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EFFECT OF SURFACE TREATMENTS ON CHEMICAL AND PHYSICAL PROPERTIES OF PORTUGUESE SMOKED DRY SAUSAGES AND DETERMINATION OF PRODUCTION COSTS

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Abstract

According to the EC legislation, benzoates, sorbates and the esters of p-hydroxy-benzoic acid (parabens) may only be used in surface treatments of dry sausages casings. However, there is no reference about these preservatives residual values in the product when applied as surface treatments. Three of these preservatives, sodium benzoate (SB), potassium sorbate (PS) and methyl p-hydroxybenzoate (MHB), were applied at 2.5% (w/v), in seven different combinations, as surface treatment in two types of Portuguese dry smoked sausages [Alentejano (A) and Ribatejano (R)]. Water activity, pH, residual values of PS, SB, MHB, NaNO₂ and P₂O₅ were determined and also production costs were studied. Surface treatments did not influence (p>0.05) results of NaNO₂ and P₂O₅ residual values, pH and water activity parameters. However, results of pH and of P₂O₅ were significantly different (p<0.05) between the two types of sausages. MHB residual levels were not detected. SB residual mean values varied between 122.3 and 233.3 mg/kg in sausage type R and, between 108.2 and 560.3 mg/kg in sausage type A. Residual mean values of PS oscillated from 93.0 to 151.7 mg/kg and from 104.0 to 345.7 mg/kg in sausage type R and A, respectively. Production costs can increase from 6 € up to 24 €, per ton of final product, in sausage type A and, from 1 € up to 30 € in sausage type R, depending of salt combination used as surface treatment. © 2005 Altaga. All rights reserved.

Keywords: Chouriço, Surface Treatments, Sodium Benzoate, Potassium Sorbate, Methyl p-hydroxybenzoate, Production Costs

Resumen

Según la legislación europea, en los tratamientos de superficie de pieles de chorizo se puede usar benzoatos, sorbatos y esteres de ácido p-hidroxibenzoico. Sin embargo, no hay estudios sobre los valores residuales de estos conservantes en el producto cuando se aplica como tratamiento de superficie. Tres de estos conservantes, benzoato sódico (SB), sorbato potásico (PS) y metil p-hidroxibenzoato (MHB), se aplicaron al 2.5% (p/v), en 7 combinaciones diferentes, como tratamiento de superficie en dos tipos de chorizos portugueses (Alentejano (A) y Ribatejano (R)). Se determinaron: Actividad de agua (Aw), pH, valores residuales de PS, SB, MHB, NaNO₂ y P₂O₅ y se estudiaron los costes de producción. Los tratamientos de superficie no afectaron a los resultados (p>0.05) de valores residuales de NaNO₂ y P₂O₅, ni a los parámetros pH y Aw. No se detectaron niveles residuales de MHB. Los valores residuales medios de SB variaron entre 122.3 y 233.3 mg/kg en chorizo tipo R y entre 108.2 y 560.3 en chorizo tipo A. Los valores residuales de PS variaron entre 93.0 y 151.7 mg/kg y entre 104.0 y 345.7 mg/kg en chorizos tipo R y A, respectivamente. Los custos de producción poden incrementarse de 6 € a 24 € por tonelada de producto final en chorizo tipo A y entre 1 € y 30 € en chorizos del tipo R, dependiendo da combinación de sales usada como tratamiento de superficie. © 2005 Altaga. Todos los derechos reservados.

Palabras clave: Chorizo, Tratamiento de superficie, Benzoato sódico, Sorbato potásico, Metil p-hidroxibenzoato, Coste de producción

