DETECTION OF IRRADIATED SPICES ADDED TO MEAT PRODUCTS

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Detection of admixtures in irradiated spices and herbs to reprocessed meat products is today a crucial analytical problem in view of European Union (EU) regulations defined in Directive 1999/2/EC [1] and in the decree issued by the Polish Ministry of Health on 15th January 2003 [2], respectively. Both documents refer to food and food ingredients treated with ionising radiation which must be labelled, while only herbs, spices and seasonings are allowed to be present in EU food market. Our proposal is to apply a method based on the thermoluminescence (TL) measurements of silicate minerals separated from foodstuff. The method is standardised to food products which contain silicate minerals but refers rather to food articles irradiated in the bulk (PN-EN 1788) [3]. Model samples of meat products with a known content of irradiated spices have been prepared in the Laboratory for Detection of Irradiated Foods (Institute of Nuclear Chemistry and Technology – INCT). Hundred grams of ground mixed (pork and beef) meat was taken to form forcemeat balls with an admixture of spices. The irradiated spices were: powdered sharp paprika exposed to 7 kGy of gamma rays in a ^{60}Co source "Issledovatel" of the Department of Radiation Chemistry and Technology (INCT) and powdered black pepper exposed to 6 kGy of 7 MeV electron beam generated in the linear electron accelerator "Elektronika 10-10" installed in the Experimental Plant for Food Irradiation (INCT).

The concentration of irradiated components in the samples of meat was 0.1, 0.3, 0.5 and 1.0%, respectively. In parallel, the samples which contained 0.1% of non-irradiated spices were also prepared.

In order to isolate silicate minerals from the samples, the hydrolysis with 6 mol/l of aqueous HCl solution was applied. The sample (forcemeat ball) was placed in a round button beaker, treated with HCl solution and heated at 50°C ±5°C in a water bath during 3 hours. Then the pulp was diluted with re-distilled water and filtered through nylon sieves 125 mesh. From the filtrate, the mineral fraction was separated by sedimentation technique. In order to separate the silicate minerals, the procedure given in the PN-EN 1788 standard and in our earlier publications was applied [4,5].

The TL of silicate minerals was measured with the use of a TL reader (model TL/OSL; Risø National Laboratory, Denmark). The measuring conditions were similar to those routinely used in the Laboratory [4,5]. After Glow 1 curve has been recorded, the minerals were irradiated with a normalised dose of 1 kGy in the gamma source. Subsequently, Glow 2 curve was registered.

For the evaluation of samples whether irradiated or not, a criterion given in PN-EN 1788 standard was adapted. The shapes of both Glow 1 and Glow 2 TL curves were analysed, while the integrated glow ratio was calculated within the temperature range 214-284°C. The TL maximum be-

Table 1. TL intensities (Glow 1 and Glow 2) integrated over the temperature range 214-284°C and TL glow ratio of silicate minerals isolated from control samples of minced meat enriched with 0.1% of non-irradiated pepper, and at different concentrations of pepper irradiated with 6 kGy by electron beam.

Percentage of pepper	TL intensity Glow 1 (214-284°C)	TL intensity Glow 2 (214-284°C)	TL glow ratio Glow 1/Glow 2 (214-284°C)
0.1 non-irradiated	12164	2436800	0.005
	9726	1200208	0.008
	8456	944000	0.009
0.1 irradiated	2036547	817409	2.49
	9130432	4929884	1.84
	7323815	3421138	2.14
0.3 irradiated	25390016	14747925	1.72
	24579191	8747223	2.81
	20873128	9324815	2.23
0.5 irradiated	20849992	6841794	3.05
	11778646	4110629	2.86
	15469327	5708239	2.71
1.0 irradiated	2949100	951925	3.10
	64210162	17189166	3.73
	117434465	4270358	2.75

Table 2. TL intensities (Glow 1 and Glow 2) integrated over the temperature range 214-284°C and TL glow ratio of silicate minerals isolated from control samples of minced meat enriched with 0.1% of non-irradiated paprika and at different concentrations of paprika irradiated with 7 kGy of gamma rays.

