Under this new situation the Laboratory is faced today (a) how to analyse the complex samples to obtain reliable results and (b) how to treat those samples which cannot deliver reliable results and hence, will not undergo classification whether irradiated or non-irradiated according to standard PN-EN 1788 [5]. First problem finds very often its solution in the modification, if necessary, of the preparation technique leading to more effective isolation of mineral fraction and/or in an increase of the mass of a single sample to be examined.

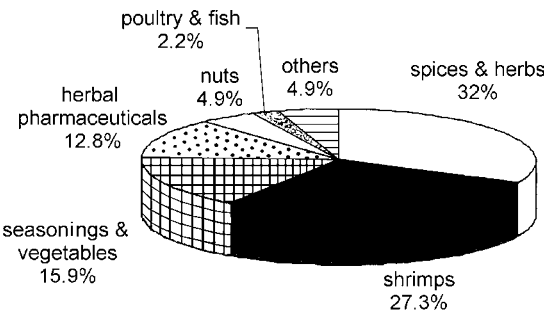

Fig.4. Assortment of foodstuffs examined in 2005.

Sometimes, however, the separation of silicate minerals remains still unsuccessful. Under such a condition, the examination of a sample is not satisfactory and thus the test report cannot include the statement whether the sample was or was not irradiated. Usually, we inform our client in advance that such situation may appear and the receiving of reliable result of the analysis may be rather problematic. This year, only 5 samples remained unclassified.

Among the 509 food samples analysed in this year, 89.6% were found unirradiated, 9.4% – irradiated, while 1% samples remained not classified (Fig.3).

The assortment of foodstuffs that were examined in 2005 (Fig.4) compiles:
- spices, herbs and their blends that may contain a small admixture of irradiated spices as a flavour ingredient (32%);
- seasonings, fresh and dried vegetables (15.9%);
- shrimps (27.3%);
- herbal pharmaceuticals, herbal extracts (12.8%);
- foods containing bone – poultry, meat and fish (2.2%);
- nuts in shell (4.9%);
- others – instant soups, red fermented rice, all purpose savoury seasoning (4.9%).

References

[1]. PN-EN 13708:2001: Foodstuffs – Detection of irradiated food containing crystalline sugar by ESR spectroscopy.
[2]. PN-EN 13751:2002: Foodstuffs – Detection of irradiated food using photostimulated luminescence.
[3]. PN-EN 1786:2000: Foodstuffs – Detection of irradiated food containing bone. Method by ESR spectroscopy.
[4]. PN-EN 1787:2001: Foodstuffs – Detection of irradiated foods containing cellulose. Method by ESR spectroscopy.
[5]. PN-EN 1788:2002 Foodstuffs – Thermoluminescence detection of irradiated food from which silicate minerals can be isolated.

PPSL – THE NEWLY INSTALLED ANALYTICAL SYSTEM FOR THE DETECTION OF IRRADIATED FOOD

Grzegorz P. Guzik, Wacław Stachowicz

The pulsed photostimulated luminescence (PPSL) system has been installed in the Laboratory for Detection of Irradiated Food at the beginning of 2005. The system, composed of two modules, was manufactured by the Scottish Universities Research and Reactor Centre – SURRC (United Kingdom) in 2004.

The PPSL system has been developed to meet the requirement of European food market that needed a relatively simple and compact device for fast control of foodstuffs whether irradiated. Indeed, two Directives of the European Parliament, 1999/2/EC and 1999/3/EC established the requirement of labelling and control of irradiated foods in all EU countries [1-3].

The method of the detection of irradiated food using photostimulated luminescence has the status of European Standard EN 13751:2003 and is recommended for the use as a control method for the detection of irradiation in foods since 2003. The corresponding Polish replica of European standard is numbered PN-EN 13751:2003 (U).

The PPSL method is today successfully used for examination of the whole spices and herbs and some other food products to detect the earlier radiation treatment in them [3,4].

Currently, the research program with the use of PPSL system in the Institute of Nuclear Chemistry and Technology (INCT) is focused on the examination of archival samples of herbs and spices stored in the Laboratory. Basil, chilli, curry, tarragon, nutmeg, mustard, clove, juniper, dill, turmeric, lovage, oregano, black pepper and white pepper, sweet pepper and cayenne pepper, parsley and rosemary have been tested so far.