Resumo

Segundo a lexislación europea, nos tratamentos de superficie de peles de chouriço pôdense empregar benzoatos, sorbatos e esteres de ácido p-hidroxibenzoico. Sen embargo, non hai estudos sobre os valores residuais destes conservantes no produto cando se emprega como tratamento de superficie. Tres destes conservantes, benzoato sódico (SB), sorbato potásico (PS) e metil p-hidroxibenzoato (MHB), se aplicaron al 2.5% (p/v), en 7 combinacións diferentes, como tratamento de superficie en dous tipos de chorizos portugueses (Alentejano (A) e Ribatejano (R)). Determináronse: Actividade de augua (Aw), pH, valores residuais de PS, SB, MHB, NaNO₂ e P₂O₅ e estudáronse os custos de producción. Os tratamentos de superficie non afectaron ós resultados (p>0.05) de valores residuais de NaNO₂ e P₂O₅ nin ós parámetros pH e Aw. Non se detectaron niveis residuais de MHB. Os valores residuais medios de SB variaron entre 122.3 e 233.3 mg/kg en chourizo tipo R e entre 108.2 e 560.3 en chourizo tipo A. Os valores residuais de PS variaron entre 93.0 e 151.7 mg/kg e entre 104.0 e 345.7 mg/kg en chourizos tipo R e A, respectivamente. Os custos de produción pueden incrementarse de 6 € a 24 € por tonelada de producto final en chourizos tipo A e entre 1 € e 30 € en chourizos do tipo R, dependendo da combinación de sales usada como tratamento de superficie. © 2005 Altaga. Tódolos dereitos reservados.
INTRODUCTION

«Chouriço» is a very popular smoked dry sausage in Portugal. In Alentejo and Ribatejo provinces particular varieties very appreciated for their sensorial characteristics are produced. These types of smoked dry sausages, based on varying combinations of ingredients, are stuffed into natural casings and heavily smoked.

Nitrite and phosphate are widely used as formulation ingredients in meat products. Phosphate is added to meat products to improve their binding properties and water-holding capacity (Lin and Chuang, 1999; Pearson and Gillett, 1996; Puolanne and Ruusunen, 1983; Offer and Knight, 1983). Sodium nitrite is responsible for the development of the typical cured meat colour and flavour as well as functioning as an antimicrobial agent, providing protection against growth and toxin production by Clostridium botulinum (Pierson and Smoot, 1982). However, the need for nitrite has to be balanced against its documented adverse effect on man, because of the risk of nitrosamine formation in vitro in foods or in vivo in man (Skovgaard, 1992).

To reduce the potential hazard of N-nitrosamine formation, nitrite removal or reduction in meat products has been one of the major issues faced by both food scientists and federal regulators. Sodium benzoate was the first chemical preservative allowed in foods by the FDA, and it is still widely used today in a large number of foods. One of its approved derivatives is an ester of p-hydroxybenzoic acid (paraben) such as methyl p-hydroxybenzoate. Esters of p-hydroxybenzoic acid differ from benzoate in their antimicrobial activity being less sensitive to pH. Sorbic acid is employed as a food preservative, usually as the calcium, sodium, or potassium salt and, like sodium benzoate, is more effective in acid foods than in neutral foods (Jay, 2000). In Portugal, as in the E.U., these preservatives [benzoates, sorbates and the esters of p-hydroxy-benzoic acid (parabens)] may only be used in surface treatments of dry sausages casings. Legislation values are only be used in surface treatments of dry sausage casings.

Nitrite and phosphate are added to the formulation ingredients used in the production of meat products, in which nitrite, in combination with phosphate, is employed as a preservative into the product. This will be useful in determining levels needed, time of exposure, expected inhibitory activity, and potential undesirable effects on product quality.

In this context, the main goals of this study were to investigate, in Portuguese smoked dry sausages, the residual amounts of the additives added as ingredient formulation and of those applied as surface treatment and also, the viability of such treatments regarding the production costs.

MATERIALS AND METHODS

Processing technology

Chouriço type Alentejano (A) and Ribatejano (R) are made with minced lean pork, mixed with fat similarly cut into small pieces together with other ingredients. This mixture, after one day maturation below 10ºC, is stuffed into natural casings (pork intestine salted for chouriço type R and beef dry casing for chouriço type A) and intensively smoked for about three days. Formulation ingredients used in both types of chouriço manufacture are presented in Table 1. Sausages are commercialised in a modified atmosphere package (55% of N₂ and 45% of CO₂).

Surface treatments

In control chouriço type R samples, surface treatment applied in casings was only cleaning with water to remove the salt and then immersion in cold water until filling. In chouriço type A control samples, surface treatment applied in casings was only cleansing with water to remove the salt and then immersion in cold water until filling.

In this study, the mainly goals of this study were to investigate, in Portuguese smoked dry sausages, the residual amounts of the additives added as ingredient formulation and of those applied as surface treatment and also, the viability of such treatments regarding the production costs.

