Estimation of residual potassium sorbate content in high moisture prunes

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**ABSTRACT**

The purpose of this study was to generate a table for high moisture prune makers to be able to estimate the residual potassium sorbate content depending on the concentration of preservative used and the type of application (immersion or spraying). Medium size plums (35 to 48 fresh units per kg) were harvested with an average maturity over 20°Brix and dehydrated in oven until they reached an average humidity of 21 ± 1% and an average water activity (aw) of 0.682 ± 0.013. Subsequently, the softening process was done in an autoclave reaching a humidity of 30 ± 2% and a aw of 0.782 ± 0.020, prunes were drained and pitted. The average performance of medium size prunes was 1.08 ± 0.01 kg of prunes to obtain 1.00 kg of pitted high moisture prunes. The average residue of pits was 14 ± 1%. 8 treatments were carried out with 4 repetitions of 20 units of high moisture prunes, in which potassium sorbate was applied using the following concentrations; 1.25; 1.50; 1.75; 2.00; 2.25; 2.50; 2.75 and 3.00% through immersion and spraying. Samples were stabilized in hermetic containers for twenty-four hours. Residual potassium sorbate was determined using ISO 5519:2008 analytical technique and a table was made with the data obtained. In both methods, immersion and spray, the residual potassium sorbate obtained, depending on the concentrations used, adjusted to linear models and were grouped by ranges. Both methods showed significant differences in residual potassium sorbate. The Argentinean Alimentary Code establishes a residual maximum content of 100 ppm, which is not enough to preserve the final product, since it was found that the antimicrobial action of sorbates occurs between 200 and 600 ppm (0.02 and 0.06%) depending on the moisture content. This was corroborated in the Codex Alimentarius International Food Standards, which allows the use of sorbates with a maximum level of 500 ppm in dried fruit.

**Keywords:** D’agen plum; Prunus domestica; (2E, 4E)-hexa-2, potassium 4-dienoate.
INTRODUCTION

The plum d’Agen is mainly destined to dehydration due to its high sugars content and excellent flavor. Worldwide, the main producing regions are California (USA), O’Higgins (Chile), Lot-et-Garonne (France) and Mendoza (Argentina). The province of Mendoza has a productive area of 15,055 hectares (ha) over the 18,280.9 implanted hectares and an average dehydrated plum production between 15 and 40 thousand tons (t).

The great variability in the production is due to the occurrence of climatic contingencies (frost, wind, rain and hail) and to red spot. The domestic market practically does not consume dehydrated plums (approximately 3,500 tons). The remaining 88% of the production is exported to countries such as Russia, Germany, Brazil and Japan (Institute of Rural Development [Instituto de Desarrollo Rural], 2015). For this reason dehydrated plum is an important product for the region.

During the elaboration of dehydrated plum, the fruit undergoes a drying process (sun or oven) that ends when it reaches a humidity of 21% or less. After that, it undergoes a tenderizing process (exposure to steam or hot water), to achieve a pleasant texture for the consumer, to eliminate microorganisms and to facilitate pitting. In this stage moisture is incorporated into the fruit (final moisture: 30-34%) and therefore it is important to use a preservative to protect the fruit from fungi and yeasts.

Sorbic acid (2,4-hexadienoic acid, CH3-CH=CHCH=CH-COOH) and its calcium and potassium salts - commonly called sorbates - inhibit or retard the growth of fungi, yeasts and certain bacteria (Chichester and Tanner, 1973; Sofos et al., 1986; Sofos, 2000; Stopforth, et al., 2005).

They are widely used due to their physiological inertness, antimicrobial effect in small concentrations and their high threshold of taste perception (Guadagni and Schade, 1973; Lück and Jager, 1997; Sofos, 2000; Stopforth, et al., 2005). They are considered safe for food use when they are used with good manufacturing practices (Bolin et al., 1980; Stopforth et al., 2005) since they are metabolized in the body through a mechanism similar to that of fatty acids. Most of them is oxidized to carbon dioxide and water, providing 6.6 Kcal/g (Bolin et al., 1980; Chichester and Tanner, 1973; Stopforth et al., 2005).

Sorbates play a key role in the conservation of intermediate moisture foods such as tenderized plums. They are usually used in concentrations between 0.02 and 0.05% (Chichester and Tanner, 1973; Stopforth et al., 2005). Its effectiveness depends on the moisture content and pH of the food: the higher the humidity and pH, the more preservative will be required to inhibit microbial growth (Bolin and Boyle, 1967).

