 g of soil are 62.5, 19.4, 1.4 and 8.0 mg, respectively. This study also demonstrates how different elements of the soil affect the grape syrup quality.

Key words: Grape syrup • Chemical analysis • White soil • Contaminant

INTRODUCTION

In geochemistry, soil is a mixture of organic and inorganic materials, air, water and micro-organisms. All of these components affect each other. Solid reactions affect air and water quality and soil micro-organisms may facilitate some of the soil reactions. Although soil chemistry takes into account the entire reactions, our emphasis is on the soil solution, i. e. the thin film of solution around the soil particles [1].

The mechanisms by which heavy metals are absorbed or desorbed include: (1) the anion and cation exchange in which ions are attracted to the opposite charges; (2) the specific absorption during which some of the cations and anions are attracted by ligands with covalent bonding; (3) co-precipitation in which ions and minerals, such as iron oxides, aluminium, manganese and calcium carbonates are placed simultaneously on the surface of the soil particles; (4) precipitation of particles on the surface of the soil as carbonates, sulfides, phosphates

and insoluble hydroxides; and (5) complex formation with organic ligands. The term “desorption of heavy metals” refers to the release of ions in the cases mentioned above and is mainly associated with changes in pH value, reduction conditions, or substances secreted from the roots of the plants [2].

Factors that affect the absorption and desorption of ions in the soil include: (1) characteristics, type and concentration of heavy metals; (2) composition of the soil, especially the type and amount of clay minerals, concentration of iron oxides, aluminium and manganese, free calcium carbonate and organic matter; and (3) the soil’s physical and chemical conditions, including pH, reduction conditions and concentrations of anions and cations [2].

More information on the development history of soil analysis techniques, especially for reasons of industry regulatory compliance and verification experimental procedures and agents used, is addressed in Refs. 8-22.

Grape Syrup Traditional Production: In the traditional method of producing grape syrup, when the grape juice is produced, some white soil is added and the mixture is boiled. It is then cooled and filtered. Thereafter, the filtered liquid is further boiled and concentrated to obtain the syrup. If the soil is not added and a so-called “mud boil-up” process is not done, the syrup appears turbid and brown (not red) and does not taste sweet. From the health point of view, it is recommended that people with low iron deficiency anemia or arthritis may use grape juice (Personal Communications with Dr. H. Eshaghi, Shahrekord Medical Association, Shahrekord, 2011). Further, from an environmental standpoint, soil pollutants may contaminate the syrup, resulting in dangerous health problems. Therefore, it is important to analyze the soil and examine it against the possible toxic and harmful elements.

The qualitative and quantitative estimates on the elements existing in soil have been studied by many authors for many years. For example some authors have used new reagents such as titan yellow for measuring of some elements in soil [8-13]. The others have used different methods such as microwave digestion for dissolving the soil and measuring particular elements in it [14-22]; but no method was performed for analysis of this especial soil used in producing grape syrup.

In this study, the qualitative methods were used for the soil added in the grape syrup production to identify its useful and harmful elements. Then, their quantities were measured by the spectrophotometric and volumetric techniques.

MATERIALS AND METHODS

All chemicals used in our analysis were of analytical reagent grade (Merck) and used without further purification and in all of the steps doubly distilled water was used.

The apparatus used for the absorption measurements is a model SHIMADZU UV-120-01 spectrophotometer.

Sampling: The white soil was randomly sampled from the Aqash hill quarries in northwest of the town of Ben in the Province of Chaharmahal Va Bakhtiari, Iran. After sieving, the soli was mixed mechanically and 15 g of the mixture was put in an oven for four hours at a temperature of 110°C. Then, the soil was ground and three samples of 2.0 g were selected for the experiments.

Dissolving: Each sample was transferred to a 400-mL beaker. Under fume hood, 25 mL of a 1:1 concentrated

sulfuric and nitric acids mixture were added to each sample and the samples were heated to dryness on an electric heater. The heating was continued until a brown vapour coming out stopped and a white solid remained. 12 mL of a mixture of the two above acids and 10 mL of concentrated hydrochloric acid were added to the residue and heating was continued to dryness. Finally, after cooling, 25 mL of a mixture of 1:1 nitric acid and water was added to each sample and the mixture was stirred and filtered. The precipitate was then washed by a nitric acid 1:3 solution [4]. The filtrated solution was transferred to a 100-mL flask and diluted to the mark with water.

In this sub-section, we briefly explain how the cations and anions were separated and identified.

The reagents were added to small volumes of solutions prepared in the previous step. According to the changes in solutions such as change in color or precipitate formation, the presence or absence of ions were demonstrated. Cations (or anions) were divided into five groups based on their common reactions. Cations (or anions) in each group were first precipitated using special reactants and later separated from other cations (or anions). This means that with the addition of an appropriate reagent to each precipitate, each existing ion was separated and identified [5, 6]. Here, the detailed description of the methods is avoided.