Product sampling

The experiments were divided in four trials. Each trial was conducted in batters of 560 kg. In the first trial were performed the surface treatments with potassium sorbate (PS), sodium benzoate (SB), methyl p-hydroxybenzoate (MHB) and control (AC1) (Table 2) in chouriço type A. The second trial was also conducted in chouriço type A and the surface treatments with potassium sorbate and sodium benzoate (PS+SB), potassium sorbate and methyl p-hydroxybenzoate (PS+MHB), sodium benzoate and methyl p-hydroxybenzoate (SB+MHB), potassium sorbate, sodium benzoate and methyl p-hydroxybenzoate (PS+SB+MHB) and, control (AC2).
Table 1.- Composition of Alentejano and Ribatejano smoked dry sausages.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Chouriço Alentejano</th>
<th>Chouriço Ribatejano</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial sausage sodium polyphosphate, E452(i); (50% of P₂O₅)</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Water</td>
<td>31.0</td>
<td>12.7</td>
</tr>
<tr>
<td>Sugar</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Olive oil</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td>Liquid smoke</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>Spice &quot;louro&quot;</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>Sweet chilli</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Powder clove</td>
<td>-</td>
<td>0.1</td>
</tr>
<tr>
<td>Garlic paste</td>
<td>11.0</td>
<td>11.3</td>
</tr>
<tr>
<td>Sweet red pepper paste</td>
<td>4.3</td>
<td>8.8</td>
</tr>
<tr>
<td>Special red pepper paste</td>
<td>44.9</td>
<td>46.1</td>
</tr>
<tr>
<td>Hot red pepper paste</td>
<td>12.9</td>
<td>2.5</td>
</tr>
<tr>
<td>White pepper (powder)</td>
<td>1.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Sodium chloride with sodium nitrite, E250, (0.6% of NaNO₃)</td>
<td>10.3</td>
<td>10.0</td>
</tr>
<tr>
<td>Salt</td>
<td>10.3</td>
<td>10.0</td>
</tr>
<tr>
<td>White wine</td>
<td>-</td>
<td>3.9</td>
</tr>
<tr>
<td>Sub-total</td>
<td>139.7</td>
<td>119.9</td>
</tr>
<tr>
<td>Total</td>
<td>1397.0</td>
<td>1409.9</td>
</tr>
</tbody>
</table>

were applied (Table 2). In the third trial were applied the treatments PS, SB, MHB and control (RC1) (Table 1) in chouriço type R and, in the fourth trial, the treatments PS+SB, PS+MHB, SB+MHB, PS+SB+MHB and control (RC2) also in Ribatejano sausage type (Table 2). From all experiments 3 samples of sausages were taken from each surface treatment and control. Sausage samples were not peeled to accomplish the physical and chemical measurements.

Chemical and physical measurements

Determination of potassium sorbate, sodium benzoate, methyl p-hydroxybenzoate, sodium nitrite (NaNO₃) and diphosphourpentoxide (P₂O₅) residual values, pH and water activity was accomplished in three product samples of control and of each surface treatment. Analyses were carried out using the following methods: pH, ISO R2917-1974 (ISO 1974) with a solid sample potentiometer, water activity (aw) at 25°C in PROTIMER øw analyser, sodium nitrite (NaNO₃) residual values according to Portuguese Standard Methods (NP 1846, 1987), diphosphourpentoxide (P₂O₅) residual values as described in NP 874 (1984). The determination of potassium sorbate, sodium benzoate and methyl p-hydroxybenzoate residual values were performed by High Performance Liquid Chromatography (HPLC) using a Nova Pack, part no°6975 (Waters). Solution A, with 3.5 kg KH₂PO₄ + 0.1% antic acid solution, pH at 4.4 (reached with 20% KOH solution), was prepared for eluent composition. Eluent for HPLC was constituted by 85% solution A and 15% ethanol. Detector of UV λ at 217 nm, oven temperature was 35°C at 1.0 ml/minute stream.

Statistical methods

Computational work was performed using a Statistic for Windows 5.0 software package (Statsoft, Inc.). Mean values were compared using ANOVA methodology (One Way ANOVA). This procedure was performed after certification of the adjustment of the results to Gauss curve (Kolmogorov-Smirnov test) and application of the Levene Median test. Statistical significance of differences between means of results was determined by a Tukey’s test. Significance was established at P<0.05. Results reports the mean ± standard deviation for n=3.

