• Food Irradiation Control with the e-scan™ Food Analyzer

Introduction

Currently, more than 240,000 tons of food and dietary supplements per year, worldwide, are treated with radiation, with spices and vegetable seasonings making up the majority. However, this amount is still small compared to the amount of food produced. For example, in Germany per capita consumption is ca. 1.4 tons per year [1]. Nevertheless, both the current standards for consumer protection and the need for a traceable and transparent food production chain demand a proper food control strategy.

European Union (EU) directives [2] clearly state that irradiated food as well as food containing irradiated ingredients (regardless of their percentage) must be labeled (Fig. 1 shows the international food irradiation symbol, the radura). Furthermore, national authorities are responsible for issuing a clearance list [3] of irradiated food (and packing materials for some countries). For example, in Germany only spices, herbs and vegetable seasonings but no poultry or shrimps are cleared for irradiation. Therefore, national or federal bodies are obliged to control dairy and imported food according to EU norms and to ensure that the corresponding laws are observed by the food industry and importers.

Figure 1: The international food irradiation symbol, referred to as the radura symbol.

Food Irradiation Control and EPR

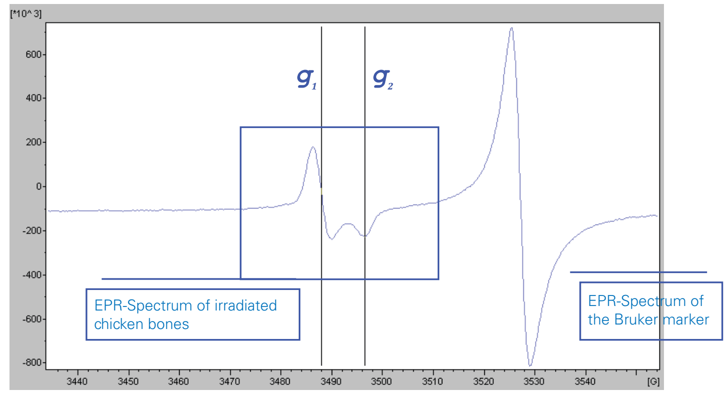
Food irradiation is used to reduce the health risk associated with food-borne pathogens such as Salmonella and to prolong shelf life (sprout inhibition, delay of ripening). In fact, ionizing radiation inhibits the division of microorganisms and creates so-called radiolytic products as well as free radicals. In a dry environment these radicals are relatively stable. For example, irradiated poultry bones or dried spices may contain a substantial amount of stable radicals which can be easily detected by EPR spectroscopy (EPR = electron paramagnetic resonance, also known as ESR). Extensive consultations and round-robin tests were conducted during the 1990s in order to set European-wide standards for sample preparation, measurement protocol and unequivocal identification of irradiated food via EPR.

Currently three EU norms exist, defining food irradiation control via EPR spectroscopy [4-6].

- EN 1786:1996 Foodstuffs – Detection of irradiated food containing bone – Method by ESR spectroscopy.
- EN 1787:2000 Foodstuffs – Detection of irradiated food containing cellulose by ESR spectroscopy.
- EN 13708:2001 Foodstuffs – Detection of irradiated food containing crystalline sugar by ESR spectroscopy.

With standard research EPR spectrometers such as Bruker's EMX and ELEXSYS series, food irradiation control can be conducted with superior sensitivity. However, experienced technicians or scientists are required to operate these complex spectrometers with their full array of technical capabilities. For food irradiation control by EPR to become a safe, reliable and accepted method, a dedicated bench-top EPR system is needed which is easy to set up and operate and which features purpose-designed protocols and applications as well as reliable calibration and self-validation as an integral part of the package. For this purpose Bruker's e-scan Food Analyzer is the product of choice and represents the successor to the successful EMS104 table-top EPR analyzer [7] with which many of the round-robin tests were conducted.

Figure 2



EPR spectrum of an irradiated chicken bone recorded with the e-scan Food Analyzer. The spectrum of the sample (axially symmetric lineshape at the center of the field sweep) is measured in parallel with the spectrum of the reference marker (isotropic signal lineshape to higher field at the right) with a known g value (1.980). The horizontal axis gives the B0 field values in Gauss.