In the sorbate application stage, the preservative is applied to plum with moisture content above 29% (aw above 0.700) by spraying or immersion (Morales Friette, 1971; Somogyi, 2005).

The immersion method involves of immersing the rehydrated plum in a potassium sorbate solute for a certain time, at a certain concentration and temperature.

One of the main drawbacks of this method is that the sugars contained in the plum are solubilized in the solution and, in turn, the fruit absorbs water (Morales Friette, 1971). This makes difficult to standardize the final moisture content of the plum, and therefore the residual dose of potassium sorbate may be lower than that required in the product, causing the development of fungi and yeast with its consequent loss of quality.

In the spraying method, the preservative is applied in vaporized form (reduced to very small drops). This system ensures an application of potassium sorbate in the required residual percentage since it does not affect the final moisture content of the plum.

Usually, the concentrations of the solutions applied by immersion or spraying are between 2% and 5% (Morales Friette, 1971; Bolin and Boyle, 1967; Stopforth et al., 2005). They are usually used at room temperature.

The Article 916 bis of the Argentine Food Code [Código Alimentario Argentino (C.A.A.)] states that: “Surface treatment of dried fruits with sorbic acid or potassium sorbate is allowed provided that the residual content (expressed in sorbic acid) does not exceed 100 mg/kg or ppm of whole fruit”. This article is incorrectly worded and lacks a zero to the residual limit. Processing industries and international regulations have always used a limit of 1,000 ppm for tenderized plums.

This is due to the fact that the antimicrobial action of sorbate is observed between 200 and 600 ppm, depending on the moisture content of the fruit to be preserved (Alagöz, et al., 2015; Chichester and Tanner, 1973; Stafford, 1976; Stopforth, et al., 2005). Now, the Codex Alimentarius in the Codex General Standard for Food Additives [Norma General del Codex para los Aditivos Alimentarios] states that: “Surface treatment of dried fruits with sorbic acid or potassium sorbate is allowed provided that the residual content (expressed in sorbic acid) does not exceed 100 mg/kg or ppm of whole fruit”.

To ensure that the high moisture plum has an adequate amount of preservative, either to prevent microbial spoilage or to comply with parameters requested by the country of destination (0 - 1,000 ppm), potassium sorbate determinations are performed using different analytical techniques. For this it is necessary to have the proper equipment and personnel.

However, not all producers and processing companies have these resources. Thus, this research work aims at generating a tool that allows developers to estimate the content of potassium sorbate in high moisture plum d’Agen, according to the applied dose and method of application (immersion and spraying).

MATERIALES Y MÉTODOS

Raw material

The plum (Prunus domestica) d’Agen variety, medium caliber (35 to 48 fresh units per kg) was harvested from
the crops of the Agricultural Experiment Station [Estación Experimental Agropecuaria (EEA)] Rama Caidá (georeference: 34°40'03.93'' S 68°23'37.80'' W). Soluble solids content: above 20%, pulp firmness: between 0.211 and 0.281 kgf/cm² (equivalent to 3-4 pounds of pressure per square inch). The dehydration process was carried out at 82 °C, with an average relative humidity of 60% for 21 hours, in the oven of the pilot plant of the EEA Rama Caidá.

Aw content, humidity (Dean Stark method), and caliber (units of dried plum in 1 kg) were determined in the dehydrated plums used to perform the tests.

**Standardization of the softening (rehydration) of the prune**

The tenderized of the dehydrated plum was performed using water and steam under pressure in an autoclave (pressure cooker). To standardize the process, the following procedure was carried out: the container contained 1 L of water, brought to boil and twenty previously weighted prunes were added. The total time of the thermal treatment was 10 minutes. Subsequently, the tenderized plum was strained and manually pitted, the stones were weighed, and the plum was conserved in a hermetically sealed container for 24 hours to stabilize the moisture. The aw, humidity, stone residues and yield were evaluated.

**Applied treatments**

Each treatment had 4 repetitions with 20 previously weighted high moisture prunes (humidity= 30 ± 2%). We used potassium sorbate p.a. (minimum title 99%) for the tests.

After the treatments, the plum was placed in hermetically sealed containers for 24 hours for stabilization.

The content of residual potassium sorbate was evaluated.

**Analytical method used to for the determination of potassium sorbate**

We used the International Standard ISO 5519:2008 Fruits, vegetables and derived products - Determination of sorbic acid content, modified by the National Institute of Industrial Technology [Instituto Nacional de Tecnología Industrial] Mendoza.