Production costs

Methodology was based on variable cost system and production costs were calculated as basic standard costs type (Rocha and Rúbio 1999; Santos, 1998; Pereira and Franco, 1994). Calculations were based on real data achieved in a meat industry, under commercial conditions. Production costs concerned with the application of surface treatments in the natural casings in both types of sausages were determined.

RESULTS AND DISCUSSION

Chemical and physical properties of sausages type Ribatejano and Alentejano are summarised in Tables 3 and 4. Surface treatments production costs are presented in Tables 5 and 6 for chouriço type A and R, respectively. In Table 7 the totality of production costs for both types of sausages is shown. Chemical and physical parameters were not affected by the application of surface treatments (p>0.05) (Table 3 - 4). Results of pH and of P₂O₅ were significantly different (p<0.05) between the two types of sausages (Table 3 - 4).

pH values

The pH mean values fluctuated between 5.43 and 5.70 in sausage type R and, between 5.47 and 5.80 in sausage type A (Table 3). On the basis of results (Table 3) there is no significant differences between samples with or without surface treatments (p>0.05). However, significant differences (p<0.05) were observed among types of product. Sousa and Ribeiro (1983) reported pH values between 5.9 and 6.4 in Portuguese chouriços and, values from 4.42 to 6.52 were observed in several types of dry-cured sausages (González and Díez, 2002; Acton and Dick, 1976; Ferrer and Arboix, 1986; Fanco et al., 2002). Some of the values obtained by these authors (4.42) are lower than those reported by Sousa and Ribeiro (1983) in Portuguese dry smoked sausages (5.9 - 6.4) and from those reported in this study (5.43-5.80). This fact can be explained considering several factors such as maturation period, microbial flora that will growth differentially (Sousa and Ribeiro, 1983), phosphates addition (Bozkurt, 2002).
Table 2.- Surface treatments applied in Alentejano and Ribatejano smoked dry sausages.

<table>
<thead>
<tr>
<th>Combinations of salts</th>
<th>Preparation</th>
<th>Amount of salt added</th>
<th>Final concentration (w/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control of Alentejano sausage (AC1 and AC2)</td>
<td>30 l of water + 1.5 l of commercial vinegar</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Control of Ribatejano sausage (RC1 and RC2)</td>
<td>Clean with water and immersion in cold water</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Potassium sorbate (PS) (SIGMA, S1751)</td>
<td>In 20 l of water at 35±5°C</td>
<td>500 g</td>
<td>2.5%</td>
</tr>
<tr>
<td>Sodium benzoate (SB) (SIGMA, B3375)</td>
<td>In 20 l of water at 35±5°C</td>
<td>500 g</td>
<td>2.5%</td>
</tr>
<tr>
<td>Methyl p-hydroxybenzoate (MHB) (SIGMA, H5501)</td>
<td>In 20 l of water at 35±5°C</td>
<td>500 g</td>
<td>2.5%</td>
</tr>
<tr>
<td>Potassium sorbate and Sodium benzoate (PS+SB)</td>
<td>In 40 l of water at 35±5°C</td>
<td>500 g of each salt</td>
<td>1.25% of each salt</td>
</tr>
<tr>
<td>Potassium sorbate + Methyl p-hydroxybenzoate (PS+MHB)</td>
<td>In 40 l of water at 35±5°C</td>
<td>500 g of each salt</td>
<td>1.25% of each salt</td>
</tr>
<tr>
<td>Sodium benzoate + Methyl p-hydroxybenzoate (SB+MHB)</td>
<td>In 40 l of water at 35±5°C</td>
<td>500 g of each salt</td>
<td>1.25% of each salt</td>
</tr>
<tr>
<td>Potassium sorbate + Sodium benzoate + Methyl p-hydroxybenzoate (PS+SB+MHB)</td>
<td>In 60 l of water at 35±5°C</td>
<td>500 g of each salt</td>
<td>0.83% of each salt</td>
</tr>
</tbody>
</table>

and Erkmen, 2002), the meat raw material pH (Kuo and Chu, 2003) and, the buffering capacity of raw materials used (Kivikari, 1996). The Portuguese «chouriço» is exposed to one very short maturation period, varying from one to three days, although Spanish sausage is exposed to a long dry period at low temperature. During this period, through lactic fermentation from meat sugars and sugar formulation ingredient, a relevant pH drop is observed (Sousa and Ribeiro, 1983). Bozkurt and Erkmen (2002) found that phosphates addition increased pH in Turkish style sausages, which was expected once these additives have buffering capacity. In Portuguese «chouriço» phosphates are normally added at 5 g/kg (Table 1).

