Collection of Official Methods under Article 35 of the German Federal Food Act		
L	Analysis of Foodstuffs Modular Multiple Analytical Method for the Determination of **Pesticide Residues** in **Foodstuffs** (Extended and Revised Version of the DFG Method S 19)	00.00 34

1 Aim and scope

This official method specifies a procedure for the residue analysis of organochlorine, organophosphorus, nitrogen-containing and other pesticides in foodstuffs. It reflects the DFG Multiresidue Method S 19 in its original [1] as well as in its modified version [2] and affords a much broader field of application.

2 Definition

The term pesticide residue content of a foodstuff is defined as the content determined by using this method. It is expressed in mg/kg.

3 Introduction

The Multiresidue Method S 19 of the DFG Manual including the Cleanup Method 6 (gel chromatographic cleanup) [3] has proved to be used successfully in many laboratories because of its broad applicability for the gas chromatographic determination of pesticide residues in foodstuffs. It was also included into the respective European Standards [4, 5].

In the meantime a modification of the extraction and partition step has been implemented [2]. It requires less experimental efforts and manages without dichloromethane which is undesirable for toxicological and ecological reasons. As the results from validation studies demonstrate, this modification has the same broad field of application as the original DFG Method S 19, and it is included in the German Collection of Official Methods as Method L 00.00-34.

In both cases the entire method consists of four stages: extraction and partition, gel permeation chromatography (GPC), mini silica gel column chromatography, and gas chromatographic determination. Except for the central GPC, several variations occur on each stage depending on the kind of the sample material and the residues to be analyzed. They can be combined with each other in a variety of ways according to the requirements.

This is difficult to realize in the references published previously. However, every laboratory analyzing pesticide residues is constrained to provide a detailed description of the specific analytical conditions used together with its results. This is easier to see when the individual stages are presented just as “modules” which can be listed in the particular test report. At the same time this facilitates the course of work in the residue laboratory, when it can be clearly specified with which modules an individual sample has to be processed. If the analyst, however, introduces any deviations, this should be recorded in the test report.

In addition, this modular form facilitates the introduction of new and approved techniques in the future, e.g. the HPLC as a module for cleanup or for determination purposes.

For all these reasons, the Analytical Working Group of the Pesticides Commission at BgVV publishes here an extended version of the latest available and reliable methodology. It takes the mentioned points into account and makes the modular structure transparent. Since each module is completely described thus avoiding complicating cross-references, the reiteration of several texts had to be accepted.

4 Sampling

4.1 Sampling study plan

The sampling procedure for the official control of residues of pesticides on and in fruit and vegetables has to comply with the provision given in L 29.00-1 in the German Collection of Official Methods.

4.2 Sample preparation

Reference is given to the recommendations of the DFG Manual [6] and of the Pesticide Working Group of “Lebensmittelchemische Gesellschaft” (GDCh) [7].

5 Procedure

The extraction and liquid/liquid partition steps are described in the Modules E. The extracts are cleaned up by gel permeation chromatography (Module GPC) and additionally – if required – on a small silica gel column (Module C).

The residue-containing eluate from the GPC step is evaporated and is analyzed by gas chromatography with the flame photometric detector (FPD) or a mass spectrometric detector (MS), under appropriate conditions also with a nitrogen/phosphorus detector (NPD) (Modules D 2 to D 4).

For gas chromatography with the electron capture detector (ECD) (Module D 1), the GPC eluate requires an additional cleanup on a small silica gel column.

The Tables 1 to 4 schedule a short description of the modules, notes for their application and several examples. The water contents of important foodstuffs are listed in Table A 1 in the Appendix. Plant foodstuffs and their fat content, which determines the extraction module to be used, are compiled in Table A 2.

The individual modules are described in the working procedures in this method.

Table 1: Extraction (E)

Module	Description	Use / Application	Examples
E 1	Extraction and subsequent liquid/liquid partition [2]	Plant material and foodstuffs with a water content exceeding 70 g/100 g and a fat content below 2.5 g/100 g	Fruit, vegetables, juices
E 2	Extraction and subsequent liquid/liquid partition [2]	Plant material and foodstuffs with a water content below 70 g/100 g and a fat content below 2.5 g/100 g	Cereals and cereal products, spices, fruit powder
E 3	Extraction and subsequent liquid/liquid partition [2]	Plant material and foodstuffs with a water content exceeding 70 g/100 g, a fat content below 2.5 g/100 g and a high acid content	Fruit, tomatoes
E 4	Two-stage extraction and liquid/liquid partition [1]	Plant material and foodstuffs with a water content exceeding 70 g/100 g and a fat content below 2.5 g/100 g	Fruit, vegetables, juices
E 5	Two-stage extraction and liquid/liquid partition [1]	Plant material and foodstuffs with a water content below 70 g/100 g and a fat content below 2.5 g/100 g	Cereals and cereal products, spices, fruit powder
E 6	Dissolving fat in GPC eluting mixture	Plant and animal fats (containing no water)	Edible fats and oils, essential oils
E 7	Extraction in the presence of large amounts of fat [8]	Plant and animal fats with low water content, if the limit of determination is not sufficient with E 6, and dry food with a fat content exceeding 2.5 g/100 g	Edible fats and oils, wheat and rye germs, oats, nuts, oil seed
E 8	Extraction of fat with hexane/acetone [9]	Fat-containing foodstuffs with high water content	Meat, fish, cheese
E 9	Accelerated solvent extraction (ASE)	Plant material and foodstuffs with a water content below 20 g/100 g and a fat content below 2.5 g/100 g	Tea, cereals and cereal products, spices

Table 2: Gel permeation chromatography

Module	Description	Use / Application	Examples
GPC	Gel permeation chromatography	Extract from E 1 to E 9	All samples

Table 3: Cleanup (C)

Module	Description	Use / Application	Examples
C 1	Column chromatography on a small silica gel column	GPC eluate, PCB residues not expected	
C 2	Column chromatography on a small silica gel column	GPC eluate, PCB residues expected	Animal fats

Table 4: Detection (D)

Module	Description	Use / Application	Examples
D 1	Gas chromatography with ECD	Eluate from C 1 or C 2	Organochlorine compounds, pyrethroids, PCB
D 2	Gas chromatography with FPD	GPC eluate or eluate from C 1 or C 2	Organophosphorus and sulfur-containing compounds
D 3	Gas chromatography with NPD	GPC eluate or eluate from C 1 or C 2	Organophosphorus and nitrogen-containing compounds
D 4	Gas chromatography with MS	GPC eluate or eluate from C 1 or C 2	Compounds containing nitrogen, compounds not detectable with D 1 to D 3

6 Evaluation

6.1 Identification and confirmation

In multiresidue analysis an analyte is identified by its relative retention time, e.g. relative to aldrin when using an ECD or relative to parathion or chlorpyrifos when using a FPD and a NPD. Such relative retention times are taken from corresponding lists for the columns used. Further evidence for the identity of an analyte is provided by the selectivity of the different detectors (modules D 1 to D 3), by its elution behaviour during column chromatography (modules C 1 and C 2) and in some cases even by the peak form in a gas chromatogram. In a specific analysis for only some individual analytes, their retention times are compared directly with the corresponding retention times of the analytes from standard solutions.

