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Biochemical changes during the ripening of *Chorizo de cebolla*, a Spanish traditional sausage. Effect of the system of manufacture (homemade or industrial)

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Abstract

Chorizo de cebolla is a dry-fermented sausage abundantly produced and consumed in Galicia (NW Spain). The gross chemical composition and the main physicochemical, proteolytic, lipolytic and fat autooxidative parameters were determined throughout the ripening process of seven homemade batches and four industrial batches. Samples from each batch of sausages were taken at 0 days (mix before stuffing), and after 2, 7, 14, 21, 28 and 42 days of ripening. Dehydration throughout ripening was more intense in the homemade batches, which showed final moisture and a_w values lower than the industrial batches. In comparison to other varieties of chorizo and other similar raw-cured sausages, *Chorizo de cebolla* is characterised by high contents of fat and hydroxyproline and low contents of protein, NaCl and ash. In both systems of manufacture (homemade and industrial), a significant decrease in the pH values is observed until the seventh day of ripening (coinciding with the period of maximum degradation of the sugars), after which the pH was practically constant until the end of ripening in the homemade batches and showed a slight, but progressive increase after the 14th day in the industrial batches. The final pH values were lower than those reported for similar sausages.

The different nitrogen fractions showed an increase during ripening and no significant differences in the final values, associated with the system of manufacture, were observed. The values of the nitrogen fractions show that proteolysis is particularly evident in the early stages of ripening, coinciding with the development of fermentation and a sharp decrease in pH.

The acidity of the fat increases considerably during ripening in both systems of manufacture; however, the final values were among the lowest previously reported. The peroxide and TBA values evolved differently in the homemade and industrial batches. At the end of ripening, no significant differences associated with the system of manufacture (homemade or industrial) were observed in the peroxide value; however, the homemade batches showed significantly higher TBA values.

Keywords: *Chorizo de cebolla*; Dry-fermented sausages; Ripening; Proteolysis; Lipolysis; Fat auto-oxidation

1. Introduction

The Spanish traditional sausages are, in almost all cases, fermented sausages that undergo a more or less prolonged process of drying–ripening before consumption. The more representative Spanish raw-cured sausages are "*Chorizo*" and "*Salchichón*", of which various types are manufactured in the different Spanish regions. The mixes used in the manufacture of these sausages are made-up of minced pork (beef, or beef and pork) and pork fat, with the addition of salt, paprika (only in the case of *Chorizo*), pepper (only in the case of *Salchichón*), and other species and additives. The

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mixes are stuffed into natural or artificial casings and, after stuffing, the sausages undergo a drying–ripening process.

During the manufacture of dry-fermented sausages, apart from microbiological modifications, chemical and physicochemical changes occur, especially dehydration, fermentation of carbohydrates and acidification, development of colour, lipolysis and fat autooxidation and proteolysis (Ordóñez, Hierro, Bruna, & de la Hoz, 1999). These changes are responsible for the organoleptic characteristics of the final products.

Chorizo de cebolla, a variety of *Chorizo*, is a fermented and dried-ripened sausage abundantly produced from raw pork in Galicia (NW of Spain). It is both home- and industrially-made and is included in the "Catalogue of cured sausages and hams of Spain" (Anonymous, 1983). The scientific knowledge of this sausage variety is limited and its quality is very variable, as there is very little uniformity in the product manufactured by different homemade processors and meat industries.

The existing information in the scientific literature on this sausage variety refers only to some microbiological aspects of the ripening process (Castaño, García Fontán, Fresno, Tornadijo, & Carballo, 2002; García Fontán et al., 1998) and to the characteristics of the fat of the end-product (Rodríguez, Carballo, & López, 2001), and there is a lack of information about the chemical and physicochemical changes that occur throughout the manufacturing process.

The aim of this article is to study the changes in the contents of the chemical components, changes of the physicochemical parameters, and the proteolysis and modifications of the lipid fraction during the manufacture of *Chorizo de cebolla*. The effect of the system of manufacture (homemade or industrial) on these changes is also studied.

2. Materials and methods

2.1. Samples

In order to carry out this study, seven homemade batches of *Chorizo de cebolla* (from seven different processors) and four industrial batches (from four different pork meat industries) were used. From each batch of sausage, samples at 0 days (mix before stuffing), and after 2, 7, 14, 21, 28 and 42 days of ripening were taken. Each sample consisted of two entire units of *Chorizo de cebolla*.

The average amounts of ingredients for the preparation of the mix, used in the manufacture of the batches, are summarized in Table 1. The supplement added to the mix of the industrially manufactured *Chorizo de cebolla* was in all cases BELL No. 2 from Laboratorios La Campana (Xirivella, Valencia, Spain), composed, in unknown proportions, of dehydrated skim milk; sugars, disodium diphosphate (E_{450i}), soya protein, salt, dextrin, sodium nitrite (E_{250}), potassium nitrate (E_{252}), monosodium citrate (E_{331i}), and colorant (E_{124}).

Table 1
Average composition of the mix used in the manufacture of the homemade and industrial *Chorizo de cebolla* (per 150 kg of mix)

Industrial sausage		Homemade sausage	
Pork jowl	70 kg	Pork jowl	50 kg
Bacon	40 kg	Bacon	20 kg
Sweet paprika	2.5 kg	Pork bloody trimmings	15 kg
Spicy paprika	0.5 kg	Cooked skin	9 kg
Salt	3 kg	Lung	17 kg
Garlic	1.5 kg	Sweet paprika	2.5 kg
Marjoram	0.075 kg	Spicy paprika	0.5 kg
Onion	30 kg	Salt	3 kg
Supplement	2.25 kg	Garlic	1.5 kg
		Marjoram	0.1 kg
		Onion	10 kg
		Pumpkin	20 kg
		Bay	*Quantum satis*
		Sugar (sucrose)	1 kg

The meat is minced and mixed with the species and the supplement (in the case of industrial manufacture), and the resulting mix is left to stand at low temperatures (below 5 °C) for 24 h when homemade and for 12 h when manufactured industrially. After standing, and immediately before stuffing, the mass is finally mixed with the onion ("cebolla") and pumpkin (in the case of the homemade product). In the homemade mixture, the onion is always added raw and finely minced. Dehydrated onion, which has previously been hydrated for 24 h after mixing 3 l of water with each kilo of dehydrated onion, is used in the industrial product. Once the mass has been properly mixed, it is stuffed into the natural large intestine of the pig and divided into units that are ≈15 cm long.

In industrial manufacture, after stuffing, the sausages are smoked over a period of ≈4–5 days, using oak and birch wood. After smoking, the sausages are transferred to a drying–ripening chamber where they are kept for the rest of the ripening period at 11 °C and 70% of relative humidity.