Separation and determination of the iron, aluminium, calcium and magnesium cations 6 M NH_3 was added to 25 mL of stock solution drop-wise to make it alkaline. In fact, after adding of each drop, pH was tested. When pH became alkaline, 1.0 mL of ammonia was additionally plused. A few drops of 1 M of sodium sulfide were added to form a black deposit. It was heated afterward in a thermal bath for 10 minutes. The overhead solution was tested with a sodium sulfide droplet. After ensuring the completeness of precipitation, the precipitate was filtered and washed with a solution containing ammonia, ammonium chloride and sodium sulfide [5]. The precipitate contains iron and aluminium (precipitate 1) and solution contains calcium and magnesium ions (solution 1).

Separating Calcium from Magnesium: 1.5 mL of 6 M HNO_3 was added to the solution 1 and heated until the sulfide was removed. The hot solution was mixed with 30 mL 6% w/v ammonium oxalate. With the addition of 6 M ammonia, the pH was set to about 5.5. The solution settled for about 20 minutes and filtered. The white colour calcium oxalate deposit was washed with distilled water.

The filtrate contained magnesium. In order to remove the ammonium salts, 1 mL of concentrated nitric acid was added to the magnesium solution and heated to near dry-out phase. The crystals formed were dissolved in water and the solution was diluted to the mark in a 50-mL volumetric flask (solution 2) [5].

Dissolution of the Calcium Oxalate Deposit: The deposit was dissolved with 1:10 of sulfuric acid solution (solution 3) [5].

Separation of Iron from Aluminium: Precipitate 1 was dissolved by adding 6 M HNO₃. The solution was boiled for five minutes until the sulfide was removed. 0.2 g of solid ammonium chloride was added and stirred until it was completely dissolved. 6 M ammonia was added drop-wise to precipitate iron. An additional 1 mL of ammonia was added to dissolve the aluminium hydroxide in an excessive alkali environment. The precipitate was filtered and washed with 1% of ammonium nitrate solution. The filtered solution contains aluminium. The pH of this solution was set at a value of about six with ammonia and hydrochloric acid solutions. Its total volume then reached 50 mL (solution 4) [5].

Dissolving Iron Hydroxide Precipitate: The iron hydroxide precipitate was first dissolved in a 6 M HCl solution and then reached a volume of 25 mL (solution 5) [5].

Determination of Iron Using Absorption Spectrophotometry, Plotting Calibration Curve: In five 25-mL numbered volumetric flasks respectively, 0.0, 2.0, 4.0, 6.0 and 8.0 mL, standard Fe³⁺ solution (20 ppm) and 5 mL of 1 M potassium thiocyanate were added and diluted with distilled water to the mark. In 25-mL volumetric flask number 6, 1 mL of unknown iron solution (solution 5) and 5.0 mL of 1 M potassium thiocyanate were added and diluted to the mark with distilled water. The apparatus wavelength was set to 480 nm and absorption set to zero with the blank (solution number 1). The absorption of all solutions was measured at this wavelength [7]. The experiment was repeated three times. The results are shown in Table 1 and Figure 1.

Determination of Aluminium Content Using Absorption Spectrophotometry, Plotting Standard Addition Curve: In five 100-ml numbered volumetric flasks, 0.0, 0.5, 1.0, 1.5 and 2.0 mL, standard Al³⁺ solution

Table 1: Iron calibration curve data. Note that absorbance is a dimensionless quantity

Solution number	1	2	3	4	5	6
Volume of 20 ppm Fe ³⁺ solution, mL	0.0	2.0	4.0	6.0	8.0	1.0 mL of unknown solution
[Fe ³⁺], ppm	0.0	1.6	3.2	4.8	6.4	Unknown
Absorbance series 1	0.0	0.363	0.673	0.988	1.267	0.657
Absorbance series 2	0.0	0.363	0.671	0.986	1.262	0.655
Absorbance series 3	0.0	0.365	0.673	0.985	1.264	0.654

Table 2: Aluminium standard addition curve data. Note that absorbance is a dimensionless quantity.

