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Determination of Sulfite in some dried fruits using colorimetric method

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A B S T R A C T

Sulfites are often used as preservatives in dried fruits to prevent discoloration and spoilage. Some individuals may be sensitive or allergic to sulfites, and exposure can lead to adverse reactions. Monitoring sulfite levels helps protect these consumers and allows researchers to evaluate the long-term health impacts of sulfite consumption and contribute to ongoing research in food safety. The goal of the current study was to determine sulphur dioxide (SO2) concentration in some widely consumed dried fruits in Zawia city, Libya. Also is to ensuring that dried fruits are safe for consumption. A nine dried fruit samples were randomly collected from local market in Zawia city, Libya. The sulfur dioxide concentration in dried fruit samples were measured by colorimetric method using ONDA TOUCH UV-21 Spectrophotometer. The mean sulphite residue in apricot, white raisins, black raisins, banana, mango, kiwi, imported fig, local fig, plum was 252.2±2.50, 154.0±2.65, 166.0±1.00. 419.0±3.71. 223.2±2.37. 352.7±2.08, 259.7±2.52, 0, 326.9±7.34 respectively. The concentrations of SO_2 in the studied samples were within the permissible limits according to FDA regulations (up to 2,000 ppm). It appears that the content of this food preservative in dried fruits consumed in Libya has no serious risk for consumers in Libya.

تقدير الكبريت في بعض الفواكه المجففة باستخدام الطريقة اللونية

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الكلمات المفتاحية:
الفواكه المجففة
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إدارة الغذاء والدواء (*FDA*)

الملخص

غالبا ما تستخدم عوامل الكبرتة كمواد حافظة في الفواكه المجففة لمنع تغير اللون والتلف. قد يعاني بعض الأفراد من الحساسية تجاه مركبات الكبريت، ويمكن أن يؤدي التعرض إلى ردود فعل سلبية. تساعد مراقبة مستويات الكبريت على حماية هؤلاء المستهلكين وتسمح للباحثين بتقييم الآثار الصحية طويلة المدى لاستهلاك الكبريت والمساهمة في الأبحاث الجارية في مجال سلامة الأغذية. كان الهدف من الدراسة الحالية هو تحديد تركيز ثاني اكسيد الكبريت في بعض الفواكه المجففة المستهلكة على نطاق واسع في مدينة الزاوية، ليبيا. وكذلك التأكد من أن الفواكه المجففة آمنة للاستهلاك. تم جمع تسع عينات من الفواكه المجففة بشكل عشوائي من السوق المحلي في مدينة الزاوية، ليبيا. تم قياس تركيز ثاني أكسيد الكبريت في عينات الفواكه المجففة بالطريقة اللونية باستخدام مقياس الطيف الضوئي. كان متوسط تراكيز الكبريت في المشمش والزبيب الأبيض والزبيب الأسود والموز والمانجو والكيوي والتين المستورد والتين المحلي والبرقوق على التوالي كالاتي 252.2±2.50، 2.65±154.0، 1.00±166.0، 3.71±419.0، 2.37±223.2، 2.08±352.7، 2.52±259.7، 0، 7.34±326.9 ppm
ثاني اكسيد الكبريت في العينات المدروسة كانت ضمن الحدود المسموح بها وفقا للوائح منظمة الغذاء والدواء (يصل إلى2000 جزء من المليون) [16,17]. من خلال النتائج نلاحظ أن محتوى هذه المادة الحافظة الغذائية في الفواكه المجففة المستهلكة في ليبيا ليس له خطر كبير على المستهلكين الليبيين.

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1. Introduction

Sulfur fumigation is a method used for preservation or treatments of solid food to maintaining visual and microbial quality. It is primarily used for the preservation of dried fruits, such as apricots, grapes (raisins), and figs. This method involves exposing the products to sulfur dioxide gas (SO_2), which has antimicrobial and antioxidant properties. It helps in extending the shelf life of food products and prevents browning and maintains the color of the fruits [1]. It is effective in controlling insects and microorganisms. However, some people may be sensitive to sulfur compounds and can experience allergic reactions [2]. There can be a residual sulfur taste or odor if not handled properly. It requires careful control to avoid excessive exposure, which can be harmful.

