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SLOVENSKI STANDARD
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Živila - Hitra metoda za analizo več visokopolarnih pesticidov in njihovih metabolitov v živilih z ekstrakcijo s kislim metanolom in merjenjem z LC- ali IC-MS/MS (QuPPe-Metoda)

Foodstuff - Quick Method for the Analysis of Multiple Highly Polar Pesticides and their Metabolites in Foodstuff Involving Extraction with Acidified Methanol and Measurement by LC- or IC-MS/MS (QuPPe-Method)

Lebensmittel - Schnellmethode zur Bestimmung mehrerer hochpolarer Pestizide und ihrer Metaboliten in Lebensmitteln nach Extraktion mit angesäuertem Methanol und Messung mittels LC- oder IC-MS/MS (QuPPe-Methode)

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Produit alimentaire - Méthode rapide pour l'analyse de plusieurs pesticides hautement polaires et de leurs métabolites dans les aliments impliquant une extraction avec du méthanol acidifié et une mesure par LC- ou IC-MS/MS (QuPPe-Methode)

Ta slovenski standard je istoveten z: **prEN 18032**

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 foreword

This document (prEN 18302:2023) has been prepared by Technical Committee CEN/TC275 “Food analysis - Horizontal methods”, the secretariat of which is held by DIN.

This document is currently submitted to the CEN Enquiry.

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1 Scope

This document specifies a procedure for the analysis of residues of highly polar pesticides and metabolites, which are not amenable to common multiresidue methods, in various food commodities of plant and animal origin, including fruits, vegetables, cereals, pulses, oily seeds, nuts, milk, liver and honey. The method was developed at the EURL-SRM hosted at CVUA Stuttgart [1], [2], [3] and has been collaboratively studied on a large number of commodity/pesticide combinations. Guidelines for calibration are outlined in CEN/TS 17061:2019.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

CEN/TS 17061:2019, *Foodstuffs - Guidelines for the calibration and quantitative determination of pesticide residues and organic contaminants using chromatographic methods*

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:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

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4 Principle

Residues are extracted from the homogeneous test portion following water adjustment and addition of acidified methanol. In the case of fruits and vegetables, the mixture is centrifuged, filtered and directly analysed by LC-MS/MS or IC-MS/MS. In the case of cereals, pulses, nuts, oily seeds and foods of animal origin, EDTA is added for the complexation of metal ions, such as calcium and magnesium, which can affect the analysis of certain compounds (e.g. glyphosate and AMPA). As such commodities also contain a substantial content of protein, they are additionally diluted with acetonitrile to precipitate proteins. Samples with high lipid content are subjected to dispersive SPE with C18-sorbent. Various LC- and IC-MS/MS methods, allowing simultaneous analysis of different combinations of pesticides, are provided in this document. Quantification is performed employing isotope labelled analogues of the target analytes as internal standards (IL-ISs), so far these are available. When adding IL-ISs directly to the test portion at the beginning of the procedure, they compensate for any factors having an influence on recovery-rates, such as volume-deviations and analyte losses during sample preparation. Matrix-effects during measurement are also corrected. The use of IL-ISs, ensures good accuracy and reproducibility. Quantification without IL-ISs is possible, but careful water adjustment and other approaches for addressing recovery losses or matrix effects are required in this case. The analytical procedure entails few working steps and involves little material consumption. A brief overview of the method is shown in the flowcharts within the "On-line Supplement" linked in Annex C.

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5 Preparation and storage of the samples

5.1 General considerations

Sample processing and storage procedures should be demonstrated to have no significant effect on the residues present in the test sample (sometimes also called "analytical sample"). Processing should also ensure, that the test sample is homogeneous enough so that sub-sampling (portion-to-portion) variability is acceptable. If a single analytical portion is unlikely to be representative of the test sample, larger or

replicate portions shall be analysed, to provide a better estimate of the true value. The degree of comminution should support a quantitative residue extraction, otherwise, extraction shall involve supplementary comminution, e.g. through a homogenizing device (A.2.2) or grinding aids (e.g. metal balls (A.2.3)).

