SLOVENSKI STANDARD
SIST EN 15742:2020

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Krma: metode vzorčenja in analize - Določevanje OCP z GC/ECD

Animal feeding stuffs: Methods of sampling and analysis - Determination of OCPs by GC/ECD

Futtermittel - Probenahme- und Untersuchungsverfahren - Bestimmung von OCP mittels GC-ECD

Aliments des animaux: Méthodes d'échantillonnage et d'analyse - Dosage des pesticides organochlorés (POC) par CPG/ECD

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

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Contents

Page

European foreword

This document (EN 15742:2020) has been prepared by Technical Committee CEN/TC 327 “Animal feeding stuffs: Methods of sampling and analysis”, the secretariat of which is held by NEN.

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of an identical text or by endorsement, at the latest by September 2020, and conflicting national standards shall be withdrawn at the latest by September 2020.

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 15742:2009.

In comparison with the previous edition, the following technical modifications have been made:

The analysis of polychlorinated biphenyls (PCBs) has been removed from this standard as current legislation on maximum limits requires sensitivity that cannot be provided by GC-ECD. Additionally, editorial changes were made.

This document has been prepared under a standardization request given to CEN by the European Commission and the European Free Trade Association.

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.

Introduction

This document was developed in response to Directive 2002/32/EC of the European Parliament and the Council of 7 May 2002 on undesirable substances in animal feed.

The previous edition of this document (EN 15742:2009) was fully validated by means of a collaborative study for aldrin, dieldrin, endrin, p,p'-DDT, o,p'-DDT, p,p'-TDE, pp-DDE, alpha-endosulfan, beta-endosulfan, HCB, alpha-HCH, beta-HCH and gamma-HCH. Attempts in the framework of the third Mandate from the European Commission to CEN/TC 327 to perform additional validation of the method through a full collaborative study (2017) for photo heptachlor, cis/trans nonachlor and keto-endrin were unsuccessful as no more than three laboratories volunteered to send in results [1].

WARNING — The use of this document can involve hazardous materials, operations and equipment. This standard does not purport to address all the safety problems associated with its use. It is the responsibility of the user of this European Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This document specifies a gas chromatographic method with electron capture detection (ECD) for the determination of organochlorine pesticides (OCPs) in compound feeds and oil and fats.

The method is applicable to animal compound feed, oils and fats and fish meals with a water content up to about 20 % by weight and oil/fatty samples containing residues of one or more of the following OCPs, toxaphene and some of their isomers and degradation products:

— aldrin;

— dieldrin;

— dichlorodiphenyltrichloroethane (DDT) (the isomers 'op'-DDT', 'pp'-DDT', 'pp'-TDE' ('pp'-DDD'), and 'pp'-DDE');

— endosulfan (as the sum of α-/β-isomers);

— endrin;

— hexachlorobenzene (HCB);

— hexachlorocyclohexane isomers α-HCH (α-BHC), β-HCH (β-BHC), γ-HCH (γ-BHC or lindane);

For the following OCPs, the method is considered a screening method. Additional in-house validation is required for reporting validated data.

— chlordane (as the sum of chlordane isomers and oxychlordane);

— endosulfan-sulphate;

— delta-keto-endrin;

— heptachlor (as the sum of heptachlor and heptachlor epoxide);

— photo-heptachlor;

— *cis*- and *trans*-nonachlor.

A limit of quantification (LOQ) for the mentioned OCPs of 5 µg/kg is intended to be obtained. However, 10 µg/kg applies for heptachlor, aldrin, endrin, dieldrin, and endosulfan (α-/β– and sulphate). Individual laboratories are responsible for ensuring that the equipment that they use, achieves these limits of quantifications. The LOQs apply to the individual OCPs.

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.

EN ISO 6498, *Animal feeding stuffs - Guidelines for sample preparation (ISO 6498)*

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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 https://www.iso.org/obp

3.1
limit of detection
smallest measured content, from which it is possible to deduce the presence of the analyte with reasonable statistical certainty

Note 1 to entry: The limit of detection is numerically equal to three times the standard deviation of the mean of blanc determinations (n > 10).

3.2
limit of quantification
lowest content of the analyte which can be measured with reasonable statistical certainty

Note 1 to entry: If both accuracy and precision are constant over a concentration range around the limit of detection, then the limit of quantification is numerically equal to 6 times the standard deviation of the mean of blanc determinations (n > 10).

