SLOVENSKI STANDARD
SIST EN 13708:2022

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Nadomešča:
SIST EN 13708:2002

Živila - Določevanje obsevanosti živil, ki vsebujejo kristalni sladkor, s spektroskopijo ESR

Foodstuffs - Detection of irradiated foodstuff 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: **EN 13708:2022**

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

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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 (EN 13708:2022) has been prepared by Technical Committee CEN/TC 275 “Food analysis - Horizontal methods”, the secretariat of which is held by DIN.

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of an identical text or by endorsement, at the latest by September 2022, and conflicting national standards shall be withdrawn at the latest by September 2022.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 13708:2001.

The predecessor of this document 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.

In comparison with the previous edition, the entire document was editorially revised according to current rules. Additionally, the following technical modifications have been made:

a) clause “Normative references” was added;

b) clause “Terms and Definitions” was added;

c) former 3.2 was scientifically refined and converted into a footnote;

d) section “Sample preparation” was slightly extended and modified by conversion of the NOTE and WARNING into main text;

e) section “Spectrometer settings” was scientifically refined, its normative character (i.e. provisions set out) modified towards more exemplary/suggestive expressions of provision and aligned with EN 1787;

f) clause “Evaluation” was amended by restructuring the subsections (subsection “G-value calculation” became 7.1 and “Identification of irradiated samples” 7.2), including refinement of the given information, designations and abbreviations including the alignment with the Annexes and EN 1787;

g) clause “Limitations” was extended;

h) layout of Figures A.1 to A.4 were revised and Figures A.5 to A.7 for irradiated fructose, glucose and saccharose were added including alignment of the given information with the main text and EN 1787;

i) the Bibliography was updated and extended by entry [8], [9] and [10].

Any feedback and questions on this document should be directed to the users’ national standards body. A complete listing of these bodies can be found on the CEN website.

According to the CEN-CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Republic of North Macedonia, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

1 Scope

This document specifies a method for the detection of foodstuff 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 foodstuff, see [1] to [7].

Interlaboratory studies have been successfully carried out on dried figs, dried mangoes, dried papayas and raisins, see [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 https://www.electropedia.org/

— ISO Online browsing platform: available at https://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 $m_S = +½$ and $m_S = -½$, 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 mostly detected in solid and dry parts of the foodstuff. 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[1].

5.2 ESR tubes, with an internal diameter of about 4,0 mm (e.g. Suprasil®[2] quartz tubes).

5.3 Balance, accuracy of 1 mg (optional).

5.4 Laboratory vacuum oven, or freeze dryer.

5.5 Scalpel.

6 Procedure

6.1 Sample preparation

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

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 (5.2) 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.

Temperatures significantly higher than 40 °C can reduce the signal.

6.2 ESR Spectroscopy

6.2.1 Spectrometer settings

The parameters shown in Table 1 have been found to be successful in interlaboratory tests (see Clause 9). The values shown (Table 1) are given as examples and should be optimized per sample and ESR spectrometer as required.

Use a time constant and sweep rate (or sweep time) appropriate for an ESR signal with a peak to peak linewidth of approximately 0,2 mT to 0,4 mT.

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1 g-value calculation unit including frequency counter magnetic field probe (magnetic resonance Teslameter) or any other built in g-value calculation unit.

2 Suprasil® is an example of a suitable product available commercially. This information is only given for the convenience of users of this document and does not constitute an endorsement by CEN or CENELEC of this product.

Table 1 — Example for ESR spectrometer settings

Parameter	Setting
Microwave radiation:	Frequency 9,78 GHz [a], power 5 mW.
Magnetic field:	348 mT centre field [a], 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 [b], 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 approximately 10^4 and 10^6.
Temperature:	Ambient temperature.
[a] 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). [b] These values are for the specified sweep rate.	

6.2.2 Analysis of sample

Analyse the sample prepared as described in 6.1 in an ESR tube (5.2).

7 Evaluation

7.1 G-value calculation

For calculating the g-value of the centre (i.e. zero point) of the multicomponent ESR spectra (Figures A.1 to A.4) it is necessary to measure the frequency ν (e.g. frequency counter) and the field B (e.g. gaussmeter) at this point.

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

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

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).

7.2 Identification of irradiated samples

7.2.1 General

Irradiated foodstuff 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 foodstuff reveal ESR spectra that 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 that are less sensitive to orientation. Typical characteristics are described in 7.2.2 and 7.2.3, and are illustrated in Figures A.2 and A.4. Where similar features are observed, the sample can be identified as irradiated.

Examples of several irradiated mono- and disaccharides are shown in Figures A.5 to A.7.

7.2.2 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:	Approximately 7,4 mT to 7,8 mT
g_S:	2,003 5 ± 0,001 0

7.2.3 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:	Approximately 8,7 mT to 9,1 mT
g_S:	2,003 5 ± 0,001 0

7.2.4 Unirradiated samples

Unirradiated dried samples (mangoes, papayas, figs and raisins) show no ESR spectrum at all or a broad singlet as shown in Figures A.1 and A.3 with g_S of 2,004 0 ± 0,001 0.

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 has been demonstrated in a number of studies, see [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 by inter-laboratory tests.

The 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.

To check the sensitivity of the sample it might be helpful to irradiate a portion of the sample with an appropriate technologically relevant dose, and examine it again.

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 document is based on two interlaboratory tests, one with dried papayas and raisins, [1], [2], and one with dried mangoes and dried figs [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 2).

Table 2 — 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 3).