Solution number	1	2	3	4	5
Volume of 75 ppm Al ³⁺ , mL	0.0	0.5	1.0	1.5	2.0
[Al ³⁺], ppm	0.000	0.375	0.750	1.125	1.500
Absorbance series 1	0.340	1.005	1.672	2.010	2.353
Absorbance series 2	0.338	1.001	1.673	2.009	2.353
Absorbance series 3	0.341	1.003	1.673	2.010	2.357

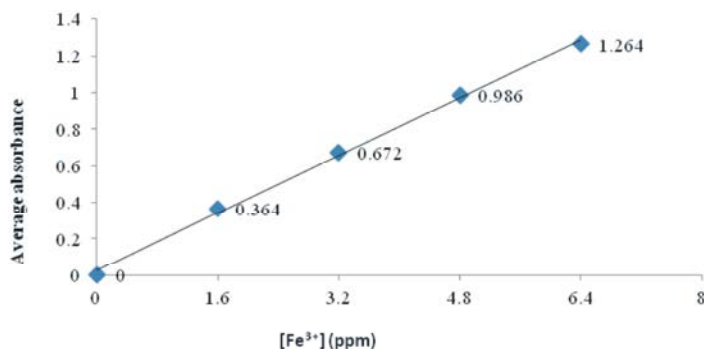


Fig. 1: Iron calibration curve. Note that absorbance is a dimensionless quantity

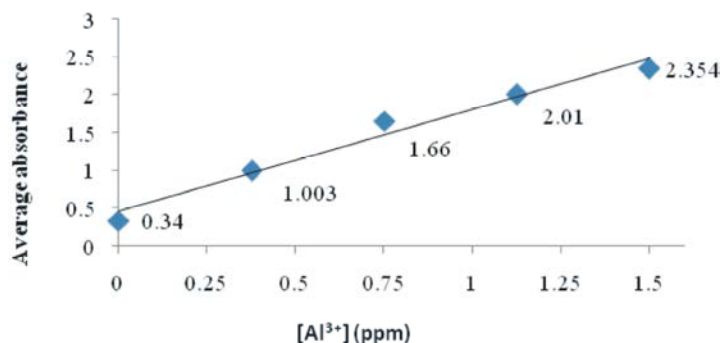
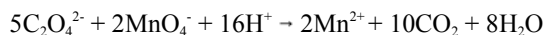


Fig. 2: Aluminium standard addition curve. Note that absorbance is a dimensionless quantity

(75 ppm) were added, respectively. In each flask, 5.0 mL of unknown solution (solution 4), 5 mL of 5% hydrogen peroxide solution, 50 mL of diluted acetate buffer solution and 5 mL of 0.1% eriochromcyanine R were added and the solution was diluted to the mark. After 30 minutes, the solutions absorption was measured at 535 nm. The absorption of the blank was set to zero at this wavelength. 100 ml of the blank solution contain 5 mL of 5% hydrogen peroxide solution, 50 mL of the acetic acid/ ammonium acetate buffer solution (pH=6.1) and 5 mL of the diluted 1% eriochromcyanine R [7]. The results are shown in Table 2 and Figure 2.

Determination of Calcium Content Using the Manganometric Titration Method: The oxalate ions are oxidized by permanganate in an acidic medium:



The molar ratio of calcium and oxalate ions in calcium oxalate is 1:1. Therefore, the amount of calcium can be calculated.

Solution 3 is formed from the dissolution of calcium oxalate in sulfuric acid (method 6). 10 mL of 1:10 sulfuric acid was added to this solution and the solution was heated up to 70°C and titrated with the standard permanganate solution. 8.1 mL of 0.0965 N permanganate were consumed [3].

Determination of Magnesium Content with Complexometric Titration: Four samples were prepared by mixing 10 mL of magnesium unknown solution (solution 2), 2 mL of buffer solution (pH = 10) and three droplets of the indicator. They were titrated with 0.01 M EDTA until the solution turned blue [3]. The average consumed titrant volume was 4.0 mL.

RESULTS AND DISCUSSION

In this section, results obtained from different methods used are discussed.

The experimental results showed the absence of the arsenate, arsenite, ferrocyanide, ferricyanide, chromate, chlorate, mercury, barium, cadmium, arsenic, cobalt, nickel, lead, manganese, copper, silver and zinc ions. This corroborates that the white soil is free from any contaminant, toxic and heavy elements. In contrast, it contains iron, aluminium, calcium and magnesium.

Quantitative Analysis

Calculating the Amount of Iron in the Sample: Both the standard iron and unknown solutions data are shown in Table 1. The calibration curve for iron is shown in Figure 1. This is obtained by plotting a mean value of absorbance of three series of solutions versus standard iron concentration. The curve is a line with an equation of $y = 0.1969x + 0.0272$ with a correlation coefficient of $R^2 = 0.9978$. Putting the unknown absorbance value of $y = 0.655$ in this equation, a value of $x = 3.2$ is obtained. This means that the iron concentration in the unknown samples (solution 6) is 3.2 ppm. Putting this value and rearrangements in volume, the amount of dissolved iron in the stock solution and finally in the soil sample, is calculated. Therefore, the iron concentration ($[Fe^{3+}]$) in the unknown sample is:

$$[Fe^{3+}] = \frac{25.0mL \times 3.2ppm}{1.0mL} = 80ppm$$

and the iron weight in 2.0 g of the soil is calculated according to:

$$\frac{80 \text{ mg Fe}^{3+}}{1 \text{ L solution}} \times \frac{0.1 \text{ L solution}}{2.0 \text{ g soil}} = \frac{8.0 \text{ mg Fe}^{3+}}{2.0 \text{ g soil}}$$

Therefore, the amount of iron in 2.0 g of the soil sample is 8 mg.

