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**Leather — Chemical tests —
Determination of pesticide residues
content**

*Cuir — Essais chimiques — Détermination de la teneur en résidus de
pesticides*

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Fax: +41 22 749 09 47
Email: copyright@iso.org
Website: www.iso.org

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by the Chemical Tests Commission of the International Union of Leather Technologists and Chemists Societies (IUC Commission, IULTCS) in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 289, *Leather*, the secretariat of which is held by UNI, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

IULTCS, originally formed in 1897, is a world-wide organization of professional leather societies to further the advancement of leather science and technology. IULTCS has three Commissions, which are responsible for establishing international methods for the sampling and testing of leather. ISO recognizes IULTCS as an international standardizing body for the preparation of test methods for leather.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Leather — Chemical tests — Determination of pesticide residues content

1 Scope

This document specifies a quantitative test method to determine 24 kinds of pesticide residues in leather by gas chromatography-mass spectrometry (GC-MS).

This document is applicable to all types of leather that could release pesticides.

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.

ISO 2418, *Leather — Chemical, physical and mechanical and fastness tests — Sampling location*

ISO 4044, *Leather — Chemical tests — Preparation of chemical test samples*

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 <http://www.electropedia.org/>

4 Principle

The leather sample is ultrasonically extracted with a mixed solution of *n*-hexane and ethyl acetate (1 + 1, volume). The extraction is detected and confirmed by GC-MS, and quantified using an external standard method.

5 Safety precautions

5.1 The compounds of pesticides are classified as high toxicity substances. Some are persistent organic pollutants (POPs) and suspected to be human carcinogens.

Any handling and disposal of these substances shall be in strict accordance with the applicable health and safety requirements.

5.2 It is the user's responsibility to use safe and proper techniques when handling materials in this test method. Consult manufacturers for specific details, such as safety data sheets and other recommendations.

5.3 Good laboratory practice should be followed. Wear safety glasses in all laboratory areas, as well as a dust respirator and single-use gloves while handling those compounds and leather samples.

6 Reagents

Unless otherwise specified, analytical grade chemicals shall be used.

6.1 ***n*-Hexane**, chromatographic pure.

6.2 **Ethyl acetate**, chromatographic pure.

6.3 **Acetonitrile**, chromatographic pure.

6.4 **Toluene**, chromatographic pure.

6.5 ***n*-Hexane and ethyl acetate** (1 + 1, volume) mixed solution.

6.6 **Acetonitrile and toluene** (3 + 1, volume) mixed solution.

6.7 **24 kinds of pesticide standards**, as listed in [Annex A](#), purity of 97 % or more. See [Annex A](#) for individual details of the 24 pesticide compounds.

6.8 **Standard solutions of pesticides**, accurately weigh the amount of each pesticide standard, and dissolve in a small amount of *n*-hexane to prepare a concentration 100 µg/ml of standard solution. A commercially available certified solution is an alternative. The shelf life of commercially available certified solution is given in the certificate. The shelf life of the solution prepared from powder is one month.

6.9 **Standard stock solutions of pesticides**, accurately pipette a certain volume of each standard pesticide solution ([6.8](#)) into a separate volumetric flask. Dilute with *n*-hexane to prepare the intermediate standard stock solution with a concentration of 1 µg/ml. The shelf life of the stock solution is one month.

6.10 **Standard calibration solutions of pesticides**, accurately pipette a certain volume of standard stock solution ([6.9](#)) into a volumetric flask and dilute with *n*-hexane to prepare standard calibration solutions with concentrations in the range of 10 ng/ml to 1 000 ng/ml. Prepare them before using.

7 Apparatus

Usual laboratory equipment and, in particular, the following.

7.1 **Gas chromatograph (GC)**, with mass-selective detector (MSD) and electron impact source (EIS).

7.2 **Analytical balance**, weighing to an accuracy of 0,1 mg.

7.3 **Laboratory balance**, weighing to an accuracy of 0,01 g.

7.4 **Vortex mixer**.

7.5 **Ultrasonic water-bath**, ultrasonic frequency 40 KHz, ultrasonic power 200 W, controllable heating.

7.6 **Vacuum rotary evaporator**, with vacuum control and water bath. Other types of evaporation apparatus may be used, e.g. a water bath with a controlled flow of nitrogen over the liquid.