The homemade sausages, after stuffing, are transferred to cool and well-ventilated rooms, where they are smoked for 8 h each day for 10 days. After this, the *chorizos* are held in these rooms for the rest of the ripening period.

Once collected, the samples were transported to the laboratory under refrigeration (below 4 °C). In order to prepare the samples for analysis, after removing and discarding the outer casing of each *Chorizo de cebolla* unit, the edible part was ground in a Moulinette mincer (Moulinex/Swan Holdings Ltd., Birmingham, England) until a homogeneous mass was obtained. After determining the moisture content, water activity and pH, the samples were stored in air-tight bottles, frozen at −80 °C, for no longer than four weeks prior to further analysis.

2.2. Analytical methods

Moisture, fat, protein (Kjeldahl $N \times 6.25$), ash, NaCl, and nitrate contents were quantified according to the ISO recommended standards 1442:1997 (ISO, 1997), 1443:1973 (ISO, 1973), 937:1978 (ISO, 1978), 936:1998 (ISO, 1998), 1841-1:1996 (ISO, 1996) and 3091:1975 (ISO, 1975), respectively.

Total carbohydrates were quantified using the phenol–sulphuric acid method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956) in an extract obtained with 0.6 N $HClO_4$ following the procedure of De Ketelaere, Demeyer, Vandekerckhove, and Vervaeke (1974). This same extract was used in the determination of the total non-protein nitrogen (NPN) using the Johnson (1941) method, the α-aminoacidic nitrogen (NH_2-N) using the Moore and Stein (1948) method, and the total basic volatile nitrogen (TBVN) using the Pearson (1968) method.

The pH was measured with a pH meter micro pH 2002 (Crison Instruments, S.A., Barcelona, Spain) after mixing 10 g of sample with 90 ml of distilled water for 2 min in a Sorvall Omnimixer homogeniser (Omni International, Waterbury, CT, USA). Determination of water activity (a_w) was performed using a Decagon CX-1 Water Activity System apparatus (Decagon Devices, Pullman, WA, USA). The titratable acidity was determined following the method described by Zaika, Zell, Smith, Palumbo, and Kissinger (1976).

The values of acidity and peroxide of the fat were determined, following the Spanish Official Standards UNE 50.011 and UNE 55.023, respectively (Presidencia del Gobierno, 1977) after extraction of the fat, following the method of Folch, Lees, and Stanley (1957). The TBA value was measured according to the method of Tarladgis, Watts, Younathan, and Dugan (1960).

2.3. Statistical methods

In order to study significant differences between the different sampling points during the ripening process in the batches of the same manufacture (homemade or industrial), and between the two systems of manufacture at each sampling point, a variance analysis (ANOVA) was performed, with a confidence interval of 95% ($P < 0.05$). Means were compared by the least squares difference (LSD) test, using the computer programme Statistica 5.1 for Windows (Statsoft Inc, 1996, Tulsa, OK, USA).

3. Results and discussion

Tables 2 and 3 show the changes in the gross chemical components during the ripening of the batches of *Chorizo de cebolla* made by homemade and industrial methods, respectively.

The average initial water contents of the homemade and industrial *Chorizo de cebolla* (63.73% and 56.44%, respectively) are similar to the values described by other authors in other varieties of *Chorizo* (Barranco Sánchez et al., 1985; Mateo, Domínguez, Aguirrezábal, & Zumalacárregui, 1996; Mendoza, Flores, & Silla, 1983), and for most of the raw-cured sausages studied (Ferrer & Arboix, 1986; Franco, Prieto, Cruz, López, & Carballo, 2002; Lizaso, Chasco, & Beriain, 1999; Roncalés, Aguilera, Beltrán, Jaime, & Peiró, 1991). This content decreases progressively during the whole of the drying–ripening period, as has also been described in other varieties of *Chorizo* (Barranco Sánchez et al., 1985; Bello et al., 1974a; Lois et al., 1987; Mateo et al., 1996) and in other similar sausages (Coppola, Iorizzo, Saotta, Sorrentino, & Grazia, 1997; Ferrer & Arboix, 1986; Franco et al., 2002; Lizaso et al., 1999; Roncalés et al., 1991; Sayas-Barberá, Pérez-Álvarez, Fernández-López, & Oñate, 1998; Serrano Moreno, 1979). The humidity losses were more marked in the first

Table 2
Changes in the chemical components during the ripening of homemade "*Chorizo de cebolla*" (average values ± standard deviation of seven batches)

	Ripening time (days)						
	0	2	7	14	21	28	42
Moisture[A]	63.73 ± 7.97[a]	54.79 ± 7.27[b]	43.48 ± 6.67[c]	33.74 ± 5.53[d]	26.22 ± 4.07[e]	23.29 ± 3.75[e]	17.17 ± 2.02[f]
Protein ($N \times 6.25$)[B]	21.2 ± 1.93[a]	21.6 ± 1.41[a]	21.7 ± 1.19[a]	20.3 ± 0.91[a]	21.7 ± 1.34[a]	21.0 ± 0.83[a]	22.1 ± 1.30[a]
Fat[B]	66.07 ± 2.02[a]	67.32 ± 1.71[ab]	66.98 ± 1.94[ab]	68.44 ± 1.67[b]	67.87 ± 2.74[ab]	67.87 ± 1.68[ab]	65.75 ± 2.29[ab]
Ash[B]	4.01 ± 0.71[a]	3.89 ± 0.79[a]	4.06 ± 0.93[a]	3.76 ± 0.85[a]	3.68 ± 0.92[a]	3.85 ± 0.83[a]	4.22 ± 0.99[a]
NaCl[B]	1.52 ± 0.42[a]	1.47 ± 0.50[a]	1.56 ± 0.57[a]	1.58 ± 0.63[a]	1.53 ± 0.57[a]	1.69 ± 0.67[a]	1.82 ± 0.70[a]
Total carbohydrates[B]	3.59 ± 2.53[a]	2.59 ± 1.30[b]	2.45 ± 1.17[b]	1.88 ± 0.88[b]	1.99 ± 0.94[b]	1.73 ± 1.07[b]	1.73 ± 1.02[b]
Hydroxyproline[B]	0.55 ± 0.15[a]	0.57 ± 0.21[a]	0.57 ± 0.17[a]	0.53 ± 0.23[a]	0.51 ± 0.24[a]	0.52 ± 0.21[a]	0.49 ± 0.17[a]
Nitrate (ppm)	65.9 ± 24.0[a]	71.6 ± 21.1[a]	60.40 ± 25.4[a]	59.9 ± 20.0[a]	64.03 ± 31.2[a]	64.0 ± 27.9[a]	67.6 ± 33.9[a]

[a–f] Mean values in the same row (corresponding to the same parameter) not followed by a common letter differ significantly ($P < 0.05$).
[A] Expressed as g/100 g.
[B] Expressed as g/100 g of dry matter.