As a rule, a confirmatory gas chromatographic measurement is performed with a capillary column of different polarity and/or a different detector. The mass selective detector [MS] (module D 4) is especially suitable for the confirmation of results.

Confirmation of the identity of an analyte should be performed particularly in those cases in which it would appear that a maximum residue limit (MRL) has been exceeded or in which a compound seems to be present, which is not to expected in the sample analyzed.

6.2 Calculation

The residue, W_R in mg/kg, of an identified analyte is calculated using the sample equivalent C_{Ex} from modules E, the dilution factors F_{GPC} and F_C from modules GPC and C, respectively, and the concentration C_A from modules D. The following equation is used:

$$W_R = \frac{C_A}{C_{Ex}} \cdot F_{GPC} \cdot F_C$$

where:

C_A	is the concentration of the identified analyte in the sample test solution from modules D, in µg/mL
C_{Ex}	is the sample equivalent in the extract from modules E, in g/mL
F_{GPC}	is the dilution factor (module GPC)
F_C	is the dilution factor (modules C)

6.3 Reliability of the method

The recoveries from untreated control samples of a wide variety of analytical materials of plant and animal origin fortified with the analytes at levels of 0.01 to 1 mg/kg generally ranged from 70 to 110 %.

Details on collaborative studies determining the precision are given in Table A 4 in the Appendix. The data was acquired in accordance with ISO 5725 : 1994 and may not be applicable to analyte concentration ranges and matrices other than as given in Table A 4 [10].

7 Test report

The test report shall contain a reference to this official method and at least the following information:

Kind, origin and description of the sample

Type and date of sampling

Date of receipt of sample in the laboratory and date of test

Enumeration of the modules and any particular points observed in course of the test

The analytical results

Reasons for any deviation from this official method

8 Explanations and notes

Reference is made to the explanations given in the introductory part of the Collection of Official Methods.

This extended, modular version was outlined by R.-D. Weeren and S. Pelz (Labor Dr. Specht & Partner, Hamburg) and was recommended for inclusion into the German Collection of Official Methods after detailed discussions in the Analytical Working Group of the Pesticides Commission at BgVV. This translation of the method L 00.00-34 was drafted by B. Walker, H.-P. Thier and J. Kirchhoff.

9 References

[1] DFG, Deutsche Forschungsgemeinschaft: Manual of Pesticide Residue Analysis, Method S 19. VCH Verlagsgesellschaft Weinheim, Vol. 1 (1987), 383–400; Vol. 2 (1992), 317–322

[2] *Specht W., Pelz, S., Gilsbach, W.*: Gaschromatographic determination of pesticide residues after clean-up by gel permeation chromatography and mini-silica gel-column chromatography. 6. Comm.: Replacement of dichloromethane by ethyl acetate/cyclohexane in liquid-liquid partition and simplified conditions for extraction and liquid-liquid partition, Fresenius J. Anal. Chem. **353**, 183–190 (1995)

[3] DFG, Deutsche Forschungsgemeinschaft: Manual of Pesticide Residue Analysis, Cleanup Method 6. VCH Verlagsgesellschaft Weinheim, Vol. 1 (1987), 75–78; Vol. 2 (1992); 31–36

[4] European Standard EN 1528-3: 1996, Fatty food – Determination of pesticides and polychlorinated biphenyls (PCBs) – Part 3: Clean-up methods, Method G

[5] European Standard EN 12393-2: 1998, Non-fatty foods – Multiresidue methods for the gas chromatographic determination of pesticide residues – Part 2: Methods for extraction and clean-up, Method N

[6] DFG, Deutsche Forschungsgemeinschaft: Manual of Pesticide Residue Analysis, Preparation of Samples. VCH Verlagsgesellschaft Weinheim, Vol. 1 (1987), 17–20

[7] Arbeitsgruppe “Pestizide”: 5. Empfehlung. Kriterien zur Vorbereitung von Proben pflanzlicher Lebensmittel für die Rückstandsanalytik von Pflanzenschutz- und Schädlingsbekämpfungsmitteln,Lebensmittelchemie **49**, 40–42 (1995)

[8] DFG, Deutsche Forschungsgemeinschaft: Manual of Pesticide Residue Analysis, Cleanup Method 5. VCH Verlagsgesellschaft Weinheim, Vol. 1 (1987), 71–74

[9] *Ernst, W., Schaefer, R. G., Goerke, H., Eder, G.*: Aufarbeitung von Meerestieren für die Bestimmung von PCB, DDT, DDE, DDD, γ-HCH und

HCB, Fresenius Z. Anal. Chem. **272**, 358–363 (1974)

[10] European Commission (1998): bcr information; report EUR 18639 EN; “Intercomparison study of two multiresidue methods for the enforcement of EU MRLs for pesticides in fruit, vegetables and grain”, ISSN 1018-5593

MODULE E 1 Extraction and subsequent liquid/liquid partition for materials with a water content exceeding 70 g/100 g and a fat content below 2.5 g/100 g

1 Outline

The sample is extracted with acetone, after addition of water, depending on the natural water content of the material, in order to ensure an acetone/water ratio of 2 + 1 (v/v) during the extraction.

For liquid/liquid partitioning, sodium chloride and a mixture of cyclohexane and ethyl acetate are added to the homogenate. The mixture is again intensively mixed and allowed to stand until the phases separate. An aliquot portion of the organic phase is dried with sodium sulfate and concentrated. To the residue obtained, ethyl acetate is added followed by the same volume of cyclohexane. Remaining water is eliminated with a mixture of sodium sulfate and sodium chloride and the solution is filtered. The extract is used for cleanup by gel permeation chromatography (module GPC).

2 Reagents

2.1 Sodium chloride, p.a.

2.2 Sodium sulfate, p.a., anhydrous, powder, heated at 550 °C for at least 2 h

2.3 Salt mixture: sodium sulfate + sodium chloride 1:1 (w/w)

2.4 Cotton wool, extracted exhaustively with acetone

2.5 Acetone, for residue analysis

2.6 Water, bi-distilled or equivalent

2.7 Cyclohexane, for residue analysis

2.8 Ethyl acetate, for residue analysis

2.9 GPC eluting mixture: cyclohexane + ethyl acetate 1:1 (v/v); alternatively, redistilled as an azeotropic mixture

3 Apparatus

3.1 High-speed homogenizer, e.g. Ultra-Turrax (Janke u. Kunkel, Staufen/Br)

3.2 Glass jar, 500 mL or 750 mL, with a screw cap lined with aluminium foil

3.3 Graduated cylinder, 250 mL

3.4 Round-bottomed flask, 500 mL, with ground joint

3.5 Glass funnels, 45 mm and 100 mm dia.

3.6 Rotary vacuum evaporator, water bath temperature 40 °C

3.7 Volumetric pipette, 10 mL

3.8 Ultrasonic bath

3.9 Fluted filter paper, 6 cm dia., fast flow rate, extracted exhaustively with acetone

3.10 Membrane filter, 0.45 µm pore size, 25 mm dia. (e.g. Chromafil, type 0-45/25 organic, Macherey-Nagel Nr. 718 005)

Note: Glassware cleaned with detergents must be thoroughly rinsed with water and acetone.

4 Procedure

In a portion of the material, determine the water content in g/100 g. As an alternative, take the approximate water content from Table A 1 in the Appendix or from a literature source.

