RESIDUAL LEVELS OF THREE PRESERVATIVES AND ECONOMICAL VIABILITY OF SURFACE TREATMENTS APPLIED IN PORTUGUESE SMOKED DRY SAUSAGES

Teresa J.S. Matos[a], António Barreto[a] and Fernando Bernardo[a]

[a] Faculdade de Medicina Veterinária. CIISA. UTL. R. Prof. Cid dos Santos - Polo Universitário, Alto da Ajuda, 1300-477 Lisboa, Portugal.

Background

In Portugal, as in the E.U., benzoates, sorbates and the esters of *p*-hydroxy-benzoic acid (parabens) may only be used in surface treatments of dry sausages casings. Legislated values are *Quantum satis* (without specified maximum level, these addictives should be added in agreement to the good manufacture practices, using the necessary amount to reach the proposed objectives) however, there is no reference about residual values in the final product (Decreto-Lei nº274, 2000; Decreto-Lei nº363, 1998). Residual levels vary with the method of application, time length of exposure, salt concentration, type of food, porosity of the food, shape and size of the food, and handling after exposure to the additive (Sofos, 1989). In this way, before a given application, tests should be conducted to determine appropriate solutions, exposure times, and handling of the necessary residual preservative levels in the product. In spray, dipping, or immersion uses, it is important to know the uptake, migration, diffusion, and residual levels of the 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.

Objectives

In this contest, the main goals of this study were to investigate, in Portuguese smoked dry sausages, the residual amounts of potassium sorbate (PS), sodium benzoate (SB) and methyl *p*-hydroxybenzoate (MHB) applied as surface treatment and also, the viability of such treatments regarding the production costs.

Materials and methods

Samples studied for this project were "chouriços" type Alentejano (A) and Ribatejano (R) produced by a large factory in Portugal as outlined by Matos et al. (2003). In control chouriço type R samples, surface treatment applied in casings was only cleansing with water to remove the salt and then immersion in cold water until fill up. In chouriço type A control samples, first casings were dipped in a solution of 30 kg of water and 1.5 l of commercial vinegar for 10 minutes, secondly cleansing with water and finally immersion in tap water until filling. These were normal plant practices for natural casings. For both sausage types, in test samples, casings were surface treated with three different salts in seven different combinations (Table 1), after water washing. Casings were immersed for 15 minutes in these solutions until filling. The experiments were divided in four trials. Each trial was conducted in batters of 560 kg. In the first trial the surface treatments were performed with potassium sorbate (PS), sodium benzoate (SB), methyl *p*-hydroxybenzoate (MHB) and control (AC1) (Table 1) 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), were applied (Table 1). 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 1). From all experiments 3 samples of sausages were taken from each surface treatment and control. Sausage samples were not peeled to accomplish the chemical measurements. The determination of PS, SB and MHB residual values were performed by High Performance Liquid Chromatography (HPLC) using a NOVA PACK, part nº36975 (Waters). Solution A, with 2.5 kg KH_2PO_4 + 0.1% acetic 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 35ºC at 1.0 ml/minute stream. Production costs concerned with the application of surface treatments in the natural casings in both types of sausages were determined according to the variable cost system and production costs were calculated as basic standard costs type (Rocha & Rúbio, 1999; Santos,

1998; Pereira & Franco, 1994). Calculations were based on real data achieved in a meat industry, under commercial conditions.

Results and discussion

Residual levels of PS, SB and MHB of sausages type Ribatejano and Alentejano are summarised in Table 2. Surface treatments production costs are presented in Tables 3 and 4 for chouriço type A and R, respectively. In Table 5 the totality of production costs for both types of sausages is shown. Values of methyl *p*-hydroxybenzoate in the accomplished analyses, were not detected (Table 2). The *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/or the non absorption of MHB by the casing during immersion time could be responsible for this MHB residual values absence. Residual levels of PS and of SB found 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 (Table 2).

For the same preservative, differences found between types of products may be related to the porosity of the natural casings used for each type of product (pork intestine salted for chouriço type R and beef dry casing for chouriço type A). In this way, it is very difficult to estimate expected values in the final product once the amount of addictive 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.

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 parabens are not potent oestrogens *in vivo.* Binstok *et al.* (1998), in a meat system containing 200 mg of sorbates and 150 mg of nitrites, heated at 60^{o}C for 5 hours, found that a mutagenic compound, ethyl-nitrolic acid (ENA) can be formed. More research is required to determine the minimum ENA amount for genotoxic activity and for establishing its health implications. Sodium benzoate toxicity in rats F344 and mice B6C3F1 was investigated by Fujitani (1993) reporting that levels of 2.4% in male rats and 3% in male mice of SB administrated in the diet for 10 days were toxic. The cost of surface treatments applied in the casings 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 (Tables 3 and 4).

Conclusions

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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Table 1
Surface treatments applied in Alentejano and Ribatejano smoked dry sausages casings.

