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SIST EN 12396-3:2001

01-februar-2001

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Non-fatty foods - Determination of dithiocarbamate and thiuram disulfide residues - Part 3: UV spectrometric xanthogenate method

Fettarme Lebensmittel - Bestimmung von Dithiocarbamat- und Thiuramdisulfid-Rückständen - Teil 3: UV-Spektralphotometrisches Xanthogenat-Verfahren

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Aliments non gras - Détermination des résidus de dithiocarbamates et de bisulfures de thiurame - Partie 3: Méthode spectrométrique UV utilisant le xanthogénate

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ICS:

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

SIST EN 12396-3:2001 **en**

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EUROPEAN STANDARD

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English version

Non-fatty foods - Determination of dithiocarbamate and thiuram disulfide residues - Part 3: UV spectrometric xanthogenate method

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This European Standard was approved by CEN on 8 April 2000.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

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COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

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Foreword

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This European Standard 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of an identical text or by endorsement, at the latest by November 2000, and conflicting national standards shall be withdrawn at the latest by November 2000.

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This European Standard EN 12396 "Non-fatty food - Determination of dithiocarbamate and thiuram disulfide residues" consists of three parts:

Part 1: Spectrometric method

Part 2: Gas chromatographic method

Part 3: UV spectrometric xanthogenate method

Annex A is informative.

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

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1 Scope

This European Standard specifies a UV spectrometric method for the determination of low-level residues of dithiocarbamate and thiuram disulfide fungicides as xanthogenate. Dithiocarbamate and thiuram disulfide fungicides release carbon disulfide under specified conditions (e.g. mancozeb, maneb, propineb, thiram, zineb). It is applicable to such compounds especially in and on those foodstuffs of plant origin for which low maximum residue levels have been set.

Only the quantification of the whole group is possible using this method and not the identification of individual compounds. Generally the maximum residue levels (MRLs) are expressed in terms of carbon disulfide.

2 Normative references

This European Standard incorporates, by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies.

ISO 1750 Pesticides and other agrochemicals - Common names

EN 12393-1:1998 Non-fatty foods - Multiresidue methods for the gas chromatographic determination of pesticide residues - Part 1: General considerations

EN 12396-1:1998 Non-fatty foods - Determination of dithiocarbamate and thiuram disulfide residues - Part 1: Spectrometric method

EN 12396-2:1998 Non-fatty foods - Determination of dithiocarbamate and thiuram disulfide residues - Part 2: Gas chromatographic method

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3 Principle

The sample is heated with hydrochloric acid and tin(II)chloride to release carbon disulfide from any dithiocarbamates and/or thiram disulfides present. The carbon disulfide is separated and purified by distillation and collected in a methanolic potassium hydroxide solution. Under these conditions, carbon disulfide forms potassium xanthogenate. The absorption of this reaction product is measured spectrometrically at a wavelength of 302 nm with base line correction at wavelengths of 272 nm and 332 nm. The mass fraction of dithiocarbamate and/or thiuram disulfide residues is calculated and expressed in terms of milligrams of carbon disulfide per kilogram of foodstuff. For further information on this method, see [1], [2], [3].

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4 Reagents

4.1 General

Unless otherwise specified, use reagents of recognized analytical grade, preferably for pesticide residue analysis and distilled or demineralized water.

Label all standard containers with the name and purity of all pesticides. For the full chemical names and structures, see ISO 1750.

Take every precaution to avoid possible contamination of water, solvents, inorganic salts etc. by plastics and rubber materials. Use only glass containers for storage and handling of all water and reagents.

4.2 Carbon disulfide, colourless, mass fraction of at least 99%. If stored at -20 °C it is stable for 2 years to 3 years.

4.3 Methanol

4.4 Hydrochloric acid, concentrated, ρ_{20} (HCl) = 1,16 g/ml.

4.5 Sulfuric acid, concentrated, ρ_{20} (H_2SO_4) = 1,84 g/ml.

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4.6 Sodium hydroxide solution, ρ (NaOH) = 100 g/l[1])

4.7 Potassium hydroxide methanolic solution I, ρ (KOH) = 28 g/l in methanol (4.3).

4.8 Potassium hydroxide methanolic solution II, ρ (KOH) = 56 g/l in methanol (4.3).

4.9 Tin(II)chloride solution, ρ ($SnCl_2$ $2H_2O$) = 40 g/100 ml in concentrated hydrochloric acid (4.4).

4.10 Tin(II)chloride - hydrochloric acid solution, ρ ($SnCl_2$ x 2 H_2O) = 3,3 g/100 ml.

Mix 20 ml of tin(II)chloride solution (4.9) with 20 ml of concentrated hydrochloric acid (4.4) and carefully add 200 ml of water.