As the test portion, weigh 25 to 100 g (m_A) of the material having a water content of x g/100 g into a glass jar. Then add sufficient water to adjust the total water present to 100 g. The amount of water m_W to be added is calculated as follows: $m_W = 100 - m_A \cdot x/100$. Next add 200 mL acetone and homogenize the mixture for 2 min with the homogenizer.

To the homogenate add 35 g sodium chloride and exactly 100 mL GPC eluting mixture and homogenize it again for 1 min. When the phases are clearly separated after 30 to 60 min, collect the upper organic phase. In case of insufficient phase separation centrifuge the mixture. Measure out exactly 200 mL (V_{R1}) of the organic phase in a graduated cylinder and filter this volume through a glass wool plug layered with approx. 100 g sodium sulfate in a funnel. Collect the filtrate in a 500-ml round-bottomed flask and rinse the graduated cylinder and the funnel four times each with approx. 20 mL GPC eluting mixture. Concentrate the combined filtrate and rinsings using the rotary evaporator. To the aqueous residue obtained, add exactly 7.5 mL ethyl acetate and swirl the flask in order to dissolve any residues adhering to the flask wall (this is facilitated by immersing the flask into an ultrasonic bath). Add approx. 5 g salt mixture for binding the remaining water. Swirl the flask and add exactly 7.5 mL cyclohexane to obtain a total volume of 15.0 mL (V_{End}). Swirl the flask again, allow the salt mixture to settle and filter the solution through a fluted filter paper or a membrane filter. With the filtrate, proceed as described in the module GPC (section 4.3).

5 Notes

It is feasible to weigh the test portion into the glass jar already one day before the extraction, if the glass jar is then tightly closed with a screw cap and is stored at –20 °C.

If several acid-sensitive analytes (e.g. bupirimate, fenarimol, myclobutanil, pirimicarb) are extracted from an acidic material (e.g. citrus fruits, berries, several sorts of apples and tomatoes), only low recoveries are obtained. If the pH value of an aqueous homogenate of the material is less than 5, it is recommended to use module E 3 where the acids are neutralized before the extraction.

For several analytes (e.g. dichlofluanid and tolylfluanid), the addition of an acid may increase the recoveries. In this case, set the pH value to less than 2 by mixing with diluted sulfuric acid (w = 10 g/100 mL) before adding the acetone.

The fat content of the material must not exceed 2.5 g/100 g, for otherwise the aqueous brine resulting in the partitioning step will retain small amounts of fat with some residues included, thus resulting in a loss of analytes.

6 Calculation

The sample equivalent C_{Ex} corresponds to the amount (in g) of sample material in one milliliter (1 mL) of extract. Calculate C_{Ex} in g/ml using the following equation:

$$C_{Ex} = \frac{m_A \cdot V_{R1}}{V_{Ex} \cdot V_{End}}$$

where:

m_A	is the sample mass, in g
V_{Ex}	is the volume of the organic phase after extraction and liquid/liquid partition, in ml (as a rule 285 mL, see Note below)
V_{R1}	is the aliquot portion of V_{Ex} taken for further processing, in mL (200 mL)
V_{End}	is the volume of the final sample test solution, in mL (15 mL)

Notes: 285 mL (V_{Ex}) result from 200 mL acetone and 100 mL GPC eluting mixture minus 15 mL caused by volume contraction and by loss of acetone in the aqueous phase.

The value for the sample equivalent C_{Ex} is required for calculating the content of an identified analyte according to section 6.2 of the basic text.

MODULE E 2 Extraction and subsequent liquid/liquid partition for materials with a water content below 70 g/100 g and a fat content below 2.5 g/100 g

1 Outline

Sufficient water is added to the sample, depending on the natural water content of the material, in order to ensure an acetone/water ratio of 2 + 1 (v/v). The mixture is allowed to stand for approx. 30 min and is then extracted with acetone.

For liquid/liquid partitioning, sodium chloride and a mixture of cyclohexane and ethyl acetate are added to the homogenate. The mixture is again intensively mixed and allowed to stand until the phases separate. An aliquot portion of the organic phase is dried with sodium sulfate and concentrated. To the residue obtained, ethyl acetate is added followed by the same volume of cyclohexane. Remaining water is eliminated with a mixture of sodium sulfate and sodium chloride and the solution is filtered. The extract is used for cleanup by gel permeation chromatography (module GPC).

2 Reagents

2.1 Sodium chloride, p.a.

2.2 Sodium sulfate, p.a., anhydrous, powder, heated at 550 °C for at least 2 h

2.3 Salt mixture: sodium sulfate + sodium chloride 1:1 (w/w)

2.4 Cotton wool, extracted exhaustively with acetone

2.5 Acetone, for residue analysis

2.6 Water, bi-distilled or equivalent

2.7 Cyclohexane, for residue analysis

2.8 Ethyl acetate, for residue analysis

2.9 GPC eluting mixture: cyclohexane + ethyl acetate 1:1 (v/v); alternatively, redistilled as an azeotropic mixture

3 Apparatus

3.1 High-speed homogenizer, e.g. Ultra-Turrax (Janke u. Kunkel, Staufen/Br)

3.2 Glass jar, 500 mL or 750 mL, with a screw cap lined with aluminium foil

3.3 Graduated cylinder, 250 mL

3.4 Round-bottomed flask, 500 mL, with ground joint

3.5 Glass funnels, 45 mm and 100 mm dia.

3.6 Rotary vacuum evaporator, water bath temperature 40 °C

3.7 Volumetric pipette, 10 mL

3.8 Ultrasonic bath

3.9 Fluted filter paper, 6 cm dia., fast flow rate, extracted exhaustively with acetone

3.10 Membrane filter, 0.45 µm pore size, 25 mm dia. (e.g. Chromafil, type 0-45/25 organic, Macherey-Nagel Nr. 718 005)

Note: Glassware cleaned with detergents must be thoroughly rinsed with water and acetone.

4 Procedure

In a portion of the material, determine the water content in g/100 g. As an alternative, take the approximate water content from Table A 1 in the Appendix or from a literature source.

As the test portion, weigh 10 to 50 g (m_A) of the material having a water content of x g/100 g into a glass jar (for example, 25 to 50 g for dried fruit and dried vegetables, 10 to 20 g for spices and tea, 50 g for cereal grains, 25 to 50 g for skimmed milk powder, and 10 to 15 g for tobacco).

Then add sufficient water, pre-heated to 40 °C, to adjust the total water present to 100 g. The amount of water m_W to be added is calculated as follows: $m_W = 100 - m_A \cdot x/100$. Thoroughly stir the mixture in the glass jar with a glass rod and allow it to stand for 30 min. Next add 200 mL acetone and homogenize the mixture for 2 min with the homogenizer.

To the homogenate add 35 g sodium chloride and exactly 100 mL GPC eluting mixture and homogenize it again for 1 min. When the phases are clearly separated after 30 to 60 min, collect the upper organic phase. In case of insufficient phase separation centrifuge the mixture. Measure out exactly 200 ml (V_{R1}) of the organic phase in a graduated cylinder and filter this volume through a glass wool plug layered with approx. 100 g sodium sulfate in a funnel. Collect the filtrate in a 500-ml round-bottomed flask and rinse the graduated cylinder and the funnel four times each with approx. 20 mL GPC eluting mixture. Concentrate the combined filtrates and rinsings using the rotary evaporator. To the aqueous residue obtained, add exactly 7.5 mL ethyl acetate and swirl the flask in order to dissolve any residues adhering to the flask wall (this is facilitated by immersing the flask into an ultrasonic bath. Add approx. 5 g salt mixture for binding the remaining water. Swirl the flask and add exactly 7.5 mL cyclohexane to obtain a total volume of 15.0 mL (V_{End}). Swirl the flask again, allow the salt mixture to settle and filter the solution through a fluted filter paper or a membrane filter. With the filtrate, proceed as described in the module GPC (section 4.3).