Table 3
Changes in the chemical components during the ripening of "*Chorizo de cebolla*" made by industrial methods (average values ± standard deviation of four batches)

	Ripening time (days)						
	0	2	7	14	21	28	42
Moisture[A]	56.44 ± 2.62^{a}	53.14 ± 3.11^{ab}	45.61 ± 8.02^{bc}	40.26 ± 9.75^{cd}	34.86 ± 9.90^{d*}	31.40 ± 7.03^{de*}	24.74 ± 7.62^{e}
Protein ($N \times 6.25$)[B]	23.0 ± 3.31^{a}	23.5 ± 3.01^{a}	24.1 ± 3.39^{a}	25.1 ± 2.56^{a*}	24.4 ± 2.59^{a*}	25.0 ± 1.64^{a*}	24.5 ± 3.76^{a}
Fat[B]	65.30 ± 1.86^{a}	64.79 ± 2.29^{a}	65.60 ± 1.81^{a}	65.53 ± 2.01^{a*}	65.63 ± 2.41^{a}	65.33 ± 1.38^{a}	65.87 ± 1.91^{a}
Ash[B]	5.71 ± 1.11^{a*}	5.70 ± 1.25^{a*}	6.04 ± 0.73^{a*}	5.73 ± 0.82^{a*}	5.95 ± 1.17^{a*}	5.94 ± 1.19^{a*}	6.02 ± 0.89^{a*}
NaCl[B]	3.07 ± 0.28^{a*}	3.23 ± 0.70^{a*}	3.03 ± 0.76^{a*}	3.07 ± 0.72^{a*}	3.04 ± 0.80^{a*}	3.31 ± 0.85^{a*}	3.34 ± 0.87^{a*}
Total carbohydrates[B]	3.01 ± 0.43^{a}	1.94 ± 0.53^{a}	0.43 ± 0.18^{b*}	0.45 ± 0.19^{b*}	0.52 ± 0.20^{b*}	0.36 ± 0.08^{b*}	0.43 ± 0.29^{b*}
Hydroxyproline[B]	0.79 ± 0.29^{a}	0.75 ± 0.35^{a}	0.70 ± 0.33^{a}	0.75 ± 0.28^{a}	0.70 ± 0.28^{a}	0.76 ± 0.31^{a}	0.76 ± 0.28^{a}
Nitrate (ppm)	120 ± 28.8^{a*}	135 ± 41.2^{a*}	132 ± 30.2^{a*}	151 ± 39.5^{ab*}	149 ± 27.7^{ab*}	182 ± 37.7^{b*}	190 ± 63.1^{b*}

[a–e] Mean values in the same row (corresponding to the same parameter) not followed by a common letter differ significantly ($P < 0.05$).
[A] Expressed as g/100 g.
[B] Expressed as g/100 g of dry matter.
[*] Sampling point with a significant difference ($P < 0.05$) between homemade and industrial sausages.

seven days, especially in the homemade product and, although after the 14th day of ripening the rates of loss were equal in both systems of manufacture, the industrial *chorizos* showed higher humidity values, reaching levels of 24.74% at 42 days, while the homemade *chorizos* showed contents of 17.7%.

The losses of moisture were, thus, more noticeable in the batches of homemade sausage. This circumstance, given that the calibre of the sausages was identical in both cases, could be motivated in the first place by slight differences in the water retention capacity of the meat, which would obviously be greater in the industrial batches due to their higher content of sodium chloride. Although some authors (Palumbo, Smith, & Zaika, 1976) maintain that the salt does not have any appreciable influence on the dehydration velocity, it is well known that salt increases the water retention capacity at pH values higher than the isoelectric point of the actomyosin, which is normally 5.1 but which decreases to 4 in the presence of sodium chloride.

Another factor that could influence the more intense dehydration experienced by the homemade batches is the relative humidity existing in the room where they are ripened. The industrial batches were, in all cases, ripened in storage chambers that allowed an exact control of the relative humidity. The homemade batches were ripened in rooms conditioned in the homes of the artisans, where the relative humidity takes the environmental values and, in many cases, these are lower than those desirable for the correct control of dehydration.

The protein levels ($N \times 6.5$) expressed as a percentage of dry matter, were constant during ripening, as has already been described in other varieties of *Chorizo* (Barranco Sánchez et al., 1985; Mendoza et al., 1983) and in other comparable sausages (Coppola et al., 1997; Ferrer & Arboix, 1986; Franco et al., 2002; Keller, Skelley, & Acton, 1974; Serrano Moreno, 1979). We have found significant differences ($P < 0.05$) in the average protein content as a function of the manufacturing process in three sampling points (14, 21, 28 days of ripening), with average values of around 21% for the homemade and of around 25% for the industrial *chorizos*. These values are clearly lower than those described by different authors in other varieties of *Chorizo* in which the evolution of these components during ripening has also been studied and which oscillate between 38.5% of dry matter (Barranco Sánchez et al., 1985) and 54.4% dry matter (Mendoza et al., 1983).

The protein content of *Chorizo de cebolla* is also lower than that shown by most raw-cured sausages (Coppola et al., 1997; Ferrer & Arboix, 1986; Franco et al., 2002; Keller et al., 1974; Marquina, Beltrán, Jaime, Peiró, & Roncalés, 1993), with the exception of *Salchichón*, which shows similar values (Serrano Moreno, 1979).

The fat content, also expressed as a percentage of dry matter, was also constant throughout ripening, showing levels in the order of 67% and 65% of dry matter in those manufactured using homemade or industrial procedures, respectively. These values are higher than those indicated in the literature for other varieties of *Chorizo* (Barranco Sánchez et al., 1985; Mendoza et al., 1983).

Lower fat contents, of between 40% and 60% of dry matter, have been described for other raw-cured sausages (Ferrer & Arboix, 1986; Franco et al., 2002; Keller et al., 1974; Serrano Moreno, 1979), with the exception of *Soppressata Molisana* that shows much lower levels, of 26% (Coppola et al., 1997).

The content of NaCl, expressed as a percentage of dry matter, was practically constant throughout ripening, with values of around 1.5% and 3%, respectively, in the homemade and industrial *Chorizo de cebolla*. These values were lower than those described in other varieties of *Chorizo* (Barranco Sánchez et al., 1985) and were also lower than those reported for different raw-cured sausages (Ferrer & Arboix, 1986; Franco et al., 2002; Keller et al., 1974; Serrano Moreno, 1979) that vary between the 3.64% found by Franco et al.