**Water activity**

In both types of sausage, water activity mean values varied between 0.91 and 0.95 (Table 3). No influence of the type of product and of the surface treatment was observed (p>0.05) on \( a_w \) results. Values of \( a_w \) observed in the final product were similar to those reported for Chinese sausages (0.93-0.96) by Kuo and Chu (2003), but were higher than those found by other authors for different sausage types (0.88-0.89) (Fanco et al., 2002; Chen et al., 1997; Chasco et al., 1996; Dominguez et al., 1988; Barranco Sánchez et al., 1985; Serrano Moreno, 1979). These differences may be related to the ripening process and period. In fact, dry-cured sausages (as Spanish and Italian sausages) are characterised by a long ripening period (30 to 45 days) at low temperatures (from 11 to 25°C) and at relative humidity of 60 to 90%. This long processing time, when compared with the short process applied in Portuguese smoked sausage (3 to 4 days) could be responsible for the lower values of water activity reported by these authors.

Also, with addition of phosphate there is a marked increase in water-holding in the range of 1.0-1.5% (Puolanne and Ruusunen, 1983). This is due to the cleavage of actomyosin bonds by phosphates thus facilitating the swelling of the filament lattice (Offer and Knight, 1983). Lin and Chuang (1999) reported higher water holding capacity (WHC) for low-fat Chinese sausage processed from trisodium phosphate-dipped raw meat materials.

**Diphosphorpentoxide (P_2O_5)**

Concerning diphosphorpentoxide (P_2O_5), the obtained values becomes not only from ingredient formulation [5 g/kg of sodium polyphosphate, E452(i) (Table 1) but also from meat raw material. Skróski (1995) appointed 1.9-2.5 g/kg of P_2O_5 as a reference value in pork meat. In agreement with this reference value the expected values of P_2O_5 in Alentejano and Ribatejano sausages were determined from the formula: g/kg P_2O_5 in sausage = [0.5 × [p_c × M/1000] / Y] + 2.5 in which p_c was the diphosphorus pentoxide concentration for pork meat (2.5 g/kg) and M was the amount of meat material (g/kg) used in each type of sausage. The Y value was the processing yield, referred as 60% and 2.5 g/kg the amount of P_2O_5 added to the product (Table 1).

In these calculations it was considered that no phosphorus will be carried in the product dehydration water and that it would remain in the final product. Considering these calculations the expected values of P_2O_5 are 6.08 g/kg for Alentejano sausage type and 6.17 g/kg for Ribatejano sausage type. Mean values obtained, 6.0 to 6.9 g/kg in Alentejano sausage and 5.5 to 6.6 g/kg in Ribatejano sausage (Table 4), were quite similar than those achieved by the presented formula. Until 1996, the maximum value allowed in the final product was 6.5 g/kg.
of P2O5 however, since 1998 the Portuguese and the EU legislation (Decreto-Lei nº363, 1998; Decreto-Lei nº274, 2000) only refer the maximum value of phosphates that can be added in these meat products (5 g/kg of product) once it is difficult to preview the exactly amount of P2O5 used in raw meat material and the processing yield of each type of meat product.

Comparing between types of product, P2O5 results were significantly different (p<0.05) however, no effect of surface treatment was observed (p>0.05). Significant differences of P2O5 residual mean values obtained between the two types of sausages could be related with the same differences observed in pH results. Addition of phosphate not only raises the pH of meat mixture, causing a shift away from the isoelectric point (pI) of myofibrillar proteins, but also increases the total negative charges on the myofibrillar proteins which increases WHC (Pearson and Gillett, 1996).