4.11 Carbon disulfide stock solution

Weigh to the nearest 10 mg a stoppered 50 ml volumetric flask with a ground glass neck containing 40 ml of methanol (4.3). Add approximately 1 ml of carbon disulfide (4.2) (equivalent to approximately 1,25 g) using a pipette, close the flask at once and re-weigh to the nearest 10 mg to obtain the exact mass of carbon disulfide by difference. Dilute to the mark with methanol and mix well. Prepare freshly for each calibration curve.

4.12 Carbon disulfide standard solution

Dilute 1 ml of carbon disulfide stock solution (4.11) with methanol (4.3) to 25 ml in a volumetric flask. Dilute 1 ml of this solution with methanol to 100 ml in a volumetric flask. 1 ml of this standard solution is equivalent to approximately 10 µg of carbon disulfide. Prepare freshly for each calibration curve.

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5 Apparatus

5.1 General

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Thoroughly clean glassware shall be used.

See 5.1 of prEN 12393-1:1998 for the cleaning of glassware.

5.2 Decomposition and distillation apparatus, consisting of a 1 l or a 2 l round bottomed three necked flask or cylindrical flask with a three necked adapter, a dropping funnel, a gas inlet tube, an ascending Liebig condenser, four absorption tubes, the last two preferably fitted with a Widmer helix, connected by spherical socket joints, the first being attached to the Liebig condenser, (see figure 1).

[1]) ρ is the mass concentration

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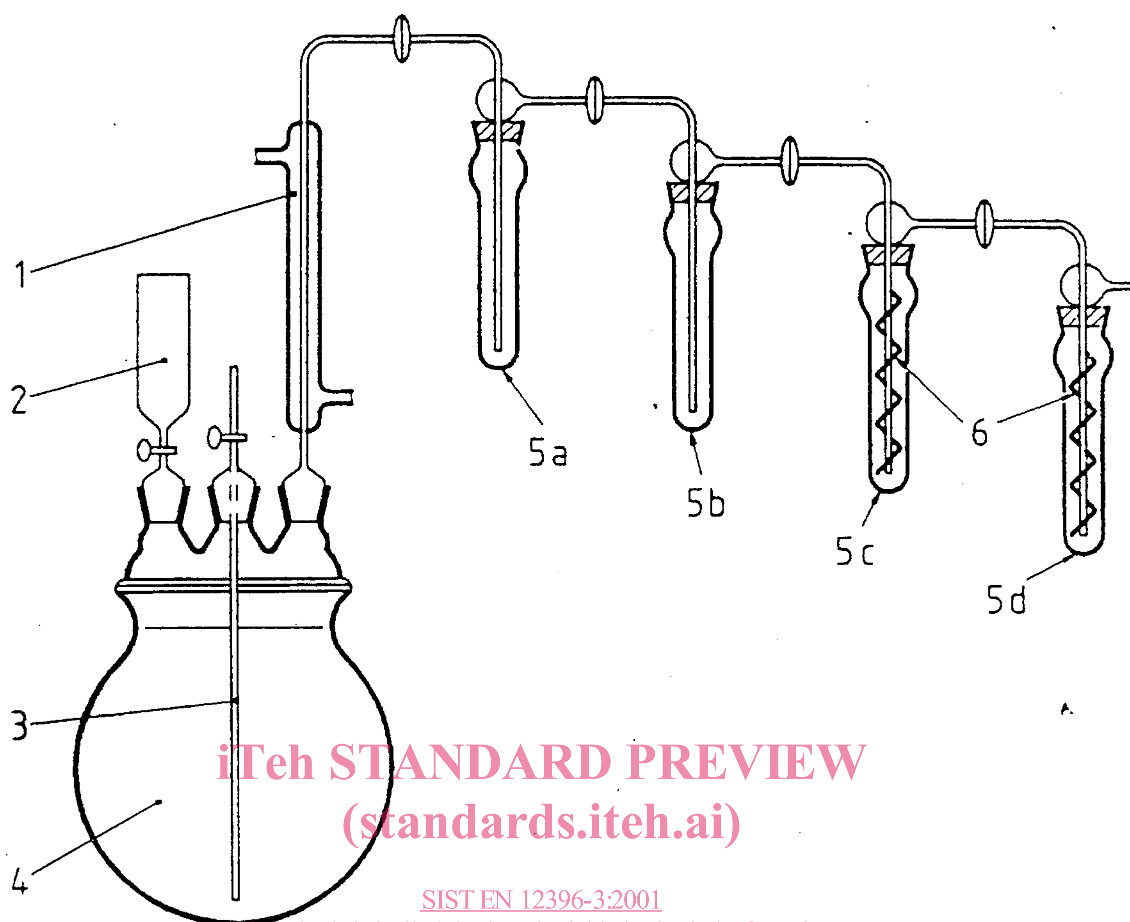