5.2 Laboratory sample

A laboratory sample is the sample arriving to the laboratory for analysis and should ideally be sampled according to international sampling protocols [4], [5]. A laboratory sample that is extensively spoiled or degraded should normally not be analysed. Samples associated with a shelf life should normally be analysed within their stated shelf life. If possible, process laboratory samples immediately after arrival and in any event, before any significant physical or chemical changes have taken place. If a laboratory sample cannot be processed without delay, it should be stored under appropriate conditions to keep it fresh and to minimize deterioration.

If the laboratory sample is in a state that does not require milling prior to analysis (e.g. juices, milk, and cereal flour), stir or shake the sample well and then withdraw the analytical test portions directly. Where the homogeneity of the sample is, however, not sufficient or the extraction of residues is expected to be significantly compromised due to the presence of larger particles, intensive comminution should be performed using appropriate means.

5.3 Treatment of laboratory samples prior to milling

For preparation of the analytical sample, take only the portion of the laboratory sample to which the maximum residue levels apply [6], [7]. If a reduction of the laboratory sample is required, out of practical reasons, it shall be carried out in a way ensuring representativeness. This, for example, applies when samples are made up of larger units, and the capacity of the available mixer is too small to process the required number of units in one go. In this case, parts of the sample can be used, i.e. wedge-shaped sections (e.g. melons) or cross sections (e.g. cucumbers) that include the skin (outer surface). Opposite sections from each unit (e.g. quarters) should then be used for mixing (see e.g. [8]). For samples of small units (e.g. small fruits such as berries, legumes, cereals), the sample shall be thoroughly mixed before taking any aliquot for further processing.

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Any parts that would cause difficulties with the homogenization process may be removed prior to milling (e.g. in the case of stone fruits, the stones). The mass of the sample before and after removing the interfering sample portions shall be recorded. Precautions should be taken to avoid any losses of juice or flesh. The sample obtained in this way is referred to as the test sample. Calculation of the residue shall be based on the mass of the original test sample (including the stones and assuming that these parts are residue free).

In case of cryogenic comminution using dry ice, cutting the samples coarsely (e.g. 3 × 3 cm) with a knife and putting them into the freezer (e.g. at ≤ −18 °C overnight) prior to comminution facilitates processing.

5.4 Sample homogenization

5.4.1 General considerations

For fresh products (e.g. fruits and vegetables), homogenization at ambient or refrigerator temperature is possible, but cryogenic milling is to be preferred in most cases, as it minimizes losses of susceptible analytes, and usually results in smaller particle sizes and a higher degree of homogeneity. In the case of fresh, non-frozen products, keep the time gap between homogenization and extraction as short as possible to minimize degradation of susceptible target analytes.

Cryogenic milling (additionally assisted by dry ice or liquid nitrogen (A.1.12)) typically further improves homogenization of commodities with tough skins (e.g. tomatoes or grapes). When test samples are processed at low temperatures, take measures to minimize the condensation of humidity on the sample. Residual carbon dioxide should be allowed to sufficiently dissipate, so that its contribution to the sample weight will be negligible. For the homogenization using liquid nitrogen, the sample material (e.g. entire units or coarsely cut units) is immersed into a suitable plastic container (e.g. PP or polystyrene) containing

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liquid nitrogen. When completely frozen, it is transferred into a powerful knife mill and ground until a fine powder is obtained. The frozen powder should be transferred quickly into a storage container. Make sure that all liquid nitrogen is evaporated before tightly closing the storage container and placing it into the freezer.

For dry commodities, the aim of milling is to produce particle sizes that are < 1 mm. Smaller particle sizes will facilitate extraction. However, be aware that friction during milling can cause very high temperatures. Cryo-milling involving addition of liquid nitrogen or dry ice helps to keep temperatures low. The use of ultra-centrifugal mills with ring-filters helps to limit the maximum particle size. Milling by a knife mill usually result in a broad particle distribution. A two-step milling typically helps to reduce the average particle size further. When dealing with dry commodities with high oil content, extensive milling with a knife mill and milling with ultra-centrifugal mills often leads to the formation of a paste due to the release of liquid oil. Cryo-milling is to be preferred for such samples. Homogenates of dry commodities should be optimally also stored in the freezer, although analyte stability under ambient conditions is typically much better than in liquid homogenates.