The use of sulfur for fumigation can be traced back to ancient civilizations, including the Greeks and Romans, who burned sulfur to disinfect and preserve food, especially wine barrels. Sulfur fumigation was used for medicinal purposes and for preserving food. It became common in drying and preserving fruits due to its effectiveness in maintaining color and preventing spoilage [1]. In 19th Century with advancements in chemistry and industrial processes sulfur fumigation became more widely used, particularly in the dried fruit industry. The common method was involved burning sulfur candles in closed spaces to produce sulfur dioxide gas for fumigation [1]. The early 20th century brought about more standardized methods and regulatory oversight. The use of sulfur dioxide in food preservation was studied and regulated to ensure safety and efficacy [3]. Improved equipment for controlled fumigation processes was developed, allowing for better regulation of sulfur dioxide levels and reducing risks associated with its use. Sulfur fumigation became a standard practice in the dried fruit industry, especially in California, which became a major producer of raisins and other dried fruits. In late 20th Century to present with increasing awareness of food safety and consumer health, there has been more scrutiny of sulfur dioxide residues on food. Regulatory agencies, such as the FDA and EU authorities, set maximum residue limits and required proper labeling for sulfur-treated products. Research into alternative preservation methods, including natural preservatives and advanced packaging technologies, has increased. However, sulfur fumigation remains widely used due to its cost-effectiveness and efficiency [4]. Sulfur dioxide (SO_2) is one of six compounds that called sulfiting agents that are approved in the United States, for use as food additives. The other five are sodium sulfite (Na_2SO_3), sodium metabisulfite ($Na_2S_2O_5$), potassium metabisulfite ($K_2S_2O_5$), sodium bisulfite($NaHSO_3$), and potassium bisulfite ($KHSO_3$) [5,6].

It's important to note that while sulfites are generally recognized as safe when used within regulatory limits, they can cause adverse reactions in sensitive individuals. Some people may be allergic to sulfites, and in rare cases, sulfite sensitivity can lead to respiratory or allergic reactions. Due to this, regulatory authorities often require labeling of sulfites in foods, and some products may be labeled as "sulfite-free" to cater to individuals with sensitivities.

Determining the sulfite content in food typically involves chemical analysis [7]. Iodometric Titration is a widely used method for determining sulfite levels. It involves titrating the sample with iodine in the presence of an acidic medium. The sulfite reacts with iodine to produce iodide ions, and the endpoint is detected by a color change using a starch indicator [8]. Monier-Williams Method is based on the reaction of sulfite with hydrochloric acid and excess iodine. The unreacted iodine is then titrated with sodium thiosulfate, and the sulfite content is calculated based on the volume of thiosulfate used [7,9]. Ripper Method involves titrating a sample with iodine in the presence of an acid and a starch indicator. This method is commonly used for quick field tests [10]. One of the colorimetric method is Methylene Blue Method. In this method, sulfite reacts with methylene blue in an acidic solution, forming a colored complex. The intensity of the color is proportional to the sulfite concentration, and it can be measured spectrophotometrically [11,12]. Enzymatic Methods involve the use of enzymes that specifically react with sulfite to produce a detectable signal. These methods are often used in combination with other analytical techniques [13]. Chromatography method such as high-performance liquid chromatography (HPLC) and ion chromatography are sophisticated techniques that can separate and quantify individual components, including sulfites, in a food sample [14,15].

When determining sulfite levels in food, it's crucial to choose a method that suits the specific requirements of the analysis. The choice may depend on factors such as the type of food matrix, the expected sulfite levels, and the available laboratory equipment. Analytical laboratories with expertise in food testing often employ a combination of methods to ensure accurate and reliable results.

The expected sulfite levels in dried fruits can vary depending on factors such as the type of fruit, the processing methods used, and any regulatory requirements in place. In many countries, including the United States and European Union, regulatory limits are set for the maximum allowable sulfite levels in certain foods, including dried fruits. These limits are in place to protect consumers and ensure food safety. FDA's food labeling regulations require that sulfites present at 10 parts per million (ppm) or more be labeled on foods [16]. According to FDA regulations, dried fruits may contain sulfite levels up to 2,000 parts per million (ppm). However, Dried fruits containing sulfites must be labeled to warn consumers of their presence [17]. FDA's food labeling regulations require that dried fruits without added sulfites can be labeled as "sulfite-free" or "no sulfites added". It's essential for manufacturers to adhere to these regulations and for consumers to be aware of the sulfite content in dried fruits, especially if they have sulfite sensitivities or allergies. Reading product labels can provide information on whether sulfites have been added and, if so, at what concentration. If someone has concerns about sulfite levels in a specific dried fruit product, they may contact the manufacturer for more detailed information.

