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Metals migration between product and metallic package in canned meat

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A B S T R A C T

The aim of this study is to investigate the migration of heavy metals in meat can under different parameters (varnish, storage time, storage temperature, storage humidity and varnish width and porosity). The physicochemical and organoleptic properties of the meat can have been analyzed. The metal content (Cd, Pb, Cu, Fe, Zn and Sn) were determined by flame and graphite furnace atomic absorption spectrometry after microwave digestion. The organoleptic and physicochemical properties of the samples have not modified significantly during the experiments. The metals migration is not influenced significantly by the varnish type. The highest level of metals in food products was observed at 4 and 50 °C. The porosity influenced significantly ($p < 0.05$) the migration of metals while the varnish width influence is not a significant one. The migration modeling using 3rd grade polynomial model achieved models with high coefficients of regression (greater than 0.9858).

1. Introduction

The stability of the system food product/package when food products are preserved in metallic packages is determined by more factors as the migration of compounds from package into the product preserved holds an important role. Tinplate corrosion depends on many factors including can material (tin coated steel, tin free steel), nature of the organic coating (epoxy, polyester, acrylic resins), enamel properties (adhesion, porosity and corrosion resistance), nature of the contacting medium (aqueous, fatty foodstuffs) and of course composition of the contained product (acid foods, sulfur and/or salt containing foods, etc.) (Barilli, Frangi, Gelati, & Montanari, 2003; Pournaras et al., 2008).

Sheet varnishing, either on one side or both, for cans manufacturing, is made in order to protect metallic surfaces from atmospheric corrosion and the reaction with the can content, thus preventing food products from metal contamination (Mariscal-Arcas et al., 2009; Poole et al., 2004).

Of all types of can inner coatings, epoxy phenol varnishes are the most used, both in cans of two and three pieces, and crimped ones. During the sterilization process the migration of bisphenols from package to food may be faster and more intense. A similar situation may be encountered, for example, in the case of heat instability of can varnishes. This aspect is very important having in view toxicity, BPA developing estrogenic activity whereas BADGE is being classified as a carcinogen and mutagenic compound. Polyester resins are used at inner coatings of cans. Polyester systems are based on both thermoplastic polyesters of high molecular weight and heat-setting polyesters of low molecular weight. The polyester structure can be modified by epoxy or phenolic resin reactions in view of increasing its performances in practice. Polyester varnishes are generally more expensive as compared with the epoxy ones, being used much more in cans, due to their properties, such as high flexibility in crimped cans. Polyester varnishes are mainly used for non-corrosive foods such as meat and liver pasty where the content in fat protects the package against the aggressive ingredients of food (Goodson, Summerfield, & Cooper, 2002; Rauter, Dickinger, Zihlarz, & Lintschinger, 1999; Simoneau, Theobald, Roncari, Hannaert, & Anklam, 2002).

The major application areas for epoxy resins are protective coatings and civil engineering. Additional uses include printed circuit hoards, composites, adhesives and tooling, while a relatively small amount of epoxy polymers are the most common varnishes used in food containing cans (Theobald et al., 2000). Epoxy-phenolic resins are often polymerization products of bisphenol

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A diglycidyl-ether (BADGE) or NOGE (Novolac glycidyl ethers). The lowest molecular weight component of NOGE is bisphenol F diglycidyl-ether (BFDGE) (Uematsu, Hirata, Suzuki, Iida, & Saito, 2001). These compounds are easily soluble in oil and food lipids and it is known that migration into oily food occurs (Goodson, Robin, Summerfield, & Cooper, 2004; Hammarling, Gustavsson, Svensson, & Oskarsson, 2000; Krishnan, Stathis, Permuth, Tokes, & Feldman, 1993; Munguia-Lopez & Soto-Valdez, 2001). Epoxy resins are used as plastic coatings in the food-packing industry. It is well documented that polymerization of epoxy resin reactions may not be fully complete and that a significant proportion of non-reacted epoxy compounds can be recovered from food packed in containers lined with these plastics (Brede et al., 2002), autoclavable flasks, and baby bottles, among other food materials and containers (Cabado et al., 2008; Moller, Helweg, Pratt, Worup, & Skak, 2004).

The aim of this study is to evaluate the organoleptic and physicochemical changes of meat cans, metal (Cd, Pb, Cu, Fe, Zn and Sn) migration in function of different parameters (storage temperature, time and humidity and varnish type, width and porosity) and to achieve migration models for each metal in function of the parameters presented above.