(2002) in *Androlla* and the 7.26% by Ferrer and Arboix (1986) in *Salchichón de Vich*.

The ash values remained constant during the whole of the ripening process and, like the chlorides, are lower than those described for other varieties of *Chorizo* (Barranco Sánchez et al., 1985). The ash content of *Chorizo de cebolla* was also higher in the batches industrially manufactured (6% of total solids) than in the homemade batches (4% of total solids).

In relation to the values reported for other similar raw-cured sausages, the ash content presented by *Chorizo de cebolla* is also low. Thus, most of these sausages have an ash content of between 7% and 10% of total solids (Coppola et al., 1997; Ferrer & Arboix, 1986; Franco et al., 2002; Keller et al., 1974; Marquina et al., 1993; Serrano Moreno, 1979).

There is a considerable variability in the amount of sugar that is added in the manufacture of homemade *Chorizo de cebolla*, reaching average amounts of 3.59 ± 2.53 g/100 g of total solids in the mix, which is about 20% higher than that added in the industrial manufacture of this product. In both cases, these sugars degrade rapidly in the first seven days of ripening, especially in the industrial batches, significant differences ($P < 0.05$) occurring at day 7 in the carbohydrate content between the different methods of manufacture. Thus, whilst in the industrial batches almost 90% of the sugars initially present have disappeared in this period (values of 0.43% of dry matter on the seventh day of ripening), in the homemade batches they continue to degrade until the 14th day of ripening, with practically constant values afterwards (around 1.8%). This different behaviour could be related to the fact that, in the industrial manufacture of the sausage, sugars are added that are more easily fermentable than the sucrose normally employed in homemade sausages.

Information about the evolution of the sugars during ripening of the raw-cured sausages is relatively scarce and it appears that the velocity of degradation depends on the type of sausage (Ferrer & Arboix, 1986; Franco et al., 2002; Lizaso et al., 1999; Lois et al., 1987).

The hydroxyproline content was constant throughout the ripening process, maintaining constant values in the order of 0.53 and 0.75 g/100 g of dry matter in the homemade and industrial batches, respectively. Although the values of the hydroxyproline content were about 50% higher in the batches manufactured industrially, this difference was not statistically significant due to the wide dispersion of the values determined in each sampling point, both in the homemade and in the industrial batches, which determined that the standard deviations reached very high values.

Our values of hydroxyproline were higher than those determined by Ferrer and Arboix (1986) during ripening of *Salchichón de Vich*, which originated in the low quality of the meat employed for the manufacture of *Chorizo de cebolla*.

The nitrate content in homemade *Chorizo de cebolla* was constant throughout the ripening process, with values of about 65 ppm. In the industrial product, it would appear that there is a tendency toward an increase of these components during ripening, possibly due to the decrease of water content as a consequence of dehydration, given that these components are expressed as ppm (mg/kg). In the homemade batches this tendency was not observed, possibly because this effect was neutralised by a partial degradation of the nitrates present (by transformation into nitrites). In other raw-cured sausages, a decrease has been observed in their nitrate content during ripening (Ferrer & Arboix, 1986; Mendoza et al., 1983) as a consequence of this degradation phenomenon that does not seem to be very intense in *Chorizo de cebolla* itself. Franco et al. (2002), studying another traditional sausage (*Androlla*), observed that the initial nitrate content (43 ppm) remained practically constant during the ripening process applied to this product, which accords with what we observed in homemade *Chorizo de cebolla*.

The phenomenon of the transformation of nitrites into nitrates could contribute to the maintenance of the concentration of nitrate during ripening and (inclusively) the increase of its concentration. The transformation of nitrites into nitrates is a fact manifested repeatedly in both raw-cured and boiled-cured meat products. The transformation of between 1% and 10% of the added nitrites into nitrates is widely accepted (Cassens, Greaser, Ito, & Lee, 1979).

However, Alley, Courst, and Demeyer (1992) observed that in the first stages of fermentation, more than 50% of the nitrites that disappeared were transformed into nitrates. Sarasíbar, Sánchez-Monge, and Bello (1989) have demonstrated that, during the stage of fermentation in *Chorizo de Pamplona*, there is a significant increase of the nitrates in sausages manufactured with 300 ppm of nitrites. On the other hand, Aguirrezábal, Mateo, Domínguez, and Zumalacárregui (1999) have demonstrated, in analytical terms, the formation of nitrates (113 ppm) in a batch of *chorizo* manufactured with 150 ppm of nitrites.

The industrial batches showed, in all the sampling points, significantly higher levels of nitrates than those observed in the homemade batches. This demonstrates a deliberate addition of nitrates into the mix during the manufacture of the industrial batches.

Fig. 1 shows the changes in some physicochemical parameters during the ripening of the homemade and industrially manufactured *Chorizo de cebolla* batches.

During the ripening process of the *Chorizo de cebolla*, a progressive decrease of a_w was observed. This decrease, fundamentally due to the decrease of the water content (although the increase that takes place in the

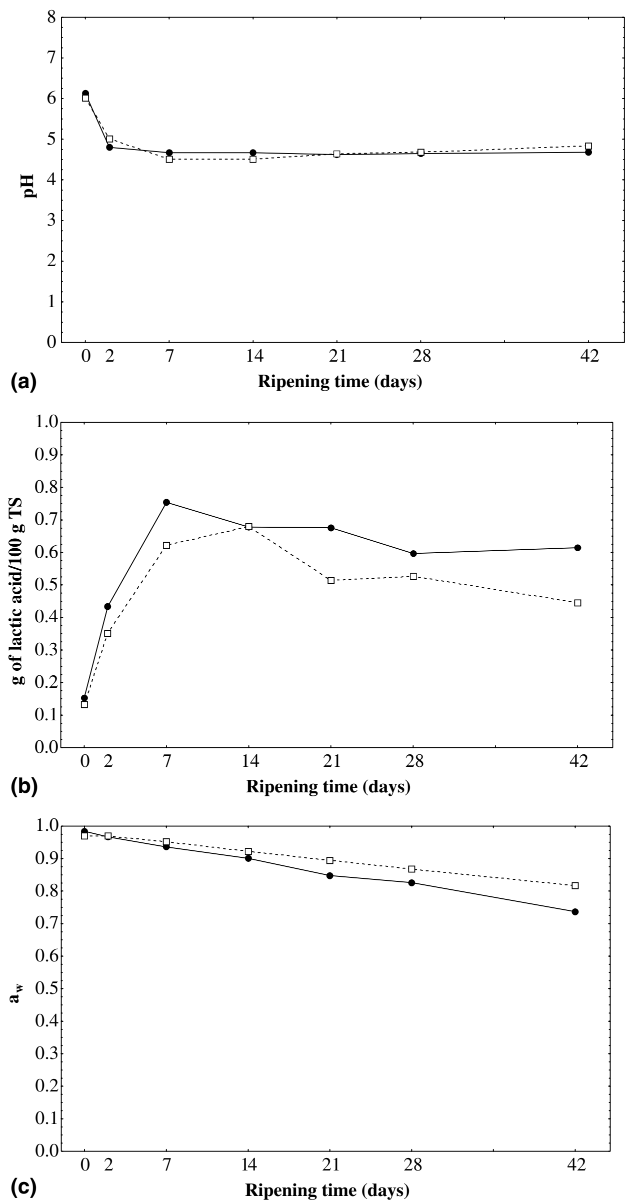

Fig. 1. Changes in pH (a), titratable acidity (b) and water activity (c) values of homemade (average of seven batches) –●– and industrial (average of four batches) –□– *Chorizo de cebolla*.