Current practices adhere strictly to regulatory guidelines to ensure consumer safety and product quality. Ongoing monitoring and research aim to assess long-term health impacts and refine safety standards. This Research study is to determine the sulfite content in dried fruits for ensuring that sulfite levels are within the legal limits set by regulatory bodies (FDA or EU authorities). This kind of research is essential to meet safety standards and avoid potential legal issues and to identify any potential long-term health risks associated with chronic exposure to sulfites and to protect public health and reduces the incidence of foodborne illnesses [18].

2. Methods

2.1 Sample Collection

Collecting representative samples of dried fruits from different batches to ensure accurate testing. Therefore, a nine dried fruit samples were randomly collected from local market in Zawia city, Libya during March 2024. The samples collected were include apricot, white raisins, Black raisins, banana, Mango, kiwi, Imported fig, Local fig, and plum.

2.2 Chemicals and Reagents

Formaldehyde solution (0-015%) prepared by diluting 40% formaldehyde. Acid bleached p-rosaniline–hydrochloride. In 1 L volumetric flask a 100 mg of p-rosaniline –hydrochloric acid was dissolved in 200 ml distilled water and a 150 ml hydrochloric acid (50%) were added then the volume was completed to the mark using distilled water. This solution must be left to stand for 12 hrs before use. Sodium tetra-chloro-mercurate, this solution was prepared by dissolving 23.4 g sodium chloride and 54.3 g mercuric chloride in a 2 L volumetric flask using distilled water. Sulphur dioxide standard solution was prepared by dissolving 170 mg sodium bisulphate in distilled water and the solution was diluted to the mark. This solution must be standardized with 0.01N iodine solution before use [19].

2.3 Preparation of standard solutions

To a series of 100 mL volumetric flasks 5 mL of mercurate ragent were added. Then a known volume (0,1,2,3 mL) of Sulphur dioxide were added and diluted using distilled water to the mark. A portion of 5 mL of each standard solution was added to a test tube containing 5 mL rosaniline reagent. Then 10 mL of 0.015% formaldehyde solution was added to each. This mixture was mixed well and hold to 30 min at 22 °C. The absorbance of these solution was read at 550 nm against the blank and the standard curve was plotted to obtained the concentration of tested samples [19].

2.4 Sample preparation

A 10 ± 0.02 g ground dried fruit were weighted and transferred to blender with a 290 mL distilled water. The mixture was blended for 2 min. A 10 mL of the fruit extract were transferred to 10 mL volumetric flask containing 5mL of 0.5 N sodium hydroxide. The solution was mixed for approximately 15-30 seconds. Then 4 mL of 0.5 N sulfuric acid and 20 ml mercurate reagent were added and diluted to the mark with distilled water. The blank solution was prepared in the same way only omit the 10 ml fruit extract [19].

A 2 ml of sample solution were transferred to a test tube containing 5 mL rosaniline reagent. Then 10 mL of 0.015% formaldehyde solution was added. This mixture was mixed well and hold to 30 min at 22 °C. The absorbance of solution was read at 550 nm against the blank. ONDA TOUCH UV-21 Spectrophotometer, ITALY, with 1 cm matched quartz cells were used for absorbance measurements, ITALY, with 1 cm matched quartz cells were used for absorbance measurements in delta technical services (Sadeem laboratory). Using the standard curve, the absorbance was converted to sulfur dioxide concentration (ppm). The analytical method used for determining sulfite concentrations in dried fruits using the Official Method 963.20 as specified at the reference [19].