7.7 **Solid phase extraction (SPE) system**, with vacuum device and graphitized carbon black (Carb), solid phase extraction column, 500 mg, 6 ml.

7.8 Small volume pipetting device, 1 ml to 5 ml, and 100 µl to 1 000 µl.

7.9 Centrifuge, with a revolution speed of more than 5 000 r/min.

7.10 Stoppered polypropylene centrifuge tube, 50 ml.

7.11 Conical flask, brown, 100 ml.

7.12 Polypropylene or polyethylene syringe, 50 ml.

7.13 Polyamide membrane filter, 0,22 µm or 0,45 µm.

8 Procedure

8.1 Sample

Sample the leather in accordance with ISO 2418. If sampling in accordance with ISO 2418 is not possible (e.g. leather from finished products like shoes, garments, etc.), details about sampling shall be given in the test report.

Cut the leather sample into small pieces or grind the leather in accordance with ISO 4044. The pieces shall be of 3 mm to 5 mm side length.

8.2 Extraction

8.2.1 Weigh accurately 2,00 g leather sample (to 0,01 g accuracy) with a laboratory balance (7.3) and place in 50 ml stoppered polypropylene centrifuge tube (7.10).

8.2.2 Add 20 ml of the *n*-hexane and ethyl acetate (1 + 1) mixed solution (6.5) into the tube, shake for 10 min with the vortex mixer (7.4).

8.2.3 Extract in the ultrasonic water-bath (7.5) for 20 min at 25 °C ± 2 °C.

8.2.4 Centrifuge for 5 min at 5 000 r/min with centrifuge (7.9). The supernatant is transferred to the conical flask (7.11).

8.2.5 With the residue, carry out the operations in 8.2.2 to 8.2.4 for a second time. Combine the supernatant in the conical flask.

8.2.6 Concentrate the combined extraction by a vacuum rotary evaporator (7.6) or under gentle flow of nitrogen at 35 °C ± 5 °C to approximately 2 ml to 5 ml.

8.3 Purification

8.3.1 Pre-rinse the Carb (7.7) with 5 ml acetonitrile and toluene (3 + 1) mixed solution (6.6).

8.3.2 Transfer the extraction solution (8.2.6) to the Carb. Rinse the conical flask twice with 3 ml acetonitrile and toluene (3 + 1) mixed solution (6.6) and transfer the washing solutions to the Carb.

8.3.3 Rinse the Carb with 15 ml acetonitrile and toluene (3 + 1) mixed solution (6.6), collecting all the eluent in a clean conical flask (7.11).

8.3.4 Evaporate the solution (8.3.3) to approximately 1 ml using a vacuum rotary evaporator (7.6) or under gentle stream of nitrogen at $35\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$.

8.3.5 Add 5,0 ml *n*-hexane (6.1) to dissolve the residue solution and re-evaporate to near dry. Repeat this operation.

NOTE Solvent displacement is to change the polarity of the solvent to protect chromatographic column.

8.3.6 Add 2,0 ml *n*-hexane (6.1) to dissolve and transfer to a clean vial for analysis in the GC-MS. Filter the solution with polyamide membrane filter (7.13).

8.4 Calibration solutions

8.4.1 Preparation of calibration solution mixture

Depending on the content of pesticide in the different leather samples, prepare at least 5 standard calibration solutions (6.10) in the range 10 ng/ml to 1 000 ng/ml, to have similar responses as the sample solution.

8.4.2 Preparation of calibration mixture for recovery rate

Measure 0,4 ml of the 1 000 ng/ml mixed standard working solution (6.10) into a 50 ml stoppered polypropylene centrifuge tube (7.10) and add 20 ml *n*-hexane and ethyl acetate (1 + 1) mixed solution (6.5). Treat this solution in the same way as the sample.

The recovery rate shall be between 70 % and 120 %.

8.5 Preparation of blank sample

An aliquot of 20 ml *n*-hexane and ethyl acetate (1 + 1) mixed solution (6.5) is placed in a sample container and treated as a sample, in all respects, including all analytical procedures.

8.6 Analysis by GC-MS

Various types of gas chromatographic equipment can be used. The chromatographic conditions given in Annex B are examples of parameters that have been successfully used for this analysis.

For each compound, one quantitative ion and two or three qualitative ions were selected. For the retention time of each compound, quantitative and qualitative ions, and ion abundance ratios, see Annex C for individual details. For the start time and dwell time of each group of detecting ions, see Annex D for individual details.