Percentage of paprika	TL intensity Glow 1 (214-284°C)	TL intensity Glow 2 (214-284°C)	TL glow ratio Glow1/Glow2 (214-284°C)
0.1 non-irradiated	10469	4068323	0.002
	7232	2169605	0.003
	14853	2970615	0.005
0.1 irradiated	3690910	2553301	1.44
	8183133	5355352	1.53
	5162432	4266473	1.21
0.3 irradiated	13224788	13036892	1.01
	15978387	17316917	0.92
	14539337	13701104	1.06
0.5 irradiated	27581269	24000815	1.15
	3897257	2938503	1.33
	12212577	11806334	1.03
1.0 irradiated	2550077	2773775	0.92
	12261268	14803812	0.83
	8347283	7258507	1.15

tween 150 and 250°C is a proof of irradiation. The TL maximum recorded over 300°C originates from natural luminescence. Glow 1/Glow 2 ratio higher than 0.1 proves a typical radiation treatment of a sample. In the case when glow ratio is lower than

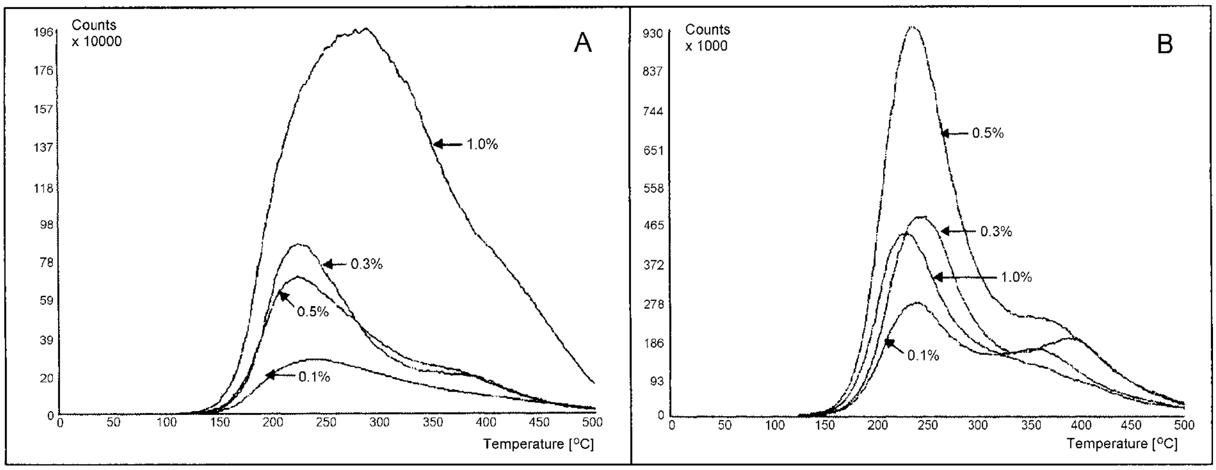

Fig.1. TL Glow 1 curves of silicate minerals isolated from the samples of minced meat containing: (A) different concentrations of pepper irradiated with a dose of 6 kGy of electron beam radiation and (B) different concentrations of paprika irradiated with a dose of 7 kGy of gamma radiation.

0.1 while the shape of Glow 1 curve is typical of an irradiated sample (maximum between 150 and 250°C) the decisive is the shape proving that the sample was irradiated.

In Tables 1, 2 and in Fig.1, the results of the TL analysis of minerals separated from model samples were comprehended. It has been proven that the concentration of irradiated paprika and pepper powders in meat at a level of 0.1% and higher are detectable by the TL method. The shapes of the Glow 1 curves have the maxima between 150 and 250°C, while the respective glow ratios were always higher than 0.1 despite the dose applied and the irradiation source used. The results document and show conclusively that the TL method could be successfully used for the detection of irradiated admixtures (spices and herbs) to meat products.

References

[1]. Directive 1999/2/EC, 22 February 1999 on the approximation of the Member States concerning foods and food ingredients treated with ionising radiation. Off. J. European Communities L 66/16-23 (13.3.1999).