Calculating the Amount of Aluminium in the Sample:

The measured aluminium data is listed in Table 2. Plotting the mean absorbance value versus the standard aluminium solution concentration ($[Al^{3+}]$) yields a line with an equation of $y = 1.3427x + 0.4664$ with a correlation coefficient of $R^2 = 0.9735$ and intercept of 0.340. Extrapolation ($y = 0$) gives 0.347 ppm for the concentration of the aluminium in 100 mL of the tested solution, which is equivalent to 5 mL of the unknown solution. Therefore we have:

$$\frac{0.347 \text{ ppm} \times 100.0 \text{ mL}}{5.0 \text{ mL}} = 6.9 \text{ ppm}$$

And the aluminium concentration ($[Al^{3+}]$) in the stock solution (unknown) is:

$$\frac{6.9 \text{ ppm} \times 50.0 \text{ mL}}{25.0 \text{ mL}} = 13.8 \text{ ppm}$$

And the aluminium weight in 2.0 g of the soil sample is obtained according to:

$$\frac{13.8 \text{ mg Al}^{3+}}{1.0 \text{ L solution}} \times \frac{0.10 \text{ L solution}}{2.0 \text{ g soil}} = \frac{1.4 \text{ mg Al}^{3+}}{2.0 \text{ g soil}}$$

Calculating the Amount of Calcium in the Sample:

$$8.1 \text{ mL MnO}_4^- \times 0.0965 \frac{\text{meq}}{\text{mL}} \text{ MnO}_4^- \times \frac{1 \text{ meq C}_2\text{O}_4^{2-}}{1 \text{ meq MnO}_4^-} = 0.7816 \text{ meq C}_2\text{O}_4^{2-}$$

$$0.7816 \text{ meq C}_2\text{O}_4^{2-} \times \frac{1 \text{ mmol C}_2\text{O}_4^{2-}}{2 \text{ meq C}_2\text{O}_4^{2-}} \times \frac{1 \text{ mmol Ca}}{1 \text{ mmol C}_2\text{O}_4^{2-}} \times \frac{40.0 \text{ mg Ca}}{1 \text{ mmol Ca}} = 15.63 \text{ mg Ca}$$

$$\frac{15.63 \text{ mg Ca}}{25.0 \text{ mL solution}} \times \frac{100 \text{ mL solution}}{2.00 \text{ g soil}} = \frac{62.5 \text{ mg Ca}}{2.00 \text{ g soil}}$$

Calculating the Amount of Magnesium in the Sample:

$$4.0 \text{ mL EDTA} \times \frac{0.01 \text{ mmol EDTA}}{1.0 \text{ mL EDTA}} \times \frac{1 \text{ mmol Mg}}{1 \text{ mmol EDTA}} \times \frac{24.31 \text{ mg Mg}}{1 \text{ mmol Mg}} = 0.9724 \text{ mg Mg}$$

$$\frac{0.9724 \text{ mg Mg}}{10.0 \text{ mL sample}} \times \frac{50.0 \text{ mL sample}}{25.0 \text{ mL stock}} \times \frac{100 \text{ mL stock}}{2.00 \text{ g soil}} = \frac{19.4 \text{ mg Mg}}{2.00 \text{ g soil}}$$

In summary, the amounts of iron, aluminium, calcium and magnesium in 2.0 g of the soil sample are 8.0, 1.4, 62.5 and 19.4 mg, respectively.

CONCLUSIONS

Methods used in this study, i. e. absorption spectrophotometry, manganometric and complexometric titrations, are rapid, precise and selective techniques for determining elements in real samples. We list the main lessons learnt from these experiments: (1) The white soil is free of toxic and harmful elements and hence can safely be used in the preparation of grape syrup; (2) From standpoints of both appearance and taste, the mud boil-up process plays a positive role. The clarity 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 the soil (during juice boiling with soil), in particular iron and aluminium, which results in the precipitation of those particles as sludges; (3) It is likely that some of the ions in soil will transfer to the syrup during the mud boil-up process. Physicians advise people with iron deficiency anemia and arthritis to use grape syrup, an argument that would be strengthened with our results. It is also possible that elements that have an important role in the human health, such as iron, calcium and magnesium transfer from the soil into the syrup. This also can be applied to aluminium. However, since the amount of aluminium is negligible in the soil, this would not be dangerous for the health; and (4) the alkaline salts in the soil decrease the acidity of the grape juice, resulting in its sweet flavor.

In conclusion, our study demonstrates how different elements of the soil affect grape syrup quality and how this may increase or decrease the public health.

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