8.7 Check of the analytical system

Select the appropriate standard calibration solution according to the content of the measured compound for each different sample. The equal volume of samples and the standard solution are alternatively analysed by means of GC-MS. It may be necessary to concentrate the response of the standard solution and the test sample solution of each pesticide within the linear response range of the instrument. For the selected ion chromatogram of a standard solution by GC-MS, see Annex E for individual details.

Under the same experimental conditions, to confirm the sample definitely contains a certain amount of any object pesticide, the deviation of the retention time of the sample and standard shall be within $\pm 2,5\%$, and both the relative abundance of the qualifier ion cannot exceed the tolerance range listed in Table 1.

Table 1 — Maximum allowable deviation for relative ion abundances as qualitatively confirmed

Relative ion abundances (%)	> 50	> 20 to 50	> 10 to 20	≤ 10
Allowable deviation (%)	±20	±25	±30	±50

9 Evaluation of results

9.1 Calculation of results

The concentration is given by the external standard curve from the data processing software. The object pesticide level is calculated as a mass fraction, w_i , in milligrams per kilogram (mg/kg) of the specimen according to the following formula:

$$w_i = \frac{(c_i - c_0) \times V}{m \times 1\,000}$$

where

- w_i is the pesticide residue content in the test samples, in mg/kg;
- c_i is the concentration of object pesticide in the calibration solution, in ng/ml;
- c_0 is the concentration of object pesticide in the blank sample, in ng/ml;
- V is the volume of the specimen according to 8.3.6 (final specimen volume), in ml;
- m is the mass of the leather specimen, in g.

The result is rounded to the nearest 0,1 mg/kg.

9.2 Reliability of the method

For the detection limit of the method for each pesticide, see [Annex C](#) for individual details.

For the fortified concentration and recoveries of 24 kinds of pesticides in leather, see [Annex F](#) for individual details.

The absolute difference of results from two independent determinations using the same conditions shall not exceed 20 % of the arithmetic mean.

For the precision of the method, see the results of an interlaboratory trial presented in [Annex G](#).

10 Test report

The test report shall include the following:

- a) reference to this document (i.e. ISO 22517);
- b) the type, origin and designation of the analysed leather sample and the sampling method used;
- c) the analytical procedure used;
- d) the analytical results in mg/kg for the pesticide content;
- e) any deviations from the analytical procedure, particularly any additional steps performed;
- f) the date of the test.

Annex A (normative)

24 kinds of pesticide compounds

Pesticides are listed according to chemical type, the numbering is according to the retention time (see [Annex C](#)).

Number	Pesticide	CAS number	Chemical formula
18	o,p'-DDT	789-02-6	C ₁₄ H ₉ Cl ₅
21	p,p'-DDT	50-29-3	C ₁₄ H ₉ Cl ₅
17	o,p'-DDD	53-19-0	C ₁₄ H ₁₀ Cl ₄
19	p,p'-DDD	72-54-8	C ₁₄ H ₈ Cl ₄
12	o,p'-DDE	3424-82-6	C ₁₄ H ₈ Cl ₄
15	p,p'-DDE	72-55-9	C ₁₄ H ₈ Cl ₄
2	α-BHC	319-84-6	C ₆ H ₆ Cl ₆
6	β-BHC	319-85-7	C ₆ H ₆ Cl ₆
7	δ-BHC	319-86-8	C ₆ H ₆ Cl ₆
3	Lindane	58-89-9	C ₆ H ₆ Cl ₆
8	Malathion	121-75-5	C ₁₀ H ₁₉ O ₆ PS ₂
23	Methoxychlor	72-43-5	C ₁₆ H ₁₅ Cl ₃ O ₂
4	Aldrin	309-00-2	C ₁₂ H ₈ Cl ₆
16	Dieldrin	60-57-1	C ₁₂ H ₈ Cl ₆ O
10	Ethylparathion	56-38-2	C ₁₀ H ₁₄ NO ₅ PS
13	α-Endosulfan	959-98-8	C ₉ H ₆ Cl ₆ O ₃ S
20	β-Endosulfan	33213-65-9	C ₉ H ₆ Cl ₆ O ₃ S
22	Mirex	2385-85-5	C ₁₀ Cl ₁₂
9	Dichlofluanide	1085-98-9	C ₉ H ₁₁ Cl ₂ FN ₂ O ₂ S ₂
11	Heptachloroepoxide	1024-57-3	C ₁₀ H ₅ Cl ₇ O
1	Pentachloroanisole	1825-21-4	C ₇ H ₃ Cl ₅ O
24	Permethrin	52645-53-1	C ₂₁ H ₂₀ Cl ₂ O ₃
14	Tolyfluanide	731-27-1	C ₁₀ H ₁₃ Cl ₂ FN ₂ O ₂ S ₂
5	Chlorthalonil	1897-45-6	C ₈ Cl ₄ N ₂