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1 = Liebig condenser

2 = dropping funnel

3 = gas inlet tube

4 = cylindrical flask or round bottomed flask

5 = absorption tubes

6 = Widmer helix

Figure 1: Decomposition and distillation apparatus

5.3 Flowmeter

5.4 Heating mantle, electrically operated, at least 450 W; or gas burner fitted with a Babo funnel and flask holder.

5.5 Spectrometer, suitable for measurements at wavelengths from 270 nm to 350 nm, with 1 cm quartz cells. A double beam spectrometer should preferably be used.

5.6 Low vacuum pump, attached to the last absorption tube, or a source of nitrogen under pressure, attached to the gas inlet tube.

6 Sampling

Prepare the laboratory sample according to a generally recommended method of sampling to achieve a representative part of the product to be analysed.

NOTE: Sampling procedures for the official control of pesticide residues in and on fruits and vegetables are given in EEC directive 79/700/EEC [4].

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7 Preparation of the samples

7.1 Test sample

If the sample reaches the laboratory frozen, store it at - 20 °C before analysis.

Where possible, carry out the analysis of fresh samples immediately after their arrival in the laboratory. Do not analyse a laboratory sample which is wholly or extensively spoiled.

For analysis take only the portion of the laboratory sample to which the maximum residue limit applies. No further plant-parts may be removed. A record of the plant-parts which have been removed shall be kept. The sample thus prepared is the analytical sample.

If the sample cannot be analyzed immediately, store it at 0 °C to 5 °C for no longer than 2 days before analysis.

The reduction of the analytical sample shall be carried out in such a way that representative portions are obtained (e.g. by division into four and selection of opposite quadrants). When the samples are in small units (e.g. small fruits, vegetables, cereals), the analytical sample shall be thoroughly mixed before weighing out the test portion. When the samples are in larger units, take wedge-shaped sections (e.g. large fruits and vegetables) or cross sections (e.g. cucumbers) which include the outer surface from each unit.

NOTE: The residues of dithiocarbamates and thiuram disulfides, which are on the surface of the plant-parts and are not systemic, decompose rapidly especially in chopped samples. Therefore precautions should be taken to avoid decomposition.

If samples have to be stored for more than 2 days, they shall be deep-frozen at - 20 °C. To ensure that even after thawing representative samples can be taken, prepare portions of the product which are each sufficient for one analysis.

7.2 Test portion

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Weigh out test portions of masses up to 200 g to an accuracy of ± 1 %. After weighing out the test portion, remove certain parts which would interfere with the analytical procedure. In the case of stone fruits, the stones may be removed after weighing out. The basis for the calculation of the residue mass fraction is the mass of the original test portion (with stones).

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The test portion shall not be cut or reduced to smaller pieces than can just pass the neck of the reaction flask, as the residues of dithiocarbamates and thiuram disulfides fall the more the test portion is cut.

Analyse the test portion immediately after cutting.

8 Procedure

8.1 Safety aspects

WARNING: Many dithiocarbamates, thiuram disulfides and carbon disulfide are toxic by various routes of exposure, especially in concentrated form. When working with dithiocarbamates, thiuram disulfides and carbon disulfide consult safety data sheets of the manufacturer for information.

Vapours from some volatile solvents are toxic. Several of these solvents are readily absorbed through skin. Use effective fume hoods to remove vapours of these solvents as they are set free.