During the application of the technique, the volumes of the solutions were reduced to reduce the amount of used inputs, the costs, and environmental pollution.

**Principle**

Tenderized prunes were homogenized, and the potassium sorbate was quantitatively extracted by steam distillation.

The potassium sorbate in the distillate was determined by a spectrophotometric reading in the UV range.

**Scope**

The technique was used to determine from 70 to 2,000 ppm of potassium sorbate in tender prunes.

**Analysis of the results**

The obtained results were analyzed using the statistical software InfoStat (Di Rienzo et al., 2016). The following statistical analyzes were performed: correlation analysis, simple linear regression analysis and variance analysis (ANAVA) (Balzarini et al., 2011).

**RESULTS**

**Raw material**

The average aw of the dehydrated plum d’Agen during its conservation in stockpiles was 0.682 ± 0.013 (19.9 ± 0.1 °C) and its average humidity was 21 ± 1%. This parameter complies with the Article 904 bis of the Argentine Food Code (C.A.A.), which states that dried fruit should not contain more than 25% of water.

According to the scale of the Article 906 of the C.A.A., the number of dehydrated plum units contained in 1 kg of fruit was 110/132 units/kg. According to the Committee of Plum Exporters of Mendoza, plums are regarded as “Medium” caliber when values range from 110/132 - 132/154 units of dry plum/kg (equivalent to 50/60 - 60/70 units by pound).

**Standardization of the softening (rehydration) of the plum**

After the tenderized and stabilization processes, the plum achieved an average aw of 0.782 ± 0.020 (19.1 ± 0.9 °C) and an average humidity of 30 ± 2%. This final moisture content complies with the Article 904 bis of the C.A.A., which regulates a maximum water content of 35% to pack fruit in hermetic containers.

The average yield during the tenderizing of medium-sized plum was 1.08 ± 0.01 kg of dried plum to obtain 1.00 kg of pitted high moisture prunes.

The yield depends on several factors, such as type of drying method (sun or oven), size, content of soluble solids, humidity, discards due to defects, and technology used during the pitting.

The average residue of pits was 14 ± 1% in regards to the weight of the dehydrated plum.

**Potassium sorbate determination**

A correlation analysis was performed to determine if there was an association between the concentration of the solutions applied by immersion and spraying, and the potassium sorbate residue obtained in the high moisture plum. The Pearson correlation coefficient (r) was positive for both
methods, with values of $r = 0.93$ for the immersion method, and $r = 0.94$ for the spraying method.

These correlation coefficients were similar to those obtained by Alagöz et al. (2015) who evaluated the correlation between potassium sorbate solutions applied to rehydrated apricots and the residual contents of the preservative in the samples.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Concentration of potassium sorbate (%)</th>
<th>Application Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.25</td>
<td>Immersion in 400 ml of potassium sorbate solution for 30 seconds at room temperature.</td>
</tr>
<tr>
<td>2</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.75</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.25</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>2.75</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>1'</td>
<td>1.25</td>
<td>Spray 10 ml of potassium sorbate solution at room temperature.</td>
</tr>
<tr>
<td>2'</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>3'</td>
<td>1.75</td>
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</tr>
<tr>
<td>4'</td>
<td>2.00</td>
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<tr>
<td>5'</td>
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<td>6'</td>
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<td>7'</td>
<td>2.75</td>
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</tr>
<tr>
<td>8'</td>
<td>3.00</td>
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</tr>
</tbody>
</table>

Table 1. Treatments applied to the high moisture prune.

These results led to the evaluation of the fit of linear regression models to the data obtained for each application method.

**Potassium sorbate: application methods. Immersion and spraying**

We performed simple linear regression analysis to develop models to estimate the means of residual potassium sorbate
content in high moisture prunes from solutions with different concentrations of the preservative (Figures 1 and 2).

For both application methods the coefficients of determination (R2) were high: 0.86 for immersion and 0.88 for spraying. This indicates that the applied concentrations of potassium sorbate solutions account for 86% and 88% of the variability observed in the residual potassium sorbate found in the high moisture prune.

Lack of fit tests were performed for both application methods. A value of p = 0.1041 was obtained for immersion, and p = 0.7258 for spraying. Therefore, since in both cases the values of p are >0.05, the linear models are appropriate for the obtained data sets.

ANAVA (DGC test with α= 0.01) of the potassium sorbate residues obtained in high moisture prunes was performed as a function of the used concentrations.

