Food Research International 100 (2017) 352–360

Contents lists available at ScienceDirect

Food Research International

journal homepage: www.elsevier.com/locate/foodres

Inhibitory effect of phosphates on magnesium lactate efflorescence formation in dry-fermented sausages

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ARTICLE INFO

Keywords:
Magnesium
Isothermal titration calorimetry
Complexation
Lactate
Creatine

ABSTRACT

This study aimed to prevent the phenomena of efflorescence formation on the surface of dry fermented sausages due to the complexation of efflorescence forming cations with phosphates. Efflorescence formation is a critical issue constituting a major quality defect, especially of dry fermented sausages. Different phosphates (di- and hexametaphosphate) were added (3.0 g/kg) to the sausage batter. As a hypothesis, these additives should complex with one of the main efflorescence-causing substances such as magnesium. The formation of efflorescences was determined for dry fermented sausages without phosphate addition, with diphosphate, or hexametaphosphate addition during 8 weeks of storage under modified atmosphere. The visual analyses of the sausage surface revealed high amounts of efflorescences for the control (42.2%) and for the sausages with added diphosphate (40.9%), whereas the sausages containing hexametaphosphate had significantly reduced amounts of efflorescence formation, showing only 11.9% efflorescences after 8 weeks of storage. This inhibition was a result of strong complexation of hexametaphosphate with magnesium ions, thus preventing the diffusion of magnesium towards the sausage surface. This can be explained by the magnesium content on the sausage surface that increased by 163.9, 127.8, and 52.8% for the sausages without phosphate, diphosphate, and hexametaphosphate addition, respectively. The mass transport of lactate and creatine was not affected by phosphate addition. Isothermal titration calorimetry confirmed that, theoretically, 4.5 g/kg of diphosphate or 2.8 g/kg hexametaphosphate are required to complex 0.2 g/kg magnesium ions naturally occurring in dry fermented sausages and, thus, the chosen overall phosphate concentration of 3.0 g/kg was enough when adding hexametaphosphate, but not for diphosphate, to inhibit the efflorescence formation.

1. Introduction

White crystals (efflorescences) on the surface of dried meat products such as dry cured hams (Arnau, Gou, & Guerrero, 1994; Arnau, Guerrero, & Gou, 1997; Arnau, Guerrero, Hortós, & García-Regueiro, 1996; Arnau, Maneja, Guerrero, & Monfort, 1993) and dry fermented sausages (Arnau, Gou, & Alvarez, 2002; Kröckel, 2004; Kröckel, Jira, Kühne, & Müller, 2003; Kühne, Stiebing, & Kolb, 1986; Walz, Gibis, Herrmann, Hinrichs, & Weiss, 2017) were first observed in the 1980s. The phenomenon of efflorescence formation can be divided into three groups: efflorescences consisting of disodium phosphate heptahydrate (Arnau et al., 1997), efflorescences consisting of creatine monohydrate (Kröckel et al., 2003), and efflorescences consisting of magnesium lactate (Kröckel, 2004; Walz et al., 2017). Efflorescences usually appear on meat products that were stored at low temperature and packed under modified atmosphere (Arnau et al., 1997). This is because of the lower solubility of the efflorescence causing substances triggering the efflorescence formation.

The main problem in dealing with the appearance of efflorescences is that consumers reject these products due to the wrong association of the white crystals with microbiological spoilage. However, efflorescence formation is a physical mass transport phenomena of minerals and acids from the core to the sausage surface, forming crystals that give the sausages a white appearance (Walz et al., 2017). Therefore, the formation of efflorescences on dry fermented sausages can lead to financial losses for the meat processing industry (Kröckel et al., 2003). To investigate the formation of efflorescences, previous studies identified the main efflorescence forming components, with magnesium being the most important substance responsible for the formation of the irreversible efflorescences *type II* (Walz et al., 2017). Magnesium