**Sodium nitrite (NaNO2)**

Sodium nitrite residual mean values did not differ significantly (p>0.05) with the type of product and with the surface treatment (Table 4). NaNO2 mean values oscillated between 1.0 and 1.3 mg/kg for both types of sausages. These values are quite lower than maximum allowed by the Portuguese and EU legislation, 100mg/kg of final product (Decreto-Lei nº363, 1998; Decreto-Lei nº274, 2000) and from the initial values of 60 mg/kg in sausages type R and of 61.8 mg/kg in sausage type A (Table 1). Freitas et al. (1992) reported results in 4 different types of Portuguese smoked sausages acquired in commercial points, in which NaNO2 values varied from 1.21 to 8.89 mg/kg in 69% of the samples and from 15.70 to 29.41 mg/kg for the remain 31% of the samples. Samelis et al. (1998), in a study of nitrite evolution in traditional Greek dry salami, observed that from an initial value of 119-128 mg/kg, after a fermentation and ripening period of 28 days, the residual value was 10 mg/kg. Nitrite decreases considerably during the fermentation. This decrease is the result of nitrite transformation into nitric oxide which, in turn, would react with myoglobin (Mb). During the drying process, the nitrites remained at trace levels as has been reported by Chasco et al., (1996). In addition, Möhler (1982) referred that when analysing nitrite transformation in pork, after addition of 150 mg/kg of meat, 3% was transformed in nitrate, 3% linked to the Mb, 27% of the nitrite was linked to the protein, 1% was involved in secondary reactions with gas production and only 66% was found as residual NaNO2.

### Table 3 - Mean values of pH and of aw in Alentejano (A) and Ribatejano (R) Portuguese dry smoked sausages, after treatments. Standard deviation is shown in parenthesis, for n=3. For each parameter, values in the same line and column with the same letter, do not differ significantly (p>0.05) by the Tuckey’s test.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>pH</th>
<th>aw</th>
<th>A</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>5.60a</td>
<td>0.93a</td>
<td>0.93a</td>
<td>0.93a</td>
</tr>
<tr>
<td>PS¹</td>
<td>5.67b</td>
<td>0.93b</td>
<td>0.93b</td>
<td>0.93b</td>
</tr>
<tr>
<td>SB¹</td>
<td>5.63b</td>
<td>0.92b</td>
<td>0.91b</td>
<td>0.91b</td>
</tr>
<tr>
<td>MHB¹</td>
<td>5.47b</td>
<td>0.94b</td>
<td>0.95b</td>
<td>0.95b</td>
</tr>
<tr>
<td>C2</td>
<td>5.67a</td>
<td>0.92a</td>
<td>0.94a</td>
<td>0.94a</td>
</tr>
<tr>
<td>PS+SB²</td>
<td>5.67b</td>
<td>0.94b</td>
<td>0.95b</td>
<td>0.95b</td>
</tr>
<tr>
<td>SB+MHB²</td>
<td>5.70b</td>
<td>0.93b</td>
<td>0.93b</td>
<td>0.93b</td>
</tr>
<tr>
<td>PS+MHB²</td>
<td>5.77b</td>
<td>0.93b</td>
<td>0.93b</td>
<td>0.93b</td>
</tr>
<tr>
<td>PS+SB+MHB³</td>
<td>5.80b</td>
<td>0.94b</td>
<td>0.93b</td>
<td>0.93b</td>
</tr>
</tbody>
</table>

**Potassium sorbate (PS), sodium benzoate (SB) and methyl p-hydroxybenzoate (MHB)**

Values of methyl p-hydroxybenzoate in the accomplished analyses, were not detected (Table 4). The analytical methodology might have influence in this absence of values. In fact, the methodology used was quite different from the one described by Rauh et al., (1996) with which obtained a recovery percentage up to 107 when compared with the theoretical values. However, in spite of the absence of values detected for the MHB, the reported methodology was effective in the detection of potassium sorbate and of sodium benzoate. It is still possible to expose two hypotheses in the attempt to explain this absence of MHB values. The first considers that p-hydroxybenzoic esters may be linked to some extent to proteins, emulsifiers and other substrate constituents on account of their phenolic OH group (Lueck, 1980) and, the second, the none absorption of MHB by the casing during immersion time.

