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Determination of organochlorine pesticide and pyrethroid pesticide multiresidues in animal original foods

动物性食品中有机氯农药和拟除虫菊酯农药多组分残留量的测定

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Determination of organochlorine pesticide and pyrethroid pesticide multiresidues in animal original foods

1 Scope

The method-1 of this standard specifies the determination method for the chromatography-mass spectrometry (GC-MS) of benzenehexachloride, DDT, hexachlorobenzene, heptachlor, heptachlor epoxide, chlordane, aldrin, dieldrin, endrin, mirex, pentachloronitrobenzene, endosulfan, fenson, allethrin, dichlorophenyl benzensulfonate, tetramethrin, fenpropathrin, permethrin, cypermethrin, fenralerate, deltamenthrin.

The method-2 of this standard spcifies the determination method of gas chromatography-electron capture device (GC-ECD) for the benzenethexzchloride, DDT, pentachloronitrobenzene, heptachlor, heptachlor epoxide, aldrin, dieldrin, fenson, ovex, tetramethrin, permethrin, cypermethrin, α-fenralerate, deltamethrin.

The method-1 of this standard applies to the confirmation analysis of α-benzenehexachloride, hexachlorobenzene, β-benzenehexachloride, γ-benzenehexachloride, pentachloronitrobenzene, δ-benzenehexachloride, pentachloraniline, heptachlor, pentachlorophenyl sulfide, aldrin, oxychlordane, heptachlor epoxide, trans-chlordane, α-endosulfan, cis-chlordane, p,p'-DDE, dieldrin, endrin, β-endosulfan, p,p'-DDD, o,p'-DDT, endrin aldehyde, endosulfan sulfate, p,p'-DDT, endrin ketone, mirex, fenson, allethrin, 2,4-dichlorophenyl benzensulfonate, ovex, tetramethrin, fenpropathrin, permethrin, cypermethrin, fenralerate, deltamenthrin in meat, egg, milk food, fat (including vegetable oil).

The method-2 of this standard applies to the analysis of 20 commonly-used organochlorine pesticides and pyrethroid pesticide residues such as α-benzenehexachloride, β-benzenehexachloride, γ-benzenehexachloride, δ-benzenehexachloride, pentachloronitrobenzene, heptachlor, heptachlor epoxide, aldrin, dieldrin, fenson, ovex, p,p'-DDE, p,p'-DDD, o,p'-DDT, p,p'-DDT, tetramethrin, permethrin, cypermethrin, α-fenralerate, deltamenthrin.

The detection limits (μg/kg) of various pesticides in method-1 of this standard are: α-benzenehexachloride 0.20; hexachlorobenzene 0.20; β-benzenehexachloride 0.20; γ-benzenehexachloride 0.20;

pentachloronitrobenzene 0.50; δ-benzenehexachloride 0.20; pentachloraniline 0.50; heptachlor 0.50; pentachlorophenyl sulfide 0.50; aldrin 0.50; oxychlordane 0.20; heptachlor epoxide 0.50; trans-chlordane 0.20; α-endosulfan 0.50; cis-chlordane 0.20; p,p'-DDE 0.20; dieldrin 0.20; endrin 0.50; β-endosulfan 0.50; p,p'-DDD 0.20; o,p'-DDT 0.20; endrin aldehyde 0.50; endosulfan sulfate 0.50; p,p'-DDT 0.20; endrin ketone 0.50; mirex 0.20; fenson 0.50; allethrin 0.50; 2,4-dichlorophenyl benzensulfonate 0.50; ovex 0.50; tetramethrin 1.00; fenpropathrin 1.00; permethrin 1.00; cypermethrin 2.00; fenralerate 2.00; deltamenthrin 2.00.