3 Results and discussion

The colorimetric method for determination of sulfur dioxide in dried fruits, is based on the well-known Schiff reaction for detecting aldehydes. The results of this study shown that the sulfur concentrations in dried fruits are ranged between 0.00 to 419.0 ppm. According to Figure (1) the sulfur dioxide concentration values obtained for apricot and imported fig are perceptually in agreement, correspondingly, Mango is relatively in agreement with them. White raisins and black raisins have almost similar concentration of sulfur put lower than apricot and imported fig. Similarly, Kiwi and plum samples have almost equally concentration of SO_2. However, bananas have dragged the highest concentration among all of them (419.0±3.71). The sulfur amount of local fig sample was the lowest which is zero. This is due to the fact that the process of drying figs in Libya is following traditional and natural methods where figs are left under direct sunlight for several days. The amount of sulfur required per day is unknown to the general population, but the recommended value, from United States Department of Agriculture: Nutrient Database Laboratory [20], ranges from a minimum of 100 mg to a maximum of 850 mg, these results emphasize the need to investigate sulfur levels in Libyan foods.

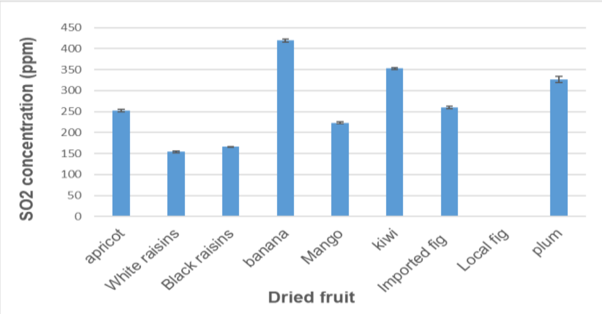

Fig. 1: Concentrations of Sulphur in dried fruits

Research on sulfur dioxide (SO_2) levels in dried fruits in Libya is limited, but general studies on SO_2 concentrations in dried fruits provide relevant insights. SO_2 is commonly used in dried fruits as a preservative to prevent spoilage, enhance color retention, and maintain quality. Studies from other regions show significant variations in SO_2 content depending on the type of fruit and packaging methods. For instance, bulk dried fruits like apricots and dates tend to have higher SO_2 concentrations than pre-packaged versions [21]. The levels of SO_2 in dried fruits must be chosen based on the expected storage conditions and length of the storage period. As Zamboni et al. [22] recommended after determine the effect of sulfur dioxide (SO_2) concentration on quality and nutritional properties of dried apricot fruits during storage using Neutron Activation Analysis. Where they found apricot fruits treated with different concentrations of SO_2 showed a rapid initial decrease in SO_2 levels, followed by a slower decline. While color darkening became more pronounced after 12 months, especially at lower SO_2 concentrations. This result is with agreement with the study [23] that founded the SO_2 concentration in the dried apricots samples decreased rapidly initially, then at a slower rate. Color darkening of the fruit became more noticeable after 12 months, particularly in the samples treated with 1.250 and 2.000 mg/kg SO_2.

4 Conclusion

The colorimetric method based on the Schiff reaction that used in this study has proven to be an effective technique for determining sulfur dioxide concentrations in dried fruits samples collected from local stores in Zawia city Libya. The study revealed a wide range of sulfur dioxide levels among different types of dried fruits, with values ranging from 0.00 to 419.0 ppm. The concentrations obtained were all at the globally acceptable level of sulfite. Dried bananas samples had the highest concentration at 419.0±3.71 ppm. The addition of SO_2 helps to inhibit the growth of mold, bacteria, and other microorganisms, preserving the fruit for longer periods. bananas brown very quickly due to enzymatic reactions, especially during the drying process. SO_2 acts as an anti-browning agent by inhibiting these reactions, helping the dried banana retain a bright, more appealing yellow color rather than turning dark brown, which could be unattractive to consumers. In addition, bananas are prone to spoilage due to their high sugar content, which can foster microbial growth. Therefore, bananas, being naturally sensitive to discoloration and spoilage, might need more sulfur dioxide compared to other dried fruits [24]. In contrast, the local fig sample contained no detectable sulfur dioxide, attributed to traditional sun-drying methods used in Libya.

Overall, the study provides valuable insights into the sulfur dioxide content in various dried fruits and emphasizes the need for appropriate SO_2 levels based on storage conditions to maintain quality and nutritional properties. Further research and monitoring are essential to ensure food safety and compliance with recommended dietary guidelines.

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