level of the low molecular weight nitrogen compounds could also contribute), was more marked in the homemade batches. At the end of the ripening period, the average value of water activity was also significantly lower in the homemade batches.

The decrease of a_w observed in our study was more marked than was found by Serrano Moreno (1979) and by Lizaso et al. (1999) in *Salchichón*, and by Franco et al. (2002) in *Androlla*.

The average pH value of the *Chorizo de cebolla* mix before stuffing was virtually similar in both systems of manufacture studied, with average values of 6.13 for the homemade *chorizos* and of 6.02 for those manufactured industrially. These initial pH values were higher than some of the values found in the literature (Coppola et al., 1997; Ferrer & Arboix, 1986; Lizaso et al., 1999; Lois, Gutiérrez, Zumalacárregui, & López, 1987; Mateo et al., 1996), but similar to the results obtained by other researchers in mixes of various sausages (Franco et al., 2002; García de Fernando & Fox, 1991; Nagy, Mihályi, & Incze, 1989; Serrano Moreno, 1979; Zaika, Zell, Palumbo, & Smith, 1978; Wardlaw, Skelley, Johnson, & Acton, 1973).

With respect to the evolution of pH during the ripening process of *Chorizo de cebolla*, substantial differences were found between the results of the two manufacturing processes. In both cases, a significant decrease was observed up to the seventh day of ripening, which coincides with the maximum degradation of the sugars, the time at which average pH values of 4.67 ± 0.14 and 4.51 ± 0.19 were observed, in the homemade and industrial batches, respectively. In the homemade batches, from this time, this parameter remained practically constant until the end of ripening, whilst the industrial batches showed a slight and progressive increase from day 14 and reached an average value of 4.84 ± 0.26 at the end of the process (42 days).

Many studies have aimed to understand the evolution of the pH during the ripening process of different raw-cured sausages (Barranco Sánchez et al., 1985; Coppola et al., 1997; Ferrer & Arboix, 1986; Franco et al., 2002; García de Fernando & Fox, 1991; Lois et al., 1987; Lizaso et al., 1999; Mateo et al., 1996; Nagy et al., 1989; Serrano Moreno, 1979; Wardlaw et al., 1973) and the data obtained were very varied. Whilst, in some studies, initial decreases of one pH unit or more have been observed (Barranco Sánchez et al., 1985; Lizaso et al., 1999; Lois et al., 1987, Wardlaw et al., 1973), in other studies, decreases of only 0.16 units have been detected in the first phase of ripening (Coppola et al., 1997; Ferrer & Arboix, 1986). After the initial decrease, as the ripening process continues, there is an increase in this parameter that can reach up to 0.6–0.8 units (Ferrer & Arboix, 1986; Lois et al., 1987; Nagy et al., 1989), although most of the increases are within the range of 0.2–0.4 pH units (Coppola et al., 1997; García de Fernando & Fox, 1991; Wardlaw et al., 1973), being in other cases even lower (Barranco Sánchez et al., 1985; Franco et al., 2002) or even inappreciable (Lizaso et al., 1999; Serrano Moreno, 1979).

In our case, as mentioned previously, the decrease of the pH during the first days of ripening was one of the largest ever observed (1.46 units, on average, in the homemade batches and 1.51 units in the industrial batches) increase during the final days being absent in the homemade batches and only moderate (0.33 units on average) in the industrial batches. Other authors (Grazia, Romano, Bagni, Roggiani, & Guglieelmi, 1986; Roncalés et al., 1991), are right to indicate that this increase in the latter stages of the ripening process

Table 4
Changes in the nitrogen fraction contents (mg/100 g of total solids) during the ripening of homemade "*Chorizo de cebolla*" (average values ± standard deviation of seven batches)

	Ripening time (days)						
	0	2	7	14	21	28	42
NPN	279 ± 110[a]	484 ± 251[a]	672 ± 324[b]	719 ± 360[b]	707 ± 330[b]	716 ± 329[b]	743 ± 271[b]
αNH_2–N	98 ± 52[a]	180 ± 116[ab]	281 ± 187[bc]	303 ± 197[bc]	320 ± 214[bc]	310 ± 213[bc]	344 ± 231[c]
TVBN	34 ± 12[a]	61 ± 32[ab]	85 ± 43[bc]	102 ± 59[c]	98 ± 48[bc]	108 ± 48[c]	112 ± 45[c]

[a–c] Mean values in the same row (corresponding to the same nitrogen fraction) not followed by a common letter differ significantly ($P < 0.05$).

Table 5
Changes in the nitrogen fraction contents (mg/100 g of total solids) during the ripening of "*Chorizo de cebolla*" made by industrial methods (average values ± standard deviation of four batches)

	Ripening time (days)						
	0	2	7	14	21	28	42
NPN	230 ± 56[a]	279 ± 46[ab]	490 ± 86[abc]	555 ± 73[abc]	620 ± 96[bc]	678 ± 102[c]	775 ± 138[c]
αNH_2–N	35 ± 12[a]	42 ± 12[a]	83 ± 22[b*]	98 ± 29[b*]	113 ± 32[b*]	113 ± 25[b*]	122 ± 14[b*]
TVBN	33 ± 9[a]	42 ± 18[a]	67 ± 31[a]	79 ± 38[a]	79 ± 30[a]	79 ± 35[a]	83 ± 34[a]

[a–c] Mean values in the same row (corresponding to the same nitrogen fraction) not followed by a common letter differ significantly ($P < 0.05$).
[*] Sampling point with a significant difference ($P < 0.05$) between homemade and industrial sausages.

appears to be more related to the decrease in lactic acid content, consumed by a microbial group that is present, than to the formation of low molecular weight nitrogen compounds.

