SLOVENSKI STANDARD
oSIST prEN 13708:2019

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Živila - Detekcija obsevane hrane, ki vsebuje kristalni sladkor, s spektroskopijo ESR

Foodstuffs - Detection of irradiated food containing crystalline sugar by ESR spectroscopy

Lebensmittel - ESR-spektroskopischer Nachweis von bestrahlten Lebensmitteln, die kristallinen Zucker enthalten

Produits alimentaires - Détection par spectroscopie RPE d'aliments ionisés contenant des sucres cristallisés

Ta slovenski standard je istoveten z: **prEN 13708**

ICS:

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

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EUROPEAN STANDARD

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English Version

Foodstuffs - Detection of irradiated food containing crystalline sugar by ESR spectroscopy

Produits alimentaires - Détection par spectroscopie RPE d'aliments ionisés contenant des sucres cristallisés

Lebensmittel - ESR-spektroskopischer Nachweis von bestrahlten Lebensmitteln, die kristallinen Zucker enthalten

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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European foreword

This document (prEN 13708:2019) has been prepared by Technical Committee CEN/TC 275 “Food analysis - Horizontal methods”, the secretariat of which is held by DIN.

This document is currently submitted to the CEN Enquiry.

This document will supersede EN 13708:2001.

This version published in 2001 has been changed by introduction of an information that this standard is not applicable to pure, grind crystalline sugar in Clause 8 (last paragraph).

1 Scope

This document specifies a method for the detection of foods containing crystalline sugars 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 [7].

Interlaboratory studies have been successfully carried out on dried figs, dried mangoes, dried papayas and raisins [1] to [3].

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

4 Principle

ESR spectroscopy detects paramagnetic centres (e.g. radicals). They are either due to irradiation or to other compounds present. An intense external magnetic field produces a difference between the energy levels of the electron spins $m_s = + 1/2$ and $m_s = - 1/2$, 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 magnetic field and microwave 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 co-ordination. For further information, see [1] to [7].

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.

5 Apparatus and equipment

Usual laboratory apparatus and, in particular, the following:

5.1 Commercially available X-Band ESR spectrometer

including magnet, microwave bridge, console with field-controller and signal-channel, rectangular or cylindrical cavity

5.2 G-value measurement unit

including frequency counter, magnetic field probe (nuclear magnetic resonance (NMR) Gaussmeter), or any other built-in g-value measurement unit.

5.3 ESR tubes,

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

5.4 Balance,

accurate to the nearest 1 mg (optional)

5.5 Laboratory vacuum oven, or freeze dryer

5.6 Scalpel

6 Procedure

6.1 Sample preparation

Prepare suitable pieces (50 mg to 100 mg) of the fruit, e.g. using a scalpel. Avoid grinding of samples.

NOTE Various parts of the fruits can contain different quantities of crystalline sugars. It can be advantageous to take the test sample from the outer parts of the fruits.

Transfer a test portion directly into the ESR tube (3.3) and start the measurement.

Difficulties in tuning the spectrometer cavity can be experienced if the sample is insufficiently dry. In this case either reduce the sample quantity or dry it further. Samples should be dried in a laboratory vacuum oven at approximately 40 °C under reduced pressure or in a freeze-dryer.

WARNING: Excessive heating can reduce the signal.

6.2 ESR Spectroscopy

6.2.1 Spectrometer settings

Use a time constant and sweep rate appropriate for ESR signals with linewidths of 0,2 mT to 0,4 mT. For example, the following ESR spectrometer settings have been found to be satisfactory:

Microwave radiation:	9,78 GHz[2)], power 5 mW
Magnetic field:	348 mT centre field[2)], sweep width 10,0 mT to 20,0 mT;
Signal channel:	50 kHz or 100 kHz modulation frequency,
	0,15 mT to 0,4 mT modulation amplitude;
	100 ms to 200 ms time constant[3)]
	sweep rate 5 mT min^{-1} to 10 mT min^{-1}

1) Suprasil® is an example of a suitable product available commercially. This information is only given for the convenience of users of this International Standard and does not constitute an endorsement by CEN of this product.

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) These values are for the specified sweep rate.

	or accumulation of 3 to 5 spectra at greater sweep rate and shorter time constant;
Gain:	between 10^4 and 10^6;
Temperature:	ambient temperature.

6.2.2 Analysis of sample

Analyse the sample prepared as described in 6.1 in an ESR tube (5.3).

7 Evaluation

7.1 Identification of irradiated samples

7.1.1 General

Irradiated food containing crystalline sugar show typical multicomponent ESR spectra reflecting the presence of radiation-induced radicals in the sample. Dried fruits often contain sugar particles in crystalline form, and therefore the appearance of a typical multicomponent ESR spectrum (see Annex A) indicates radiation treatment. Due to different mono- and disaccharides and due to the changes in saccharide composition various ESR spectrum types can occur.

Other irradiated sugar-containing foodstuffs reveal ESR spectra which have similar structures. Since the overall spectrum structure depends on the radical composition and on the crystallinity of the mono- and disaccharides present in the sample, variations in the spectrum characteristics occur.