Combinations of salts	Preparation	Amount of salt added	Final concentration (w/v)
Control of Alentejano sausage (AC1 and AC2)	30 l of water + 1.5 l of commercial vinegar	-	–
Control of Ribatejano sausage (RC1 and RC2)	Clean with water and immersion in cold water	-	–
Potassium sorbate (PS) (SIGMA, S1751)	In 20 l of water at 35±5^{0}C	500 g	2.5%
Sodium benzoate (SB) (SIGMA, B3375)	In 20 l of water at 35±5^{0}C	500 g	2.5%
Methyl *p*-hydroxybenzoate (MHB). (SIGMA, H5501)	In 20 l of water at 35±5^{0}C	500 g	2.5%
Potassium sorbate and Sodium benzoate (PS+SB)	In 40 l of water at 35±5^{0}C	500 g of each salt	1.25% of each salt
Potassium sorbate + Methyl *p*-hydroxybenzoate (PS+MHB)	In 40 l of water at 35±5^{0}C	500 g of each salt	1.25% of each salt
Sodium benzoate + Methyl *p*-hydroxybenzoate (SB+MHB)	In 40 l of water at 35±5^{0}C	500 g of each salt	1.25% of each salt
Potassium sorbate + Sodium benzoate + Methyl *p*-hydroxybenzoate (PS+SB+MHB)	In 60 l of water at 35±5^{0}C	500 g of each salt	0.83% of each salt

Table 2
Residual mean values of 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.

Treatments	PS (mg/kg)		SB (mg/kg)		MHB (mg/kg)	
	A	R	A	R	A	R
C1	-	-	-	-	-	-
PS	345.7 (14.2)	151.7 (14.6)	-	-	-	-
SB	-	-	560.3 (305.5)	233.3 (3.5)	-	-
MHB	-	-	-	-	nd	nd
C2	-	-	-	-	-	-
PS+SB	121.3 (85.6)	101.7 (13.2)	151.3 (57.7)	122.3 (31.2)	-	-
SB+MHB	-	-	144.3 (44.2)	131.3 (78.6)	nd	nd
PS+MHB	109.3 (54.1)	93.0 (5.3)	-	-	nd	nd
PS+SB+MHB	104.0 (5.2)	133.0 (11.3)	108.2 (5.3)	166.7 (12.4)	nd	nd

nd - not detected

Table 3
Production costs of surface treatments applied to beef dry casings in chouriço type Alentejano.

Components[a]	€ / kg	Surface treatments[b] (kg)							
		Control	PS	SB	MHB	PS+SB	PS+MHB	SB+MHB	PS+SB+ MHB
Water	0,005	30,000	20,000	20,000	20,000	20,000	20,000	20,000	30,000
Commercial vinegar	0,818	1,500							
Potassium sorbate	10,260	0,000	0,250			0,250	0,250		0,250
Sodium benzoate	1,915	0,000		0,250		0,250		0,250	0,250
Methyl *p*-hydroxybenzoate	9,477	0,000			0,250		0,250	0,250	0,250
Total value [c] (€)		1,377	2,665	0,579	2,469	3,144	5,034	2,948	5,563
Production cost per kg [d] (€)		0,0008	0,0015	0,0003	0,0014	0,0018	0,0029	0,0017	0,0032

[a]The labour costs were considered in Table 7.
[b]Surface treatments are described in Table 2.
[c]Total value (€) = Value (€ / kg) X Surface treatment (kg)
[d]Production cost per kg (€)= Total value of each surface treatment / kilograms of meat batter processed (1740,64 kg)

Table 4
Production costs of surface treatments applied to pork salted casings in chouriço type Ribatejano

Components[a]	€ / kg	Surface treatments[b] (kg)							
		Control	PS	SB	MHB	PS+SB	PS+MHB	SB+MHB	PS+SB+ MHB
Water	0,005	60,000	20,000	20,000	20,000	20,000	20,000	20,000	30,000
Commercial vinegar	0,818	0,000							
Potassium sorbate	10,260	0,000	0,250			0,250	0,250		0,250
Sodium benzoate	1,915	0,000		0,250		0,250		0,250	0,250
Methyl *p*-hydroxybenzoate	9,477	0,000			0,250		0,250	0,250	0,250
Total value [c] (€)		0,299	2,665	0,579	2,469	3,144	5,034	2,948	5,563
Production cost per kg [d] (€)		0,0002	0,0015	0,0003	0,0014	0,0018	0,0029	0,0017	0,0032

[a]The labour costs were considered in Table 7.
[b]CSurface treatments are described in Table 2.
[c]Total value (€) = Value (€ / kg) X Surface treatment (kg)
[d]Production cost per kg (€) = Total value of each surface treatment / kilograms of meat batter processed (1733,67 kg)

Table 5
Distribution of the production costs by components for both types of sausages (Alentejano and Ribatejano).

Chouriço Type Alentejano	€ / kg	Percentage (%) of the total cost
Raw meat material	2,697	66,18
Formulation ingredients.	0,239	5,86
Packaging material	0,754	18,50
Labour	0,305	7,48
Sanitation	0,020	0,49
Energy	0,060	1,48
TOTAL	**4,075**	**100**
Chouriço Type Ribatejano	**€ / kg**	**Percentage (%) of the total cost**
Raw meat material	2,629	64,58
Formulation ingredients.	0,286	7,02
Packaging material	0,762	18,72
Labour	0,314	7,71
Sanitation	0,020	0,49
Energy	0,060	1,47
TOTAL	**4,071**	**100**