NOTE Upon comminution (including the coarse cutting mentioned above) of non-frozen high moisture content samples (e.g. fruits and vegetables) matrix-juices are released that can accelerate the degradation of certain susceptible pesticides with which they come in contact. This includes pesticides located on the skin of products, which get exposed to fruit juices when coarsely cut pieces (later used for cryo-milling) are mixed in a bag.

5.4.2 Preparation of homogenates of dried fruit and similar commodities

Dried fruits and similar commodities (~15 % to ≤ 40 % moisture-content) can be processed as a slurry or in deep frozen state without addition of water. For the processing as a slurry, weigh 500 g of frozen dried fruits, add X g of cold water (A.1.1) (see Table 1 and Table B.1) and homogenize the mixture using a strong mixer (A.2.1), if possible, with addition of dry ice (A.1.12) to prevent or slow-down any chemical and enzymatic reactions. For extractions according to E3 (See Table 2), weigh Y g of homogenate (see Table 1 and Table B.1 corresponding to 5 g sample). Alternatively, immerse the sample material into a plastic or polystyrene container containing liquid nitrogen. When completely frozen, transfer it into a powerful knife mill and grind until a fine powder is obtained. Do not mill for too long and quickly transfer the frozen powder into a storage container and place it into the freezer to avoid that it becomes clumpy and more difficult to handle.

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Table 1 — Dried fruits/water proportion during homogenization

Moisture content of product	Amount of sample	Water amount added	Weight of analytical portion (Y g; corresponding to 5 g of original dry sample)
%	g	X g	g
~15 to < 25	500	900	14
25 to < 35	500	850	13,5
≥ 35 to 40	500	800	13

Freeze-dried fruit and vegetables (typical moisture content 0,3 % to 4 %) are homogenized with a high speed knife mill (A.2.1), preferably after adding dry ice or liquid nitrogen (A.1.12) to keep the material cool. Thereof, 2 g sample is employed for analysis (as in the case of other dry extract-rich commodities such as spices and dried herbs).

5.5 Analytical test portion

One or more individual test portions, each sufficient for one analysis, should be taken from the sample homogenate, prepared as described above. If the test sample was stored prior to weighing the analytical portions and it is noticed, that the homogeneity of the test sample has been compromised during storage, the test sample shall be mixed again before taking test portions, to ensure that homogeneity has been re-established.

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If fresh products are homogenized in a non-frozen state, the test portions should be weighed and analysed immediately after milling, unless it could be demonstrated, that no significant degradation of target analytes occurs in the time period between comminution and start of analysis. If the test portions cannot be analysed directly, they shall be frozen until required. Keep in mind that in such non-frozen liquid homogenates a separation of flesh and juice can occur and potentially increase portion-to-portion variability. Thus stir the homogenate well before weighing.

6 Procedure

The extraction is described in modules E1 to E7 (Table 2). Depending on the commodity, the centrifuged raw extracts are either filtered and directly subjected to the measurement modules M1 to M5 (Table 5) or cleaned-up prior to measurement by one or more of the clean-up modules C1 to C4 (Table 3). A dilution module DL (Table 4) prior to measurement is either indicated or recommended, but this also depends on the sensitivity of the instrumentation used. The residue concentrations in the samples can be calculated using the quantification approaches described under Q1 to Q6 (see Table 6 with reference to calibration procedures in CEN/TS 17061:2019). For the application of the Q-Modules a decision tree can be found under [11]. Further calibration/quantification procedures can be found under CEN/TS 17061:2019.

Preferred combinations of modules for a multitude of raw and processed commodities, concerning the extraction of samples and clean-up of raw extracts are listed in Table B.1.

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Table 2 — Extraction modules