4 Principle

In order to check for the presence of OCPs, a test portion of animal feeding stuff is fortified with internal standard (PCB 198), and is extracted with ethyl acetate. The extract is concentrated and subsequently purified by:

— gel permeation chromatography (GPC), with cyclohexane or ethyl acetate as eluting solvent;

— chromatography on partially deactivated silica gel.

The collected fraction containing the compounds of interest is concentrated and re-dissolved in a solution containing another internal standard (PCB 209) as a reference standard. After clean up, the analytes are measured using GC-ECD. Identification is done on the basis of comparing retention times on capillary columns of different polarity. Quantification is done using the internal standard method.

5 Reagents and materials

5.1 General

Use only reagents of recognized analytical grade and with a purity suitable for OCP and PCB residue analysis. Check the purity of the reagents by performing a blanc test under the same conditions as used in the method. The chromatogram should not show any interfering impurity at the retention time of compounds of interest.

5.2 Chemicals

5.2.1 Cyclohexane

5.2.2 Ethyl acetate

5.2.3 Hexane

5.2.4 Dichloromethane

5.2.5 Iso-octane

5.2.6 Toluene

5.2.7 Hexane/toluene = 3+7, parts by volume

Mix 30 ml of hexane (5.2.3) with 70 ml of toluene (5.2.6) thoroughly. Store at room temperature in a tightly closed glass bottle.

5.2.8 Sodium sulphate, anhydrous

Heated to 160 °C to 200 °C during at least 24 h.

5.2.9 Ethyl acetate/cyclohexane = 1+1, parts by volume

Mix 500 ml of ethyl acetate (5.2.2) with 500 ml of cyclohexane (5.2.1) thoroughly. Store at room temperature in a tightly closed glass bottle.

5.2.10 Silica gel, deactivated with 3,5 % water

Heat silica gel 60 (63 µm to 200 µm = 70 mesh to 230 mesh), at 130 °C for at least 5 h, allow to cool in a desiccator, and store in a tightly stopped container in the desiccator.

Add 3,5 ml water dropwise from a burette, with continuous swirling, to 96,5 g dried silica gel in a 300 ml Erlenmeyer flask with a ground joint.

Immediately stopper the flask with a ground stopper and shake vigorously for 5 min until all lumps have disappeared.

Next, shake for 2 h on a mechanical shaker, and then store in a tightly stoppered container.

Deactivated silica gel is tenable during approximately 2 weeks if carefully stored.

5.2.11 Internal standard (PCB 198)

5.2.12 Internal Standard (PCB 209)

5.2.13 OCP reference standards, each with a purity not less than 99 %:

Aldrin

(1R,4S,4aS,5S,8R,8aR)-1,2,3,4,10,10-hexachloro-1,4,4a,5,8,8a-hexahydro-1,4:5,8-dimethanonaphthalene; CAS Number: 309-00-2.

Dieldrin

(1R,4S,4aS,5R,6R,7S,8S,8aR)-1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-6,7epoxy-1,4:5,8-dimethanonaphthalene; CAS Number: 60-57-1.

Delta-keto-endrin

CAS Number 53494-70-5.

Chlordane, α isomer

|1,2,4,5,6,7,8,8 octachloro-2,3,3a,4,7,7a-hexahydro-4,7-ethano-1H-indene; α isomer; CAS Number: 5103-71-9.

Chlordane, β isomer

1,2,4,5,6,7,8,8-octachloro-2,3,3a,4,7,7a-hexahydro-4,7-ethano-1H-indene; β isomer; CAS Number: 5103-74-2.

Oxychlordane

4,7-Methanoindan, 1,2,4,5,6,7,8,8-octachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-, exo, endo-; CAS Number: 27304-13-8.

'op'-DDT' 1,1,1-trichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane ; CAS Number: 789-02-6.

'pp'-DDT' 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane ; CAS Number: 50-29-3.

'pp'-TDE'

('p,p'-DDD')1,1-dichloro-2,2-bis(4-chlorophenyl) ethane; CAS Number: 72-54-8.

'pp'-DDE' 1,1-dichloro-2,2-bis(4-chlorophenyl) ethylene; CAS Number: 72-55-9.