Sodium benzoate mean values varied between 122.3 and 233.3 mg/kg (0.012 and 0.023%) in sausage type R and, between 108.2 mg/kg (0.011%) and 560.3 mg/kg (0.056%) in sausage type A (Table 4). Residual mean values of PS oscillated from 93.0 mg/kg (0.009%) to 151.7 mg/kg (0.015%) and from 104.0 mg/kg (0.010%) to 345.7 mg/kg (0.034%) in sausage type R and A, respectively (Table 4). Concerning salts combination in treatments PS+SB and PS+SB+MHB, the total amount of PS and SB residual mean values obtained was 272.6 mg/kg in sausage type A, 224 mg/kg in sausage type R and, 212.2 mg/kg in sausage type A and 299.7 mg/kg in sausage type R, respectively (Table 4).

Many factors such as, the method of application, time length of exposure, preservative concentration, type of food, porosity of the food, shape and size of the food and handling after exposure to preservative, all contributes for the amount of residual levels found in the product (Sofos, 1989; Giannakopoulos and Guilbert, 1986). For the same preservative, differences founded between types of product may be related with the porosity of the natural casings used for each type of product (porcine intestine salted.
Table 4- Residual mean values of \( P_2O_5 \), NaNO\(_2\), potassium sorbate (PS), sodium benzoate (SB) and methyl p-hydroxybenzoate (MHB) in Alentejano (A) and Ribatejano (R) Portuguese types of sausages, after treatments. Standard deviation is shown in parenthesis, for \( n=3 \). For each parameter, values in the same line and column with the same letter, do not differ significantly (p<0.05) by the Tuckey’s test. nd - not detected

<table>
<thead>
<tr>
<th>Treatments</th>
<th>( P_2O_5 ) (g/kg)</th>
<th>NaNO(_2) (mg/kg)</th>
<th>PS (mg/kg)</th>
<th>SB (mg/kg)</th>
<th>MHB (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>R</td>
<td>A</td>
<td>R</td>
<td>A</td>
</tr>
<tr>
<td>C1</td>
<td>6.2(^a)</td>
<td>6.1(^b)</td>
<td>1.0(^a)</td>
<td>1.0(^a)</td>
<td>-</td>
</tr>
<tr>
<td>PS(^1)</td>
<td>6.6(^a)</td>
<td>6.1(^b)</td>
<td>1.0(^a)</td>
<td>1.2(^b)</td>
<td>345.7</td>
</tr>
<tr>
<td>SB(^1)</td>
<td>6.7(^a)</td>
<td>5.7(^b)</td>
<td>1.0(^a)</td>
<td>1.0(^b)</td>
<td>-</td>
</tr>
<tr>
<td>MHB(^1)</td>
<td>6.0(^a)</td>
<td>6.3(^b)</td>
<td>1.0(^a)</td>
<td>1.0(^b)</td>
<td>-</td>
</tr>
<tr>
<td>C2</td>
<td>6.9(^a)</td>
<td>6.6(^b)</td>
<td>1.3(^a)</td>
<td>1.0(^b)</td>
<td>-</td>
</tr>
<tr>
<td>PS+SB(^2)</td>
<td>6.9(^a)</td>
<td>6.3(^b)</td>
<td>1.0(^a)</td>
<td>1.0(^b)</td>
<td>121.3</td>
</tr>
<tr>
<td>SB+MHB(^2)</td>
<td>6.9(^a)</td>
<td>6.6(^b)</td>
<td>1.0(^a)</td>
<td>1.3(^b)</td>
<td>-</td>
</tr>
<tr>
<td>PS+MHB(^2)</td>
<td>6.8(^a)</td>
<td>5.9(^b)</td>
<td>1.0(^a)</td>
<td>1.0(^b)</td>
<td>109.3</td>
</tr>
<tr>
<td>PS+SB+MHB(^3)</td>
<td>6.5(^a)</td>
<td>5.5(^b)</td>
<td>1.0(^a)</td>
<td>1.0(^b)</td>
<td>104.0</td>
</tr>
</tbody>
</table>

For chouriço type R and beef dry casing for chouriço type A). In this way, is very difficult to estimate expected values in the final product once the amount of additive that will remain in the casing after dipping in salts solutions and which amount will migrate from the surface to the interior of the product are ignored.

