

# **Egyptian Journal of Chemistry**

http://ejchem.journals.ekb.eg/



CrossMark

## **Removal of Sulfur Dioxide from Dried Grapes before Handling**

Magdy F. Tawfik<sup>a</sup>, Eman E. Yousef<sup>b</sup>, M.M. Aboul Fotouh<sup>a</sup>\* and Hanaa R.M. Farag<sup>a</sup> <sup>a</sup>Department of Biochemistry, Faculty of Agriculture, Ain Shams University, Cairo, Egypt <sup>b</sup>Department of Food science, Faculty of Agriculture, Ain Shams University, Cairo, Egypt

## Abstract

Dried grapes or raisins are usually treated with sulfur dioxide in high concentrations to prevent enzymatic and non-enzymatic browning reactions and keep golden yellow color of these dried fruits. Sulfur dioxide and sulfite salts are good food preservatives but have high risk on human health especially when using in high concentrations. Thus, this work was achieved to remove sulfur dioxide and sulfite salts from over sulfur raisins before handling in different food industries into lower concentrations by soaking of raisins in water,  $H_2O_2$  (1%), citric acid (5%) and a sol<sup>o</sup>C for 15 and 30 minutes. These treatments led to removing high amounts of sulfur dioxide and sulfite salts from raisins especially with treatment by citric acid (5%) at 50°C for 15 min. Comparatively, soaking of raisins in citric acid (5%) was the best treatment followed by acetic acid (5%) and  $H_2O_2$  (1%) then water. This work also aimed to desulfurization of raisins with minimal effects on their constituents e.g., total phenols, tannins, flavonoids and color features. The loss rates of these constituents from raisins were obtained by  $H_2O_2$  because it is oxidizing and bleaching agent. Therefore, this work was achieved to vorcome this problem by using citric acid or acetic acid instead of  $H_2O_2$ . *Keywords:* Removal; Sulfur dioxide; Dried grapes; Raisins.

## 1. Introduction

Raisin varieties depend on the type of grape and appear in a variety of sizes and colors including green, black, brown, purple, blue, and yellow. Commercial raisins are produced in three steps including pretreatment, drying, and post-drying processes. Pretreatment is a necessary step in raisin production to ensure the increased rate of water removal during the drying process. A faster water removal rate decreases the rate of browning and helps to produce more desirable raisins. Drying methods are sun drying, shade drying, and mechanical drying. Mechanical drying is the best method where it can be done in a safer and more controlled environment, and rapid drying is guaranteed. One type of mechanical drying is to use microwave drying. Water molecules in the grapes absorb microwave energy resulting in rapid evaporation [1]. All steps in the production of raisins are very important in determining the quality of raisins. Sulfur dioxide is applied to raisins after the pretreatment step and before drying to decrease the rate of browning caused by the reaction between polyphenol oxidase and phenolic compounds. Sulfur dioxide also helps to preserve flavor and prevent the loss of certain vitamins during the drying process [2]. Dried grapes or raisins contain about 15% water, 65% total sugars including glucose, fructose and tiny amount of sucrose, 4.5% fibers, 3.3% protein, and 0.25% fats. Raisins also contain several minerals and vitamins besides phenolic compounds including phenolic acids, flavonoids, tannins and others [3].

Dried fruits such as apricots and grapes are usually treated with sulfur dioxide in high concentrations to prevent enzymatic and non-enzymatic browning reactions and keep golden yellow color of these dried fruits. This treatment also prevents microbial spoilage during drying and storage, and prolongs shelf life. In the sulfurization process of raisins, either directly the SO<sub>2</sub> gas is used or by burning various sulfur salts [4]. The sulfurization process is carried by keeping fresh fruits in a closed room in the SO<sub>2</sub> gas atmosphere obtained by burning elementary sulfur. In this application, controlling the SO<sub>2</sub> amount absorbed by raisins is difficult. In sulfurization, factors such as temperature, sulfurization time, elementary sulfur amount, fruits maturity levels, and fruit sizes cause the SO<sub>2</sub> amount absorbed to differ. For these reasons, the SO<sub>2</sub> amount in the final product can reach undesirable levels. Besides, the SO<sub>2</sub> amount is kept high for preserving the fruit color and storing for a long time [5, 6].

Sulfur dioxide and sulfite salts as sodium sulfite, sodium bisulfite and sodium meta-bisulfite have been used as food preservatives in the food industry for centuries, besides acting as anti-browning and antioxidant agents. Sulfur dioxide gas is more efficient than sulfite salts in the sulfurization process of dried fruits while sulfite salts are usually used in other foods such as beer, wines, gelatin, sausage and some fruit juices. Sulfite salts are used by certain concentrations such as 70 ppm in beer, 500 ppm in wines and sausage, and 1000 ppm in gelatin while the concentration of sulfur dioxide in dried fruits is about

\*Corresponding author e-mail: mohamed\_mesalhi@agr.asu.edu.eg.; (M.M. Aboul Fotouh).