2. Materials and methods

2.1. Materials

In order to study the interaction product – metallic package and check at the same time the stability of protective varnish applied on the surface of cans, the preserved products were periodically analyzed during storage period from the organoleptic, physicochemical and microbiological point of view. The cans have been made special for this study at a local factory from Buftea, Romania, as: 90 cans Ø 99 × 48 mm VS (varnished inside with white varnish PL 1333) – of "pork meat in own juice"; and 90 cans Ø 99 × 48 mm DV (varnished inside and outside with gold HE1526-13) – of "pork meat in own juice".

The filling and sterilization of cans was made as follows: pork meat in own juice: 35–65–35 min at 121 °C, at 1.8×10^5 Pa pressure.

For the production of canned meat, beside beef or pork there are also used by-products, in is own juice. The rind is in a proportion of 5 pct that can be stored as frozen in cold storage's. The compositions preparation is mechanical processing, in case of canned meat in own juice, namely shredding meat, specific to the manufactured assortment, by Volf, using sieve with $\Phi = 20$ mm. The boiled and cooled rind is divided with the meat grinder, using sieve with $\Phi = 3$ mm, then it is passed, along with the minced meat, salt solution and pepper, respecting the quantities, according to the recipe, true the mixer, for standardization and homogenization of the composition, operation after witch it is performed the "welding", followed by filling and dosing of canes. Storage is performed in dry spaces, safe from frost, with temperatures ranging from 2 to 25 °C, and relative humidity of 75 pct.

2.2. Methods

2.2.1. Testing of organoleptic properties

The testing was made on a lot taken from the production of meat cans (pork meat in own juice). The cans were stored according to the conditions stipulated by the norms of the product. The sample taken from each packed product was analyzed, piece by piece, from the point of view of their exterior aspect and can's tightness. Organoleptic, physico-chemical and microbiological properties were tested accordingly with the standard methodology of the product. The aspect of varnish film specific to each varnishing system was characterized at the same time with the testing of the previously mentioned properties.

2.2.1.1. The sensorial analysis – the marking scale method. The sensorial analysis was led by tasting the meat samples respecting the same tasting conditions and marking the results and consequently using the marking scale method. The method consisted in evaluating each organoleptic property by comparing it with point scales from 0 to 5 and obtaining the average marks for the tasters group. For this purpose a testing committee was established being formed by 30 members (15 females and 15 male), all of them were between 18 and 35 years old; they were previously instructed regarding the organization of the testing meeting, its purpose and marking system used in the tasting papers for to remove the eventual errors that could appear in appreciating the samples subdued to analysis. The organoleptic properties of the meat were appreciated in the following order: aspect, color, smell and taste respectively.

The results of the appreciations led by the tasting committee members were written in the tasting papers for each sample of meat presented and then the average percentage was calculated.

$$Pmp = Pm \times fp \quad (1)$$

where Pm – average marks; fp – ratio factor.

2.2.2. Physicochemical analysis

The fat content has been analyzed using AOAC 991.36, total protein substances AOAC 2011.04, NaCl AOAC 24.010, easy hydrolyzable nitrogen using a titrimetric method and pH using a potentiometer method.

2.2.3. AAS determination of heavy metals migration

2.2.3.1. Microwave digestion. One gram of sample was digested with 6 ml of concentrated HNO_3 (65 pct) (Suprapure, Merck) and 2 ml of concentrated H_2O_2 (30 pct) (Suprapure, Merck) in microwave digestion system and diluted to 10 ml with double deionized water (Milli-Q Millipore 18.2 MΩ/cm resistivity). A blank digest was carried out in the same way (digestion conditions for microwave system were applied as 2 min for 250 W, 2 min for 0 W, 6 min for 250 W, 5 min for 400 W, 8 min for 550 W, vent: 8 min, respectively).

2.2.3.2. Trace metals determination. A Perkin–Elmer Analyst 400 atomic absorption spectrometer, with found correction absorbance (D_2 lamp), for all metals analysis was used, except tin, which was analyzed using an ICP-AES spectrophotometer. The operating parameters for working elements were set as recommended by the manufacturer. Copper, Cadmium, Iron, Lead, tin and Zinc in canned pea food during 36 months storage were determined by HGA graphite furnace using argon as inert gas. The elements were determined by using air–acetylene flame. Milestone Ethos D microwave closed system (maximum pressure 1450 psi, maximum temperature 300 °C) was used.

2.3. Statistical analysis

In order to establish statistical differences between the means of the heavy metals concentration, a multi-factor analysis of variance, with least significant difference (LSD) at significance level 0.05 calculated by Fisher's test was applied using the Statgraphics trial version. The variables were weighted with the inverse of the standard deviation of all objects in order to compensate for the different scales of the variables.