Zamora and Zaritzky (1987) found in beef slices, 1.5 cm thick and 10 cm in diameter, of 117 g and 200 cm\(^2\) surface area, residual levels of sorbate varied from 0.003 to 0.13% for 0.21 to 10% of PS spraying solutions. Myers et al., (1983) reported residual sorbate mean levels (%) in pork loins (5 x 8 x 10 cm) of 0.03 and of 0.053 after sprayed for 10 s with 5 and 10% of PS solutions, respectively and, of 0.67 and 0.13 after dipping for 30 s in 5 and 10% PS solutions, respectively. Poultry breast pieces (2 x 5 x 10 cm) with intact skin or without skin, after immersed in 5% PS solution for 30 s and drained for 2 min and packaged, presented mean sorbate levels of 0.31 and of 0.39%, respectively (McMeekin et al., 1984). Residual sorbate concentrations obtained in chicken breasts dipped for 1 min in 2.5, 5 and 10% PS solutions were 0.5, 0.13 and 0.32% (Robach and Ivey, 1978).

Concerning eventually toxicological effects, Hossaini et al., (2000) in mouse uterotrophic assay found no oestrogenic response of methyl p-hydroxybenzoate and of propyl p-hydroxybenzoate at doses of 100 mg/kg body weight per day and for the ethyl congener even at 1000 mg/kg body weight per day. The authors concluded that both methyl and propyl esters might be considered as non oestrogenic.

Eventually, Fujitani (1993) reported that levels of 2.4% for 5 hours in male rats and 3% in male mice of SB administrated in the diet for 10 days were toxic.

Currently, the EU legislation does not refer maximum residual values for none of these preservatives. As a reference, values allowed to be use in Portuguese legislation vary from 200 mg/l in drinks to 2000 mg/kg in different products such as fat emulsions and cheese for potassium sorbate, from 150 mg/l in drinks to 500 mg/kg in different products such as fat emulsions and cheese for sodium benzoate and, from 300 mg/kg in bakery to 2000 mg/kg in dietetic food supplements for methyl p-hydroxybenzoate (Decreto-Lei n°363, 1998; Decreto-Lei n°274, 2000).

Production costs

According to the values presented in Table 5, for Alentejano dry sausage casings, the minimum cost was verified with application of the treatment SB followed by increasing values in the control, MHB, PS, SB+MHB, PS+SB, PS+MHB and PS+SB+MHB treatment. The cost of surface treatments applied in the casings of dry smoked sausage type Ribatejano (Table 6) varied between 0.0002 € in Control and 0.0002 € in PS+SB+MHB treatment.
Among these, increasing values were verified for the treatments SB, MHB, PS, SB+MHB, PS+SB and PS+MHB (Table 6). Results obtained with these calculations revealed that the production costs can increase from 0.0006 € up to 0.0024 €, per kilogram of final product, in sausage type Alentejano and, from 0.0001 € up to 0.003 € in sausage type Ribatejano, depending on the salt combination used for surface treatment. Comparing the production costs obtained for each type of product, the difference founded is of 0.004 € per kg of final product (Table 7). This difference can increase or reduce according to the surface treatment applied in the natural product casings. It is still important to refer that to these production costs will be added fixed costs, administration costs, financial costs, distribution costs, figurative and net profit until the product’s sell price is attained. The most important production cost components concerning their influence on total costs are raw meat (> 64%) and packaging materials (18%).

In summary, residual levels of PS and of SB (MHB was not detected) founded in the product after immersion of sausage dry smoked natural casings for 15 min in 2.5% (w/v) solutions of these three preservatives in seven different combinations varied from 0.009 to 0.056% (w/w) in treatments with PS, SB, PS+MHB and SB+MHB and, from 0.021 to 0.030% (w/w) (addition of residual mean values obtained for both salts, PS and SB) in treatments with combination of salts PS+SB and PS+SB+MHB.

Regarding potential undesirable effects on product quality it would seem indispensable to accomplish more...
experiments to establish maximum legislated values for these preservatives applied as surface treatments to dry smoked sausage casings. Also, determination of the accurate amounts to be added, time of exposure, diffusion and migration must be performed in order to obtain the expected residual levels into the product.

Surface treatments represent less than 0.5% of the production costs in both types of sausages. Nevertheless, treatment selection should be supported through a technical and economical decision well based once, meat industries, due to the specific technologies used and the smaller commercialization margins, must assure their competitiveness in a very demanding market.

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REFERENCES