The final pH values that we observed are the lowest that have been found in the studies performed on the evolution of this parameter during the ripening of raw-cured sausages (Coppola et al., 1997; Ferrer & Arboix, 1986; Franco et al., 2002; García de Fernando & Fox, 1991; Lizaso et al., 1999; Lois et al., 1987; Mateo et al., 1996; Nagy et al., 1989; Wardlaw et al., 1973). Only Barranco Sánchez et al. (1985) have found, at the end of the ripening process, values that are slightly lower than ours (4.48 on average).

As was to be expected, the values of titratable acidity had an inverse relationship to pH during the ripening process. The titratable acidity increased significantly ($P < 0.05$) in the first seven days of ripening and, afterwards, more slowly until the 14th day of ripening, when it gradually decreased (more pronounced in the industrial batches) until the end of the ripening process.

Literature information about the evolution of titratable acidity during ripening of raw-cured sausages is not very abundant and neither are the discussions about the phenomena implied in the evolution of this parameter. The decrease observed in *Chorizo de cebolla* after the 14th day of ripening could be related to the development of microbial flora, fundamentally moulds and yeasts, capable of consuming lactic acid.

If we take into account the low pH values found in *Chorizo de cebolla*, higher values of titratable acidity would be expected. Such an apparent discrepancy could be explained by the low buffer capacity of this sausage that would cause the mix to reach lower pH values than would be expected from the amounts of acids present.

Tables 4 and 5 show the changes in the different nitrogen fractions during the ripening of the batches of homemade and industrially manufactured *Chorizo de cebolla*, respectively.

The content of non-protein nitrogen (NPN) (279 ± 110 and 230 ± 56 mg/100 g of dry matter, representing about 8.30% and about 6.25% of total nitrogen in the mix of homemade and industrial *Chorizo de cebolla*, respectively) increased significantly during ripening, reaching (in both systems of manufacture) similar average final values (743 ± 271 and 775 ± 138 mg/100 g of dry matter, representing 22.1% and 21.1% of total nitrogen in the homemade and industrial *Chorizo de cebolla*, respectively). However, the evolutional behaviour of this nitrogen fraction was different in the two systems of manufacture. Whilst in the *chorizos* manufactured industrially this fraction increased progressively during the ripening process, in the homemade *chorizos* this increase was more marked in the first seven days of ripening.

The existing information in the bibliography on the evolution of the NPN in different cured sausages indicates that an increase in this fraction is produced in all of them during ripening, although at different rates. In some sausages, there is a rapid increase in the first few days, after which it remains more or less stable (Dierick, Vandekerckhove, & Demeyer, 1974; Domínguez Fernández & Zumalacárregui Rodríguez, 1992-94; León Crespo, Millán, & Serrano Moreno, 1978; León Crespo et al., 1985; Lois et al., 1987). In others it can be seen that the increase is constant during the whole of the process (Franco et al., 2002) and, sometimes, a slight but continuous decrease has been reported in the latter stages (León Crespo et al., 1985; Lois et al., 1987).

Likewise, differences in the magnitudes of the NPN increases during ripening can be seen. Thus, in the *Androlla* this fraction increases about 2.1 times (Franco et al., 2002), in *Chorizo de León* around 1.7 times (Domínguez Fernández & Zumalacárregui Rodríguez, 1992-94; Lois et al., 1987), whilst in *Salchichón de Vich* this increase is only 1.5 times (Ferrer & Arboix, 1986). In *Chorizo de cebolla* we have confirmed that this fraction undergoes a larger increase, of about 2.7 and 3.4 times, in the homemade and industrial batches, respectively. Flores, Marcus, Nieto, and Navarro (1997) demonstrated that, the lower the pH value in the sausage, the higher was the NPN content, which could justify our results, as the *Chorizo de cebolla* shows, throughout the manufacturing process, lower pH values and higher NPN values than those described in most of the previously cited sausages. From this observation and from the data contributed by different authors who have studied the evolution of the NPN during the manufacturing process of various raw-cured sausages (Astiasarán, Villanueva, & Bello, 1990; Bello, Larralde, & Sáenz de Buruaga, 1974a; DeMasi, Wardlaw, Dick, & Acton, 1990; Dierick et al., 1974; Franco et al., 2002; Garriga, Calsina, & Monfort, 1986; Johansson, Berdagué, Larsson, Tran, & Borch, 1994), it could be deduced that the proteolysis is particularly evident in the first stages of ripening, coinciding with the development of fermentation and the more marked decrease in the pH value.

The importance of microorganisms and tissue enzymes in the proteolysis is a source of controversy. Many authors maintain that the formation of NPN is due to the action of bacterial enzymes (Cantoni, D'Aubert, Bianchi, & Beretta, 1975; DeMasi et al., 1990; Dierick et al., 1974; Lücke, 1985; Reuter, Langner, & Sinell, 1968). However, the studies of other authors (see Ordóñez et al., 1999) also suggest an implication of the muscular proteases.

Our final values for this nitrogen fraction were within the range of those described in the literature for other varieties of *Chorizo* at the end of their ripening periods (León Crespo et al., 1985; Lois et al., 1987). However, our values were higher than in other types of raw-cured sausages, such as *Longaniza de Aragón* (Marquina et al., 1993), *Fuet* (Roncalés et al., 1991) and *Androlla* (Franco et al., 2002) and lower than those found in *Salchichón de Vich* (Ferrer & Arboix, 1986).

The content of α-aminoacidic nitrogen also underwent an increase during the ripening process of *Chorizo de cebolla*, such that the average initial value (98 and 35 mg/100 g of dry matter in the homemade and industrial batches, respectively) was multiplied by a factor of ≈3.5 in both systems of manufacture.

Studies focussed on the understanding of the evolution shown by the α-aminoacidic nitrogen during ripening of raw-cured sausages are not abundant (Bello et al., 1974a; Dierick et al., 1974; Domínguez Fernández & Zumalacárregui Rodríguez, 1992-94; Ferrer & Arboix, 1986; Franco et al., 2002; Mateo et al., 1996). Although an increase has been detected in all of them, the behaviour of this nitrogen fraction is different. While, in some sausages, it has been observed that the increase is produced at a similar rate during the whole of the process (Bello et al., 1974a; Dierick et al., 1974; Ferrer & Arboix, 1986; Mateo et al., 1996), in others a very marked increase has been found in the early stages (7–14 days); it then remains more or less stable until the end of the ripening period (Domínguez Fernández & Zumalacárregui Rodríguez, 1992-94; Franco et al., 2002).

Our results show that, during the ripening of *Chorizo de cebolla*, the increase of α-aminoacidic nitrogen is fundamentally produced in the first seven days, where the initial rates almost triple. Other authors (Dierick et al., 1974; Domínguez Fernández & Zumalacárregui Rodríguez, 1992-94; Körmendy & Gantner, 1962) have observed the same phenomenon, working with different raw-cured sausages. This maximum level of production of free amino acids coincides with the period of fermentation (more intense metabolism of the carbohydrates) and maximum microbial growth, which appears to suggest that the participation of the microorganisms is fundamental in the formation of this nitrogen fraction.