Module	Short description[a]	Preferred application[b] and restrictions	Examples / Remarks [b]
E1	Extraction of 10 g sample without water addition	Commodities with high water content (≥80 %)	Fruit, vegetables, juices
E2	Extraction of 10 g sample after addition of, e.g. I. Two ml water II. 2,5 ml water III. Three ml water IV. 3,5 ml water	Commodities with average water content (>40 % to < 80 %)	I. Potato, parsley II. Banana, horseradish, fresh peas, ginger III. Avocado, olive, IV. Garlic
E3	Extraction of e.g. 13,5 g homogenate that was prepared with the addition of water, see Table 1	Commodities with low water content (15 % to 40 %)	Dried fruits and similar products (e.g. jams)
E4	Extraction of 5 g honey after addition of 7,5 ml water	Honey	
E5a	Extraction of 2 g or 5 g sample after addition of 10 ml water	Commodities with very low water content (<15 %). **Restrictions**: Not recommended for pesticides and metabolites containing a phosphonic acid moiety (e.g. glyphosate, AMPA, MPPA) see E5b.	<u>Low lipid content:</u> Refined cereals, pseudo cereals, pulses, skimmed milk powder. <u>High lipid content:</u> Whole grain cereals, oilseeds, nuts, spices, herbs, milk powder, infant formula.
E5b	Extraction of 2 g or 5 g sample after addition of 9 ml water, 1 ml 10 % EDTA, 0,1 ml formic acid	Commodities with very low water content (<15 %). Recommended for pesticides and metabolites containing a phosphonic acid moiety (e.g. glyphosate, AMPA, MPPA).	
E6a	Extraction of 10 g sample after addition of, e.g. … I. One ml water II. 1,5 ml water III. Two ml water IV. 2,5 ml water V. Three ml water	Commodities of animal origin with water content (>30 %). **Restrictions**: Not recommended for pesticides and metabolites containing a phosphonic acid moiety (e.g. glyphosate, AMPA, MPPA) see E6b.	I. Skimmed milk (low lipid content) II. Whole fat milk III. Kidney, fish IV. Egg, muscle V. Liver

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Module	Short description[a]	Preferred application[b] and restrictions	Examples / Remarks [b]
E6b	Extraction of 10 g sample after addition of water/10 % EDTA / formic acid, e.g. as follows: I. 0/1/0,1 ml II. 0,5/1/0,1 ml III. 1/1/0,1 ml IV. 1,5/1/0,1 ml V. 2/1/0,1 ml	Commodities of animal origin with water content (>30 %). Recommended for pesticides and metabolites containing a phosphonic acid moiety (e.g. glyphosate, AMPA, MPPA).	In the case of processed meat products increase the amount of water (e.g.: in the case of cured ham with 50 % moisture add 5 ml of water or 4/1/0,1 ml of water/10 % EDTA/formic acid to 10 g sample)
E7	Extraction of 5 g fat sample assisted by mechanical aids (e.g. metal balls)	Fats (lipids that have a non-liquid, e.g. solid, waxy or pasty consistency at room temperature)	Fats of animal and plant origin

[a] The indication “without water addition” refers to procedures where IL-IS is added before any aliquotation of the extract. Where IL-IS is not used or where it is added to an aliquot of the extract, water adjustment is indicated up to a total volume of 10 ml (sample water + added water) to reduce the bias

[b] Water contents of the various commodities can be found in Table B.1

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Table 3 — Clean-up modules

Module	Description	Preferred applications	Examples
C0	No clean-up	Most fruits and vegetables	
C1	Freeze-out for the precipitation of poorly soluble co-extractives or to assist filtration	Commodities, of which the extracts show difficulties in filtration or contain co-extractives that precipitate at low temperatures (e.g. lipids, sugars, proteins)	Raw extracts of e.g. pineapples, potatoes, cereal flours (especially if finely milled), avocado, olives, strawberries
C2	Dispersive SPE with C18-sorbent	Commodities containing high lipid and low protein content	Avocado, olives
C3a	Precipitation with acetonitrile for removal of proteins and other co-extractives with limited solubility in acetonitrile	Commodities containing high protein content	Refined cereals, pseudo cereals, pulses, skimmed milk powder
C3b	Precipitation with acetonitrile combined with C18 sorbent for removal of proteins, lipids and other co-extractives with limited solubility in acetonitrile	Commodities containing high protein and high lipid content	Oilseeds, nuts, cereals, liver, kidney, whole fat milk, muscle
C4	Ultrafiltration using cut-off filters of 5 kDa or 10 kDa	Commodities with high protein content	Oilseeds, nuts, pulses, cereals, pseudo cereals, liver, kidney, whole fat milk, muscle

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Table 4 — Dilution modules - exemplary