Received date 08 July 2024; revised date 04 September 2024; accepted date 29 September 2024 DOI: 10.21608/EJCHEM.2024.302677.9969

©2025 National Information and Documentation Center (NIDOC)

2000 ppm [7]. The controlling of SO<sub>2</sub> amount absorbed by dried fruits during the sulfurization process is difficult thus it can reach to 6000 ppm [8]. Legally, the maximum limit of SO<sub>2</sub> concentration is about 2000 mg/kg. Different countries only allowed to certain amounts of sulfur dioxide in dried apricots and raisins such as 2000 mg/kg in Germany and England, 1000 mg/kg in France and Denmark, 600 mg/kg in Italy and 300 mg/kg in Austria. Legal restrictions and the demand for dried fruits containing low SO<sub>2</sub> content have revealed the need to reduce subsequently the SO<sub>2</sub> content. Various methods have been tried for desulfurization of dried apricots by dipping these fruits into  $H_2O_2$  with different concentrations at different temperatures for different times [8, 9, 10, 11, 12].

This work was performed to remove sulfur dioxide from over sulfite dried grapes or raisins which contain much higher  $SO_2$  levels (up to 6000 mg/kg) than legal limits (usually 2000 mg/kg) into lower concentrations by soaking of raisins in water,  $H_2O_2$  (1%), citric acid (5%) and acetic acid (5%) at 30 and 50°C for 15 and 30 minutes. This work also aimed to desulfurization of raisins with minimal effects on their constituents e.g. total sugars, total phenols, tannins, flavonoids and color.

## 2. Materials and Methods

## 2.1. Materials

Golden yellow raisins (*Vitis vinifera* L.) were purchased from a local market, Cairo, Egypt. Folin-Ciocalteu reagent, gallic acid, tannic acid and quercetin were purchased from PioChem Chemical Company, 6 October City, Egypt. All other chemicals used in this work were of analytical grade.

#### 2.2. Determination of total sulfur dioxide in raisins

Total sulfur dioxide in samples of raisins was determined according to the Monier Williams method. The distillation and titration of sulfur dioxide from various samples were performed according to [13]. Comparatively, free forms of sulfur dioxide (molecular SO<sub>2</sub>, sulfite and bisulfite salts) can be determined by direct titration with iodine solution (0.02 N) in the presence of starch indicator after grinding the sample in water while total SO<sub>2</sub> which includes free and bound forms of SO<sub>2</sub> can be determined after steam distillation of the sample in the acidic medium of HCl solution (7%) for 6 min then titration of the distillation product with iodine solution (0.02 N) in the presence of starch indicator.

#### 2.3. Color measurements

After various soaking treatments of raisins in water,  $H_2O_2$  (1%), acetic acid (5%) and citric acid (5%) at 30 and 50°C for 15 and 30 minutes, skin color of raisins was determined in the CIE Lab system by using spectrophotometer (MOM, 100D, Hungary). In the CIE Lab color space, L\* indicates the brightness, ranging from black (0) to white (100), a\* ranging from green (-a) to red (+a), and b\* ranging from blue (-b) to yellow (+b) as described by [14].

#### 2.4. Preparation of raisins extracts

Five grams of frozen raisins were ground and extracted twice with 5:1 of ethanol (70%) for 24 hours at room temperature (25°C), and the samples were filtered after each extraction. Solvent was removed from the combined extracts with a vacuum rotary evaporator at 40°C to obtain crude extracts. The dried extracts were weighed and stored at  $-20^{\circ}$ C until use [15]. 2.5. Determination of total sugars

Total sugars of the dry extracts of raisins were determined by the phenol-sulfuric acid method. Each sample was dissolved in distilled water to make 100 ml and then 0.5 ml portion of the solution was mixed with 1.0 ml of phenol solution (5%) and 1.0 ml of distilled water for 1 min, 5.0 ml of concentrated  $H_2SO_4$  was then added, shaken for 3 minutes. After settling down for 30 minutes, the resulting solution was cooled by water for 20 minutes and then measured at 485 nm. Standard curve of glucose was prepared and the results were expressed as glucose equivalents (g/100g) as described by [16].

#### 2.6. Determination of total phenols

Briefly, total phenols of the dry extracts of raisins were determined by the Folin-Ciocalteu reagent and sodium carbonate solution (7%). The mixture was incubated at room temperature for 90 min and the absorbance at 760 nm was measured. The results were expressed as gallic acid equivalents (mg/100 g) as described by [17].

## 2.7. Determination of total tannins

Briefly, total tannins of the dry extracts of raisins were determined by the Folin-Ciocalteu reagent and sodium carbonate solution (35%). The mixture was incubated at room temperature for 30 min and the absorbance at 700 nm was measured. The results were expressed as Tannic acid equivalents (mg/100 g) as described by [18].

