Sen F, Aksoy U, Tan G (2012) Determining effect of sulfuryl fluoride fumigation on dried apricots, raisins, and hazelnuts quality. In: Navarro S, Banks HJ, Jayas DS, Bell CH, Noyes RT, Ferizli AG, Emekci M, Isikber AA, Alagusundaram K, [Eds.] Proc 9th. Int. Conf. on Controlled Atmosphere and Fumigation in Stored Products, Antalya, Turkey. 15 – 19 October 2012, ARBER Professional Congress Services, Turkey pp: 315-320

DETERMINING EFFECT OF SULFURYL FLUORIDE FUMIGATION ON DRIED APRICOTS, RAISINS, AND HAZELNUTS QUALITY

Fatih Sen[1*], Uygun Aksoy[1], Gurler Tan[2]

[1]Ege University, Faculty of Agriculture, Department of Horticulture, 35100 Izmir, Turkey
[2]Dow AgroSciences, 34742 Kozyatagi, Istanbul, Turkey
*Corresponding author'S e-mail: *fatih.sen@ege.edu.tr*

ABSTRACT

Dried fruits and nuts have a long shelf life but many factors including storage pests or quality losses may limit their marketability. Storage pests pose significant threat for the dried fruits and nuts industry especially after the phase out of methyl bromide (MB). Research on MB alternatives is carried out intensively in Turkey as the major producer and trader of dried apricots, figs, raisins, and hazelnuts in the world market. Sulfuryl fluoride (SF) (ProFume, Dow AgroScience, USA) was tested on dried apricots, raisins, and hazelnuts as a MB alternative. The present study aimed at assessing the effect of SF treatments on dried apricots (cv. Hacıhaliloğlu), raisins (cv. Sultana) and hazelnuts (cv. Tombul) quality. Dried fruits and nuts samples were treated with SF at commercial scale at the storage units of TARİŞ Dried Fig Processing Plant in containers at a dosage of 100 $g.m^{-3}$. The temperature and relative humidity levels were monitored during fumigation and later in storage. After assessing SF as an effective fumigant, major quality parameters were analyzed right after the treatments, and after 7 months of storage under ambient conditions. Post-harvest SF treatment did not exert any negative effects on surface colour, water content, total soluble solids and titratable acidity contents of dried apricot and raisin fruits. Similarly, no negative effects were determined on colour and fatty acid composition of hazelnut kernels after 7 months of storage. Analysis also showed no SO_2 residues in treated dried apricot, raisins fruit and hazelnut kernels.

Key words: MB alternatives, ProFume, dried fruit, nut, quality, storage, residue

INTRODUCTION

Dried fruits and nuts are traditional export goods in Turkey. A major problem faced in the trade of dried fruits and nuts is the damage and losses caused by storage pests infesting fruit especially during ripening, drying and/or storage. Methyl bromide was used as the unique fumigant for disinfestations however it was banned in developed countries since 2005 and since January 1, 2008 in Turkey. It is scheduled for worldwide withdrawal from routine use as a fumigant in 2015 under the directive of the Montreal Protocol on Substances that Deplete Ozone Layer (Schneider et al., 2003) except for quarantine and pre-shipment purposes.

Integrated pest management, chemicals (phosphine, carbonyl sulfide, SF, ozone, cyfluthrin, iodomethane etc.) and physical (modified atmospheres, high pressure, heat/cold treatments, sanitation, radio frequency, long-wave energy, irradiation) methods were tested on various commodities and against different pests (Fields and White, 2002; Johnson et al., 2000; Schneider et al., 2003; Aksoy et al., 2004; Çetinkaya et al., 2006). Although there are a large number of potential alternatives to MB, each has limitations in terms of efficiency, cost, penetration or residues that prevent it from being a direct replacement for MB in all its current uses. In many of the research works, the main target is to provide control of storage pests, however quality is generally underestimated due to more stable nature of dried produce.

Dow AgroSciences released ProFume gas fumigant (SF) as an alternative to MB for the control of stored product insect pests in food storage, processing, milling and warehousing (Fields and White, 2002).

Food residue studies have already been conducted on key dried fruits and tree nuts. After testing efficacy of SF on major storage pests in Turkey, this study was designed to determine the effect of SF on the quality of dried apricots, raisins and hazelnuts.