For both application methods we obtained a value of p= 0.0001. Therefore, as p is <0.01, there were significant differences, which could be grouped by ranges. For the immersion method: solutions with a concentration between 1.25-1.75% generate residues between 489 and 641 ppm; 2.00-2.25% between 855 and 926 ppm; 2.50-2.75% between 1126 and 1143 ppm and finally, 3.00% an average residue of 1473 ppm (Figure 3).

For the spraying method: a solution with a concentration of 1.25% generated an average residue of 390 ppm; 1.50-
Figure 4. ANAVA between the used concentration of sorbate p.a and the residue obtained in the tenderized prune using the spraying method.

2.00% between 598 and 735 ppm; 2.25-2.50% between 862 and 1006 ppm and finally, 2.75-3.00% between 1166 and 1327 ppm (Figure 4).

When we compared the ANAVA results for both methods, we observed that higher potassium sorbate residues in the plum were obtained when the immersion method, when compared to the spraying method. Therefore, an ANAVA was performed to compare if the differences between application methods were significant.

Figure 5. ANAVA between the application methods for potassium sorbate.

Comparison between potassium sorbate application methods

An ANAVA was conducted (Fisher’s LSD test with α= 0.05) and we obtained a value of p= 0.0272. Thus, as p<0.05, there were significant differences between the application methods of sorbate of potassium. The immersion method presented a greater mean value (909.47 ppm) than that of the spraying (844.11 ppm) (Figure 5). Therefore, this result allowed us to conclude that when using the immersion
A higher residual concentration of potassium sorbate in the high moisture prune is obtained.

**Table to estimate the residual potassium sorbate content**

Table 2 shows the data obtained to estimate the content of residual potassium sorbate in prune plum as a function of the concentration and application of the preservative. The table is valid exclusively for plum processed with a final moisture of 30 ± 2% - aw 0,782 ± 0,020.

Alagöz et al. (2015) observed that when fruits with different moisture contents are immersed in potassium sorbate solutions, at the same concentration those with the highest moisture content absorbed more preservative. This phenomenon was due to the fact that the fruit with a higher moisture content had a lower content of dry matter, therefore, the flow of the potassium sorbate solution was higher than in the sample with a lower percentage of humidity.

**DISCUSSION AND CONCLUSIONS**

There is a strong correlation between the content of residual potassium sorbate in prune plum with respect to the concentration and application method of the preservative.

For the immersion and spraying methods, the potassium sorbate residues obtained based on the concentrations used were adjusted to linear models and grouped by ranges. For the immersion method, solutions with concentrations between 1.25-1.75% generate residues between 489 and 641 ppm, 2.00-2.25% between 855 and 926 ppm, 2.50-2.75% between 1126 and 1143 ppm and finally, 3.00% an average residue of 1473 ppm.

For the spraying method, a solution with a concentration of 1.25% generated an average residue of 390 ppm, 1.50-2.00% between 598 and 735 ppm, 2.25-2.50% between 862 and 1006 ppm and finally, 2.75-3.00% between 1166 and 1327 ppm. Both methods presented significant differences in potassium sorbate residues obtained in the product.

The immersion method presented a mean value (909.47 ppm) greater than that of the spraying method (844.11 ppm). This result allowed us to conclude that, when using the immersion method, a higher residual concentration of potassium sorbate is obtained in the high moisture plum.

That is, in the application by immersion a lower dose is required to obtain the same final sorbate concentration in the product. However, the application of preservative by spraying is recommended since it does not modify the final moisture of the tender plum and is more aseptic.

The table obtained would serve as a reference tool to processors to estimate the residual content of potassium sorbate in high moisture prune, with a humidity of 30 ± 2% - aw 0,782 ± 0,020, depending on the concentration and type of application of preservative.

Also, this research could be considered as a precedent to modify the Article 916 bis of the C.A.A, which regulates the surface treatment of dried fruits with sorbic acid or potassium sorbate, provided that the residual content (expressed in sorbic acid) does not exceed 100 ppm of whole fruit. This
concentration is insufficient to achieve the conservation of the final product.

A bibliographic analysis showed that the antimicrobial action of the sorbates takes place between 200 and 600 ppm depending on the moisture content of the fruit. This could be corroborated in the Codex Alimentarius International Food Standards, which establishes in the “Codex General Standard for Food Additives” (NGAA, CODEX STAN 192-1995) that the use of sorbates is allowed (INS 200-203) with a maximum level of 500 ppm in dehydrated fruit.

A future research line in the processing of high moisture prune should be aimed at obtaining new conservation methods that do not involve the addition of potassium sorbate. This would allow to satisfy the current market trend that increasingly demands natural or organic products.

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