## 2.8. Determination of total flavonoids

Flavonoids of the dry extracts of raisins were determined according to the colorimetric method described by [19]. Briefly, each sample was mixed with distilled water and subsequently with sodium nitrite solution (10%). After 5 min, aluminum chloride solution (10%) was added followed by sodium hydroxide solution (1%) to the mixture. Immediately the mixture was thoroughly mixed and absorbance was then determined at 510 nm. Standard curve of quercetin was prepared and the results were expressed as quercetin equivalents (mg/100g).

#### 2.9. Statistical analysis

All data are expressed as means  $\pm$  standard deviation from three replicates. The recorded data were treated statistically using the one-way analysis of variance (ANOVA). The means were compared by Least Significant Difference test (LSD) at P<0.05. Statistical analyses were performed using SPSS statistical software (IBM SPSS Statistics, version 20) [20].

#### 3. Results and Discussion

Dried grapes or raisins are usually treated with SO<sub>2</sub> for inhibiting the enzymatic and non-enzymatic browning reactions during drying and storage as well as prevention of microbial deterioration. Dried grapes sometimes contain much higher SO<sub>2</sub> levels (up to 6000 mg/kg) than legal limits (usually 2000 mg/kg). It is important to note that the acceptable daily intake (ADI) of sulfites expressed as SO<sub>2</sub> is very low (0.7 mg/kg) [21, 22, 23, 24]. Thus, it may become necessary to decrease the final SO<sub>2</sub> level in dried grapes. Therefore, this work was carried out to remove SO2 from over sulfite dried grapes into lower concentrations by soaking of raisins in water, H<sub>2</sub>O<sub>2</sub> (1%), citric acid (5%) and acetic acid (5%) at 30 and 50°C for 15 and 30 min. This work also aimed to desulfurization of raisins with minimal effects on their constituents e.g., total sugars, total phenols, tannins, flavonoids and color features. The obtained data were classified into the following items:

#### Effect of soaking treatments of raisins on total sulfur dioxide content

Table (1) shows the effect of soaking of raisins in water,  $H_2O_2$  (1%), citric acid (5%) and acetic acid (5%) at 30 and 50oC for 15 and 30 minutes on the residual concentration of total sulfur dioxide in these samples of raisins compared to that in the control samples (untreated raisins). The results showed significant (P<0.05) decreases in the levels of total SO<sub>2</sub> in the samples of raisins in all treatments compared to that in the control samples (5828 ±12 mg/kg). Water treatments at 30°C exhibited weak potency of SO<sub>2</sub> removal from raisins as indicated by the highest concentrations of residual SO<sub>2</sub> in the samples of raisins either for 15 min (5628 ±12 mg/kg) or 30 min (5244 ±11 mg/kg). This may be due to that soaking of raisins in water at room temperature (30°C) led to releasing of free forms only of sulfur dioxide. Free forms of SO2 include molecular SO<sub>2</sub>, sulfite and bisulfite salts while combined forms include sulfites attached to acids, sugars, acetaldehyde and polyphenols. Comparatively, the amounts of combined forms were much more than those of free forms in the dried fruits. Clearly, soaking of raisins in hot water at 50°C exhibited sharp decrease in the levels of residual SO<sub>2</sub> in these samples of raisins either for 15 min (3242  $\pm$ 18 mg/kg) or 30 min (3045 ±13 mg/kg). It means that soaking of raisins in hot water was more potent than cold water for removal of SO<sub>2</sub> from raisins. This may be ascribed to that increasing of soaking temperature led to increase releasing of bound forms of SO<sub>2</sub> from raisins. The data also indicate that the amount of residual SO<sub>2</sub> in the samples of raisins more decreased, and the efficiency of SO<sub>2</sub> removal more increased by increasing of soaking temperature from 30°C to 50°C, and increasing of soaking time from 15 min to 30 min in all treatments as in shown in Table (1). Evidently, the potency of water treatment at 50oC was approximately equal the soaking treatments in  $H_2O_2$  (1%) and acetic acid (5%) at 30°C but less than the soaking treatment in citric acid (5%) at 30°C. It can be noticed that the efficacy of soaking treatment in  $H_2O_2$  (1%) at 50oC was approximately equal the soaking treatment in acetic acid (5%) at 50oC but less than the soaking treatments in citric acid (5%) at the same temperature. Efficiency of SO<sub>2</sub> removal from raisins by various treatments was in the following order; citric acid (5%) followed by acetic acid (5%) and hydrogen peroxide (1%) then water. The treatments with citric acid (5%) gave the best results and the lowest concentrations of residual SO<sub>2</sub> in the samples of raisins especially at 50°C for 15 and 30 min of soaking time (1428  $\pm$ 12 and 1409  $\pm$ 11 mg/kg, respectively).