MATERIALS AND METHODS

Sun-dried apricots (cv. Hacıhaliloğlu), raisins (cv. Sultana) and in-shell hazelnuts (cv. Tombul) packed in 50 and 25 kg (cross stitch bags for dried fruits and net for in-shell hazelnuts) bags were fumigated using SF (ProFume, Dow AgroScience, USA) at commercial scale in containers at TARİŞ Dried Fig Processing Plant in İzmir Turkey. During fumigation, SF concentration was 100 $g.m^{-3}$ for exposure of 24 h at a temperature ranging between 11^{o}C and 23^{o}C. Pooled sub-samples were prepared from the treated lots of 4 kg of hazelnut kernels and 7 kg of apricots and raisins for quality assessment. Quality of SF treated samples was compared with samples from the same lots treated with MB applying 60 $g.m^{-3}$ for 24 h. Quality tests were carried out as five replicates right after the fumigation and after 7 months of storage at ambient conditions. The temperature and relative humidity were monitored in the container during exposure and later in storage by data loggers (Hobo U12-013, Onset, USA).

Moisture content was measured by drying samples in a vacuum oven to a constant weight (AOAC, 1990) and calculated based on the percentage of weight loss. A water activity meter (TH 500, Novasina, Switzerland) was used to measure water activity values at 25°C. The surface color of dried fruits and kernels were measured on the two opposite sides of 20 fruits/kernels with a colorimeter (CR-300, Minolta Co., Japan), and average scores were recorded in terms of CIE L* a* b* values. Chroma (C*) value and hue angle (h^{o}) were calculated from a* and b* values. Total soluble solids content (TSS) was determined with a refractometer (ATC-1, Atago, Japan). Titratable acidity (TA) was determined by titration with 0.1 N NaOH up to pH 8.1 and expressed as g citric acid/100 g. Five trained panelists conducted the sensory analysis in discriminative evaluation of dried apricots and raisins. Visual appearance, flavor and texture of dried apricots and raisins were evaluated on a five-point scale (1: extremely poor; 9: excellent). The fatty acid composition of hazelnuts was determined on the lipid extracts after methylation to form fatty acid methyl esters (FAME) (AOAC, 1997) were analyzed by using a Hewlett Packard 6890N gas chromatograph equipped with a Spelco SPB-5 capillary column (Supelco, Bellefonte, PA) and a flame ionization detector (FID). Sulphur dioxide residue level was determined in duplicate by modified Monier Williams distillation method (AOAC, 1995).

The experiments were conducted as completely randomized design with five replicates. Significant differences among groups were determined using Duncan's multiple range tests at $P \leq 0.05$. Standard deviation of the mean (*SD*) was also calculated from the replicates. All computation and statistical analyses were done using SPSS package version 19.0 (SPSS Inc., Chicago, IL, USA).

RESULTS AND DISCUSSION

Dried apricots

Sulphuryl fluoride treatment did not have any adverse effect on surface colour of dried apricot (cv. Hacıhaliloğlu) fruits and the analyzed colour parameters (L*, a*, b*, C*, h^o) were similar to the control fruits after storage (Table 1). Both SF and MB treated fruits were darkened during the storage period as revealed by lowered a*, b* and C* values.

Table 1. Changes in fruit colour (L*, a*, b*, C*, h^o) of sulphuryl fluoride (SF) or methyl bromide (MB) treated dried apricots after treatment and after 7 months of ambient storage[a]

Time	Treatment	L*	a*	b*	C*	h^o
After Treatment	MB	40.44±0.22^{NS}	5.98±0.45^{NS}	29.70±0.46^{NS}	30.30±0.37^{NS}	78.62±0.99^{NS}
	SF	40.41±0.21	6.55±0.42	28.30±0.55	29.05±0.51	76.97±0.91
After 7 months storage	MB	35.58±0.61^{NS}	4.64±0.59^{NS}	20.17±0.47^{NS}	20.70±0.52^{NS}	77.07±1.52^{NS}
	SF	36.40±0.60	5.28±0.66	21.34±0.94	21.99±1.22	76.13±1.22

^{NS} Nonsignificant.

[a] Results are the means of five replicate samples ±SD.

Sulphuryl fluoride treatment did not influence moisture, TSS or TA contents and sensory quality of dried apricot fruits. At the end of the storage period, moisture content decreased significantly by about 37% due to the dry conditions prevailing in the ambient. Such moisture decrease triggered the increase in TSS and TA. The sensory quality scores of SF and MB treated samples were similar and both decreased at the end of the storage period due to darkening of colour and hardening of texture (Table 2).