Significantly higher rates of α-aminoacidic nitrogen during the whole of the ripening period were determined in the homemade *chorizo*, which could be related to the fact that additives are added during the industrial process and these could inhibit microbial growth.

The average final values obtained (344 and 122 mg/100 g of dry matter in the homemade and industrial batches, respectively) are within the wide range of values described in *Chorizo de León* (Domínguez Fernández & Zumalacárregui Rodríguez, 1992-94) and in other similar sausages (Dierick et al., 1974; Ferrer & Arboix, 1986; Franco et al., 2002) and which vary between the 119 mg/100 g of DM observed by Franco et al. (2002) in *Androlla* and the 1259 mg/100 g of DM found by Ferrer and Arboix (1986) in *Salchichón de Vich*.

The total volatile basic nitrogen (TVBN) increases markedly up to the 14th day of ripening and less markedly during the rest of the process. As with the α-aminoacidic nitrogen, the average values during the whole of the ripening process were also higher in the homemade batches than in the industrial batches, reaching final values of 112 and 83 mg/100 g of DM, respectively.

There is very little information available about the evolution of TVBN during the process of ripening and different behaviours are observed, not only with regard to the magnitude of the increase of this fraction, but also regarding the pattern followed by this increase. Thus, Domínguez Fernández and Zumalacárregui Rodríguez (1992-94) obtained increases of 2.3 and 2.6 times in *Chorizo de León* industrially manufactured and homemade, respectively, while Franco et al. (2002) observed that, at the end of the ripening period of *Androlla*, the initial content of TVBN was increased by a factor of 6. On the other hand, whilst, in the industrially manufactured *Chorizo de León* Lois et al. (1987) and Domínguez Fernández and Zumalacárregui Rodríguez (1992-94) have observed that the increase of TVBN is constant over the whole of the ripening period, in the *Androlla*, Franco et al. (2002) observed that this increase was produced fundamentally in the first 21 days. Domínguez Fernández and Zumalacárregui Rodríguez (1992-94), in homemade *Chorizo de León*, and León Crespo et al. (1978), in *Salchichón*, observed a gradual decrease of this nitrogen fraction during the final periods of ripening. León Crespo et al. (1978) attributed this decrease to the volatility of the NH_3.

Our final average values of TVBN (112 mg/100 g of DM in the homemade batches and 83 mg/100 g of DM in the industrial batches) are of the same order as those determined in *Chorizo de León* (Lois et al., 1987). These values were higher than those previously observed by other authors (Dierick et al., 1974; Franco et al., 2002; Körmendy & Gantner, 1962; Stanculescu et al., 1970).

As mentioned previously, the average values of TVBN, both the final average and the averages during the ripening process, were slightly higher in the homemade batches of *Chorizo de cebolla*. These differences are probably due to the higher free amino acid content of the homemade batches (as previously mentioned) that would have served as the substrate of the deamination reactions.

During ripening of meat products, the lipid fraction suffers different degradation processes (fundamentally hydrolytic and autooxidative) in the course of which compounds are generated that are responsible for the aroma and taste of the final product (Gandemer, 1998).

Fig. 2 shows the changes in some parameters of the fat during the ripening of the homemade and industrially manufactured *Chorizo de cebolla* batches.

In this study, independently of the system of manufacture, a progressive liberation of fatty acids is produced in *Chorizo de cebolla* during the ripening process, as has been described for numerous types of sausages (Domínguez, 1988; Ferrer & Arboix, 1986; Franco et al., 2002; León Crespo et al., 1985; Lois et al., 1987; Nagy et al., 1989).

The acidity of the fat increases from initial values of 0.095 and 0.190 to final values of 2.36 and 1.98 mg KOH/g of fat in the homemade and industrial sausage, respectively, which is a considerable increase. Similar increases have been described in *Salchichón de Vich* (Ferrer & Arboix, 1986). However, other authors have found

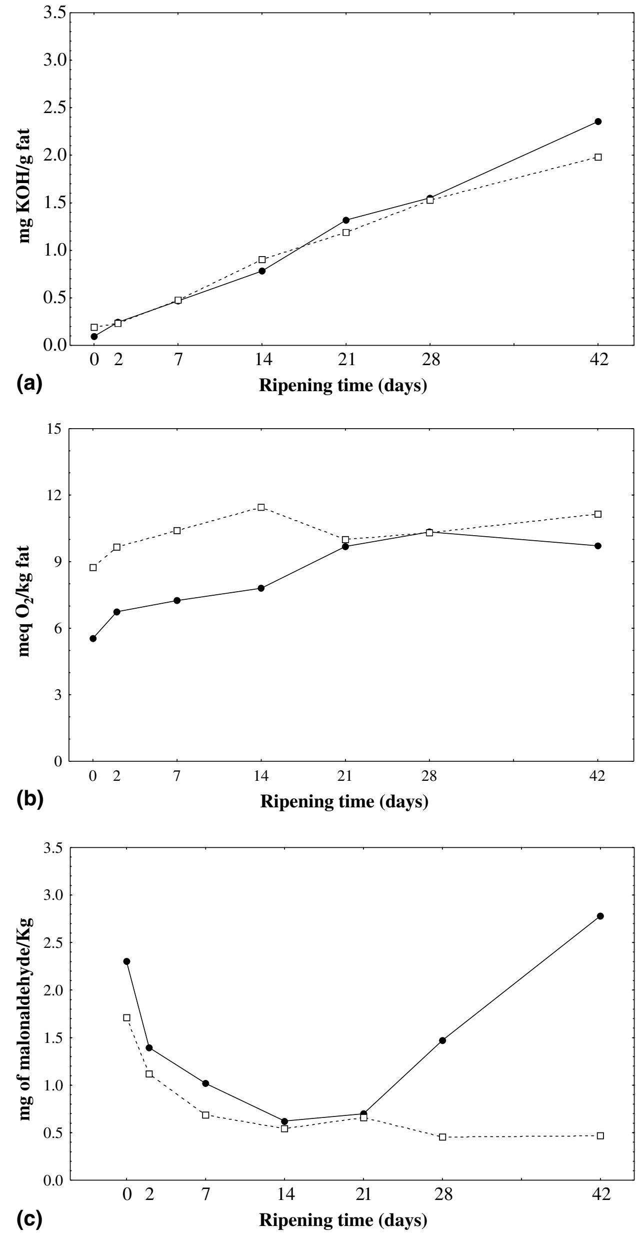

Fig. 2. Changes in the fat acidity value (a), peroxide value (b) and TBA value (c) of homemade (average of seven batches) –●– and industrial (average of four batches) –□– *Chorizo de cebolla.*

less marked increases. Thus, Domínguez (1988) and León Crespo et al. (1985) have described average increases, in the order of 6–7 times, in other types of *Chorizo*, while Franco et al. (2002) have obtained lower increases in Androlla (around 4 times) and Fernández-Fernández, Rozas-Barrero, Romero-Rodríguez, and Vázquez-Odériz (1997) obtained an increase of only 1.7 times in *Galician Chorizo.*