There were no significant (P<0.05) differences in the levels of residual SO<sub>2</sub> between the soaking treatments in citric acid (5%) at 50°C for 15 min and 30 min. Thus, the soaking for 15 min was considered the best. It can be observed that the concentration of residual SO<sub>2</sub> in the samples of raisins became less than legal limits (usually 2000 mg/kg) and the efficiency of SO<sub>2</sub> removal from raisins by these treatments were about 75% which accounted by the following equation:

Efficiency of SO<sub>2</sub> removal =  $100 - [(SO_2 \text{ in the treatment})/(SO_2 \text{ in the control}) \times 100]$ 

Our results are supported by those obtained with [8, 9, 10, 25]. The removal of sulfites from excessively sulfited dried apricots (over 4000 mg/kg) using H<sub>2</sub>O<sub>2</sub> (0.5, 1.0 and 1.5%) at 20, 40 and 60°C for various times was studied by [8] and found that the removal of SO<sub>2</sub> from dried apricots increased as H<sub>2</sub>O<sub>2</sub> concentration, temperature and time increased, and this increase ranged from 12 to 66%. The best results observed with  $H_2O_2$  (1%) where the potency of SO<sub>2</sub> removal from dried apricots increased from 32% at 20°C to 53% at 40°C and 66% at 60°C for the same time (12 min). The removal of SO<sub>2</sub> from dried apricots exposed to hot air flows at 40, 50 and 60°C for various times was studied by [25] and indicate that exposure of dried apricots to hot air flow was effective in reducing the SO<sub>2</sub> content where the potency of SO<sub>2</sub> removal from dried apricots increased from 34% by exposing to hot air flow at 50°C for 144 hours to 67.6% at 60°C for 100 hours. Using of H<sub>2</sub>O<sub>2</sub> (0.5, 1.0 & 1.5%) to remove SO<sub>2</sub> from over sulfite dried apricots at 20, 40 & 60°C for various times was examined by [9] and indicate that removal of SO<sub>2</sub> increased as H<sub>2</sub>O<sub>2</sub> concentration and temperature increased. When using H<sub>2</sub>O<sub>2</sub> (1%) at 40°C for 12 min, SO<sub>2</sub> content of dried apricots decreased from 4184 to 2138 mg/kg. They also indicate that using H<sub>2</sub>O<sub>2</sub> (1%) for 10 min with increasing temperature resulted in a considerable increase in the removal of SO<sub>2</sub> from 31% at 20°C, 47% at 40°C to 61% at 60°C. Effect of H<sub>2</sub>O<sub>2</sub> used in desulfurization of dried apricots on the antioxidant capacity and phenolic compound content of the fruit whereas dried apricots were immersed in 0.5, 1.0 and 2% H<sub>2</sub>O<sub>2</sub> solutions at 20, 30 and 40°C for 5 min was investigated by [10] and indicate that H<sub>2</sub>O<sub>2</sub> was effective in desulfurizing, by decreasing up to 61% rate the SO<sub>2</sub> content in dried apricots.

The above-mentioned data reveals that using  $H_2O_2$  was the official method for desulfurization of dried apricots in most countries especially in Turkey which supplies about 75% of dried apricots consumed in the world. This work studied the possibility of using edible organic acids e.g., citric acid and acetic acid to remove SO<sub>2</sub> from over sulfite dried grapes into lower concentrations instead of  $H_2O_2$  because it is oxidizing and bleaching agent other than it removes SO<sub>2</sub> and sulfites from dried fruits e.g. apricots and grapes by converting them into sulfuric acid which is considered a harmful metallic acid for these

fruits, and consequently it may diminish their nutritional values and quality features. Our results illustrate that the removal of SO<sub>2</sub> from dried grapes by soaking treatments in citric acid (5%) were more efficient than those in  $H_2O_2$  (1%) at 30 and 50°C for 15 and 30 min while the potency of soaking treatments in acetic acid (5%) was approximately equal to those in  $H_2O_2$  (1%) at the same temperatures for the same times. It can be also noticed that the removal of SO<sub>2</sub> from dried grapes by soaking treatments in water exhibited the lowest potency compared to other soaking treatments.

#### Effect of soaking treatments of raisins on the total sugar content

Data presented in Table (2) reveals the effect of soaking of raisins in water,  $H_2O_2$  (1%), citric acid (5%) and acetic acid (5%) at 30 and 50°C for 15 and 30 minutes on the total sugars content in these samples of raisins compared to that in the control samples (untreated raisins). The results indicated slight changes in the total sugar content in the samples of raisins in all treatments compared to that in the control samples (65.1 ± 0.4 g/100g). The percentage of total sugars in raisins was recorded by [3] and indicates that raisins are sweet as they consist of about 60% sugar, predominantly fructose and glucose. It means that soaking treatments of raisins. This may be attributed to the short time of soaking treatments (15 and 30 min) and temperatures did not exceed 50°C.

## Effect of soaking treatments of raisins on the total phenols content

Table (3) indicates the effect of soaking treatments of raisins in water,  $H_2O_2$  (1%), citric acid (5%) and acetic acid (5%) at 30 and 50°C for 15 and 30 minutes on the total phenols content in these samples of raisins compared to that in the control samples. The results illustrated significant (P<0.05) decreases in the levels of total phenols in the samples of raisins obtained by the soaking treatments in water were lower than those obtained by citric acid (5%) then acetic acid (5%) while the maximum loss rates of phenols from raisins were obtained by  $H_2O_2$  because it is oxidizing agent, and consequently it can oxidize some phenols. These results are in agreement with those obtained by [10] who reported that soaking treatments of apricots in  $H_2O_2$  caused a considerable decrease of total phenols and antioxidant capacity in these fruits. They also recorded that the development and use of methods to preserve the nutritional content of the fruit are important. Therefore, this work was achieved to overcome this problem by using citric acid instead of  $H_2O_2$ .