5 Notes

If several acid-sensitive analytes (e.g. bupirimate, fenarimol, myclobutanil, pirimicarb) are extracted from an acidic material (e.g. citrus peel, fruit powder), only low recoveries are obtained. If the pH value of an aqueous homogenate of the material is less than 5, it is recommended to use module E 3 where acids are neutralized before the extraction.

For several analytes (e.g. dichlofluanid and tolylfluanid), the addition of an acid may increase the recoveries. In this case, set the pH value to less than 2 by mixing with diluted sulfuric acid (w = 10 g/100 mL) before adding the acetone.

With several materials, e.g. skimmed milk powder and some spices, this procedure can not be used or only with a smaller test portion because of insufficient phase separation after extraction. In this case module E 5 is better suitable.

6 Calculation

The sample equivalent C_{Ex} corresponds to the amount (in g) of sample material in one milliliter (1 mL) of extract. Calculate C_{Ex} in g/ml using the following equation:

$$C_{Ex} = \frac{m_A \cdot V_{R1}}{V_{Ex} \cdot V_{End}}$$

where:

m_A	is the sample mass, in g
V_{Ex}	is the volume of the organic phase after extraction and liquid/liquid partition, in ml (as a rule 285 mL, see Note below)
V_{R1}	is the aliquot portion of V_{Ex} taken for further processing, in mL (200 mL)
V_{End}	is the volume of the final sample test solution, in mL (15 mL)

Notes: 285 mL (V_{Ex}) result from 200 mL acetone and 100 mL GPC eluting mixture minus 15 mL caused by volume contraction and by loss of acetone in the aqueous phase.

The value for the sample equivalent C_{Ex} is required for calculating the content of an identified analyte according to section 6.2 of the basic text.

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MODULE E 3 Extraction and subsequent liquid/liquid partition for materials with a water content exceeding 70 g/100 g, a fat content below2.5 g/100 g and a high acid content

1 Outline

A sample having a pH value of less than 5 is adjusted to approx. pH 7 by adding sodium hydrogen carbonate. Sufficient water is added to the sample depending on the natural water content of the material in order to ensure an acetone/water ratio of 2 + 1 (v/v). The mixture is then extracted with acetone.

For liquid/liquid partitioning, sodium chloride and a mixture of cyclohexane and ethyl acetate are added to the homogenate. The mixture is again intensively mixed and allowed to stand until the phases separate. An aliquot portion of the organic phase is dried with sodium sulfate and concentrated. To the residue obtained, ethyl acetate is added followed by the same volume of cyclohexane. Remaining water is eliminated with a mixture of sodium sulfate and sodium chloride and the solution is filtered. The extract is used for cleanup by gel permeation chromatography (module GPC).

2 Reagents

2.1 Sodium hydrogen carbonate, p.a.

2.2 Sodium chloride, p.a.

2.3 Sodium sulfate, p.a., anhydrous, powder, heated at 550 °C for at least 2 h

2.4 Salt mixture: sodium sulfate + sodium chloride 1:1 (w/w)

2.5 Cotton wool, extracted exhaustively with acetone

2.6 Acetone, for residue analysis

2.7 Water, bi-distilled or equivalent

2.8 Cyclohexane, for residue analysis

2.9 Ethyl acetate, for residue analysis

2.10 GPC eluting mixture: cyclohexane + ethyl acetate 1:1 (v/v); alternatively, redistilled as an azeotropic mixture

3 Apparatus

3.1 High-speed homogenizer, e.g. Ultra-Turrax (Janke u. Kunkel, Staufen/Br)

3.2 Glass jar, 500 mL or 750 mL, with a screw cap lined with aluminium foil

3.3 Graduated cylinder, 250 mL

3.4 Round-bottomed flask, 500 mL, with ground joint

3.5 Glass funnels, 45 mm and 100 mm dia.

3.6 Rotary vacuum evaporator, water bath temperature 40 °C

3.7 Volumetric pipette, 10 mL

3.8 Ultrasonic bath

3.9 Fluted filter paper, 6 cm dia., fast flow rate, extracted exhaustively with acetone

3.10 Membrane filter, 0.45 µm pore size, 25 mm dia. (e.g. Chromafil, type 0-45/25 organic, Macherey-Nagel Nr. 718 005)

Note: Glassware cleaned with detergents must be thoroughly rinsed with water and acetone.

4 Procedure

In a portion of the material, determine the water content in g/100 g. As an alternative take the approximate water content from Table A 1 in the Appendix or from a literature source.

As the test portion, weigh 25 to 100 g (m_A) of the material having a water content of x g/100 g into a glass jar. Adjust the pH value to approx. 7 (using pH indicator paper) by adding small portions of sodium hydrogen carbonate. Then add sufficient water to adjust the total water present to 100 g. The amount of water m_W to be added is calculated as follows: $m_W = 100 - m_A \cdot x/100$. Next add 200 mL acetone and homogenize the mixture for 2 min with the homogenizer.

To the homogenate add 35 g sodium chloride and exactly 100 mL GPC eluting mixture and homogenize it again for 1 min. When the phases are clearly separated after 30 to 60 min, collect the upper organic phase. In case of insufficient phase separation centrifuge the mixture. Measure out exactly 200 ml (V_{R1}) of the organic phase in a graduated cylinder and filter this volume through a glass wool plug layered with approx. 100 g sodium sulfate in a funnel. Collect the filtrate in a 500-ml round-bottomed flask and rinse the graduated cylinder and the funnel four times each with approx. 20 mL GPC eluting mixture. Concentrate the combined filtrates and rinsings using the rotary evaporator. To the aqueous residue obtained, add exactly 7.5 mL ethyl acetate and swirl the flask in order to dissolve any residues adhering to the flask wall (this is facilitated by immersing the flask into an ultrasonic bath. Add approx. 5 g salt mixture for binding the remaining water. Swirl the flask and add exactly 7.5 mL cyclohexane to obtain a total volume of 15.0 mL (V_{End}). Swirl the flask again, allow the salt mixture to settle and filter the solution through a fluted filter paper or a membrane filter. With the filtrate, proceed as described in the module GPC (section 4.3).

5 Notes

It is feasible to weigh the test portion into the glass jar already one day before the extraction, if the glass jar is then tightly closed with a screw cap and is stored at – 20 °C.

The extraction described above is highly recommended for determining acid-sensitive analytes, e.g. bupirimate, fenarimol, myclobutanil, and pirimicarb.