Principle of the PPSL method

Mineral debris of silicates and bioinorganic composites (calcite and hydroxyapatite) are the natural contaminants of most foods, *e.g.* of spices, herbs and seasonings that belong to most frequently irradiated food products. They are mainly composed of quartz and feldspar, as proved in earlier works [1-3]. This debris stores steadily the energy of ionising radiation in charge carriers trapped at structural, interstitial or impurity sites [4]. Charge carriers which are very stable at ambient temperatures are released from mineral debris with increasing temperature – thermoluminescence (TL)

Fig.1. Irradiated Food Screening System SURRC PPSL installed in this Laboratory. Placing of a Petri dish with a sample inside into a sample chamber by means of tweezers.

method and/or under illumination – optically stimulated luminescence (OSL) measurements [1,2,5,6] and PPSL method [4,7,8].

Methodology of the PPSL examination of food is simple. The analysed sample is dispensed into a Petri dish in a thin layer and then placed into a sample chamber (Fig.1). After switching on the system, the sample is exposed to pulsed laser infra-red light emitted by an array of diodes (IR LEDs). The PPSL signal produced in the system by luminescence released from photostimulated mineral debris of the sample is stored by a photomultiplier (PMT; bialcali cathode photomultiplier tube) and intensified. Numerical signal is transmitted to PC computer and printed by the use of PPSL DOS program delivered from the producer (Fig.1). Optical filtering of light is adapted to define both stimulation and detection wavebands [4]. Schematic diagram of the PPSL system is shown in Fig.2.

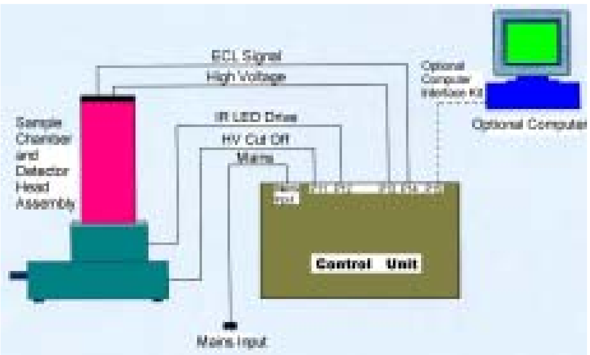

Fig.2. Block schematic and interconnection diagram [4].

Depending on the requirement two pathways of the PPSL examination are in use, screening or calibrated PPSL measurement.

Screening PPSL measurement

In screening measurement, signal intensity of luminescence produced by a sample is compared with two threshold values.

For herbs and spices as examined in the interlaboratory tests [9 – Part 10. Validation], the threshold settings of T_1=700 counts/60 s and T_2=5000 counts/60 s have been shown to be satisfactory. These thresholds refer to the use of 5 cm Petri dishes. This kind of dishes is also used now in the Laboratory.

For shellfish tested in an interlaboratory trial [9 – Part 10. Validation], slightly different threshold settings T_1=1000 counts/60 s and T_2=4000 counts/60 s have been shown to be better acceptable [4,10-12].

Typically, irradiated samples give rise to a strong signal much above the upper threshold level. The unirradiated ones, in turn, generate signals with the intensities below the lower threshold level. Samples that produce luminescence signals with the intensities between two thresholds cannot be classified by the PPSL method and should be investigated by means of the TL method according to the European Standard EN 1788, or, if suitable, by another validated method for the detection of irradiated food [12,13].

Fig.3. Irradiated Food Screening System SURRC PPSL installed in this Laboratory. From the right to the left: control unit and detector head assembly with sample chamber. Note three colour diodes (red, amber, green) on front panel of control unit.

Three diodes on the front panel of the apparatus indicate the actual status of a sample that undergoes examination: green light indicates negative result of examination, red light – positive result, while amber indicates intermediate result (Fig.3).

Calibrated PPSL measurement

Calibrated PPSL measurements deliver more adequate results and are carried out before and after exposing the sample to a defined dose of ionising radiation.

The recommended calibrating dose is 1-4 kGy or a dose comparable to that used for radiation treatment of food species examined [10]. Calibrating irradiation of samples is accomplished in the INCT with gamma rays from two ^{60}Co sources: “Issledovatel” (dose rate *ca*. 1.4 kGy/h) or “Mineyola” (dose rate *ca*. 0.6 kGy/h).

Irradiated samples indicate only a small increase of the PPSL signal, whereas with unirradiated ones the increase of the signal is significant.

Application and limitations of measures

The method of detection of irradiated food by means of PPSL has been positively tested in interlaboratory tests for samples of shellfish (*e.g.* prawns), herbs, spices and seasoning [9-11].

PPSL sensitivity depends on the quantity and type of minerals present in the individual sample. Signals of the intensity below the lower threshold (T_1) are generally associated with unirradiated material, but sometimes can be also derived from low sensitivity irradiated materials. In general, calibrated PPSL measurements are recommended for shellfish with low mineral contents and „clean" spices (*e.g.* nutmeg, white and black pepper) to avoid false negative results [9,14]. According to our experience, for the examination of any sample delivered from our clients the calibrated PPSL measurement should be always adapted.