### Effect of soaking treatments of raisins on the tannins content

Table (4) illustrates the effect of soaking treatments of raisins in water,  $H_2O_2$  (1%), citric acid (5%) and acetic acid (5%) at 30 and 50°C for 15 and 30 minutes on the tannins content in these samples of raisins compared to that in the control samples (untreated raisins). The results elucidated significant (P<0.05) decreases in the levels of tannins in the samples of raisins in all treatments compared to that in the control samples (93.2 ± 3.3 mg/100g). The loss rates of tannins from raisins obtained by the soaking treatments in water were lower than those obtained by citric acid (5%) then acetic acid (5%) while the maximum loss rates of tannins from raisins were obtained by  $H_2O_2$  because it is oxidizing agent, and consequently it can oxidize some tannins.

#### Effect of soaking treatments of raisins on the flavonoids content

Table (5) elucidates the effect of soaking treatments of raisins in water,  $H_2O_2(1\%)$ , citric acid (5%) and acetic acid (5%) at 30 and 50°C for 15 and 30 minutes on the flavonoids content in these samples of raisins compared to that in the control samples. The results demonstrated significant (P<0.05) decreases in the levels of flavonoids in the samples of raisins obtained by the soaking treatments in water were lower than those obtained by citric acid (5%) then acetic acid (5%) while the maximum loss rates of flavonoids from raisins were obtained by  $H_2O_2$  because it is oxidizing agent, and consequently it can oxidize some flavonoids. The data also indicate that the levels of flavonoids in the samples of raisins decreased by increasing of soaking time from 15 min to 30 min in all treatments. The most abundant flavonoids in raisins are quercetin and kaempferol [26].

#### Effect of soaking treatments of raisins on the color features

The grapes are exposed to sulfur dioxide for 6 to 8 hours, preserving their light color which can range from yellow to light amber. Figures (1 - 4) reveals the effect of soaking treatments of raisins in water,  $H_2O_2$  (1%), citric acid (5%) and acetic acid (5%) at 30 and 50°C for 15 and 30 minutes on the color features of these samples of raisins compared to that of the control samples (untreated raisins). The results indicated slight changes in the surface color parameters of raisins in all treatments compared to those in the control samples (L\*, a\* & b\* were 34.0, 1.88 & 9.73 respectively). It is obvious that the various soaking treatments of raisins led to increases of the L\* values, and decreases of the a\* and b\* values. The data also indicate that the changes in the surface color parameters of raisins obtained by the soaking treatments in water were lower than those obtained by acetic acid (5%) then citric acid (5%) while the maximum changes in the surface color parameters of raisins were obtained by the soaking treatments in  $H_2O_2$  because it is bleaching agent, and consequently it can decolorize these dried fruits. Therefore, this work was carried out to overcome this problem by using citric acid instead of  $H_2O_2$ . These results are in accordance with those obtained by [8, 9, 25, 27].

Treatments	30°C		50°C	
	15 min	30 min	15 min	30 min
Water	$5628 \pm 12^{a}$	$5244 \pm 11^{a}$	$3242 \pm 18^{b}$	$3045 \pm 13^{b}$
H <sub>2</sub> O <sub>2</sub> (1%)	$3420 \pm 14^{b}$	$3125 \pm 15^{b}$	$2816 \pm 14^{c}$	$2542 \pm 18^{\circ}$
Citric acid (5%)	$2320 \pm 17^{\rm d}$	$2155 \pm 15^{d}$	$1428 \pm 12^{e}$	$1409 \pm 11^{e}$
Acetic acid (5%)	$3250 \pm 20^{\rm b}$	$3128 \pm 22^{b}$	$2891 \pm 14^{\circ}$	$2742 \pm 18^{\circ}$

Table 1: Effect of soaking treatments of raisins on sulfur dioxide content (mg/kg)

<sup>a</sup>Sulfur dioxide content in untreated raisins (control) was  $5828 \pm 12 \text{ mg/kg}$ <sup>b</sup>The data are presented as means  $\pm$  SD calculated from three replicates.