However, despite the sizeable increase of this parameter during ripening, our final values are, together with those described in *Fuet* (2.0 mg KOH/g of fat (Roncalés et al., 1991)), the lowest indicated in the literature for raw-cured sausages (Bello et al., 1974a, Bello, Sáenz de Buruaga, & Larralde, 1974b; Domínguez Fernández & Zumalacárregui Rodríguez, 1991; Fernández-Fernández et al., 1997; Ferrer & Arboix, 1986; Franco et al., 2002; León Crespo et al., 1985; Nagy et al., 1989). There were no significant differences in the acidity of the fat associated with the system of manufacture (homemade or industrial).

From the results obtained in this study and from those previously reported, it can be deduced that the intensity with which lipolysis is developed during ripening varies considerably between different varieties of sausage as a function of the manufacturing procedure employed (Domínguez, 1988; Domínguez Fernández & Zumalacárregui Rodríguez, 1991) and the raw material used (Lois et al., 1987). This variation is produced, as we have also confirmed, even between batches of the same variety (Domínguez Fernández & Zumalacárregui Rodríguez, 1991; Franco et al., 2002) and this is not surprising, because liberation of fatty acids is a phenomenon catalysed by tissue lipases and by lipases of microbial origin (Ordóñez et al., 1999) and because the activity of these enzymes depends on different factors, such as the saline content and temperature.

The peroxide value was similar at the end of the ripening process for both types of sausage manufacturing processes (9.71 meq of O_2/kg of fat in the homemade *chorizos* and 11.6 meq of O_2/kg of fat in the industrial *chorizos*) and no significant differences associated with the system of manufacture were observed. However, evolution was different in the two systems of manufacture studied. Thus, whilst in the industrial *chorizos*, this value remained practically constant during the whole of the ripening process, in the homemade *chorizos* a progressive increase was produced that, in the latter stages, reached values similar to those observed in the industrial batches. However, this difference in evolution was not statistically significant, due to the wide variability between batches that produced very high standard deviation values. This difference in behaviour appears to be related to the fact that, in the industrial manufacture of our sausage, in two of the batches studied, there were initially very high peroxide values in the mix, which indicates a high level of autooxidation of the fat used in the formulation of the mixture. The peroxide value did not increase during the ripening process, possibly due to the fact that antioxidants are added to the mix during formulation when manufactured industrially.

A detailed analysis of the literature focussed on the evaluation of the degree of autooxidative rancidity suffered by the fat during the ripening of raw-cured sausages, shows differences in the evolution of the peroxide value during ripening of the different types of sausages. Thus, in *Androlla* (Franco et al., 2002), it has been observed that the initial value suffers a rapid increase from the third day of manufacture, reaching values that are 50% higher than the initial values, and they remain practically constant until the 21st day and then decrease at the final stage of ripening, to levels close to those present in the mix. However, in *Salchichón de Vich* (Ferrer & Arboix, 1986) it was discovered that the peroxide value increased gradually during ripening. For their part, Nagy et al. (1989) found that the peroxide content of *Hungarian Salami* decreased rapidly in the first 10 days of manufacture, reaching values that were five times lower than the initial values, remaining constant thereafter until the end of the ripening process.

The average final peroxide values of the fat from *Chorizo de cebolla* were much higher than those described by Nagy et al. (1989) in *Hungarian Salami* at the end of 100 days of ripening (0.18–0.90 meq of O_2/kg of fat) and also higher than tose determined by Ferrer and Arboix (1986) in *Salchichón de Vich* (3.52 meq O_2/kg of fat after 12 months ripening) and by Fernández-Fernández et al. (1997) in *Galician Chorizo* (4.84 meq O_2/kg of fat after 30 days of ripening). However, our values were lower than those observed by Lizaso et al. (1999) in *Salchichón* (56.8 meq O_2/kg of fat after four weeks of drying) and by Franco et al. (2002) in *Androlla* (18.9 meq O_2/kg of fat after 42 days of ripening).

During the ripening of *Chorizo de cebolla*, the TBA value shows similar behaviour in both systems of manufacture until the 21st day, at which time the initial concentrations of malonaldehyde (2.30 and 1.72 mg/kg of *chorizo* for the homemade and industrial *chorizos*, respectively) were reduced until both of them almost reached the same value (0.70 and 0.66 mg/kg of *chorizo*, respectively). This value remained practically constant until the end of ripening in the industrial products and increased in the homemade *chorizos* to a final average value of 2.72 mg/kg of product. At 42 days of ripening (end of the ripening process), the TBA value was significantly higher in the homemade than in the industrial *chorizos*.

The evolution of the TBA value during the ripening process of the sausages is very variable, as can be seen in the studies in which the autooxidation reactions suffered by the lipids have been noted by determination of this parameter. Thus, whilst in *Androlla* (Franco et al., 2002) it has been observed that the malonaldehyde content increases gradually during ripening, in industrially manufactured *Chorizo de León* it remains practically constant throughout the process (Domínguez, 1988). For their part, Nagy et al. (1989) found that the concentrations of malonaldehyde that were initially present in *Hungarian Salami* decreased rapidly in the first 10 days and then increased, which coincides with our observations in the homemade batches of *chorizo*.

The most frequent concentrations of malonaldehyde described at the end of ripening in this type of sausage is about 1 mg/kg (Aguirrezábal, 1993; Domínguez, 1988; Holley, Jui, Wittmann, & Kwan, 1988; Nagy et al., 1989) and frequently much lower values (Franco et al., 2002; Nagy et al., 1989). The final average content of malonaldehyde in industrial *Chorizo de cebolla* is found to be within this range, but in the homemade *Chorizo de cebolla* it is much higher. In a batch of homemade *Chorizo de León* Domínguez (1988) and Domínguez Fernández and Zumalacárregui Rodríguez (1991) observed a TBA value of 2.21 mg de malonaldehyde/kg of *chorizo* after 35 days of ripening, very similar to the average value observed in the homemade batches at the end of the ripening process. However, the authors indicate that this value is insufficient for the sensorial detection of rancidity (Domínguez Fernández & Zumalacárregui Rodríguez, 1991).

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