Annex B

(informative)

GC-MS chromatographic conditions and parameters

Various types of gas chromatographic equipment can be used. The chromatographic conditions given in this annex are examples of parameters that have been successfully used for this analysis.

Gas chromatograph (GC) with mass-selective detector (MSD) and electron impact source (EIS).

- a) Capillary column: (14 %-cyanide propyl-phenyl)-methyl polyethylene oxide silane, or a column with a similar performance; length: 30 m; inside diameter: 0,25 mm; film thickness: 0,25 μ m.
- b) Temperature programme: 50 °C (hold 2 min), 30 °C/min to 185 °C (hold 1 min), 4 °C/min to 240 °C, 20 °C/min to 270 °C (hold 5 min), then 280 °C post run 2 min.
- c) Injector temperature: 270 °C.
- d) Injection volume: 1,0 μ l, without split.
- e) GC-MS interface temperature: 280 °C.
- f) Carrier gas: helium, purity $\geq$ 99,999 %, flow rate: 1,2 ml/min.
- g) Solvent delay: 9 min.

Annex C (informative)

Retention time, quantitative and qualitative ions and ion abundance ratios

The pesticides are listed according to the retention time.

Series number	Pesticide	Retention time min	Characteristic fragment ion amu			Limit of detection mg/kg
			Quantitative	Qualitative	Abundance ratio	
1	Pentachloroanisole	10,52	280	265, 237, 263	100:100:82:63	0,03
2	α -BHC	11,26	181	183, 217, 254	100:97:69:4	0,05
3	Lindane	12,41	181	183, 217, 254	100:98:64:11	0,05
4	Aldrin	13,78	263	265, 261, 293	100:67:65:38	0,10
5	Chlorthalonil	14,64	266	264, 268	100:78:48	0,10
6	β -BHC	14,87	181	183, 217, 254	100:98:74:9	0,05
7	δ -BHC	15,65	181	183, 217, 254	100:97:70:8	0,05
8	Malathion	15,84	173	158, 256, 285	100:48:8:5	0,10
9	Dichlofluanide	16,05	123	224, 226, 332	100:37:26:5	0,15
10	Ethylparathion	16,10	275	220, 247, 232	100:82:77:68	0,10
11	Heptachloroepoxide	16,36	353	355, 351, 317	100:81:52:68	0,05
12	o,p'-DDE	16,74	246	318, 176, 248	100:34:29:65	0,01
13	α -Endosulfan	17,16	241	265, 277, 339	100:63:57:40	0,10
14	Tolyfluanide	17,85	238	240, 181	100:69:63	0,15
15	p,p'-DDE	17,97	318	316, 246, 248	100:78:130:84	0,01
16	Dieldrin	18,55	263	277, 345, 380	100:79:27:24	0,05
17	o,p'-DDD	19,21	235	237, 165, 199	100:65:44:17	0,03
18	o,p'-DDT	19,72	235	237, 165, 199	100:65:40:15	0,03
19	p,p'-DDD	21,10	235	237, 165, 199	100:64:42:12	0,03
20	β -Endosulfan	21,30	241	265, 237, 339	100:49:84:35	0,10
21	p,p'-DDT	21,68	235	237, 165, 199	100:65:39:12	0,03
22	Mirex	22,85	272	274, 237, 332	100:80:53:11	0,02
23	Methoxychlor	23,41	227	228, 212, 274	100:20:17:15	0,02
24	Permethrin (cis- and trans-isomers)	25,70	183	163, 165, 184	100:20:17:15	0,02
		26,13	183	163, 165, 184	100:27:22:15	

