Effect of sulphur forms on colour and residue of sulphur during the storage at drying grapes by sulphur

Özlem Boztepe[1], Ahmet Altındişli[2], and Burçak İşçi[2]

[1] Hazelnut Research Institute, 28200 Giresun, Turkey
[2] Ege University Department of Horticulture, 35100 Izmir, Turkey

Abstract. Turkey is the world leader in the manufacture and export of seedless raisins. Requirement of golden bleached raisins is increasing in food Industry of especially cake, bread and pastry year by year. In this research, the lowest residual value and the practical realization of such production was intended to determine by drying grapes with application of sulphur. In this case, sulphur residue and colour situations were determined during 12-mounth-storage according to sulphur forms. In this study sulphur studies were applied by *Vitis Vinifera* cv. "Sultani Çekirdeksiz" with $Na_2S_2O_5$, which is liquid source of sulphur and SO_2, which is gas source of sulphur. SO_2 application were studied during 3, 6 and 8 hours and liquid form of sulphur is $Na_2S_2O_5$ that was used during by 10, 20 and 30 minutes. Applications were prepared with 3 replicates which contain 20 kg fresh grape in each replicate. In conclusion, changes in dried grape have been identified in point of colour (chroma and hue) and the sulphur content was determined according to sulphur forms in packing. Gas form of sulphur (SO_2) which was applied 3 hours, gave the best result during 12-mounth-storage for colour and sulphur residue.

1. Introduction

Grape is an important fruit crop and is grown in countries that fall between the latitudes of 20–520 in the north hemisphere and the latitudes of 20–400 in the south hemisphere; thus almost in all regions of the world except the poles and the equator. In our country, a total of 4,175,356 tons of fresh grapes is produced in a vineyard area of 467,093 ha. 2,166,749 tons of this production is used as table grapes, 1,563,480 as raisins, and 445,127 as wine grapes [1]. Raisins have become increasingly important because of their use for visual and flavour improvement in the pastry sector, which has developed during the recent years. With this purpose, a demand for seedless raisins with different colours arose and different processes have been applied in order to obtain light coloured raisins. As a result, the demand for Golden Bleach (golden yellow – bleached raisins) increased [2]. In the present study, colour changes that take place in fruits as a result of darkening and browning was prevented through sulphurization treatment and a golden yellow product colour was obtained.

2. Material

2.1. Plant materials

The *V. vinifera* L. "Sultana Seedless" grape ripens during mid-season; has strong growth, conical-shaped and winged bunch with normal density, oval shaped small berries, and a skin with normal thickness.

2.2. Powder sulphur

Sulphur is a lemon coloured, non-metallic chemical element with a symbol of S. In the research, sulphur of 99% purity was used.

2.3. Sodium metabisulphite

Sodium metabisulphite or sodium pyrosulfite is known as disodium salt and is an inorganic material. Its molecular formula is $Na_2S_2O_5$. Its molecular weight is 190.1 g/mol. Its density changes between 1.1–1.2 g/cm^3 . Upon contact with air, it oxidizes to sodium sulfate (Na_2SO_4). It has an acrid odor, since it releases SO_2 when mixed with the humidity in air. In the research, sodium metabisulphite of 99.6% purity was used.

2.4. Dip solution

In order to dry the "Sultana Seedless" grapes rapidly, they are dipped into a dip solution after harvesting. The dip solution (1.5%) is prepared with 5 kg potassium carbonate in 100 liters of water and an olive oil dose of 1–1.5 liters [3–6].

3. Method

3.1. Sulphurization treatment carried out with SO_2 gas that is released by burning powder sulphur

The unhealthy and damaged berries of *V. vinifera* L. "Sultana Seedless" grape bunches harvested at brix in the range of 20–22 were removed. Dipped and undipped grapes were prepared for treatment with powder sulphur at

treatment periods of 3, 6, and 8 hours. Treatment tents were established for the grapes based on the treatment periods. A total of 120 kg fresh grapes were placed in the tents in 3 repetitions, each repetition consisting of 20 kg grapes. The powder sulphur dose was calculated as 1.6 g for 1 kg of fresh grapes. 192 g powder sulphur was burned for each tent. The sulphurization tents were kept close for periods of 3, 6, and 8 hours and the amount of sulphur used per kilogram of grapes was kept constant at each treatment.

3.2. Sulphurization process with liquid sulphur

Dipped and undipped grapes were prepared for the liquid sulphur treatment in a similar manner as the plant material powder sulphur treatment by applying treatment periods of 10, 20, and 30 minutes and using 8% sodium metabisulphite solution for the liquid sulphur treatment. The grapes were kept in liquid sulphur at specified periods.

3.3. Drying

Fresh grapes that were treated by burning with powder sulphur and dipping in sodium metabisulphite were transferred to a shadowy area with their plastic stands in order to dry. The drying process was carried out in the of Ege University Agricultural Faculty, Menemen Research and Application Farm facility, which is closed above and open on the sides. In addition, the raisins were subjected to quality and sulphur analyses according to the Monnier Williams Method.

4. Results

4.1. Results obtained from grapes that were dried by sulphurization with SO_2 gas

While the grapes that were dried through dipping were brighter with a chroma value 17.05, those that were dried without dipping were more dull in appearance compared to those that were dried through dipping and had a chroma value of 9.519. The grapes that were dried by treatment after dipping into the dip solution were more yellow, bright, and had more homogeneous appearance, while those that were subjected to SO_2 treatment without dipping were darker, duller, and heterogeneous in colour. With a chroma value of 19.005, the best result was obtained for the treatment of power sulphur and potash. The chroma values for other sulphur treatments were 16.706, 15.43, 10.089, 9.939, and 8.530, respectively. According to these results, the brightness of the raisins decreased with holding period in the SO^2 treatment tent. The storing period had a statistically significant effect on the chroma value of the berries ($p < 0.01$). While the initial chroma value was 15.688; in storage samples obtained after 3 months the chroma values were determined as 13.783, 12.321, 12.274, and 12.356, respectively. With increase in the storage period the brightness of the berries decreased considerably.

