Proposition 65

Interpretive Guideline No. 2012-02

Consumption of Sulfur Dioxide in Dried Fruits

June 2012

Summary

Under Proposition 65[1], a warning for exposure to sulfur dioxide (SO_2) from consumption of dried fruit is not required because SO_2 exposure will be below the proposed Maximum Allowable Dose Level (MADL) when the reasonably anticipated rate of intake by the average user of the product is considered.[2]

Scope of Interpretive Guideline

The Office of Environmental Health Hazard Assessment (OEHHA) may issue an Interpretive Guideline that interprets Proposition 65 and its implementing regulations, as applied to specific facts. The Interpretive Guideline reflects OEHHA's scientific interpretation of the available information as the lead agency for implementation of the Act.[3]

SO_2 was listed as a chemical known to cause reproductive toxicity under Proposition 65, effective July 29, 2011.[4] This interpretative guideline applies only to SO_2 in dried fruit resulting from the use of SO_2 on fruit during the production process. This guideline calculates average exposures to SO_2 in various dried fruits and compares them to the proposed Maximum Allowable Dose Level (MADL) for the chemical. Exposures at or below a MADL are exempt from the warning requirements of Proposition 65.

Sulfur Dioxide in Dried Fruit

SO_2 is used to preserve the color and flavor of dried fruit and to act as an antimicrobial agent.[5] Fruits treated with SO_2 are light in color and include, but are not limited to, golden raisins, dried apricots, dried peaches, dried apples, dried pineapple, dried papaya and dried mango.[6] California, the primary contributor of dried fruit to the U.S. market[7], uses SO_2 in approximately 15% of its dried fruit products.[8]

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[1] Safe Drinking Water and Toxics Enforcement Act of 1986, Health and Safety Code section 25821.C.2 *et seq.*
[2] Title 27, California Code of Regulations, section 25821(c)(2).
[3] Health and Safety Code section 25249.12
[4] California Proposition 65 list of chemicals known to cause cancer and reproductive toxicity. Most recent list is available at: http://www.oehha.ca.gov/prop65/prop65_list/Newlist.html
[5] Papadopoulou-Mourkidou, E. (1991). "Postharvest-applied agrochemicals and their residues in fresh fruits and vegetables." *Journal - Association of Official Analytical Chemists* 74(5): 745-765
[6] Freedman, B. J. (1980). "Sulphur dioxide in foods and beverages: its use as a preservative and its effect on asthma." *British journal of diseases of the chest* 74(2): 128-134.
[7] USDA: "Noncitrus Fruits and Nuts 07.07.2011", *National Agricultural Statistics Service*
[8] Data provided by SunMaid© Corporation.

Dried fruit has residual water that comprises 30% or less of the total weight of the product. The presence of this residual water allows SO_2 to dissolve into solution.[9] SO_2 in the dried fruit is either bound or free and the combination is referred to as total sulfites, or sometimes as "total SO_2."[10] Total sulfite includes sulfur compounds both reversibly and irreversibly bound to food components.[11,12] The bound form constitutes the majority of the total sulfites in fruit.

Free sulfite (sometimes referred to as "free SO_2") represents the total dissolved SO_2 which exists as an equilibrium among molecular SO_2 (which is a dissolved gas), bisulfite ion (HSO_3^-), and sulfite ion (SO_3^{2-}).[13] Only the molecular SO_2 falls under the Proposition 65 listing of sulfur dioxide. Free sulfite is used to calculate the amount of molecular SO_2 in dried fruit, as discussed below.