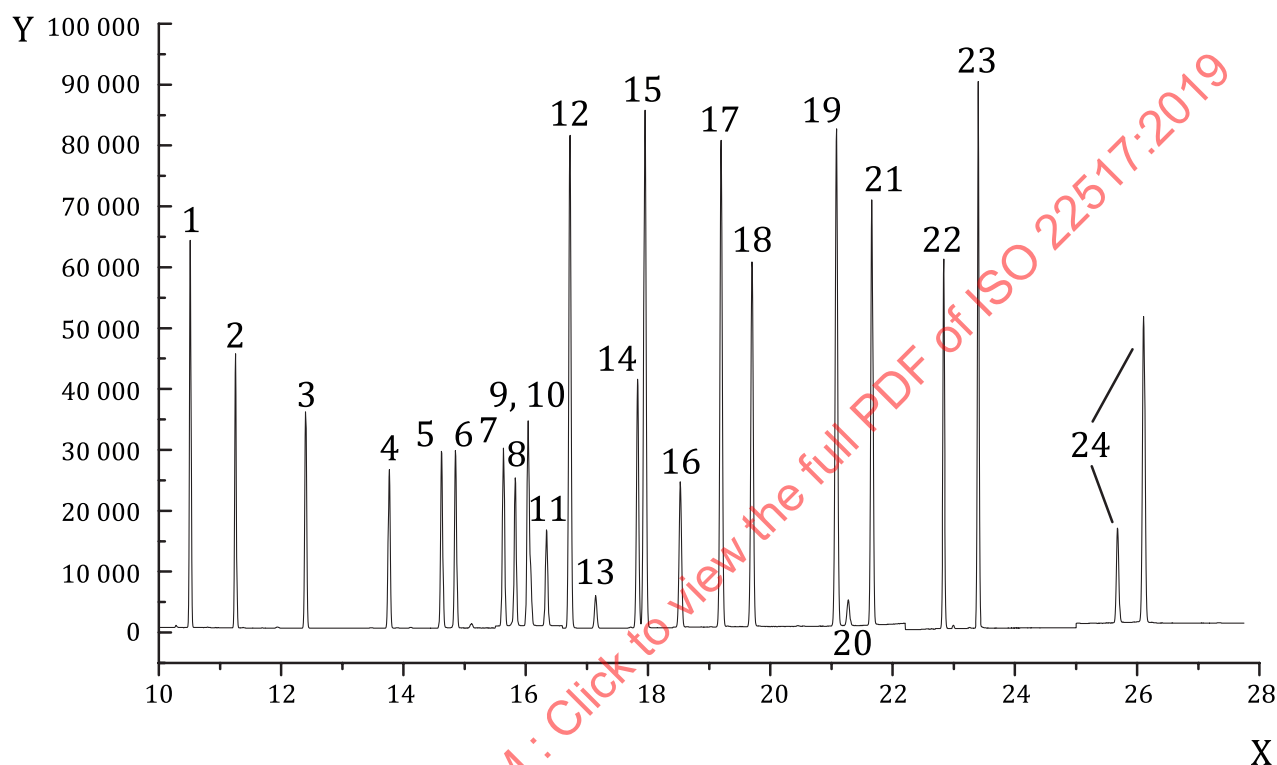
Annex D (informative)

Start time and dwell time of each group of detecting ions

Ion channels	Time min	Dwell time ms	Selective ion amu
1	9,00	25	181, 183, 217, 237, 254, 261, 263, 264, 265, 266, 268, 280, 293
2	15,20	20	123, 158, 173, 181, 183, 217, 220, 224, 226, 232, 247, 254, 256, 275, 285, 317, 332, 351, 353, 355
3	16,50	25	176, 181, 238, 240, 241, 246, 248, 265, 277, 316, 318, 339
4	18,20	25	165, 199, 235, 237, 241, 246, 263, 265, 277, 339, 345, 380
5	22,20	40	212, 227, 228, 237, 272, 274, 332
6	25,00	70	163, 165, 183, 184

Annex E (informative)

Chromatogram and selected ion of the 24 pesticides standard obtained by GC-MS



Key

X time, in min
Y resolution

Peak No.	Pesticide	Peak No.	Pesticide
1	pentachloroanisole	13	α -endosulfan
2	α -BHC	14	tolyfluanide
3	lindane	15	p,p'-DDE
4	aldrin	16	dieldrin
5	chlorthalonil	17	o,p'-DDD
6	β -BHC	18	o,p'-DDT
7	δ -BHC	19	p,p'-DDD
8	malathion	20	β -endosulfan
9	dichlofluanide	21	p,p'-DDT
10	ethylparathion	22	mirex
11	heptachloroepoxide	23	methoxychlor
12	o,p'-DDE	24	permethrin (cis- and trans-isomers)