8.2 Preparation of blanks

Prepare reagent and matrix blanks. Spiked recovery tests at levels appropriate to the maximum residue levels shall be carried out and shall lead to satisfying results.

The absorption for the reagent blanks measured at a wavelength of 302 nm against the methanolic potassium hydroxide solution I (4.7) shall be zero or near zero.

NOTE 1: Analysts should thoroughly familiarize themselves with the method before starting the analysis.

NOTE 2: Some vegetables (e.g. of the family Cruciferae) contain naturally occurring compounds which release carbon disulfide under the conditions described in this European Standard. Therefore the analysis of such vegetables can lead to false positive results.

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8.3 Preparation of the calibration curve

Add 5 ml of methanolic potassium hydroxide solution II (4.8) to each of sixteen 10 ml volumetric flasks. Then add 0,1 ml, 0,2 ml, 0,4 ml, 0,8 ml, 1,2 ml, 1,6 ml, 2 ml and 4 ml of the carbon disulfide standard solution (4.12) (equivalent to 1 µg, 2 µg, 4 µg, 8 µg, 12 µg, 16 µg, 20 µg and 40 µg of CS_2) from a graduated pipette or a burette to each of two volumetric flasks. Dilute to the mark with methanol, mix well, and let the 16 mixtures stand for 45 min. Perform the spectrometric measurement as described in 8.4.3.

Plot the values obtained for the corrected absorption on the ordinate (y axis) against the mass of carbon disulfide in each mixture on the abscissa (x axis) to obtain a calibration curve.

The calibration curve shall be linear over the range 1 µg to 40 µg carbon disulfide.

If these requirements are not fulfilled, prepare a new calibration curve using a freshly prepared set of reaction mixtures.

Alternatively carry out a regression analysis on the 16 values and plot the regression line as the calibration curve.

8.4 Measurement of the sample

8.4.1 Preparation of the apparatus

Add 20 ml of sodium hydroxide solution (4.6) to the first absorption tube in the decomposition and distillation apparatus (see figure 1) and 20 ml of sulfuric acid (4.5) to the second. To the third and the fourth absorption tubes, fitted with a Widmer helix, add 8 ml each of methanolic potassium hydroxide solution I (4.7). These tubes shall be cooled with ice water, to avoid losses of methanol.

NOTE: The fourth absorption tube containing methanolic potassium hydroxide solution is attached to check the complete absorption of the evolved carbon disulfide.

Turn on the water flow through the reflux condenser and adjust the nitrogen flow or the low vacuum pump (5.6) to give approximately 150 ml of nitrogen or air per minute passing through the absorption tubes.

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8.4.2 Decomposition and distillation

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Add a test portion of up to 200 g to the three necked flask (400 g in case of baby food). Close the apparatus. Take care to avoid any losses of carbon disulfide from the apparatus. Then add 240 ml of tin(II)chloride - hydrochloric acid solution (4.10) through the dropping funnel. If the amount of liquid is not enough for a sample of bulky crop material (e.g. lettuce) to be fully immersed, add more tin(II)chloride - hydrochloric acid solution. Then immediately heat flask contents rapidly to boiling. To reach this rapidly, especially if the material to be analysed is deep frozen, heat the tin(II)chloride - hydrochloric acid solution to boiling before adding it carefully to the flask. Continue boiling for a total period of 30 min. Then disconnect the absorption tubes containing the potassium hydroxide solution and turn off the gas flow.

8.4.3 Spectrometric measurement

Transfer the contents of the third and fourth absorption tube each to 10 ml volumetric flasks, rinse the absorption tubes with methanolic potassium hydroxide solution I (4.7) and transfer this to the flasks also. Dilute to the mark with methanolic potassium hydroxide solution I, mix and allow to stand for 15 min. Measure the absorption of this sample test solution obtained from the third absorption tube at wavelengths of 272 nm, 302 nm and 332 nm in a 1 cm path cell in the spectrometer against the methanolic potassium hydroxide solution I. From the absorption units measured at the three wavelengths, calculate the corrected absorption A_{corr} with equation (1):

$$A_{corr} = A_{302} - \frac{(A_{272} + A_{332})}{2} \qquad (1)$$

where:

A_{302} is the absorption value measured at a wavelength of 302 nm;

A_{272} is the absorption value measured at a wavelength of 272 nm;

A_{332} is the absorption value measured at a wavelength of 332 nm.