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ków spożywczych, dozwolonych substancji dodatkowych lub innych składników żywności, które mogą być poddane działaniu promieniowania jonizującego, ich wykazów, maksymalnych dawek napromieniowania oraz wymagań w zakresie znakowania i wprowadzania do obrotu. Dz. U. z 2003 r. Nr 37, poz. 327.
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PROPERTIES OF THE FILMS BASED ON MILK PROTEINS RELATED TO THE INTERACTION IN THE NON-IRRADIATED AND GAMMA-IRRADIATED PROTEIN-POLYSACCHARIDE SYSTEM

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Our work concerns the current problem of the edible packaging materials and methods for improvement of their functional properties using modified composition and gamma irradiation [1-4]. Our previous results dealing with the films prepared using non-irradiated and irradiated solutions of calcium caseinate-whey protein isolate (WPI)-glycerol (1:1:1) have shown that improvement of the films properties after irradiation corresponds to the changes in protein conformation. Reorganisation of aperiodic helical phase and β-sheets, in particular the increase in β-strands content [3] was discovered after irradiation. It was also found that addition of polysaccharides (at the level of 10% of total protein mass) led to an essential modification of films properties [4].

The present studies were directed to the interaction between calcium caseinate and WPI taking place in a mixed calcium caseinate-WPI-glycerol system. For this purpose, the properties of gels formed in the presence of calcium salt using a mixed composition were examined and related to the properties of gels prepared using separately calcium caseinate and WPI. Modification resulting in this composition after irradiation were related to the structural changes occurring in calcium caseinate-glycerol and in WPI-glycerol compositions. Moreover, the studies were carried out concerning the influence of polysachaccharide addition on the properties of gels formed using non-irradiated and irradiated proteins. The following polysaccharides were selected for this purpose: potato starch, soluble potato starch and sodium alginate. Structural properties of proteins and interactions with polysaccharides in gels were related to the functional properties and microstructure of the films resulting as the final product.

Calcium caseinate (New Zealand Milk Product Inc.) and WPI (BiPro Davisco) and chemical grade glycerol were used. Potato starch, soluble potato starch and sodium alginate were all Sigma products. Irradiation of solutions was carried out with gamma rays from Co-60 applying a dose of 32 kGy at a dose rate of 7 Gys^{-1}. The control non-irradiated solutions, were also prepared. Gel formation in calcium salt solutions and gel fracture strength measurements were realised according to the procedure described in [2,4]. The films were prepared and examined according to the procedures described in [1] and [4]. In particular, water vapour permeability (WVP) and puncture strength were determined.

FTIR (Fourier transform infrared spectroscopy) measurements were done using a Perkin-Elmer spectrophotometer in conditions described in [3]. TEM (transmission electron microscopy) studies were carried out using a Hitachi 7100 transmission electron microscope. A Stevens LFRA Texture Analyser Model TA/100 was applied for mechanical measurements of gels and films. The SAS statistical package was applied to analyse statistically the results dealing with gel fracture strength and functional properties of the films [1,4]. Differences between means were considered significant when $p \leq 0.05$.

The irradiation increased capability to connect calcium ions by mixed calcium caseinate-WPI system results due to the increase in β-structure content and to its further ordering [3], accompanied by a decrease in the content of aperiodic phase and turns rather than α-helices. It is connected to the fact that calcium binding leading to gel formation is more possible in the cases when the more strongly crosslinked β-sheets and β-strand are present.

Table 1. Strength of gels formed after addition of calcium salt to the non-irradiated and irradiated proteins compositions. Means followed by different letters are significantly different.

Dose [kGy]	CC[1)]	WPI	CC[1)]-WPI
0	16.7 ± 2.0[a]	189.7 ± 10.4[d]	48.0 ± 4.7[b]
32	120.9 ± 7.0[c]	293.3 ± 2.0[e]	413.6 ± 30.5[f]

[1)] calcium caseinate.

Gels formed after addition of calcium salt to the non-irradiated calcium caseinate are soft (Table 1) in regard to the small content of β-structure in these proteins resulting after heating. On the contrary, large strength of gels formed using the non-irra-