The equilibrium between molecular SO_2 and the ionic forms is dependent on pH. As shown in Figure 1,[14] since the pH of dried fruit is generally in the range of 3.2 – 5.5[15], the proportion of unbound SO_2 in dried fruit in the form of molecular SO_2 is expected to be very small. Further, there is evidence that the amount of free SO_2 in the dried fruit decreases over storage time, resulting in even lower levels of available molecular SO_2.[16]

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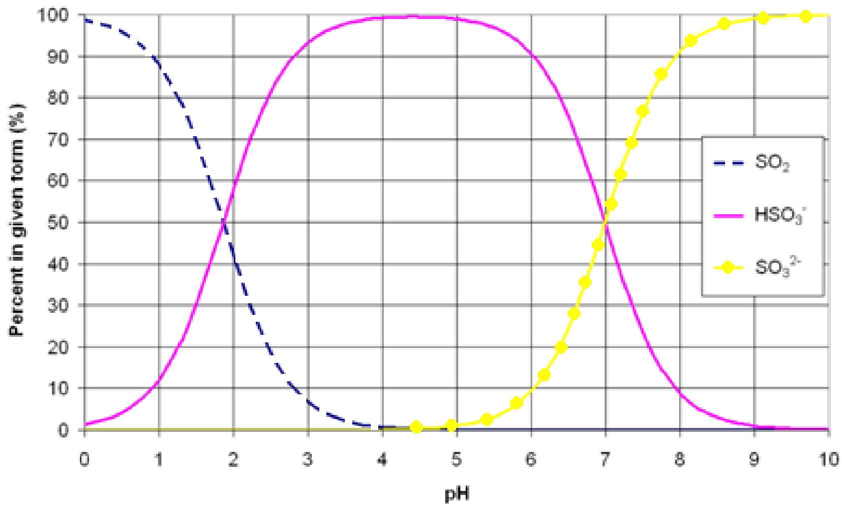
[9] Brown, A. (2010). "Understanding Food: Principles and Preparation". Belmont, CA, Wadsworth.
[10] DeMan, J. M., Ed. (1999). "Principles of food chemistry." Aspen Publishers.
[11] Wedzicha B.L. (1992). "Chemistry of sulfating agents in food". *Food Additives and Contaminants* 9(5):449-459.
[12] Wedzicha, B. L., I. Bellion, and S.J. Goddard (1991). "Inhibition of browning by sulfites." In: *Nutritional and Toxicological Consequences of Food Processing* M. Friedman (Ed). Pub. Plenum Press.
[13] Rotter, B. (Jan 2001). "Sulfur Dioxide" available at http://www.brsquared.org/wine/)
[14] Carswell, D.R. (1977). The Determination of Sulfur Dioxide in Food – a Literature Review. Scientific & Technical Surveys No. 103
[15] U.S. Food and Drug Administration. "Bad Bug Book: Foodborne Pathogenic Organisms and Natural Toxins Handbook. pH Value of Various Foods." Available at http://www.fda.gov/Food/FoodSafety/FoodborneIllness/FoodborneIllnessFoodbornePathogensNaturalToxins/BadBugBook/ucm122561.htm
[16] Bolin, H.R. and R. Jackson (1985). "Factors Affecting Sulfur Dioxide Binding in Dried Apples and Apricots." *Journal of Food Processing and Preservation* 9:25-34.

Figure 1. Percent of Free SO_2 forms in solution at a given pH



Current analytical methods to determine the concentration of SO_2 in dried fruit are indirect. One method analyzes the amount of free (unbound) SO_2, which includes molecular SO_2, bisulfite ion and sulfite ion (ETS Method MIW 008: aeration-oxidation)[17] that is released from fruit pureed with deionized water and then acidified to release SO_2 gas. The amount of molecular SO_2 cannot be directly measured, but can be calculated by means of the equation:

$$\text{Molecular } SO_2 = \text{Free } SO_2 / (10^{(pH-1.81)}+1)$$ [18]

The pH used in the equation is the pH of the fruit slurry prior to acidification.

Another method measures total sulfites, including both bound and free forms (ETS Method MIA 024: flow injection)[11], is not relevant in this context since it does not quantify free SO_2. A measure of free SO_2 is needed to calculate the amount of molecular SO_2 in dried fruit.