6 Calculation

The sample equivalent C_{Ex} corresponds to the amount (in g) of sample material in one milliliter (1 mL) of extract. Calculate C_{Ex} in g/ml using the following equation:

$$C_{Ex} = \frac{m_A \cdot V_{R1}}{V_{Ex} \cdot V_{End}}$$

where:

m_A is the sample mass, in g

V_{Ex} is the volume of the organic phase after extraction and liquid/liquid partition, in ml (as a rule 285 mL, see Note below)

V_{R1} is the aliquot portion of V_{Ex} taken for further processing, in mL (200 mL)

V_{End} is the volume of the final sample test solution, in mL (15 mL)

Notes: 285 mL (V_{Ex}) result from 200 mL acetone and 100 mL GPC eluting mixture minus 15 mL caused by volume contraction and by loss of acetone in the aqueous phase.

The value for the sample equivalent C_{Ex} is required for calculating the content of an identified analyte according to section 6.2 of the basic text.

MODULE E 4 Two-stage extraction and liquid/liquid partition for materials with a water content exceeding 70 g/100 g and a fat content below 2.5 g/100 g

1 Outline

The sample is extracted with acetone, after addition of water depending on the natural water content of the material in order to ensure an acetone/water ratio of 2 + 1 (v/v) during the extraction.

The filtered extract is mixed with sodium chloride and is extracted with dichloromethane, resulting in the separation of excess water. An aliquot portion of the organic phase is dried with sodium sulfate and evaporated to dryness. The residue is dissolved in ethyl acetate and the solution is mixed with the same volume of cyclohexane. Remaining water is removed with sodium sulfate and the solution is filtered. The extract is used for cleanup by gel permeation chromatography (module GPC).

2 Reagents

2.1 Sodium chloride, p.a.

2.2 Sodium sulfate, p.a., anhydrous, powder, heated at 550 °C for at least 2 h

2.3 Filter aid, e.g. Celite 545 (Roth, Karlsruhe)

2.4 Cotton wool, exhaustively extracted with acetone

2.5 Acetone, for residue analysis

2.6 Water, bi-distilled or equivalent

2.7 Dichloromethane, for residue analysis

2.8 Ethyl acetate, for residue analyis

2.9 Cyclohexane, for residue analysis

3 Apparatus

3.1 High-speed homogenizer, e.g. Ultra-Turrax (Janke u. Kunkel, Staufen/Br)

3.2 Glass jar, 500 mL or 750 mL, with a screw cap lined with aluminium foil

3.3 Buchner porcelain funnel, 13.5 cm dia.

3.4 Filtration flask, 1 L

3.5 Round filter paper, 13.5 cm dia., fast flow rate, extracted exhaustively with acetone

3.6 Separatory funnel, 500 mL, with ground stopper and PTFE stopcock

3.7 Erlenmeyer flask, 300 mL

3.8 Round-bottomed flasks, 250 mL and 500 mL, with ground joints

3.9 Graduated cylinder, 250 mL

3.10 Volumetric pipette, 10 mL

3.11 Glass funnels, 45 mm and 100 mm dia.

3.12 Rotary vacuum evaporator, water bath temperature 40 °C

3.13 Fluted filter paper, 6 cm dia., fast flow rate, extracted exhaustively with acetone

3.14 Membrane filter, 0.45 µm pore size, 25 mm dia. (e.g. Chromafil, type 0-45/25 organic, Macherey-Nagel Nr. 718 005)

Note: Glassware cleaned with detergents must be thoroughly rinsed with water and acetone.

4 Procedure

In a portion of the material, determine the water content in g/100 g. As an alternative take the approximate water content from Table A 1 in the Appendix or from a literature source.

As the test portion, weigh 25 to 100 g (m_A) of the material having a water content of x g/100 g into a glass jar. Then add sufficient water to adjust the total water present to 100 g. The amount of water m_W to be added is calculated as follows: $m_W = 100 - m_A \cdot x/100$. Next add 200 mL acetone and homogenize the mixture for 2 min with the homogenizer. Add 10 g Celite to the mixture and homogenize again for 10 s.

Filter the homogenate with suction through a fast flow rate filter paper in a Buchner funnel until more than 200 mL of filtrate is obtained. Apply only gentle suction to avoid the loss of acetone by evaporation; therefore do not allow the filter cake to pull dry. The filtration should take not more than 1 min.

Measure out exactly 200 mL of the filtrate (V_{R1}) in a graduated cylinder and transfer this volume to a 500-mL separatory funnel. Add 20 g sodium chloride and shake vigorously for 3 min. Then add 100 mL dichloromethane, shake for 2 min and allow to stand for 10 min. (When using a mechanical shaker, add sodium chloride and dichloromethane simultaneously, ventilate the separatory funnel and shake the mixture for 5 min.) Usually after shaking some sodium chloride will remain undissolved. Discard the lower aqueous phase. Draw off the organic phase into a 300-mL Erlenmeyer flask, add approx. 25 g sodium sulfate and allow the flask to stand for about 30 min with occasional swirling. Filter the solution through a cotton wool plug layered with 3 cm of sodium sulfate in a funnel (100 mm dia.) and collect the filtrate in a 500-mL round-bottomed flask. Rinse the Erlenmeyer flask and filter twice with 20-mL portions of ethyl acetate. Concentrate the solution to 2 mL in a rotary evaporator, then evaporate the remaining solvent to dryness using a gentle stream of nitrogen. The residue must be free of dichloromethane.

To the residue, add exactly 7.5 mL ethyl acetate and dissolve it by gently swirling the flask. Add 2 g sodium sulfate, swirl the flask again and add exactly 7.5 mL cyclohexane to obtain a total volume of 15.0 mL (V_{End}). Shake for approx. 20 s and filter the solution through a fluted filter paper or a membrane filter. With the filtrate, proceed as described in the module GPC (section 4.3).

5 Notes

If clogging of the extract occurs, collect only a smaller volume of filtrate and take the portion which runs quickly through the filter paper. Reduce the amounts of sodium chloride and dichloromethane to be added according to the volume collected and consider the smaller volume (V_{R1}) in the calculation.

It is feasible to weigh the test portion into the glass jar already one day before the extraction, if the glass jar is then tightly closed with a screw cap and is stored at – 20 °C.

For several analytes (e.g. dichlofluanid and tolylfluanid), the addition of an acid may increase the recoveries. In

this case, set the pH value to less than 2 by mixing with diluted sulfuric acid (w = 10 g/100 mL) before adding the acetone.

The fat content of the material must not exceed 2.5 g/100 g, for otherwise the aqueous brine resulting in the partitioning step will retain small amounts of fat with some residues included, thus resulting in a loss of analytes.

6 Calculation

The sample equivalent C_{Ex} corresponds to the amount (in g) of sample material in one milliliter (1 mL) of extract. Calculate C_{Ex} in g/mL using the following equation:

$$C_{Ex} = \frac{m_A \cdot V_{R1}}{V_{Ex} \cdot V_{End}}$$

where:

m_A is the sample mass , in g

V_{Ex} is the total volume of extract, in mL (as a rule 295 mL, see Note below)

V_{R1} is the aliquot portion of V_{Ex} taken for further processing, in mL (200 mL)

V_{End} is the volume of the final sample test solution, in mL (15 mL)

Notes: 295 mL for V_{Ex} result from 200 mL acetone and 100 mL water minus 5 mL caused by volume contraction.

The value for the sample equivalent C_{Ex} is required for calculating the content of an identified analyte according to section 6.2 of the basic text.