The detection limits (μg/kg) of various pesticides in method-2 of this standard are: α-benzenehexachloride 0.25; β-benzenehexachloride 0.50; γ-benzenehexachloride 0.25; δ-benzenehexachloride 0.25; pentachloronitrobenzene 0.25; heptachlor 0.50; heptachlor epoxide 0.50; aldrin 0.25; dieldrin 0.50; fenson 1.25; ovex 1.25; p,p'-DDT 0.50; o,p'-DDT 0.50; p,p'-DDE 0.60; p,p'-DDD 0.75, tetramethrin 12.50; permethrin 7.50; cypermethrin 2.00; α-fenralerate 2.50; deltamenthrin 2.50.

Method-1 -- Gas chromatography-mass spectrometry

2 Principles

In the homogeneous sample solution, quantitatively add the stable isotope internal standard of ^{13}C-hexachlorobenzene and ^{13}C-mirex. It is oscillated and extracted by organic solvent, purified by gel chromatography. It is determined by the gas chromatography-mass spectrometry (GC-MS) with selective ion monitoring, quantified by internal standard method.

3 Reagents

3.1 Acetone (CH_3COCH_3): Analytically pure, re-steamed.

3.2 Petroleum ether: Boiling range 30 °C ~ 60 °C, analytical pure, re-steamed.

3.3 Ethyl acetate ($CH_3COOC_2H_5$): Analytically pure, re-steamed.

3.4 Cyclohexane (C_6H_{12}): Analytically pure, re-steamed.

3.5 n-hexane ($n\text{-}C_6H_{14}$): Analytically pure, re-steamed.

3.6 Sodium chloride (NaCl): Analytically pure.

3.7 Anhydrous sodium sulfate (Na_2SO_4): Analytically pure. Place the anhydrous

$^{13}C_6$-hexachlorobenzene (6 mg/L) and 5 mL of $^{13}C_{10}$-mirex (6 mg/L). Add 40 mL of acetone. Shake it for 30 min. The rest of the operation is the same as the operation of eggs in 5.2.1 starting from “Add 6 g of sodium chloride”.

5.2.4 Fat: Weigh 1 g (accurate to 0.01 g). Add 5 μL of $^{13}C_6$-hexachlorobenzene (6 mg/L) and 5 mL of $^{13}C_{10}$-mirex (6 mg/L). Add 30 mL of petroleum ether. Shake it for 30 min. Transfer all the organic phase into a rotary evaporation flask. Concentrate it to about 1 mL. Add 2 mL of ethyl acetate-cyclohexane (1 + 1) solution for re-concentration. Repeat this operation for 3 times to concentrate it to about 1 mL, to prepare for use by gel chromatographic purification. Or otherwise transfer the concentrated solution into the sample-injection test-tube of the fully-automatic gel permeation chromatography system. Use ethyl acetate - cyclohexane (1 + 1) solution to rinse the rotary evaporation flask for several times. Combine the rinsing solution into the test-tube. Make its volume reach to 10 mL.

5.3 Purification

Choose either manual or fully-automatic purification methods.

5.3.1 Purification by manual gel column: Make the sample concentrate pass through the gel column. Use ethyl acetate-cyclohexane (1 + 1) solution to elute it. Discard the 0 mL ~ 35 mL fraction. Collect the 35 mL ~ 70 mL fraction. Make it subject to rotatory evaporation and concentration to about 1 mL. Repeat the above procedures. Collect the 35 mL ~ 70 mL fraction. Make it subject to evaporation-concentration. Use nitrogen to purge the solvent. Then use n-hexane to make its volume reach to 1 mL. Prepare for GC-MS analysis.

5.3.2 Purification by fully-automatic gel permeation chromatography system (GPC): Inject the specimen through a 5 mL sample ring into the GPC column. The pump’s flow rate is 0.5 mL/min. Use ethyl acetate-cyclohexane (1 + 1) solution to elute it. The time program is: Discard the 0 min ~ 7.5 min fraction, collect the 7.5 min ~ 15 min fraction, rinse the GPC column at 15 min ~ 20 min. Make the collected fractions subject to rotatory evaporation and concentration to about 1 mL. Use nitrogen to blow it almost dry. Use n-hexane to make its volume reach to 1 mL. Prepare for GC-MS analysis.

