

- stances by the EPR spectroscopy method (Documented testing procedure PB SLINZ 01 edition 1);
- food containing cellulose (nuts, spices, fruits): Qualitative analysis for the presence of the specific radiation induced paramagnetic substances by the EPR spectroscopy method (Documented testing procedure PB SLINZ 02 edition 1);
 - food containing silicate minerals (spices, herbs, fruits, vegetables): Qualitative analysis of silicate minerals for the presence of radiation induced centres detected by the thermoluminescence measurement method (Documented testing procedure PB SLINZ 03 edition 1).

The accredited methods as well as other methods for the detection of irradiated food presently adapted in our Laboratory have been described in earlier publications [1]. Here, we would like to point out to the highlights of the methods which have been accredited. Food, containing paramagnetic species, characterised by the presence of unpaired electrons is detected by electron paramagnetic resonance spectrometry (EPR/ESR). Many years of investigations have shown that unpaired electrons are present in many stable components of irradiated foodstuffs such as bones, stones, dried fruits, spices etc. The high sensitivity of the method allowing the detection of 10^{-12} mol/sample and its reproducibility enables to detect efficaciously a small concentration of paramagnetic centres in irradiated foodstuffs, being in the order of 10^{-8} mol per sample isolated for measurement. Detection of irradiation by EPR in all kinds of meat containing bones, eggshells, fishbones and scales is based on finding in the analysed sample a characteristic singlet ($g_a=2.003$, $g_z=1.997$ and $\Delta h_{pp}=0.85$ mT. In food containing cellulose, in turn, as, for example, nuts (husks), strawberries and some spices, detection of irradiation is based on finding in the EPR signal a symmetrical triplet which has its centre at about $g_b=2.004-2.006$ and the distance between the outer satellite peaks ($g_a=2.020$, $g_c=1.983$) of 6.0 mT. The presence of these outer peaks in an EPR signal is taken as evidence that food has been irradiated. Such peaks have never been found in non-irradiated samples.

In foodstuffs containing silicate minerals (as inherent components or admixtures) irradiation can

be detected by measuring the intensity of luminescence of isolated minerals subjected to heating (thermoluminescence-TL). Irradiation produces free electrons which are trapped in the crystalline lattice of minerals. During heating electrons absorb thermal energy and pass from the excited to basic state emitting photons. The intensity of luminescence at a chosen temperature interval is compared with the luminescence of the same sample subjected to reirradiation with a standard dose of gamma radiation (usually 1 kGy). The value obtained from relation of these two TL measurements is taken as indication of irradiation, when it is higher than 0.5. When this value is lower than 0.1 the foodstuff has not been irradiated. When the intermediate values are obtained an additional evaluation, taking into consideration the shape of luminescence curve is to be made. Glow curves for unirradiated samples have peaks at higher temperature interval while that for irradiated ones have their peaks around 150-200°C. Before accreditation a comprehensive investigation of thermoluminescence of irradiated various herbs and spices has been made in this Laboratory [2].

In the course of certification procedure the testing analyses of unirradiated and irradiated foodstuffs have been performed according to the procedures indicated above. The results obtained fully confirmed the reliability of these methods and their applicability for detecting whether a given food has been irradiated or not.

Recently in the Laboratory a new EPR spectrometer MINI-10 has been installed addressed exclusively to the accredited methods of the detection of irradiated foods based on the EPR spectroscopy. The purchase of the instrument was financed by the Foundation for Polish Science under the Agreement "SUBIN" No 13/99.

References

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DETECTION OF IRRADIATED FOODS WITH THE USE OF GAS CHROMATOGRAPHY - EXPERIMENTS WITH POULTRY CARCASSES

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The treatment of foodstuffs, which contain fats, with ionising radiation induces a series of chemical changes. These changes cannot be classified as radiation-specific since they also appear in oxidation processes. There is, however, a preferential cleavage of certain chemical bonds in triglycerides when treated with ionising radiation. Among others two types of volatile hydrocarbons produced in this matter can be

detected in fairly large quantities: hydrocarbons which have one C atom less than the original fatty acid (C_{n-1}) and those which have two C atoms less and an additional double bond in 1-position ($C_{n-2:1}$). The main fatty acids of chicken carcasses, pork and beef are palmitic acid, stearic acid, oleic acid and linoleic acid. After the treatment, the following radiation induced hydrocarbons appear in abundance (a)



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C_{n-1}: 15:0, 17:0, 8-17:1, 6,9-17:2 and (b) C_{n-2}: 1-14:1, 1-16:1, 1,7-16:2, 1,7,10-16:3. The presence in abundance of these hydrocarbons in the examined sample is a proof of its irradiation. The best method of the detection of hydrocarbons is gas chromatography. However, to be detected the volatile hydrocarbons have to be separated beforehand from the sample. Firstly, it is necessary to separate fat from the sample and then to extract hydrocarbons in pentane or hexane with a Florosil column.