Figure E.1 — Chromatogram and selected ion of the 24 pesticides standard obtained by GC-MS

Annex F (informative)

Recovery range of pesticides in leather ($n = 6$)

No.	Concentration µg/kg	Test value µg/kg						Average µg/kg	Recovery range %	Standard deviation µg/kg	Coefficient of variation %
		1	2	3	4	5	6				
1	100	104,82	104,38	110,68	106,82	108,94	106,78	107,1	107,1	2,41	2,25
	300	318,28	309,22	326,48	323,16	323,69	335,06	322,6	107,5	8,61	2,66
	600	636,62	639,78	681,74	677,02	677,43	686,97	666,6	111,1	22,3	3,35
2	100	109,85	100,37	113,23	118,39	107,76	109,63	109,9	109,9	5,98	5,44
	300	327,21	317,45	338,52	334,91	331,40	341,38	331,8	110,6	8,62	2,61
	600	648,38	652,08	688,85	687,70	687,30	693,73	676,3	112,7	20,4	3,01
3	100	85,18	77,30	74,93	67,40	80,85	84,58	78,4	78,4	6,70	8,55
	300	287,21	283,85	325,19	297,12	319,81	305,60	303,1	101,0	16,9	5,58
	600	607,83	609,95	646,35	653,77	645,26	654,94	636,4	106,1	21,6	3,40
4	100	110,96	104,01	119,73	109,97	123,82	111,07	113,3	113,3	7,21	6,37
	300	334,97	321,51	337,56	341,04	340,49	350,81	337,7	112,6	9,61	2,84
	600	675,45	678,21	711,10	711,93	708,28	720,59	700,9	116,8	19,1	2,73
5	100	86,97	83,05	77,88	71,58	74,32	76,76	78,4	78,4	5,68	7,24
	300	304,99	254,67	308,45	308,32	348,20	349,42	312,3	104,1	34,8	11,16
	600	641,60	673,02	744,66	767,52	767,94	803,11	733,0	122,2	62,3	8,50
6	100	81,63	78,76	84,53	80,78	88,71	87,16	83,6	83,6	3,87	4,63
	300	302,09	291,98	310,99	308,32	308,09	318,69	306,7	102,2	9,00	2,93
	600	623,89	633,22	676,93	673,99	671,39	681,53	660,2	110,0	24,9	3,77
7	100	92,36	82,78	87,15	94,43	94,00	100,06	91,8	91,8	6,05	6,60
	300	329,35	319,65	340,34	335,97	345,02	346,19	336,1	112,0	10,2	3,02
	600	653,34	656,45	695,04	695,95	691,75	696,94	681,6	113,6	20,8	3,05
8	100	106,66	101,93	129,89	123,74	117,89	109,03	114,9	114,9	10,8	9,40
	300	376,77	366,53	392,05	358,81	429,19	445,49	394,8	131,6	35,2	8,90
	600	642,69	647,13	688,26	691,59	687,02	697,96	675,8	112,6	24,2	3,59
9	100	105,65	108,00	117,28	118,75	115,22	120,72	114,3	114,3	6,09	5,33
	300	315,61	314,33	329,19	307,40	332,09	385,47	330,7	110,2	28,4	8,60
	600	727,84	704,70	738,58	739,31	736,92	746,94	732,4	122,1	14,9	2,03
10	100	122,17	109,74	117,84	97,45	118,82	120,49	114,4	114,4	9,36	8,18
	300	334,50	326,12	342,18	335,06	330,87	341,48	335,0	111,7	6,2	1,84
	600	684,42	687,77	717,25	711,94	702,44	709,71	702,3	117,0	13,4	1,91
11	100	117,29	113,80	120,19	112,93	123,96	114,67	117,1	117,1	4,26	3,64
	300	336,75	331,23	349,52	348,65	345,17	347,20	343,1	114,4	7,41	2,16
	600	675,82	692,65	715,01	717,33	721,97	732,42	709,2	118,2	20,9	2,95
12	100	104,50	102,74	111,07	115,82	110,78	108,95	109,0	109,0	4,76	4,37
	300	335,60	320,10	339,86	337,43	337,00	354,70	337,4	112,5	11,0	3,27
	600	663,89	668,07	704,65	705,12	706,79	713,85	693,7	115,6	21,8	3,14