Level of Exposure to Sulfur Dioxide in Fruit

Table 1 below provides the concentration of free SO_2 measured in slurry for different products using the methods described in AOAC Official Method 990.30[19], and the amount of molecular SO_2 calculated from the free SO_2 using the equation given above.

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[17] ETS Laboratories Reports #527775R, 529613, 535705 and 535711.

[18] University of California at Davis, Cooperative Extension. Enology Briefs Vol 1(1), 1982. Available at http://www.moundtop.com/so2/EnologyBriefs-1-1.pdf

Table 1. Concentration of Free and Molecular SO_2 in dried fruit products[20]

Product	Measured pH of Slurry	Mean Free SO_2 Measured in Slurry (ppm)	Molecular SO_2 Calculated from Free SO_2 (ppm)
Golden Raisins	3.44 – 3.45	505	11.37
Dried Apricots	3.90 – 3.97	240	1.82
Dried Peaches	3.43 – 3.53	355	7.35
Dried Apples	4.31 – 4.34	635	1.94
Dried Pineapple	3.84 – 3.87	20	0.19
Tropical Trio (dried Pineapple, Papaya, Mango)	3.92 – 3.96	37.5	0.26
Dried Mango	3.90 – 3.93	35	0.27
Fruit Bits	3.58 – 3.68	192.5	2.86
Mixed Fruit	3.82 – 4.02	272.5	2.25

Level of Exposure to Proposition 65 Chemicals that Cause Reproductive Toxicity

Proposition 65 regulations address how to calculate the exposure to chemicals listed as known to cause reproductive toxicity:

> "For purposes of Section 25249.10(c) of the Act, the level of exposure to a chemical listed as causing reproductive toxicity shall be determined by multiplying the level in question (stated in terms of a concentration of a chemical in a given medium) times the reasonably anticipated rate of exposure for an individual to a given medium."[21]

By this provision, the reasonably anticipated rate of exposure to a chemical for a given individual is used in exposure calculations. The regulations give further guidance for calculating the reasonably anticipated rate of exposure for chemical exposures from consumer products:

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[19] AOAC Official Method 990.30 (2007). "Sulfite (Free) in Wines Flow Injection Analysis Method." In *Official Methods of Analysis, 18th ed (V.2).* Association of Official Analytical Chemists International, Gaithersburg, MD.

[20] ETS Laboratories, Report No. 527775R, 899 Adams St., Suite A, St. Helena, California, 94574, available at http://www.oehha.ca.gov/prop65/law/pdf_zip/ETSrpt_527775R.pdf

[21] Title 27, Cal. Code of Regs., section 25821(b)

> "For exposures to consumer products, the level of exposure shall be calculated using the reasonably anticipated rate of intake or exposure for average users of the consumer product, and not on a per capita basis for the general population. The rate of intake or exposure shall be based on data for use of a general category or categories of consumer products, such as the United States Department of Agriculture Home Economic Research Report, Foods Commonly Eaten by Individuals: Amount Per Day and Per Eating Occasion, where such data are available."[22]

Table 2 provides estimates of average intake by the average consumer of each specified dried fruit product. With one exception, values provided were calculated by OEHHA from the data collected in the National Health and Nutrition Examination Survey (NHANES). This is a dietary survey of individuals throughout the United States reported by the US Centers for Disease Control and Prevention. The values used to estimate average intakes were for any individual that reported consuming the food on the first day of a 2-day, 24 hour Dietary Recall, for the data years 1999-2008.[23] Data for consumption of golden raisins are not available in NHANES. Estimated consumption by the average consumer of golden raisins was based on information on sales and usage of golden raisins provided by Exponent.[24]

Exposure of the average consumer to molecular SO_2 in dried fruit can be calculated based on these average intake values for consumers of the food and the concentrations provided in Table 1. These values are also provided in Table 2.