Endosulfan, α stereoisomer

6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3-oxide, (3α, 5aβ, 6α, 9α, 9aβ); CAS Number: 959-98-8.

Endosulfan, β stereoisomer

6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3-oxide, (3α,5aα,6β,9β,9aα); CAS Number: 33213-65-9;

Endosulfan sulphate

6,9-Methano-2,4,3-benzodioxathiepin, 6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-, 3,3-dioxide; CAS Number: 1031-07-8.

Endrin
(1R,4S,4aS,5S,6S,7R,8R,8aR)-1,2,3,4,10,10-hexachloro-1,4,4a,5,6,7,8,8a-octahydro-6,7-epoxy-1,4:5,8-dimethanonaphthalene; CAS Number: 72-20-8;

Delta-keto endrin

2,5,7-Metheno-3H-cyclopenta[a]pentalen-3-one,3b,4,5,6,6,6a-hexachlorodecahydro-, (2α, 3aβ,3bβ,4β,5β,6aβ,7α7aβ,8R); CAS 53494-70-5;

Heptachlor

1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene; CAS Number: 76-44-8.

β-Heptachlor epoxide

1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene(exo); CAS Number: 1024-57-3.

HCB
hexachlorobenzene; CAS Number: 118-74-1.

α-HCH (α-BHC)

α-1,2,3,4,5,6-hexachlorocyclohexane; CAS Number: 319-84-6.

β-HCH (β-BHC)

β-1,2,3,4,5,6-hexachlorocyclohexane; CAS Number: 319-85-7.

γ-HCH (γ-BHC; lindane)

γ-1,2,3,4,5,6-hexachlorocyclohexane; CAS Number: 58-89-9.

Photoheptachlor

CAS Number 33442-83-0.

Cis-nonachlor

CAS Number 5103-73-1.

Trans-nonachlor

CAS Number 39765-80-5.

Alternatively to each individual OCP reference standard listed above, use a certified mixture at a concentration of 10 µg/ml.

5.2.14 Chlorocamphene (toxaphene)

5.3 Stock solutions, 100 µg/ml

Weigh 5 mg–10 mg (±0,01 mg) of each compound (5.2.11, 5.2.12, 5.2.13 and 5.2.14) in separate brown medicine glass bottles of 100 ml and add iso-octane (5.2.5.) to achieve a concentration of 100 µg/ml.

Store the solutions in a refrigerator at 4 °C (±3 °C). The solution is tenable under these conditions during at least 5 years if the weight is carefully controlled.

Dissolve ß-HCH in 10 ml toluene (5.3), to achieve complete solvability and dilute further with iso-octane (5.2.5) to achieve a concentration of 100 µg/ml.

5.4 Mixed stock solutions

5.4.1 Mixed stock solution OCP (without endosulfan and toxaphene)

Pipet of each OCP-stock solution (5.3) the indicated volume (Table 1) in a volumetric flask of 100 ml. Fill up to 100 ml with iso-octane (5.2.5) and mix. The achieved concentration is given in Table 1. Transport this solution to a brown medicine glass bottle of 100 ml and store it in a refrigerator at 4 °C (±3 °C). The solution is tenable under these conditions during at least 5 years if the weight is carefully controlled.

5.4.2 Mixed stock solution endosulfan

Pipet of each endosulfan-stock solution (5.3) the indicated volume (Table 1) in a volumetric flask of 100 ml. Fill up to 100 ml with iso-octane (5.2.5) and mix. The achieved concentration is given in Table 1. Transport this solution to a brown medicine glass bottle of 100 ml and store it in a refrigerator at 4 °C (±3 °C). The solution is tenable under these conditions during at least 5 years if the weight is carefully controlled.

Table 1 — Concentration of OCPs in mixed stock solution (5.4) and mixed standard solution (5.5)

Compound	Pipet volume (ml)	Mixed stock solution (5.4.1 and 5.4.2) (µg/ml)	Mixed standard solution (5.5.1 and 5.5.2) (µg/ml)
aldrin	2,0	2,0	0,10
dieldrin	2,0	2,0	0,10
α-chlordane	1,0	1,0	0,05
γ-chlordane	1,0	1,0	0,05
oxychlordane	1,0	1,0	0,05