SLOVENSKI STANDARD
SIST EN 1787:1998

01-november-1998

Živila - Detekcija obsevane hrane, ki vsebuje celulozo - Metoda z ESR spektroskopijo

Foodstuffs - Detection of irradiated food containing cellulose - Method by ESR spectroscopy

Lebensmittel - Nachweis von bestrahlten cellulosehaltigen Lebensmitteln - Verfahren mittels ESR-Spectroscopy

Produits alimentaires - Détection d'aliments ionisés contenant de la cellulose - Méthode par specroscopie RPE

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67.050	Splošne preskusne in analizne metode za živilske proizvode	General methods of tests and analysis for food products

SIST EN 1787:1998 **en**

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English version

Foodstuffs - Detection of irradiated food containing cellulose - Method by ESR spectroscopy

Produits alimentaires - Détection d'aliments ionisés contenant de la cellulose - Méthode par spectroscopie RPE

Lebensmittel - Nachweis von bestrahlten cellulosehaltigen Lebensmitteln - Verfahren mittels ESR-Spektroskopie

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CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

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Foreword

This European Standard has been prepared by CEN/TC 275 "Food analysis - Horizontal methods" the secretariat of which is held by DIN.

This European Standard was elaborated on the basis of a protocol developed following a concerted action supported by the Commission of European Union (XII C.). Experts and laboratories from E.U. and EFTA countries, contributed jointly to the development of this protocol.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 1997, and conflicting national standards shall be withdrawn at the latest by June 1997.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

1 Scope

This European Standard specifies a method for the detection of foods containing cellulose which have been treated with ionizing radiation, by analysing the electron spin resonance (ESR) spectrum, also called electron paramagnetic resonance (EPR) spectrum, of the food, see [1] to [13].

Interlaboratory studies have been successfully carried out with pistachio nut shells, see [13] to [17], and paprika powder, see [18] and [19].

2 Definition

For the purposes of this standard, the following definition applies:

ESR spectrum: The signals obtained by the method described in this European Standard. They are either due to paramagnetic compounds formed by irradiation or to compounds originally present.

3 Principle

ESR spectroscopy detects paramagnetic centres (e.g. radicals). An intense external magnetic field produces a difference between the energy levels of the electron spins $m_s = +\frac{1}{2}$ and $m_s = -\frac{1}{2}$, leading to resonance absorption of an applied microwave beam in the spectrometer. ESR spectra are conventionally displayed as the first derivative of the absorption with respect to the applied magnetic field.

The field and frequency values depend on the experimental arrangements (sample size and sample holder), while their ratio (i.e. g value) is an intrinsic characteristic of the paramagnetic centre and its local coordination. For further information, see [1] to [13].

Radiation treatment produces radicals which can be detected in solid and dry parts of the food. The intensity of the signal obtained increases with the concentration of the paramagnetic compounds and thus with the applied dose.

4 Apparatus

Usual laboratory apparatus and, in particular, the following:

4.1 Commercially available X-Band ESR spectrometer including magnet, microwave bridge, console with field-controller and signal-channel, rectangular or cylindrical cavity

4.2 ESR tubes, of internal diameter about 4,0 mm (e.g. Suprasil®[1]) quartz tubes)

4.3 Balance, accurate to the nearest 1 mg (optional)

4.4 Vacuum laboratory oven, or freeze dryer

5 Sampling plan

(No specification yet)

6 Procedure

6.1 Sample preparation

NOTE: Storing samples in the frozen state will not adversely affect the detection of treatment with radiation.

6.1.1 Shells and stones

Remove pieces of suitable size (about 50 mg to 100 mg, 3,0 mm to 3,5 mm in diameter) from the shells or stones of the food. Drying (e. g. in a freeze-dryer or at approximately 40 °C in a laboratory vacuum oven (4.4)) is usually not necessary in the case of nutshells but recommended for pips and kernels of fruits.

6.1.2 Spices

Use about 150 mg to 200 mg of the spice sample. Drying (e. g. in a freeze-dryer or at approximately 40 °C in a laboratory vacuum oven (4.4)) is usually not necessary.

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[1]) Superasil is an example of a product available commercially. This information is given for the convenience of users of this standard and does not constitute an endorsement of CEN of this product.

6.2 ESR Spectroscopy

6.2.1 Spectrometer settings

Use a time constant and sweep rate appropriate for an ESR signal with a peak to peak linewidth of approximately 0,8 mT. For example, the following ESR spectrometer settings have been found to be satisfactory:

Microwave radiation:	9,78 GHz[2]), power 0,4 mW (for pistachio nuts), to 0,8 mW (for paprika powder)[3])
Magnetic field:	348 mT centre field[2]), sweep width 20,0 mT;
Signal channel:	50 kHz or 100 kHz modulation frequency, 0,4 mT to 1 mT modulation amplitude; 100 ms to 200 ms time constant[4]) sweep rate 5 mT min^{-1} to 10 mT min^{-1} or accumulation of 3 to 5 spectra at greater sweep rate and shorter time constant;
Gain:	between about 1,0 x 10^4 and 1,0 x 10^6
Temperature:	room temperature.

6.2.2 Analysis of sample

Analyse the sample prepared as described in 6.1 in an ESR tube (4.2).

7 Evaluation

A single signal Z (see figure A.1) is observed in the ESR spectra of all food containing cellulose, including unirradiated samples. In the case of irradiated samples, the intensity of this signal is usually much greater and, in addition, a pair of lines occurs to the left (at lower field) and right (at higher field) of the central signal.