The hue value of grapes that were dried trough dipping was 64.838 and the value obtained after treatment without potash was 47.235. The grapes that were dried without dipping were darker in colour. The grapes that were dried after dipping was lighter yellow. With increase in the storage duration the berry colour becomes darker. This is especially clear when the values of 45.867 and 45.375 obtained in the 9th and 12th months of storage, respectively are compared with the initial value of 75.899.

The sulphur amount of grapes that were subjected to powder sulphur treatment after dipping in dip solution was 466.044, and much higher than the sulphur amount of 349.689 determined in the grapes that were subjected to sulphurization without dipping. The waxy layer around the fresh grapes becomes thinner after dipping in the dip solution; as a result, the amount of sulphur adsorbed by these grapes during the SO_2 treatment is much higher than that absorbed by grapes that are treated without dipping in the dip solution. While after the 8 hour SO_2 treatment with potash the mean sulphur remaining in the grapes was 437.467 ppm, the highest number after this was obtained for powder sulphur treatment of 8 hours without potash as 402.133 ppm. Lower sulphur amounts were detected in grapes after 3 hour SO_2 treatments. According to these results, as the duration of SO_2 treatment increased, the amount of sulphur in the grapes increased as well. After the SO_2 treatment, the sulphur amount in the grapes decreases with storage period. While the initial mean sulphur amount was 883.889 ppm, it decreased to the values of 611.111 ppm in 3 months, 337.222 ppm in 6 months, 146.667 ppm in 9 months, and 60.444 ppm in 12 months.

4.2. Results obtained from the liquid sulphur treatment

The mean chroma value of the grapes that were treated with liquid sulphur after being dipping into the dip solution was determined as 14.022, while the mean chroma value of the grapes that were dried after treated with $Na_2S_2O_5$ without dipping was determined as 11.055. It was observed that grapes that were dried with treatments after dipping in potash solution were brighter. As the duration period of raisins in the storage increased, changes in the chroma value was detected. While the initial value was 14.364, the mean values obtained after storage at the specified months were 12.978, 12.012, 11.678, and 11.661, respectively. The chroma value which was 14.364 at the beginning of storage was measured as 11.661 at the end of 12 months. As the duration of the raisins in the storage increased, their chroma value decreased. As the duration of the raisins in the storage increased, their brightness decreased.

The hue value of the grapes that were dried after dipping into the dip solution and then treating with liquid sulphur was determined as 60.223, and this higher than the value of 52.421 that was obtained for grapes that were dried without dipping and after sulphurization with $Na_2S_2O_5$ solution. The hue value which was 77.644 initially was measured in the analyses as 61.727 after 3-month storage, 50.376 after 6-month storage, 47.237 after 9-month storage, and 44.628 after 2-month storage, respectively. According to these values, as the storage period increased darkening was observed in the berries of the grapes.

The sulphur amount of grapes was 372.444 when they were dried after dipping into dip solution and subjecting to treatment, which was much higher than the value of 327.467 that was obtained for grapes that were dried after treatment with $Na_2S_2O_5$ that is not preceded with a dipping process into potash dip solution. According to the research result, as the duration in the $Na_2S_2O_5$ solution

increased, the sulphur amount of the raisins increased as well. The highest mean sulphur amounts were as follows: 437 ppm for 30 minute $Na_2S_2O_5$ treatment with potash and 402.133 ppm for 30 minute $Na_2S_2O_5$ treatment without potash. The mean sulphur amounts in the dry raisins were 385.333 for 20 minute $Na_2S_2O_5$ treatment with potash, 310.267 for 20 minute $Na_2S_2O_5$ treatment without potash, 294.533 for 10 minute Na2S2O5 treatment with potash, 270.000 for 10 minute Na2S2O5 treatment without potash. As the holding period in the $Na_2S_2O_5$ solution increased, the adsorbed sulphur amount increased as well. In addition, when the storage periods were observed, decrease in the sulphur amount was observed with increase in the storage period of the raisins. The sulphur amount that was measured initially as 787.222 ppm, decreased to 58.611 ppm at the end of the 12th month. This value was 522.222 ppm after 3 months, 270.611 ppm after 6 months, and 111.111 ppm after 9 months, respectively. Since the sulphur in the raisin berry continues to be released with time, the sulphur present in the raisins decreases with storage duration.

According to the results of this study carried out with the purpose of covering the demand of the pastry industry for light yellow colored raisins that are obtained by drying fresh grapes after sulphurization process:

- The SO_2 treatment with a gas form after burning powder sulphur for sulphurization processes in grapes is a practical and applicable method. The 1.6 g powder sulphur value that was used in the study for 1 kg fresh grapes is an adequate value.
- It can be claimed that drying after sulphurization with 8% $Na_2S_2O_5$ (Sodium Metabisulphite) solution is not an adequate method because of the observed heterogeneous light and dark colors in the grape berries.
- Regarding sulphurization applications, it can be claimed that dipping into 1.5% potash dip solution either prior sulphurization via burning powder sulphur or dipping into 8% $Na_2S_2O_5$ solution, leads to positive results with respect to the quality criteria of the raisins.
- Because of the observed decline in the total sulphur amount of the raisins throughout the storage process, it can be claimed that the storage process can be used as a tool to manage the sulphur dose in raisins.

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