<sup>c</sup>Different letters refer to significant differences at (P<0.05)

Table 2: Effect of soaking treatments of raisins on total sugars content (g/100g)	
<b>Tuble 2.</b> Effect of southing freatments of fulshis on total sugars content (groog)	

Treatments	30°C		50°C	
	15 min	30 min	15 min	30 min
Water	$64.6 \pm 0.5^{a}$	$63.9 \pm 0.4^{a}$	$62.5 \pm 0.3^{b}$	$62.2 \pm 0.1^{b}$
$H_2O_2(1\%)$	$62.5 \pm 0.4^{b}$	$62.3 \pm 0.5^{b}$	$61.7 \pm 0.3^{\circ}$	$61.5 \pm 0.2^{\circ}$
Citric acid (5%)	$62.3 \pm 0.4^{b}$	$62.1 \pm 0.2^{b}$	$60.6 \pm 0.4^{\circ}$	$60.0 \pm 0.2^{\circ}$
Acetic acid (5%)	$62.5 \pm 0.5^{b}$	$62.3 \pm 0.3^{b}$	$60.7 \pm 0.4^{c}$	$60.3 \pm 0.3^{\circ}$

<sup>a</sup>Total sugars content in untreated raisins (control) was  $65.1 \pm 0.4 \text{ g/100g}$ <sup>b</sup>The data are presented as means  $\pm$  SD calculated from three replicates.

<sup>c</sup>Different letters refer to significant differences at (P<0.05)

Table 3: Effect of soaking treatments or	f raisins on total phenols content (1	mg/100g)
--	---------------------------------------	----------

Treatments	30°C		50°C	
-	15 min	30 min	15 min	30 min
Water	$245.3 \pm 5.5^{a}$	$240.2 \pm 4.2^{a}$	$225.9 \pm 3.6^{b}$	$215.3 \pm 3.6^{\circ}$
H <sub>2</sub> O <sub>2</sub> (1%)	$233.8 \pm 5.6^{b}$	$230.3 \pm 3.3^{b}$	$212.3 \pm 5.1^{\circ}$	$205.0 \pm 4.5^{d}$
Citric acid (5%)	$242.8 \pm 4.3^{a}$	$238.7 \pm 3.4^{a}$	$220.6 \pm 3.1^{\circ}$	$210.7 \pm 5.4^{\circ}$
Acetic acid (5%)	$234.1 \pm 3.7^{b}$	$231.7 \pm 5.7^{b}$	$215.7 \pm 5.5^{\circ}$	$207.5 \pm 3.3^{d}$

<sup>a</sup>Total phenols content in untreated raisins (control) was  $250.3 \pm 3.6 \text{ mg}/100\text{g}$ 

<sup>b</sup>The data are presented as means  $\pm$  SD calculated from three replicates.

<sup>c</sup>Different letters refer to significant differences at (P<0.05)

Table 4: Effect of soaking treatments of raisins on tannins content (mg/100g)

Treatments	30°C		50°C	
=	15 min	30 min	15 min	30 min
Water	$90.4 \pm 3.5^{a}$	$88.3 \pm 4.3^{a}$	$82.6 \pm 3.4^{ab}$	$79.1 \pm 3.3^{ab}$
$H_2O_2(1\%)$	$85.6 \pm 4.4^{a}$	$82.5 \pm 4.6^{ab}$	$77.4 \pm 3.6^{bc}$	$73.3 \pm 3.3^{\circ}$
Citric acid (5%)	$88.7 \pm 3.7^{a}$	$85.7 \pm 4.5^{a}$	$80.5 \pm 5.3^{ab}$	$77.4 \pm 4.4^{bc}$
Acetic acid (5%)	$86.9 \pm 4.6^{\rm a}$	$83.8 \pm 5.4^{ab}$	$79.7 \pm 4.7^{ab}$	$75.6 \pm 5.5^{bc}$

<sup>a</sup>Tannins content in untreated raisins (control) was  $93.2 \pm 3.3 \text{ mg}/100\text{g}$ 

<sup>b</sup>The data are presented as means ± SD calculated from three replicates.

<sup>c</sup>Different letters refer to significant differences at (P<0.05)

Treatments	30°C		50°C	
-	15 min	30 min	15 min	30 min
Water	$44.3 \pm 2.4a$	$42.5 \pm 4.5a$	$37.7 \pm 3.3$ ab	$35.3 \pm 2.5b$
$H_2O_2(1\%)$	$38.6 \pm 3.7$ ab	$35.5 \pm 3.3b$	$33.3 \pm 4.5c$	$30.0 \pm 3.6c$
Citric acid (5%)	$43.8 \pm 3.6a$	$41.7 \pm 4.4a$	$36.6 \pm 2.6b$	$33.5 \pm 4.4c$
Acetic acid (5%)	$39.6 \pm 4.3$ ab	$37.4 \pm 2.5$ ab	$35.7 \pm 5.4$ b	$32.4 \pm 4.5c$

Table 5: Effect of soaking treatments of raisins on flavonoids content (mg/100g)

<sup>a</sup>Flavonoids content in untreated raisins (control) was  $45.3 \pm 3.5 \text{ mg/100g}$ <sup>b</sup>The data are presented as means  $\pm$  SD calculated from three replicates.