Table 2. Changes in water content, TSS and TA contents of sulphuryl fluoride (SF) or methyl bromide (MB) treated dried apricots after treatment and after 7 months of ambient storage[a]

Time	Treatment	Water content (%)	TSS (%)	TA (%)	Sensory score
After Treatment	MB	27.05±0.14^{NS}	60.3±0.47^{NS}	1.51±0.05^{NS}	4.60±0.55
	SF	25.02±0.55	61.3±0.00	1.57±0.02	4.80±0.45
After 7 months storage	MB	15.79±0.16^{NS}	68.44±0.38^{NS}	1.98±0.08^{NS}	3.20±0.45
	SF	17.03±0.13	68.44±0.38	1.77±0.01	3.40±0.55

^{NS} Nonsignificant.

[a] Results are the means of five replicate samples ±SD.

Raisins

Raisins (cv. Sultana) colour values (L*, a*, b*, C*, h^o) were similar for SF and MB treated samples. Colour a*, b* and C* values increased during storage whereas h^o decreased (Table 3).

Table 3. Changes in fruit colour (L*, a*, b*, C*, h°) of sulphuryl fluoride (SF) or methyl bromide (MB) treated raisins after treatment and after 7 months of ambient storage[a]

Time	Treatment	L*	a*	b*	C*	h°
After Treatment	MB	25.89±0.49 [NS]	6.35±0.50 [NS]	14.45±2.46 [NS]	15.78±2.09 [NS]	66.28±2.95 [NS]
	SF	25.97±0.85	5.88±0.10	13.46±1.25	14.69±1.17	66.40±1.80
After 7 months storage	MB	25.94±2.63 [NS]	11.58±0.67 [NS]	17.06±1.10 [NS]	20.63±0.94 [NS]	55.79±2.41 [NS]
	SF	26.72±1.20	12.66±0.79	18.45±0.94	22.37±1.22	55.54±1.31

[NS] Nonsignificant.
[a] Results are the means of five replicate samples ±SD.

Sulphuryl fluoride and MB treatments did not exert significant effects on moisture, TSS, TA content and sensory attributes. Water content of raisins decreased from ca 16 % to 13 % after 7 months of storage which led to the increase of TSS and TA. Sensory quality scores were lower after storage mainly due to appearance (Table 4).

Table 4. Changes in water content, TSS and TA contents of sulphuryl fluoride (SF) or methyl bromide (MB) treated raisins after treatment and after 7 months of ambient storage[a]

Time	Treatment	Water content (%)	TSS (%)	TA (%)	Sensory score
After Treatment	MB	16.33±0.64 [NS]	71.5±0.77 [NS]	1.50±0.04 [NS]	4.80±0.45 [NS]
	SF	16.06±0.52	70.2±1.54	1.46±0.05	4.80±0.45
After 7 months storage	MB	13.03±0.08 [NS]	72.44±1.54 [NS]	2.00±0.07 [NS]	4.40±0.55 [NS]
	SF	12.78±0.07	72.89±0.77	1.90±0.03	4.20±0.45

[NS] Nonsignificant.
[a] Results are the means of five replicate samples ±SD.

Hazelnut kernels

Post-harvest SF treatment had no negative effect on colour value of hazelnut (cv. Tombul) kernels. The changes that occurred during storage were similar in SF and MB treated hazelnut kernels (Table 5). The fatty acid composition of SF treated kernels was statistically similar to MB treated samples after storage (Table 6).

Table 5. Changes in fruit colour (L*, a*, b*, C*, h°) of sulphuryl fluoride (SF) or methyl bromide (MB) treated hazelnut kernels after treatment and after 7 months of ambient storage[a]

Time	Treatment	L*	a*	b*	C*	h°
After Treatment	MB	28.04±1.77 [NS]	11.09±0.30 [NS]	18.21±0.81 [NS]	21.32±0.87 [NS]	58.66±0.54 [NS]
	SF	28.07±1.15	10.44±0.11	19.75±0.32	22.34±0.30	62.14±0.38
After 7 months storage	MB	22.48±0.64 [NS]	5.77±0.26 [NS]	11.13±0.69 [NS]	12.55±0.52 [NS]	62.54±2.34 [NS]
	SF	24.15±1.48	5.91±0.31	11.03±0.71	12.21±0.57	61.80±1.60

[NS] Nonsignificant.
[a] Results are the means of five replicate samples ±SD.