This pair of lines is due to cellulose radicals formed by the ionizing radiation. The spacing of this radiation-induced signal pair is about 6,0 mT and is symptomatic of radiation treatment having taken place (see figure A.2).

In some species of food, broad, low-intensity lines due to Mn^{2+} ions (paramagnetic) are observed in addition to the signals mentioned. However, there is no danger of misinterpretation of the spectra because the intensity is low, the position in the magnetic field is different and the spacing is different, the spacing between two manganese lines from one another (coupling constant) being about 9,0 mT.

8 Limitations

Detection limits and stability are influenced by the crystalline cellulose content and the moisture content of the samples. Positive identification of the cellulose radicals is evidence of irradiation but the absence of this signal does not constitute evidence that the sample is unirradiated.

Detection of irradiated pistachio nuts has been validated for doses of 2 kGy and above and stability is not expected to present limitations for detection of irradiation for at least one year after treatment.

Detection of irradiated paprika powder has been validated for doses of 5 kGy and above. Stability of cellulose radicals in paprika powder is largely dependent on storage conditions, (especially humidity), and may be shorter than the shelf-life of the products.

Detection of irradiated berries has been tested for doses of 0,5 kGy and above. Detection is typically limited to about the first 20 days after treatment.

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[2]) These values are for the specified microwave frequency and magnetic field; if the frequency is higher (lower) the magnetic field strength will be higher (lower).

[3]) If saturation is suspected, the microwave power should be reduced, see [10].

[4]) These values are for the specified sweep rate.

9 Validation

This European Standard is based on two interlaboratory tests with pistachio nut shells [13] to [17] and one with paprika powder [18], [19].

In an interlaboratory test carried out by the Community Bureau of Reference (BCR) [16], [17], 21 laboratories identified coded samples of pistachio shells which were either unirradiated or irradiated to about 2 kGy, 4 kGy or 7 kGy (see table 1).

Table 1: Interlaboratory data

Product	No of samples	No of false negative[1])	No of false positive[2])
Pistachio shells	84	15	2

[1]) False negatives are irradiated samples identified as unirradiated.
[2]) False positives are unirradiated samples identified as irradiated.

After improvement of the first protocol, in an interlaboratory test carried out by the German Federal Health Office (Bundesgesundheitsamt, BGA) [15], 17 laboratories identified coded samples of pistachio shells which were either unirradiated or irradiated to about 4 kGy or 6 kGy (see table 2).

Table 2: Interlaboratory data

Product	No of samples	No of false negative[1])	No of false positive[2])
Pistachio shells	68	0	1[3])

[1]) False negatives are irradiated samples identified as unirradiated.
[2]) False positives are unirradiated samples identified as irradiated.
[3]) The false positive was due to a misinterpretation of the spectra.

In a further interlaboratory test carried out by the BGA [18], [19], 20 laboratories identified coded samples of paprika powder which were either unirradiated or irradiated to about 5 kGy or 10 kGy (see table 3).

Table 3: Interlaboratory data

Product	No of samples	No of false negative[1])	No of false positive[2])
Paprika powder	160	0	1[3])

[1]) False negatives are irradiated samples identified as unirradiated.
[2]) False positives are unirradiated samples identified as irradiated.
[3]) The false positive was due to a misinterpretation of the spectra.

10 Test report

The test report shall contain at least the following:

a) information for identification of the sample;
b) a reference to this European Standard;
c) the result;
d) date of sampling and sampling procedure (if known);
e) date of receipt;
f) date of test;
g) any particular points observed in the course of the test;
h) any operations not specified in the method or regarded as optional which might have affected the results.

Annex A (normative)

Figures

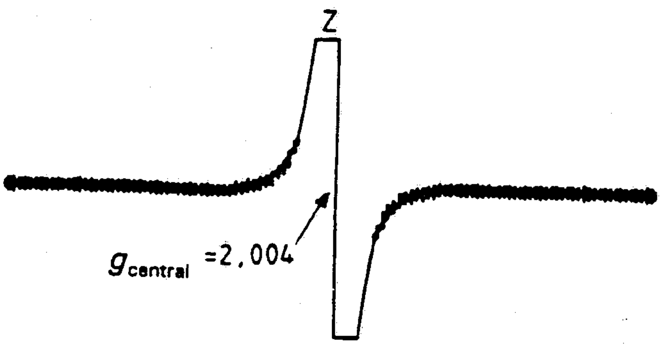

Figure A.1: ESR spectrum of an unirradiated pistachio nut shell

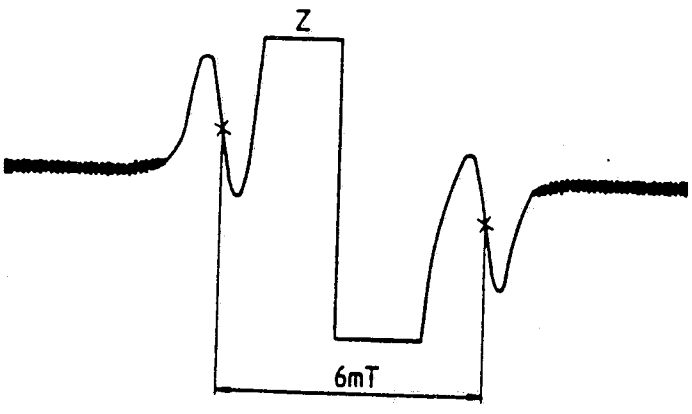

Figure A.2: ESR spectrum of an irradiated pistachio nut shell

Annex B (informative)

Further information on the applicability

Laboratory experience has been gained to support the application of this method to the following sample types:

Strawberries, raspberries, blueberries (chilled or frozen), french prunes, coconuts, almonds and walnuts.