MODULE E 5 Two-stage extraction and liquid/liquid partition for materials with a water content below 70 g/100 g and a fat content below 2.5 g/100 g

1 Outline

Sufficient water is added to the sample, dependent on the natural water content of the material in order to ensure an acetone/water ratio of 2 + 1 (v/v). The mixture is allowed to stand for approx. 30 min and is then extracted with acetone.

The filtered extract is mixed with sodium chloride and is extracted with dichloromethane, resulting in the separation of excess water. An aliquot portion of the organic phase is dried with sodium sulfate and evaporated to dryness. The residue is dissolved in ethyl acetate and the solution is mixed with the same volume of cyclohexane. Remaining water is removed with sodium sulfate and the solution is filtered. The extract is used for cleanup by gel permeation chromatography (module GPC).

2 Reagents

2.1 Sodium chloride, p.a.

2.2 Sodium sulfate, p.a., anhydrous, powder, heated at 550 °C for at least 2 h

2.3 Filter aid, e.g. Celite 545 (Roth, Karlsruhe)

2.4 Cotton wool, exhaustively extracted with acetone

2.5 Acetone, for residue analysis

2.6 Water, bi-distilled or equivalent

2.7 Dichloromethane, for residue analysis

2.8 Ethyl acetate, for residue analyis

2.9 Cyclohexane, for residue analysis

3 Apparatus

3.1 High-speed homogenizer, e.g. Ultra-Turrax (Janke u. Kunkel, Staufen/Br)

3.2 Glass jar, 500 mL or 750 mL, with a screw cap lined with aluminium foil

3.3 Buchner porcelain funnel, 13.5 cm dia.

3.4 Filtration flask, 1 L

3.5 Round filter paper, 13.5 cm dia., fast flow rate, extracted exhaustively with acetone

3.6 Separatory funnel, 500 mL, with ground stopper and PTFE stopcock

3.7 Erlenmeyer flask, 300 mL

3.8 Round-bottomed flasks, 250 mL and 500 mL, with ground joints

3.9 Graduated cylinder, 250 mL

3.10 Volumetric pipette, 10 mL

3.11 Glass funnels, 45 mm and 100 mm dia.

3.12 Rotary vacuum evaporator, water bath temperature 40 °C

3.13 Fluted filter paper, 6 cm dia., fast flow rate, extracted exhaustively with acetone

3.14 Membrane filter, 0.45 µm pore size, 25 mm dia. (e.g. Chromafil, type 0-45/25 organic, Macherey-Nagel Nr. 718 005)

Note: Glassware cleaned with detergents must be thoroughly rinsed with water and acetone.

4 Procedure

In a portion of the material, determine the water content in g/100 g. As an alternative, take the approximate water content from Table A 1 in the Appendix or from a literature source.

As the test portion, weigh 10 to 50 g (m_A) of the material having a water content of x g/100 g into a glass jar (for example, 25 to 50 g for dried fruit and dried vegetables, 10 to 20 g for spices and tea, 50 g for cereal grains, 25 to 50 g for skimmed milk powder, and 10 to 15 g for tobacco).

Then add sufficient water, pre-heated to 40 °C, to adjust the total water present to 100 g. The amount of water m_W to be added is calculated as follows: $m_W = 100 - m_A \cdot x/100$. Thoroughly stir the mixture in the glass jar with a glass rod and allow it to stand for 30 min. Next add 200 mL acetone and homogenize the mixture for 2 min with the homogenizer. Add 10 g Celite to the mixture and homogenize again for 10 s.

Filter the homogenate with suction through a fast flow filter paper in a Buchner funnel until more than 200 mL of filtrate is obtained. Apply only gentle suction to avoid the loss of acetone by evaporation; therefore do not allow the filter cake to pull dry. The filtration should take not more than 1 min.

Measure out exactly 200 mL of the filtrate (V_{R1}) in a graduated cylinder and transfer this volume to a 500-mL separatory funnel. Add 20 g sodium chloride and shake vigorously for 3 min. Then add 100 mL dichloromethane, shake for 2 min and allow to stand for 10 min. (When using a mechanical shaker, add sodium chloride and dichloromethane simultaneously, ventilate the separatory funnel and shake the mixture for 5 min.) Usually after shaking some sodium chloride will remain undissolved. Discard the lower aqueous phase. Draw off the organic phase into a 300-mL Erlenmeyer flask, add approx. 25 g sodium sulfate and allow the flask to stand for about 30 min with occasional swirling. Filter the solution through a cotton wool plug layered with 3 cm of sodium sulfate in a funnel (100 mm dia.) and collect the filtrate in a 500-mL round-bottomed flask. Rinse the Erlenmeyer flask and filter twice with 20-mL portions of ethyl acetate. Concentrate the solution to 2 mL in a rotary evaporator, then evaporate the remaining solvent to dryness using a gentle stream of nitrogen. The residue must be free of dichloromethane.

To the residue, add exactly 7.5 mL ethyl acetate and dissolve it by gently swirling the flask. Add 2 g sodium sulfate, swirl the flask again and add exactly 7.5 mL cyclohexane to obtain a total volume of 15.0 mL (V_{End}). Shake for approx. 20 s and filter the solution through a fluted filter paper or a membrane filter. With the filtrate, proceed as described in the module GPC (section 4.3).

5 Notes

If clogging of the extract occurs, collect only a smaller volume of filtrate and take the portion which runs quickly through the filter paper. Reduce the amounts of sodium

chloride and dichloromethane to be added according to the volume collected and consider the smaller volume (V_{R1}) in the calculation.

For several analytes (e.g. dichlofluanid and tolylfluanid), the addition of an acid may increase the recoveries. In this case, set the pH value to less than 2 by mixing with diluted sulfuric acid (w = 10 g/100 mL) before adding the acetone.

6 Calculation

The sample equivalent C_{Ex} corresponds to the amount (in g) of sample material in one milliliter (1 mL) of extract. Calculate C_{Ex} in g/mL using the following equation:

$$C_{Ex} = \frac{m_A \cdot V_{R1}}{V_{Ex} \cdot V_{End}}$$

where:

m_A is the sample mass, in g

V_{Ex} is the total volume of extract, in mL (as a rule 295 mL, see Note below)

V_{R1} is the aliquot portion of V_{Ex} taken for further processing, in mL (200 mL)

V_{End} is the volume of the final sample test solution, in mL (15 mL)

Notes: 295 mL for V_{Ex} result from 200 mL acetone and 100 mL water minus 5 mL caused by volume contraction.

The value for the sample equivalent C_{Ex} is required for calculating the content of an identified analyte according to section 6.2 of the basic text.

MODULE E 6 Dissolving fat in GPC eluting mixture

1 Outline

Plant and animal fats are dissolved in a GPC eluting mixture. The solution is used for cleanup by gel permeation chromatography (module GPC).

2 Reagents

2.1 Cyclohexane, for residue analysis

2.2 Ethyl acetate, for residue analysis

2.3 GPC eluting mixture: cyclohexane + ethyl acetate 1:1 (v/v); alternatively, redistilled as an azeotropic mixture

3 Apparatus

3.1 Volumetric flask, 25 mL

4 Procedure

Weigh 2.5 to 5 g (m_A) of fat into the volumetric flask (V_{End}) and dissolve it in 15 to 20 mL of GPC eluting mixture. Make up the solution to the mark (V_{End}) with GPC eluting mixture. With the solution, proceed as described in the module GPC (section 4.3).