°Different letters refer to significant differences at (P<0.05)

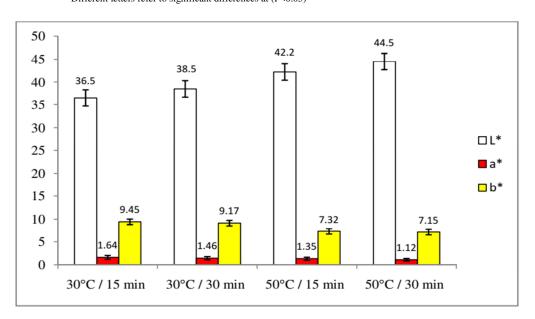


Figure 1:Effect of soaking treatments in water on the color features of raisins recorded in L\* (lightness), +a\* (redness) and +b\* (yellowness)

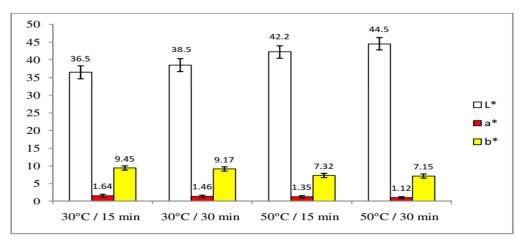


Figure 2: Effect of soaking treatments in  $H_2O_2$  (1%) on the color features of raisins recorded in L\* (lightness), +a\* (redness) and +b\* (yellowness)

Egypt. J. Chem.68, No. 5 (2025)

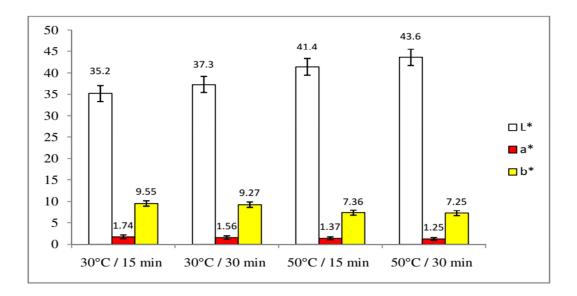


Figure 3: Effect of soaking treatments in citric acid (5%) on the color features of raisins recorded in L\* (lightness), +a\* (redness) and +b\* (yellowness)

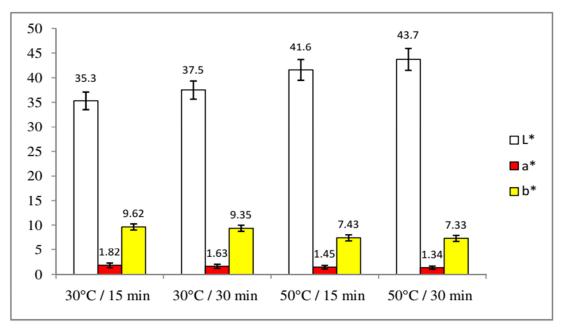


Figure 4: Effect of soaking treatments in acetic acid (5%) on the color features of raisins recorded in L\* (lightness), +a\* (redness) and +b\* (yellowness)

## 4. Conclusions

The data reveals that efficiency of SO<sub>2</sub> removal from raisins by various treatments was in the following order; citric acid (5%) followed by acetic acid (5%) and  $H_2O_2$  (1%) then water. The treatments with citric acid (5%) gave the best results and the lowest concentrations of residual SO<sub>2</sub> in the samples of raisins especially at 50°C for 15 min. This treatment decreased the levels of residual SO<sub>2</sub> in the samples of raisins to become less than legal limits and the efficiency of SO<sub>2</sub> removal from raisins by this treatment was about 75%. Moreover, the soaking treatment of raisins in citric acid (5%) caused the minimal effects on the chemical constituents of raisins e.g., total sugars, total phenols, tannins, flavonoids and color features compared to other treatments.

Egypt. J. Chem. 68, No. 5 (2025)

## 5. Conflicts of interest

No conflict of interest to declare

## 6. Acknowledgments

Great thanks to the department of biochemistry, and the department of food science, Faculty of Agriculture, Ain Shams University for providing all facilities required to successfully finish this work.