Multicomponent food products like curry powder, for example, and blended seasonings may contain the debris of minerals of low PPSL sensitivities, in which case calibrated PPSL may also provide unclear results. In such a case it is necessary to turn to TL measurements.

Food products classified in the course of our investigation as such that may provide unclear results of PPSL measurements are: garlic powder, carrot pepper (leaves), sweet pepper (powder), black pepper (grains), black pepper (ground), clove (whole), dried dill (powder).

The presence of salt in a product given for examination intensifies so much the PPSL signal intensity that its contribution dominates to an extent which masks effectively signals from any irradiated ingredient. The dominance of the luminescence from crystalline salts in a product makes the signals from irradiated components undetectable. An admixture to a product of the following salts makes the examination of by PPSL method not rational: sodium chloride (domestic salt), natrium sorbitan, sodium benzoate, monosodium glutamate, Arabic gum.

It has to be strongly stressed that the examination of samples containing the above ingredients may also cause the damage of photomultiplier and is prohibited.

Sometimes hydration of a product leading to full dilution of salt and its elimination followed by drying and PPSL measurement can both identify and rectify this situation.

Conclusions

The PPSL method can be successfully used for the detection of irradiation in pure spices, herbs and seasonings as well as in most of multicomponent blends of spices, herbs and seasonings [6,14,15].

Screening by means of the PPSL apparatus is easy, effective and first and above all inexpensive. The method provides the fastest way to gain final results whether food product is irradiated. By comparison with the TL method, preparation of samples is simple, much quicker and takes not longer than one hour instead of few days by the TL method. However, in ambiguous results of PPSL, the validated TL method should be always used [16].

References

[1]. Pinnioja S., Siitari-Kauppi M., Jernström J., Lindberg A.: Radiat. Phys. Chem., 55, 743-747 (1999).

[2]. Sanderson D.C.W., Slater C., Cairns K.J.: Radiat. Phys. Chem., 34, 915-924 (1989).

[3]. Soika Ch., Delincée H.: Lebensm.-Wiss. Technol., 33, 440-443 (2000), in German.

[4]. The SURRC Pulsed Photostimulated Luminescence (PPSL) Irradiated Food Screening System. Users Manual. Royal Society of Chemistry, Cambridge 2004, 17 p.

[5]. Bluszcz A.: Zeszyty Naukowe Politechniki Śląskiej, 86(1434), 11-17, 25-47 (2000), in Polish.

[6]. EN 1788:2001: Foodstuffs – Thermoluminescence detection of irradiated food from which silicate minerals can be isolated.

[7]. Directive 1999/3/EC of the European Parliament and of the Council of 22 February 1999 on the establishment of a Community list of food and food ingredients treated with ionising radiation. Off. J. European Communities L 66/24-25 (13.3.1999).

[8]. CEN/TC 275/WG 8 N 127: Detection of irradiated food using photostimulated luminescence. 1999.

[9]. Detection of irradiated samples. European Patent No. 0 699 299 B1.

[10]. PN-EN 13751:2003 (U): Artykuły żywnościowe – Wykrywanie napromieniowania żywności za pomocą fotoluminescencji.

[11]. Sanderson D.C.W, Carmichael L., Fisk S.: Food Sci. Technol. Today, 12(2), 97-102 (1998).

[12]. Sanderson D.C.W., Carmichael L.A., Naylor J.D.: Food Sci. Technol. Today, 9(3), 150-154 (1995).

[13]. Sanderson D.C.W., Carmichael L.A., Naylor J.D.: Recent advances in thermoluminescence and photostimulated luminescence detection methods for irradiated foods. In: Detection methods for irradiated foods – current status. Royal Society of Chemistry, Cambridge 1996, pp.124-138.

[14]. Huntley D.J., Godfrey Smith D.I., Thewald M.L.W.: Nature, 313, 105-107 (1985).

[15]. Sanderson D.C.W.: Detection of irradiated samples. Great Britain Patent No. 93-8542 GB 9308542.

[16]. Guzik G.P., Stachowicz W.: Pomiar luminescencji stymulowanej światłem, szybka metoda identyfikacji napromieniowania żywności. Instytut Chemii i Techniki Jądrowej, Warszawa 2005, 16 s. Raporty IChTJ. Seria B nr 3/2005 (in Polish).

DETECTION OF IRRADIATION IN CUTICLES OF COMMERCIAL SHRIMPS

Katarzyna Lehner, Wacław Stachowicz

The detection of stable EPR (electron paramagnetic resonance) signal produced by the action of ionising radiation in crustacea has been reported by several authors elsewhere [1,2]. The signal ob-