5 Note

If the fat contains a little water, dry the solution with sodium sulfate.

6 Calculation

The sample equivalent C_{Ex} corresponds to the amount (in g) of sample material in one milliliter (1 mL) of extract. Calculate C_{Ex} in g/mL using the following equation:

$$C_{Ex} = \frac{m_A}{V_{End}}$$

where:

m_A is the sample mass, in g

V_{End} is the volume of the fat solution, in mL (25 mL)

Note: The value for the sample equivalent C_{Ex} is required for calculating the content of an identified analyte according to section 6.2 of the basic text.

MODULE E 7 Extraction in the presence of large amounts of fat

1 Outline

Fat or a dry sample with high fat content (e.g. oil seed) is mixed intensely with the suspension of a synthetic calcium silicate (trade name: Calflo E) in acetonitrile. The suspension is filtered and the volume of the filtrate measured. The solution is evaporated to dryness and the remaining residue is dissolved in GPC eluting mixture. The extract is used for cleanup by gel permeation chromatography (module GPC).

2 Reagents

2.1 Calflo E (Johns-Manville Prod. Corp. New York; obtainable from Dr. Ehrenstorfer, Augsburg), heated at 550 °C for at least 2 h

2.2 Filter aid, e.g. Celite 545 (Roth, Karlsruhe), heated at 550 °C for at least 2 h

2.3 Acetone, for residue analysis

2.4 Acetonitrile, for residue analysis

2.5 Cyclohexane, for residue analysis

2.6 Ethyl acetate, for residue analysis

2.7 Isooctane, for residue analysis

2.8 GPC eluting mixture: cyclohexane + ethyl acetate 1:1 (v/v); alternatively, redistilled as an azeotropic mixture

3 Apparatus

3.1 High-speed homogenizer, e.g. Ultra-Turrax (Janke u. Kunkel, Staufen/Br)

3.2 Glass jar, 500 mL or 750 mL, with a screw cap lined with aluminium foil

3.3 Buchner porcelain funnel, 12.5 cm dia., or glass filter funnel, 9.0 cm dia.

3.4 Filtration flask, 1 L

3.5 Glass funnel, 100 mm dia.

3.6 Graduated cylinders, 250 mL and 25 mL

3.7 Volumetric pipette, 10 mL

3.8 Round-bottomed flask, 250 mL, with ground joint

3.9 Rotary vacuum evaporator, water bath temperature 40 °C

3.10 Round filter paper, 12.5 cm or 9.0 cm dia., fast flow rate, extracted exhaustively with acetone

3.11 Fluted filter paper, 20 cm dia., extracted exhaustively with acetone

3.12 Membrane filter, 0.45 µm pore size, 25 mm dia. (e.g. Chromafil, type 0-45/25 organic, Macherey-Nagel Nr. 718 005)

Note: Glassware cleaned with detergents must be thoroughly rinsed with water and acetone.

4 Procedure

Weigh 5 to 30 g (m_A) of fat or an equivalent amount of a high-fat material into a glass jar containing 20 g Calflo E and 10 g Celite 545. Add 225 mL acetonitrile and 25 mL acetone (sum : V_{Ex}). Homogenize the mixture for 2 min with the homogenizer and filter the suspension with suction through a filter paper in a porcelain or glass filter funnel. Apply only gentle suction to ensure that not more than minimal portions of the filtrate evaporate. In addition, filter only for a short time, even if only 100 to 150 ml of filtrate are collected. With less than 100 ml of filtrate, repeat the procedure with a smaller amount of sample.

Then filter the filtrate through a dry fluted filter paper, covered with 0.5 g Calflo E, into a 250-mL graduated cylinder and measure the volume obtained (V_{R1}). Transfer the filtrate quantitatively, rinsing with acetone, into a weighed round-bottomed flask, add 10 mL isooctane and evaporate the solution to 0.5 to 1 mL using a rotary evaporator. Evaporate the remaining traces of solvent with a gentle stream of air. Weigh the flask again and calculate the mass of the residue.

If less than 2 g of fat remain, dissolve it in approx. 10 mL GPC eluting mixture. Transfer the solution into a 25-mL graduated cylinder, make up to 15 mL (V_{End}) with GPC eluting mixture and filter through a membrane filter, if necessary. If more than 2 g of fat remain, dissolve it in GPC eluting mixture and make up to an appropriate larger volume (V_{End}). With the solution, proceed as described in the module GPC (section 4.3).

5 Notes

This procedure is suitable for dry, high-fat foodstuffs (e.g. dried egg yolk, cocoa powder), for high-fat feedstuffs and for oil seed crops (rape, poppy, peanuts).

If Calflo E and Celite 545 are only heated at 130 °C overnight [8], occasionally interfering peaks in the gas chromatogram (module D 1) are observed.

6 Calculation

The sample equivalent C_{Ex} corresponds to the amount (in g) of sample material in one milliliter (1 mL) of extract. Calculate C_{Ex} in g/mL using the following equation:

$$C_{Ex} = \frac{m_A \cdot V_{R1}}{V_{Ex} \cdot V_{End}}$$

where:

m_A is the sample mass, in g

V_{Ex} is the total volume of acetone and acetonitrile added, in mL (250 mL)

V_{R1} is the volume of the filtrate after cleanup, in mL

V_{End} is the final volume of extract, in mL

Note: The value for the sample equivalent C_{Ex} is required for calculating the content of an identified analyte according to section 6.2 of the basic text.

MODULE E 8 Extraction of fat with hexane/acetone

1 Outline

The chopped sample is mixed with sodium sulfate and quartz sand. The mixture is filled into a column and is extracted with a mixture of hexane and acetone (2:1, v/v). The extracted amount of fat is weighed. An aliquot containing at most 2 g of fat is dissolved in the GPC eluting mixture.

2 Reagents

2.1 Acetone, for residue analysis

2.2 n-Hexane, for residue analysis

2.3 Extraction mixture: n-hexane + acetone 2:1 (v/v)

2.4 Cyclohexane, for residue analysis

2.5 Ethyl acetate, for residue analysis

2.6 GPC eluting mixture: cyclohexane + ethyl acetate 1:1 (v/v); alternatively, redistilled as an azeotropic mixture

2.7 Sodium sulfate, p.a., anhydrous, powder, heated at 550 °C for at least 2 h

2.8 Quartz sand, p.a.

2.9 Sodium sulfate + quartz sand mixture 1:1 (w/w)

2.10 Cotton wool, extracted exhaustively with acetone

3 Apparatus

3.1 Mortar and pestle

3.2 Glass tube, 1.2 cm i.d., length 30 cm, upper part extended at a length of 20 cm by 5 cm i.d., lower part fitted with stopcock

3.3 Round-bottomed flasks, 100 mL and 500 mL, with ground joints

3.4 Graduated cylinders, 500 mL and 25 mL

3.5 Volumetric pipette, 10 mL

3.6 Rotary vacuum evaporator, water bath temperature 40 °C

3.7 Volumetric flask, 100 mL

3.8 Metal evaporating dish, e.g. steel 18/8 or platinum

3.9 Water bath

3.10 Drying cabinet, set at 105 °C

Note: Glassware cleaned with detergents must be thoroughly rinsed with water and acetone.

4 Procedure

Depending on the fat content of the material, weigh 5 to 30 g (m_A) for the test portion so that the extract will contain 2 to 4 g of fat.