### 7. References

- [1] Esmaiili M., R.S. Gharebagh, K. Cronin, M.A.E. Mousavi and G. Rezazadeh (2007) Grape Drying: A Review. Food Reviews International, 23, 3, 257.
- [2] Christensen L.P. and W.L. Peacock (2013) Raisin drying process at the wayback machine. Raisin Production Manual, Univ. of California at Davis.
- [3] United States Department of Agriculture (2019) National Nutrient Database for Standard Reference. Nutrient Laboratory Homepage.
- [4] Turkyilmaz M., S. Tagi and M. Ozkan (2013) Changes in chemical and microbial qualities of dried apricots containing sulfur dioxide at different levels during storage. Food Bioprocess Technol. 6, 1526-1538.
- [5] Ough C.S. and L. Were, (2005) Sulfur dioxide and sulfites. Antimicrobials in Foods, P.M. Davidson, J.N. Sofos, A.L. Branen (eds.) (Taylor & Francis Publication Co, Boca Raton FL) pp. 143–167.
- [6] Li Z., J. Huang, L. Wang, D. Li, Y. Chen, Y. Xu, L. Li, H. Xiao, Z. Luo (2023) Novel insight into the role of sulfur dioxide in fruits and vegetables: Chemical interactions, biological activity, metabolism, applications, and safety. Crit Rev Food Sci Nutr. 27, 1-25.
- [7] Dordevic D., J. Capikova, S. Dordevic, B. Tremlová, M. Gajdács, I. Kushkevych (2023) Sulfur content in foods and beverages and its role in human and animal metabolism: A scoping review of recent studies. Heliyon 9 (4), 15452.
- [8] Ozkan M. and B. Cemeroglu (2002a) Desulfiting dried apricots by hydrogen peroxide. J. Food Sci., 67, 5, 1631 1635.
- [9] Hamzaoglu F., M. Turkyilmaz and M. Ozkan (2017) Use of hydrogen peroxide to remove sulfur dioxide from over sulfite dried apricots. 19th International Conference on J. Food Process Technol., 8, 9, 117.
- [10] Ugur Y. and S. Erdogan (2021) Effect of hydrogen peroxide used in desulfurization of dried apricot on the antioxidant capacity and phenolic compound content of the fruit. J. Food Measurement characterization, 15, 3708 3719.
- [11] Hajri Z., Oussama A., Chigr M., Kzaiber F. and Boutoial K. (2022) Effect of cooking and washing on sulfitess (SO<sub>2</sub>) content of dried fruits, presented at the 1st International Conference on Chemical and Biological Sciences. Istanbul, Turkey: Sciendo.
- [12] Rustamova R., F. Mamatsabirov, S. Sulaymanova, A. Rakhmatov, A. Babayev, I. Allenova, H. Isomiddinova (2024) Study on sulfitation of fruits and berries: Methods of sulfitation and desulfitation. E3S Web of Conferences 497.
- [13] AOAC (2010) Official Methods of Analysis of Association of Official Analytical Chemists. 18th Edition, Washington, DC, USA.
- [14]Ruiz D., J. Egea, F.A. Tomás Barberán and M.I. Gil (2005) Carotenoids from new apricot (Prunus armeniaca L.) varieties and their relationship with flesh and skin color. J. Agric. Food Chem., 53, 6368 6374.
- [15] Mnari A.B., A. Harzallah, Z. Amri, S.D. Aguir and M. Hammami (2016) Phytochemical content, antioxidant properties and phenolic profile of Tunisian raisin varieties (vitis vinifera L.). International J. Food Properties, 19, 3, 578 – 590.
- [16] Lam H.H., T.M.T. Nguyen, T.A.S. Do, T.H. Dinh and T.D. Bao (2021) Quantification of total sugars and reducing sugars of dragon fruit derived sugar samples by UV-Vis spectrophotometric method. IOP Conf. Ser.: Earth Environ. Sci. 947
- [17]Singleton V.L. and J.A. Rossi (1965) Colorimetry of total phenolics with phosphomolybodic phosphotungestic acid reagents. Amer. J. Enol. Vitic. 16:144-158.
- [18]Saeed N., M.R. Khan and M. Shabbir (2012) Antioxdant activity, total phenolic and total flavonoid contents of whole plant extracts Torilis leptophylla L. BMC Complementary and Alternative Medicine, 12, 221.
- [19]Zhishen J., T. Mengcheng, W. Jianming (1999) Determination of flavonoid contents in mulberry and their scavenging effects on superoxide radicals. Food Chemistry, 64, 555 – 559.
- [20] Snedecor, G.M. and W.G. Cochran (1980) Statistical methods, Sixth Edition, Iowa State Univ. press, Amer. Iowa, USA.
- [21] Joint FAO/WHO Expert Committee on Food Additives (2000) Evaluation of certain food additives, WHO Technical Report Series, No. 891. Geneva: WHO; p. 30–35.
- [22]Shoaei F., A. Heshmati, M. Khorshidi (2019) The risk assessment of sulphite intake through dried fruit consumption in Hamadan, Iran. J. Food Quality and Hazards Control 6, 121-127.
- [23]FAO/WHO, Codex Alimentarius (2021) General standard for food additives. CODEX STAN 192 195. Rome, Italy: FAO/WHO.
- [24] Hajri Z., Chigr M., Oussama A., Kzaiber F. and Boutoial K. (2023) Dietary exposure assessment to sulfites (SO2) in the Moroccan adult population. Food Research 7 (6): 1-10.
- [25] Ozkan M. and B. Cemeroglu (2002b) Desulfiting dried apricots by exposure to hot air flow. J. Sci. Food Agric., 82, 1823 – 1828.
- [26] Williamson G. and A. Carughi (2010) Polyphenol content and health benefits of raisins. Nutrition Research, 30, 511 519.
- [27]Guine R.P.F., I.C. Almeida, A.C. Correia and F.J. Goncalves (2015) Evaluation of the physical, chemical and sensory properties of raisins produced from grapes of the cultivar Crimson. Food Measure, 9, 337 – 346.