Table 6. Changes in fatty acid composition of sulphuryl fluoride (SF) or methyl bromide (MB) treated hazelnut kernels after treatment and after 7 months of ambient storage[a]

Time	Treatment	Palmitic	Stearic	Oleic	Linoleic	Linolenic	Myristic
After 7 months storage	MB	4.93 [NS]	2.31 [NS]	82.26 [NS]	10.21 [NS]	0.11 [NS]	0.18 [NS]
	SF	5.13	2.59	82.85	9.16	0.11	0.17

[NS] Nonsignificant.
[a] Results are the means of five replicate samples ±SD.

The quality analyses showed that SF fumigation has no negative impact on dried apricots and raisins as well as hazelnut kernels. Among quality attributes, color is considered as one of the major parameters for dried apricots, raisins and hazelnut kernels. SF exposure did not create any significant impact on colour of the tested commodities even after 7 months of storage under ambient conditions. Fruit colour changed during storage irrespective of the fumigant used due to a number of chemical and biochemical reactions. Storage period had marked effect on quality. Enzymatic and non-enzymatic browning may occur during drying and storage (Roos and Himberg, 1994; Perera and Baldwin, 2001). The darkening rate in storage is related to the substrate and the storage conditions e.g. water content, a_w, temperature and oxygen (Perera, 2005). The uncontrolled storage conditions promoted water loss in dried apricots and raisins which further concentrated TSS and TA contents. Dried fruits have direct interaction with the storage atmosphere and high temperature and low relative humidity levels (data not shown), which especially towards the end of the storage period have fastened water loss resulting in lower sensory scores (Mc Bean et al., 1971; Fennema, 1976).

Sulphur dioxide is accepted as an additive and there is a tendency for the reduction of its permissible maximum limits and labeling in case of treatment. The analysis showed no residual sulphur dioxide in SF treated raisins fruit analyzed one week after SF treatment.

Based upon the quality results SF can be recommended as a fumigant alternative to MB to control storage pests in dried fruits and nuts industry. Controlled storage conditions will further contribute to the preservation of quality even during extended storage conditions.

ACKNOWLEDGMENTS

The research is a part of the project partially supported by Dow AgroScience (France) and TARIS Fig Agricultural Sales Cooperative (Turkey).

REFERENCES

Aksoy U, Meyvacı KB, Sen F, Altındişli A (2004) Impact of fumigants applied to control storage pests on fruit quality of dried figs. IOBC WPRS Bulletin. 27: 203-209.

AOAC (1990) Official Method of Analysis, 15th ed., Association of Official Analytical Chemists, Arlington, VA.

AOAC (1995) Official Method 990.28 Sulfites in Foods Optimized Monier-Williams Method.

AOAC (1997) Official Method 996.06 Fat (Total, Saturated, and Unsaturated) in Foods

Fennema OR (1976). Principles of Food Science, Part I. Food Chemistry. Marcel Decker Inc., New York.

Fields PG, White NDG (2002) Alternatives to methyl bromide treatments for stored-product and quarantine insects. Ann. Rev. Entomol. 47: 331-359.

Johnson JA, Valero KA, Hannel MM, Gill RF (2000) Seasonal occurrence of postharvest dried fruit insects and their parasitoids in a culled fig warehouse. Journal of Economic Entomology 93: 1380-1390.

Mc Bean DMcG, Joslyn MA, Nury FS (1971) Dehydrated Fruit. In: Hulme AC (Ed) The Biochemistry of Fruits and Their Products. Academic Press, London, pp. 623-648.

Perera CO (2005) Selected quality attributes of dried foods. Dry. Technol. 23: 717-730.

Perera CO, Baldwin EA (2001). Biochemistry of fruits and its implications on processing. In: Arthey D, Ashusrt PR (Eds) Fruit Processing; Nutrition, Products and Quality Management, Aspen Publishers, Gaithersburg, MD, pp.19-36.

Roos YH, Himberg MJ (1994) Nonenzymatic browning behavior, as related to glass transition, of a food model at chilling temperatures. J. Agr. Food Chem. 42: 893-898.

Schneider SM, Rosskopf EN, Leesch JG, Chellemi DO, Bull CT, Mazzola M (2003) Research on alternatives to methyl bromide: pre-plant and post-harvest. Pest Management Science, 59: 814-826.

Cetinkaya N, Ozyardımcı B, Denli E, Ic E (2006) Radiation processing as a post-harvest quarantine control for raisins, dried figs and dried apricots. Radiation Physics and Chemistry 75: 424-431.