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http://dx.doi.org/10.1016/j.foodres.2017.07.015
Received 23 May 2017; Received in revised form 3 July 2017; Accepted 4 July 2017
Available online 05 July 2017
0963-9969/

originating from the meat itself constitutes up to 0.2 g/kg (8.23 mmol/kg) in dry fermented sausages (Ockerman & Basu, 2008). In the present study only pepper was added as a spice, and it contains insignificant amounts of magnesium. However, in other regions such as e.g. in the Mediterranean, dry fermented sausages are often produced with paprika or (smoked) red peppers that contain often high amounts of magnesium (Arnau et al., 2002). Furthermore, salt-reduced meat products are increasingly produced using non-sodium containing salts, such as e.g. $MgCl_2$ thereby elevating the level of incorporated magnesium (Zanardi, Ghidini, Conter, & Ianieri, 2010). The addition of meat extrinsic magnesium sources should be considered as a potential cause when observing magnesium-based efflorescence formation.

Phosphates are inorganic salts of phosphoric acid and able to form complexes with alkaline earth metals, i.e. magnesium ions (Hänssgen & Eicher, 1991; Van Wazer & Callis, 1958). They are commonly used as additives in the food industry, for instance, in various meat, poultry, seafood, and dairy products (Dziezak, 1990). Diphosphate and hexametaphosphate were chosen to be implemented into the sausage batter to complex magnesium. Diphosphate was chosen based on its high chelating activity for bivalent cations such as calcium and magnesium. The formation constants of magnesium diphosphate complexes have been determined at different magnesium and phosphate concentrations as well as varying pH values (pH 4.76–8.93) in a water system. The determined constants varied between 3.02 and 5.44 (Lambert & Watters, 1957). The formation of magnesium complexes with diphosphate is attributed to changes in the entropy (Irani, 1961). Hexametaphosphates are cyclic molecules consisting of six phosphorous and oxygen atoms (Van Wazer & Karl-Kroupa, 1956). Hexametaphosphate was chosen due to its formation of complexes with various multivalent cations and thereby reducing their solubilized concentration to a great extent (Hatch & Rice, 1939). It has been observed that long-chain polyphosphates are generally more efficient to chelate bivalent ions (calcium) than diphosphates (Rulliere, Perenes, Senocq, Dodi, & Marchesseau, 2012). The formed magnesium-phosphate complexes are hypothesized to remain in the sausage matrix and prevented from diffusing towards the sausage surface. Thus, magnesium cations cannot react with lactate that build the efflorescence crystals. Based on this, the present study aims at preventing efflorescence formation by complexation of magnesium with suitable phosphates added to the meat batter.

2. Materials and methods

2.1. Materials

The pork meat and pork fat were purchased from a local wholesaler (MEGA, Stuttgart, Germany) and standardized to S II and S VIII, according to the GEHA meat classification system (Hack, Gerhardt, & Staffe, 1976). Spices (white pepper), additives (ascorbic acid and dextrose), nitrite curing salt (0.5% nitrite), and starter cultures (LS 25) were generously provided by Gewürzmüller (Korntal-Münchingen, Germany). The added phosphates trisodium hydrogen diphosphate ($Na_3HP_2O_7$) and sodium hexametaphosphate ($[NaPO_3]_6$, BUDAL Na 637) were provided by Chemische Fabrik Budenheim (Budenheim, Germany). Collagen casings (NDC-D, Cal. 21 mm) were received from Naturin Viscofan (Weinheim, Germany). Vacuum bags (SL 135 × 180 PA/PE 90 MY) were obtained from MEGA (Stuttgart, Germany) and modified atmosphere gas (Protadur C20, Westfalen AG, Münster, Germany) composed of 80% N_2 and 20% CO_2 was used for the packaging. The glass carafes (Art. No. 902.797.19) used for visual sensory analysis were obtained from Ikea (Sindelfingen, Germany). Sea sand (SiO_2, #7897.2, purity > 99%), calcium chloride ($CaCl_2$, #A119.1, purity > 94%), zinc sulphate heptahydrate ($ZnSO_4{\cdot}7\ H_2O$, #7316.2, purity > 97%), and acetonitrile (C_2H_3N, #HN44.2, purity > 99.9%) were purchased from Carl Roth GmbH & Co. KG (Karlsruhe, Germany). Orthophosphoric acid ($H3PO_4$, #1005521000, purity > 85%), lactic acid lithium salt ($C_3H_5LiO_3$, #8220840100, purity > 98%), creatine monohydrate ($C_4H_9N_3O_2{\cdot}H_2O$, #8414700250, purity > 99%), and magnesium chloride hexahydrate ($MgCl_2{\cdot}6\ H_2O$, #105833, purity > 99%) were obtained from Merck (Darmstadt, Germany). Potassium hexacyanoferrate tri-hydrate ($C_6FeK_4N_6{\cdot}3\ H_2O$, #1049821000, purity > 99%) was purchased from Sigma-Aldrich (Munich, Germany). Ash less round filters (Cat No 1441185), pleated filters (MN 615 FF ¼, Ø 185 mm), and membrane filters (Chromafil Xtra PTFE-45/25, pore size: 0.45 μm) were obtained from Whatman (Maidstone Kent, England), and Machery-Nagel (Düren, Germany), respectively.