Module DLx[a]	Description of dilution [b]	Circumstances (indicative)[c]	Examples / Recommendations
DL1	Undiluted extracts	• Measurement of undiluted extracts possible with satisfactory performance • Analyte sensitivity does not allow dilution, but matrix effects (compared to calibration) are negligible (<ca. ± 20 %) or sufficiently compensated (e.g. via IL-IS or matrix matching)	
DL2	2-fold dilution (V_1 + V_2, 1 + 1)	• Considerable (non-negligible) matrix effects (e.g. between ± 20 % and ± 40 %), that are not sufficiently compensated otherwise (e.g. via IL-IS or matrix matching) • See also general goals and preconditions below	• DL2 prior to analysis by M3a or M3b of sample extracts of E5b and E6b (with EDTA) following C3 or C3a (instrument sensitivity allowing)
DLx 5 to 10 e.g. x = 5 (DL5); x = 10 (DL10)	5-fold dilution (V_1 + V_2, 1+4) 10-fold (V_1 + V_2, 1+9)	• Strong matrix effects (e.g. between ± 40 % and ± 90 %) that are not sufficiently compensated otherwise (e.g. via IL-IS or matrix matching) • Heavy matrix load in extract, that affects performance or robustness of measurement • See also general goals and preconditions below	• DL10 for analysis of chlorate, perchlorate, phosphonic acid, bromide by M3b • DL5 when using IC-MS/MS (M4 or M5) • DL5 prior to analysis by M3a or M3b of sample extracts of E5b and E6b (with EDTA) following C3a or C3b (instrument sensitivity allowing)
DLx > 10 e.g. x = 50 (DL50)	50-fold dilution (V_1 + V_2, 1+49)	• Very strong matrix effects (e.g. > ± 90 %) that are not sufficiently compensated otherwise (e.g. via IL-IS or matrix matching) • Heavy matrix load in extract, that affects performance or robustness of measurement • See also general goals and preconditions below	• For quantitation of bromide (high MRLs and high background levels) (instrument sensitivity allowing)

[a] The module number indicates the dilution factor and serves the documentation of the procedure. Any dilution factor can be used as long as preconditions (see list after Table 4) are met.

[b] Dilutions can be accomplished by mixing a certain volume of the extract (V_1) with a certain volume of a water-miscible solvent (V_2), which may be a LC-mobile phase eluent (see A.6). Dilution can be part of the LC- or IC-injection process. In case the dilution induces a precipitation, filtration with syringe filter (A.2.11) is recommended after dilution. Dilutions with blank sample extracts are also possible and sometimes reasonable (e.g. for keeping matrix effects similar).

[c] Explanation on matrix effects: A signal shift (i.e. suppression or enhancement) of e.g. 90 % is specified as follows in this document: ± 90 %

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When applying Table 4, general goals of dilution are to:

- reduce matrix effects,
- reduce retention time shifts,
- improve peak shapes,
- improve chromatographic separation from interfering compounds,
- obtain a signal within the calibration range/ linear range,
- reduce exposure of measurement instrument to matrix (increase long term robustness and reduce maintenance intervals).

Thereby, general preconditions for dilution are that the:

- signal intensities of analyte(s) and IL-IS(s) remain satisfactory after dilution,
- any shifts of matrix effects are adequately addressed.

Table 5 — Measurement modules

Module	Instrument details	Exemplary Analytes	Exemplary Columns
M1	LC-MS/MS HILIC phase ESI neg. mode	Glyphosate, Glufosinate, Fosetyl, Chlorate, Perchlorate, etc.	APPC[a] Torus DEA[a] Raptor Polar X[c] Obelisc N[d] Trinity Q1[b] Luna Polar Pesticide[e]
M2	LC-MS/MS HILIC phase ESI pos. mode	Chlormequat, Mepiquat, Cyromazine, Matrine, Nicotine, etc.	Amide BEH[a] Obelisc R[d] Trinity P1[b]
M3	LC-MS/MS Porous graphitic carbon phase ESI neg. mode	Glyphosate, Glufosinate, Fosetyl, Chlorate, Perchlorate, etc.	Hypercarb[b]
M4	IC-MS/MS Anion exchange phase ESI neg. mode	Glyphosate, Glufosinate, Fosetyl, Chlorate, Perchlorate, etc.	AS19[b] AS24[b]

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