5.4 Determination

5.4.1 Reference conditions for gas chromatography

5.4.1.1 Column: CP-sil 8 capillary column or equivalent column. The column length is 30 m. The film thickness is 0.25 μm. The inner diameter is 0.25 mm.

5.4.1.2 Temperature at sample inlet: 230 °C.

5.4.1.3 Column temperature program: The initial temperature is 50 °C. Keep

Where:

X - The content of each pesticide component in the specimen, in micrograms per kilogram (μg/kg);

A - The mass of the target compound corresponding to the area ratio of the chromatographic peak of the specimen to the internal standard's chromatographic peak, in nanograms (ng);

f - The dilution factor of the sample solution;

m - The size of the sample, in grams (g).

For the calculation results, it retains three significant figures.

7 Precision

The absolute difference between two independent determinations obtained under repetitive conditions shall not exceed 20% of the arithmetic mean. The method uncertainty is as shown in Appendix C.

Method-2 -- Gas chromatography-electron capture detector method (GC-ECD)

8 Principle

The sample is extracted, purified, concentrated, constant-volume, separated by capillary column gas chromatography, detected by electron capture detector, qualitative-determined by the retention time, quantified by external standard method. Peak order: α-HCH, β-HCH, γ-HCH, pentachloronitrobenzene, δ-HCH, heptachlor, aldrin, fenson, heptachlor epoxide, ovex, dieldrin, p, p'-DDE, p, p'-DDD, o,p'-DDT, p,p'-DDT, tetramethrin, permethrin, cypermethrin, α-fenralerate, deltamethrin.

9 Reagents

9.1 Acetone: Re-steamed.

9.2 Dichloromethane: Re-steamed.

9.3 Ethyl acetate: Re-steamed.

10 Instruments

10.1 Gas Chromatograph: It is equipped with electron capture detector, capillary column.

10.2 Rotary evaporator.

10.3 Gel purification column: The glass chromatographic column with piston which has a length of 30 cm and an inner diameter of 2.5 cm. Fill a little glass wool at the bottom of the column. Use the wet method to put the gel which had been immersed in the eluent ethyl acetate-cyclohexane (1 + 1) in the column. The height of column is about 26 cm. Make the gel always be maintained in the eluent.

11 Analytical procedures

11.1 Preparation of specimen

Remove the shell of egg. Make it into a homogenate. Remove the tendon from meat. Cut it into small pieces. Make it into meat paste. Mix the milk products uniformly to prepare for use.

11.2 Extraction and distribution

11.2.1 Weigh 20 g of specimen (accurate to 0.01 g). Place it in a 100 mL stoppered conical flask. Add 5 mL of water (add water depending on the moisture content of the specimen, to make the total moisture content be about 20 g. Fresh egg generally contains about 75% water, so it needs adding 5 mL of water). Add 40 mL of acetone. Shake it for 30 min. Add 6 g of sodium chloride. Shake it uniformly. Then add 30 mL of petroleum ether. Shake it for 30 min. Take 35 mL of supernatant. Use anhydrous sodium sulfate to filter it into a rotary evaporation flask. Concentrate it to about 1 mL. Add 2 mL of ethyl acetate-cyclohexane (1 + 1) for re-concentration. Repeat this for 3 times. Concentrate it to about 1 mL.

11.2.2 Weigh 20 g of specimen (accurate to 0.01 g). Add 6 mL of water (add water depending on the moisture content of the specimen, to make the total moisture content be about 20 g. Fresh meat generally contains about 70% water, so it needs adding 6 mL of water). The rest of the operation is the same as the operation in 11.2.1 in terms of the procedures of extraction and distribution of egg samples.

11.2.3 Weigh 20 g of specimen (accurate to 0.01 g. Fresh milk does not need to add water, which is extracted by adding acetone directly). The rest of the operation is the same as the operation in 11.2.1 in terms of the procedures of

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