2.2. Sausage production and sample preparation

Three different batches of dry fermented sausages were produced from the same raw material. The meat batter was prepared in a bowl chopper (type K64 DC, Seydelmann, Aalen, Germany) by chopping 45% frozen fist-sized lean pork meat SII and 20% pork back fat SVIII. Subsequently, starter cultures (0.5 g/kg meat + fat), ascorbic acid (0.5 g/kg meat + fat), white pepper (3 g/kg meat + fat), and dextrose (5 g/kg meat + fat) were added. Afterwards, 35% ground (3 mm, type WD 114, Seydelmann, Aalen, Germany) lean pork meat SII was added. Finally, nitrite curing salt (28 g/kg) was added and the meat batter was mixed for 30 s to party solubilize the meat proteins. The other batches were produced using the same recipe but additionally 3 g/kg of different phosphates (DP: trisodium diphosphate and HMP: sodium hexametaphosphate) as well as spices and starter cultures were added. The sausage batter was filled into collagen casings using a vacuum filler (type VF 80/165-1, Handtmann, Biberach, Germany). Afterwards, the sausages were transferred into climatic chambers (type Air Master UK-1800 BE, Reich, Urbach, Germany and type Unigar 1800 BE, Ness, Remshalden, Germany) for the ripening and drying process, which was carried out as described in a previous study (Walz et al., 2017). Shortly, within the first 24 h high humidity (94%) and temperature (24 °C) were applied to ensure a high activity of the starter cultures. Afterwards, temperature and humidity were stepwise reduced to prevent the formation of a dry edge until a final temperature of 18 °C and 70% humidity were reached at the end of drying. The weight loss was determined by differential weighting (type U4100, Sartorius, Göppingen, Germany) of all sausages that were produced and the pH was measured (pH 573, WTW, Weilheim, Germany) in the center of two sausages per batch during processing. As soon as 42.5% weight loss ($a_w = 0.839 \pm 0.003$) was reached, which was defined to be the typical weight loss for these products by our industrial partners, two pairs of sausages were packed into a vacuum bag, which was then filled with modified atmosphere (20% CO_2 and 80% N_2) using a vacuum packaging device (C 400, Multivac, Wolfertschwenden, Germany). A total of 100 bags were obtained for each batch, which were selected randomly for chemical and visual analyses. The sausages were stored at 4 °C prior to analyses. The sample preparation was carried out as described already in previous studies (Walz et al., 2017). In short, 36 randomly selected sausages were sectioned into 4 different layers (0.6, 1.2, 1.2, and 3.0 mm thickness) using a food slicer (VS8A, Bizerba, Balingen, Germany). The individual layers were homogenized and shredded using a kitchen blender (Moulinette Moulinex D56, Braun, Frankfurt, Germany). Subsequently they were packed under vacuum and stored at − 20 °C until they were used for chemical analysis.

2.3. Visual analyses

2.3.1. Sensory analysis

A trained sensory panel consisting of 20 persons (55% female, 45% male, age of 25–55) performed the sensory analysis. The panelists were trained by preliminary tests using samples and images of sausages with different amounts of efflorescences. Panelists had to rate the amount of efflorescences on a scale of 0 to 10 with 0 indicating that no efflorescence was present and 10 representing samples having high