In the present study, the experiments were done with chicken carcasses purchased in the market. Each carcass was cut into four pieces. Three pieces were irradiated with doses of 0.5, 3 and 7 kGy, respectively, while the fourth one remained nonirradiated. All the samples were examined in parallel. Fats were separated at 50°C from the homogenised samples, centrifuged for 10 minutes with 900 g (1400 rot/min). A hydrocarbon fraction was separated from the fat with hexane and then with the Florosil column. 100 ml of each eluant was concentrated to 0.25 ml and examined by gas chromatography. As interior standard hexane eicosan so-

lution, while as exterior one the solution of 11 adequately selected hydrocarbons in hexane were applied. The gas chromatography examination was done with a capillary column PE-5 installed in a Perkin Elmer Model 8700 apparatus equipped with a flame-ionisation detector.

The results obtained show conclusively that in the chicken carcasses irradiated with the doses of 3 and 7 kGy the irradiation treatment has been proved with a high level of certainty while in the samples irradiated with 0.5 kGy the detection of irradiation was not satisfactory. All the separation and GC examination were proceeded in agreement with the procedures recommended in BC EN 1784 standard.

The aim of this study was to adapt the chemical method of detection of irradiation in foods which contain fats, based on gas chromatography as a routine analytical method for the use in the Laboratory for Detection of Irradiated Foods. The adaptation will be proceeded by the accreditation of this method within the frames of existing Quality Assurance System.

DSC STUDIES OF GELATINIZATION AND AMYLOSE-LIPID COMPLEX DECOMPOSITION OCCURRING IN INITIAL AND GAMMA IRRADIATED WHEAT AND CORN STARCHES

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The course of gelatinization and amylose-lipid complex transition, occurring during heating of starch and flour suspensions depends on the structure of starch granules. Therefore, decrease in order of starch granules [1, 2] and the possible changes in lipids surrounding, brought about by degradation resulting from gamma irradiation was expected to influence these processes. Our preliminary DSC studies of the processes occurring during the first heating of potato starch and wheat flour suspensions [3] showed the essential differences between gelatinization occurring in the irradiated and nonirradiated potato starch samples and of the gelatinization and amylose-lipid complex transition taking place in the irradiated and nonirradiated wheat flour. Significant differences between the maximum viscosities were also detected during heating of water suspensions of nonirradiated and irradiated wheat and rye flour. The influence on the results of the conditions applied in DSC experiments (concentration of suspensions, heating rate) appeared to be essential.

At present, DSC studies were continued for pure samples of wheat and corn starches. Wheat and corn starches (both Sigma products) were irradiated with Co⁶⁰ radiation applying a dose of 30 kGy with a dose rate of 3.62 kGy/h in a gamma cell Isledovatel in the Department of Radiation Chemistry, INCT. With the purpose of examination of the reversible amylose-lipid complex transition, characterised by a weak

thermal effect, DSC studies were carried out during heating-cooling-heating cycles (up to 3 heating processes). DSC measurements were carried out in the temperature range 10-150°C at a heating and cooling rates 10 and 2.5 °C/min for the suspensions at concentration of 20-25% (10 °/min) and 45-50% (10 and 2.5 °C/min) closed hermetically in Al pans. A Seiko DSC 6200 calorimeter with a cooling system installed in the University of Lund was used.

In the case of 20-25% concentrated starch suspensions a single effect of gelatinization is observed, while in the case of the suspensions at concentration of 45-50% two gelatinization processes occur (Fig.1, curves 1, 3). The phenomenon is connected with the existence of two types of ordered regions in starch granules. Smaller values of enthalpy were determined for gelatinization taking place in the irradiated samples in comparison with the process occurring in the nonirradiated sample under the same condition, like in the case of potato starch. Differences in the irradiation influence on the gelatinization occurring in corn, wheat and potato starch were observed, caused by the differences in granules ordering.

Only gelatinization was observed during the first heating of corn starch. It was stated that gelatinization occurs always at lower temperature in the case of the irradiated sample than in the nonirradiated one under the same experimental conditions, contrary to the results obtained for potato starch. For



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