For monocrystalline samples the orientation within the ESR cavity can influence the relative intensities of the ESR lines and thus the spectral shape. However in the majority of dried fruit samples randomly oriented microcrystalline sugars produce a powder type spectrum. This produces broader lines and spectral shapes which are less sensitive to orientation. Typical characteristics are described in 6.1.2 and 6.1.3, and illustrated in Figures A.2 and A.4. Where similar features are observed the sample can be identified as irradiated.

7.1.2 Irradiated dried mangoes and dried papayas

An ESR spectrum shown in Figure A.2 and having the following characteristics is significant for irradiated dried mangoes and dried papayas:

overall spectrum width:	7,4 mT to 7,8 mT
g-value (centre of spectrum):	2,0035 ± 0,0010

7.1.3 Irradiated dried figs and raisins

An ESR spectrum shown in Figure A.4 and having the following characteristics is significant for irradiated dried figs and raisins:

overall spectrum width:	8,7 mT to 9,1 mT
g-value (centre of spectrum):	2,0035 ± 0,0010

7.1.4 Unirradiated samples

Unirradiated samples of dried mangoes, dried papayas, dried figs and raisins show no ESR spectrum at all or a broad singlet as shown in Figures A.1 and A.3 with a g-value of 2,0040 ± 0,0010.

7.2 G-value measurement

For the characterization of the ESR spectrum, especially as regards the identification of irradiated samples, it is helpful to measure the g-values of the ESR-signals.

A g-value of a signal, g_{signal}, is calculated using Formula (1):

$$g_{signal} = \frac{71,448 \cdot \nu_{ESR}}{B} \quad (1)$$

where:

ν_{ESR} is the microwave frequency, in gigahertz (GHz);

B is the magnetic flux density (magnetic field setting of the spectrometer), in millitesla (mT) (10 Gauss = 10 G = 1 mT).

The procedure for calculating the g-value of the ESR spectrum of dried fruits is to position the field in the centre of the ESR spectrum (CF in Figures A.1 to A.4) and to measure the frequency ν (e.g. frequency counter) and the field B (e.g. gaussmeter) at this point.

8 Limitations

While the general formation processes of radiation-induced radicals are known, identification of the specific radicals responsible for individual signals has not yet been achieved. Nevertheless, the association between radiation treatment and the signals illustrated in Clause 5 and Figures A.2 and A.4 has been demonstrated in a number of studies [1] to [7].

Multicomponent ESR spectra prove prior irradiation but the absence of the specific spectrum does not constitute evidence that the sample is unirradiated. Different mono- or disaccharides may dominate in the sample producing different ESR spectra after irradiation. Moreover, if no sugar crystals are present in the sample, irradiation will not produce specific ESR signals.

Detection of irradiated dried figs, dried mangoes, dried papayas and raisins has been validated. The lower limit of detection mainly depends on the crystallinity of the sugar in the sample. Detection of irradiation treatment is not significantly influenced by storage of at least several months.

The applicability of this method depends on the presence of sufficient quantities of crystalline sugar in the sample at all stages of handling between irradiation and testing. Confirmation of sensitivity to radiation can be achieved, where necessary, by irradiating a portion of the sample and re-testing. It is important that dried fruits have not been re-hydrated prior to testing.

It should be noted that the scope of this standard does not cover pure crystalline sugar. It has been reported in [8], [9] and [10], that grinding unirradiated crystalline sugar can induce ESR signals with similar shapes to radiation induced signals.

9 Validation

This European Standard is based on two interlaboratory tests, one with dried papayas and raisins, [1], [2], and one with dried mangoes and dried Figures [3].

In an interlaboratory test carried out by the Community Bureau of Reference (BCR) [1], [2], 21 laboratories identified coded samples of dried papayas and raisins which were either unirradiated or irradiated to about 0,5 kGy, 1 kGy, 2 kGy, 4 kGy or 7 kGy (see Table 1).

Table 1 — Interlaboratory data

Product	No of samples	No of false negatives[a]	No of false positives[b]
Raisins	126	7[c]	1
Dried papayas	126	2[d]	0

[a] False negatives are irradiated samples identified as unirradiated.

[b] False positives are unirradiated samples identified as irradiated.

[c] Obtained from the 19 samples irradiated at 0,5 kGy.

[d] Obtained from the 21 samples irradiated at 0,5 kGy

In another interlaboratory test carried out by the German Federal Institute for Health Protection and Veterinary Medicine (BgVV) [3], 17 laboratories identified coded samples of dried mangoes and dried figs which were either unirradiated or irradiated to about 1 kGy, 3 kGy or 5 kGy (see Table 2)

Table 2 — Interlaboratory data

Product	No of samples	No of false negatives[a]	No of false positives[b]
Dried mangoes	184	0	0
Dried figs	184	2	0

[a] False negatives are irradiated samples identified as unirradiated.

[b] False positives are unirradiated samples identified as irradiated.

10 Test report

The test report shall contain at least the following:

a) information necessary for identification of the sample;

b) a reference to this document;

c) date of sampling and sampling procedure (if known);

d) date of receipt;

e) date of test;

f) the result;

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.