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[22] Title 27, Cal. Code of Regs., section 25821(c)(2)

[23] Data available at http://www.cdc.gov/nchs/nhanes/nhanes_questionnaires.htm

[24] Exponent, Response to Information Request — SO_2 Analytical Methods and Golden Raisin Consumption Data, Project No. 0805389.000 I0T0 letter to Dr. James Donald, OEHHA, March 27, 2012,33 pages with attachment, available at http://www.oehha.ca.gov/prop65/law/pdf_zip/SO2ExponentAnaylitic.pdf

Table 2. Estimates of the Intake of Specific Dried Fruits and the Resulting Intake of Molecular SO_2

	Average Dried Fruit Intake by the Average Consumer (g/day)[25]	Estimated Exposure to Molecular SO_2 in Fruit (µg/day)
Golden Raisins	9-12[26]	103-136
Dried Apricots	16.1	29
Dried Peaches	26.0	191
Dried Apples	26.5	51
Dried Pineapple	37.4	7
Dried Papaya	30.5	8
Dried Mango	49.8	13
Fruit Bites	12[a]	34
Mixed Fruit	12[a]	27

[a] Consumption values were not available for these foods from the NHANES survey. The value provided is the largest serving size noted on packages of these fruits.

SO_2 Exposure of the Average Dried Fruit User Compared to the MADL

Table 2 shows that the highest estimate of exposure to SO_2 through consumption of any dried fruit for which consumption data are available is 191 micrograms per day (µg/day) (dried peaches). OEHHA has developed a proposed MADL for SO_2 of 220 µg/day.[27] This MADL is based on inhalation data. All of the studies that formed the basis for listing SO_2 were of exposure to SO_2 as a gas. There are currently no available studies on exposure to SO_2 solely by the oral route. However, based on review of relevant information[28], OEHHA has concluded that exposure to SO_2 by the oral route is expected to pose no more risk, and may pose less risk, than exposure to the equivalent amount by the inhalation route.

[25] Derived by OEHHA from the National Health and Nutrition Examination Survey (NHANES), Dietary Interview Data – Individual Foods, First Day of 24 hour Dietary Recall, Data Years 1999-2008. Data available at http://www.cdc.gov/nchs/nhanes/nhanes_questionnaires.htm

[26] Exponent, Response to Information Request — SO_2 Analytical Methods and Golden Raisin Consumption Data, Project No. 0805389.000 I0T0 letter to Dr. James Donald, OEHHA, March 27, 2012,33 pages with attachment, available at http://www.oehha.ca.gov/prop65/law/pdf_zip/SO2ExponentAnaylitic.pdf.

[27] The Initial Statement of Reasons for the proposed MADL regulation and information on the opportunity for public comment are available at http://www.oehha.ca.gov/prop65/law/pdf_zip/062812SulfurdioxideISOR.pdf

[28] Office of Environmental Health Hazard Assessment. Evidence on the Developmental and Reproductive Toxicity of Sulfur Dioxide, 2011. Available at http://www.oehha.ca.gov/prop65/hazard_ident/pdf_zip/So2HID022511.pdf

The analysis in this Interpretive Guidance applies only to the specific compound SO_2, and does not apply to sulfites, bisulfites and metabisulfites. These chemicals are not listed under Proposition 65 and are therefore not subject to the law's warning requirement. As stated previously, only a small percentage of the total sulfite in the treated fruit is molecular SO_2.

OEHHA concludes that consumption by the average consumer of dried fruit treated with SO_2 will not result in an exposure to SO_2 exceeding the proposed MADL. Therefore, a warning is not required under Proposition 65 at this time for exposure to SO_2 from consumption of dried fruit.

OEHHA released the proposed MADL for public review and comment concurrent with the release of this Interpretive Guideline. OEHHA will review any public comments, determine if revisions are necessary and adopt the final MADL as soon as feasible. OEHHA may revise this Interpretive Guideline, as appropriate, upon or following adoption of the MADL, or when other relevant information becomes available.[29]

[29] Title 27, Cal. Code of Regs., section 25203(c)