Detection of irradiated food containing bone

The implemented method for detecting irradiated food containing bone [4] serves as an example of how the e-scan Food Analyzer can be used in food testing. Animal bones are predominately hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$. If hydroxyapatite is exposed to ionizing radiation (x-rays, gamma-rays, or accelerated electrons), stable radicals (mainly from impuries such as CO_2 –) are generated and exhibit quite distinct and characteristic EPR spectra [8]. Thus, when bones have been irradiated, the characteristic EPR signal obtained can be described by an axially symmetric g-tensor with $g_1 = 2.002(1)$ and $g_2 = 1.998(1)$ [4]. On the other hand, bones that have not been irradiated generally give a signal corresponding to an isotropic g = 2.005(1) [4]. The "axial" EPR signal due to irradiation is stable for 12 months or more and even withstands heating. Therefore, this signal provides the basis for identifying irradiated food containing bone, e.g., poultry, rabbit, pig, and fish.

The task for an EPR instrument in this context is to precisely determine the g values according to the relationship:

$$g = h\nu/\beta B_0$$

where h is Planck's constant, ν the microwave resonance frequency, β the Bohr magneton, and B_0 the magnetic field at resonance.

Thus, the accuracy of g depends on the accuracy with which one can measure the microwave frequency and the magnetic field. Frequency can be measured very accurately with a frequency counter or can be simply set using DDS (direct digital synthesis) hardware. The magnetic field can be determined directly or indirectly. An NMR field measurement provides a direct readout of B_0, whereas the EPR measurement of a reference sample with known g value provides an indirect determination of B_0. Although a direct field measurement can provide the ultimate accuracy, the additional hardware and software required represent a significant financial burden.

The indirect method of field calibration is readily available on the e-scan in the form of a reference marker patented by Bruker. Fig. 2 displays a typical EPR spectrum of an irradiated chicken bone as acquired on the e-scan Food Analyzer. Clearly, the spectrum consists of two components, an axial spectrum in the center with two g values and an isotropic line to the right at higher field. The latter is from the reference marker with known g = 1.980. Assuming that the field sweep is linear (validated in the self-test mode, see below), the g values for the signal from the sample can be calculated automatically.

To make this analysis tool as automatic and reliable as possible, the spectral lineshape is taken into account as well. Semiquantitative analysis is also possible via the relative intensities of the signals from sample and marker. However, a direct quantitative comparison of signals from different bone samples is not straightforward since the degree of mineralization depends on the animal species [4].

The e-scan Concept

The e-scan Food Analyzer is one member of the Bruker e-scan product line, which features table-top EPR analyzers tailored for dedicated applications. In fact, the e-scan Food Analyzer can be easily upgraded to operate also as an e-scan EPR/Alanine Dosimeter Reader, whose general e-scan concept has been described [9].

Figure 3: e-scan food control inserts (left) and the cavity template (right).

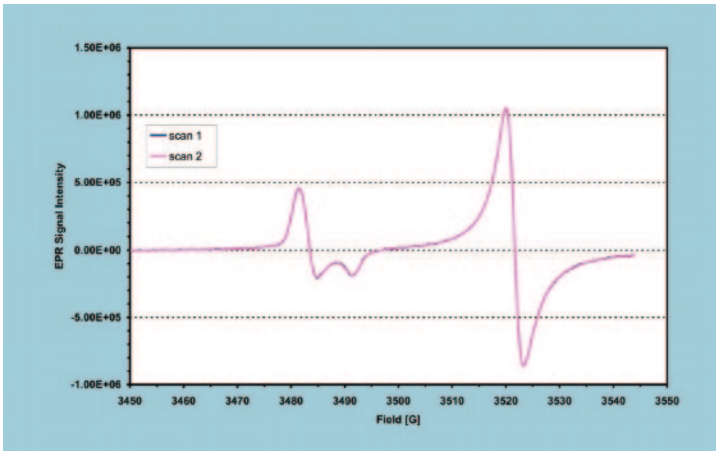
Clearly, one of the e-scan design advantages is the ability to optimally configure the instrument for the application of interest. In the context of food irradiation control, two features are most important:

- Optimal sensitivity and configuration for convenient and reliable detection of irradiated food (reliability meaning that neither false negative nor false positive identifications occur)

- Self-testing of the system and validation via an alanine dose measurement using an alanine film dosimeter insert with a Kodak BioMax® alanine film dosimeter [10] that has been irradiated with a calibrated dose [9]

To facilitate optimal detection of irradiated food, sample holders and a cavity template have been developed for the two major application areas: bone-containing and cellulose-containing food (Fig. 3). The key features of the two holders are as follows:

- A unique barcode label unequivocally identifies the food control holder (via the e-scan's internal barcode reader) and software prohibits the accidental analysis with the wrong holder
- Guided insertion of the sample tube (5 mm o.d.) via the food control holder
- Optimal positioning of samples with different filling heights using the e-scan cavity template
- Permanent EPR intensity reference marker (patent pending) for the analysis of bone-containing food;
- Quick & easy exchange of holders
- Optional use of customized barcode sample labels for automatic sample identification



Microsoft Excel generated graphic showing an overlay of two EPR spectra obtained from the same irradiated chicken bone sample, demonstrating the data export feature of the e-scan Food Analyzer and the excellent reproducibility of the results (the two traces superimpose).

In order to provide these capabilities, the same software concept (Microsoft's Visual Basic Script (VBS®) and ActiveX features) has been implemented as for the e-scan Alanine Dosimeter Reader [8]. Convenient and traceable operation is ensured since all raw data and system logging data are stored along with the automatically generated results (operator name, signal intensity, g value, etc.). Moreover, all important data and results are automatically exported to Microsoft Excel® for convenient reporting and further analysis. In Fig. 4 an example of the e-scan software features is shown. The individual Excel graphics of the acquired EPR spectra are created automatically, and overlay of spectra is possible with a macro from within Excel. This example demonstrates the excellent reproducibility of the e-scan Food Analyzer; the two overlayed scans of the same sample cannot be distinguished separately.

References

[1] http://www.bfa-ernaehrung.de/Bfe-Deutsch/Institute/IOES/Poster/Wieviel.pdf (in german). Federal Research Center for Nutrition, Institute of Nutritional Economics and Sociology, Karlsruhe, Germany.

[2] CODEX General Standard for Irradiated Foods, CODEX STAN 106-1983, rev. 1-2003.

[3] http://www.iaea.org/icgfi/ International Consultative Group on Food Irradiation.

[4] EN 1786:1996. Foodstuffs – Detection of irradiated food containing bone –Method by ESR spectroscopy.

[5] EN 1787:2000. Foodstuffs – Detection of irradiated food containing cellulose by ESR spectroscopy.

[6] EN 13708:2001. Foodstuffs – Detection of irradiated food containing crystalline sugar by ESR spectroscopy.

[7] Helle N, Maier D, Linke B, Such P, Gögl KW, Schreiber GA. Elektronen- Spin-Resonanzmessungen mit einem Kompakt-ESR-Spektrometer, Bundesgesundheitsblatt 7 (1992) 331-336.

[8] Ikeya M. New Applications of Electron Spin Resonance, Dating, Dosimetry and Microscopy, World Scientific, London (1993).

[9] Kamlowski A, Maier DC, Barr D, Heiss AH. Industrial EPR: The escan ™Alanine Dosimeter Reader, Bruker SpinReport 152/153 (2003)33-36.

[10] The BioMax® Alanine film dosimeters from Kodak originated from a cooperation between Bruker and the Scientific Div. of Eastman Kodak and are exclusively distributed by Bruker

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Bruker Corporation

Billerica, MA · USA
Phone (+1) (978) 663-7406
epr@bruker.com
www.bruker.com

Bruker BioSpin GmbH

Rheinstetten · Germany
Phone (+49) (721) 5161 - 0
epr@bruker-biospin.de
www.bruker.com