No.	Concentration µg/kg	Test value µg/kg						Average µg/kg	Recovery range %	Standard deviation µg/kg	Coefficient of variation %
		1	2	3	4	5	6				
13	100	114,08	110,13	112,40	118,10	120,73	115,88	115,2	115,2	3,85	3,34
	300	365,76	425,34	385,49	416,08	383,07	388,30	394,0	131,3	22,3	5,67
	600	718,00	760,67	741,35	785,23	814,22	753,83	762,2	127,0	33,8	4,43
14	100	112,68	91,24	108,77	112,45	115,42	120,54	110,2	110,2	10,1	9,14
	300	303,82	294,52	361,95	334,05	358,47	398,88	341,9	114,0	39,2	11,46
	600	543,13	560,93	587,19	576,49	582,19	597,35	574,5	95,8	19,6	3,41
15	100	114,80	112,28	121,45	119,48	122,35	118,92	118,2	118,2	3,91	3,31
	300	336,16	323,28	344,27	342,30	343,06	351,92	340,2	113,4	9,72	2,85
	600	664,70	666,96	709,04	707,91	710,27	713,82	695,5	115,9	23,0	3,31
16	100	91,65	99,21	92,79	97,53	81,28	81,17	90,6	90,6	7,80	8,60
	300	189,64	186,91	214,49	243,54	236,14	231,69	217,1	72,4	24,3	11,18
	600	444,66	445,46	519,73	530,00	458,33	494,34	482,1	80,3	37,9	7,85
17	100	121,63	121,59	135,00	127,56	123,45	135,78	127,5	127,5	6,49	5,09
	300	370,48	360,37	403,69	404,49	405,20	412,48	392,8	130,9	21,7	5,52
	600	678,39	678,86	764,16	763,80	765,45	771,60	737,0	122,8	45,3	6,15
18	100	113,48	112,57	109,61	105,37	107,68	103,49	108,7	108,7	3,95	3,63
	300	348,09	337,21	314,38	311,92	311,42	320,10	323,9	108,0	15,3	4,72
	600	684,67	685,29	636,12	634,61	635,84	641,81	653,1	108,8	24,9	3,81
19	100	107,38	104,67	108,01	111,81	124,94	124,04	113,5	113,5	8,84	7,79
	300	339,64	332,31	383,40	382,25	382,49	392,20	368,7	122,9	25,73	6,98
	600	617,11	615,85	710,35	711,11	710,67	715,92	680,2	113,4	49,4	7,26
20	100	97,56	84,31	89,71	99,45	101,35	99,13	95,2	95,2	6,72	7,05
	300	271,26	325,76	253,56	331,05	266,05	293,68	290,2	96,7	32,3	11,14
	600	463,13	535,41	600,88	552,06	562,28	602,02	552,6	92,1	51,3	9,29
21	100	119,86	113,84	104,48	98,01	102,86	96,78	106,0	106,0	9,11	8,59
	300	351,60	348,39	291,08	298,82	296,96	301,70	314,8	104,9	27,5	8,75
	600	680,51	686,53	580,52	580,53	579,23	590,20	616,3	102,7	52,3	8,48
22	100	101,45	102,05	107,12	105,38	106,77	104,73	104,6	104,6	2,37	2,27
	300	316,36	306,54	319,69	319,59	319,54	328,57	318,4	106,1	7,1	2,23
	600	633,38	634,61	663,98	666,99	664,06	672,27	655,9	109,3	17,2	2,63
23	100	112,56	110,35	103,28	89,72	91,94	107,17	102,5	102,5	9,59	9,36
	300	345,21	336,85	314,49	314,98	316,51	322,67	325,1	108,4	12,9	3,98
	600	676,71	679,86	624,34	626,26	627,59	635,34	645,0	107,5	26,1	4,04
24	100	116,34	114,44	133,51	131,08	131,49	121,74	124,8	124,8	8,35	6,69
	300	366,22	355,29	376,09	375,22	376,61	393,77	373,9	124,6	12,8	3,41
	600	732,07	731,63	776,16	773,49	775,17	793,54	763,7	127,3	25,7	3,37