Transfer the test portion to a mortar containing approx. 30 to 50 g of a sodium sulfate/quartz sand mixture. Grind the mixture with the pestle and add a further 80 to 100 g of sodium sulfate/quartz sand mixture in small portions until a dry fine free-flowing mass is obtained. Fill the glass tube in the following order: an approx. 1-cm layer of cotton wool, an approx. 2-cm layer of sodium sulfate and then the finely ground mass. Place a 500-mL round-bottomed flask under the column. Add approx. 350 to 400 mL extraction mixture in small portions onto the dry column (use a portion of the extraction mixture to rinse the mortar and pestle). Allow the extraction mixture to drain through the column at a rate of 2 to 3 mL/min. Shortly before all of the extraction mixture has drained through, collect a few drops of eluate on filter paper and check if the fat extraction is completed. Concentrate the eluate to approx. 20 mL using a rotary evaporator. Transfer the concentrated solution quantitatively into a 100-mL volumetric flask (V_{Ex}) with hexane, make up to the mark with hexane and mix well.

For determining the fat content of the sample, pipet 10 mL of this extract into a dried and weighed evaporating dish and carefully evaporate the extract on a boiling water bath. Dry the evaporation residue in a drying cabinet for approx. 30 min at 105 °C to obtain a constant weight and weigh.

For further cleanup, pipet an aliquot portion (V_{R1}) of the extract, containing at most 2 g of fat, into a 100-mL round-bottomed flask. Concentrate the solution to approx. 2 mL using a rotary evaporator and evaporate the remaining solvent with a gentle stream of air. Dissolve the residue in a small amount of GPC eluting mixture, transfer the solution quantitatively into a 25-mL graduated cylinder and make up to 15.0 mL (V_{End}) with GPC eluting mixture. With the solution, proceed as described in the module GPC (section 4.3).

5 Notes

For a smaller test portion, use smaller amounts of sodium sulfate/quartz sand mixture and of extraction mixture.

Mix dry products, e.g. milk powder, with a few milliliters of water (about 2.5 to 3 mL/10 g) to form a paste and grind this paste with the sodium sulfate/quartz sand mixture.

6 Calculation

The sample equivalent C_{Ex} corresponds to the amount (in g) of sample material in one milliliter (1 mL) of extract. Calculate C_{Ex} in g/mL using the following equation:

$$C_{Ex} = \frac{m_A \cdot V_{R1}}{V_{Ex} \cdot V_{End}}$$

where:

m_A is the sample mass, in g

V_{Ex} is the volume of the eluate after concentration and filling up with hexane, in mL (100 mL)

V_{R1} is the aliquot portion of V_{Ex} taken for further processing, in mL

V_{End} is the final volume of the extract solution, in mL

Notes: The value for the sample equivalent C_{Ex} is required for calculating the content of an identified analyte according to section 6.2 of the basic text.

If the analytical result shall be based on the fat content of the material, m_A corresponds to the amount of fat in g in the eluate volume V_{Ex}.

MODULE E 9 Accelerated solvent extraction (ASE)

1 Outline

The chopped sample is transferred into an extraction cell and is extracted with the GPC eluting mixture at high temperature under pressure.

2 Reagents

2.1 Cyclohexane, for residue analysis

2.2 Ethyl acetate, for residue analysis

2.3 GPC eluting mixture: cyclohexane + ethyl acetate 1:1 (v/v); alternatively, redistilled as an azeotropic mixture

2.4 Diatomaceous earth, e.g. Isolute HM-N (Separtis GmbH, Grenzach-Wyhlen), or kieselguhr

2.5 Quartz sand, p.a.

2.6 Sodium sulfate, p.a., anhydrous, heated at 550 °C for at least 2 h

3 Apparatus

3.1 Equipment for Accelerated solvent extraction (ASE 200, Dionex, Idstein)

3.2 Extraction cells, 33 mL

3.3 Funnel, 50 mm dia.

3.4 Powder funnel, 75 mm dia.

3.5 Long-neck round-bottomed flask, 100 mL, with ground joint

3.6 Rotary vacuum evaporator, water bath temperature 40 °C

3.7 Graduated test tubes, e.g. 12 to 15 mL, with ground stopper and graduation mark at 10 mL

Note: Glassware cleaned with detergents must be thoroughly rinsed with water and acetone.

4 Procedure

Weigh 5 to 10 g (m_A) of dry material into an extraction cell. Mix powdery material in a small beaker with diatomaceous earth or kieselguhr beforehand. If necessary, fill up the cell with quartz sand. For the extraction, use the following conditions:

Solvent	GPC eluting mixture
Extraction temperature	120 °C
Extraction pressure	14 MPa
Static time	5 min
Number of extraction cycles	1
Flush volume (with solvent)	60 % of cell volume
Purge time with nitrogen	140 s

Transfer the extract through a funnel containing sodium sulfate into a 100-mL long-neck round-bottomed flask and concentrate it to approx. 2 mL in a rotary evaporator. Transfer the remaining solution quantitatively with GPC eluting mixture into a graduated test tube and make up to 10 mL (V_{End}). With the solution, proceed as described in the module GPC (section 4.3).

5 Note

The procedure is suitable for dry and water-containing foodstuffs. For materials containing water, weigh 5 to 10 g (m_A) into a small beaker. Add 2 to 5 g diatomaceous earth or kieselguhr and grind until a free-flowing mixture is obtained.

6 Calculation

The sample equivalent C_{Ex} corresponds to the amount (in g) of sample material in one milliliter (1 mL) of extract. Calculate C_{Ex} in g/mL using the following equation:

$$C_{Ex} = \frac{m_A}{V_{End}}$$

where:

m_A is the sample mass, in g

V_{End} is the final volume of extract, in mL

Note: The value for the sample equivalent C_{Ex} is required for calculating the content of an identified analyte according to section 6.2 of the basic text.

MODULE GPC Gel permeation chromatography

1 Outline

The extract solution derived from one of the modules E is cleaned up by gel permeation chromatography using the polystyrene gel Bio-Beads S-X3 and elution with a mixture of cyclohexane and ethyl acetate.

2 Reagents

2.1 Bio-Beads S-X3, 200-400 mesh (Bio-Rad Laboratories GmbH, München)

2.2 Cyclohexane, for residue analysis

2.3 Ethyl acetate, for residue analysis

2.4 GPC eluting mixture: cyclohexane + ethyl acetate 1:1 (v/v); alternatively, redistilled as an azeotropic mixture

2.5 GPC test solution, e.g. approx. ρ = 0.035 µg/mL HCB, 0.13 µg/mL trifluralin, 0.2 µg/mL flucythrinate and 0.25 µg/mL chinomethionat in GPC eluting mixture

3 Apparatus

3.1 Automated equipment for gel permeation chromatography, e.g. Gilson/Abimed Clean-Up XL system (ABIMED Analysen-Technik GmbH, Langenfeld)
or
Gel chromatograph GPC Autoprep 1002 (Analytical Biochemistry Laboratories, Columbia, Mo., USA, Supplier ANTEC GmbH, Pinneberg)
in both cases: chromatography column with end adapters, length 40 cm, 25 mm i.d., sample loop 5.0 mL

3.2 Glass syringe, 10 mL, with Luer-lock fitting (or disposable polypropylene syringes)

3.3 Long-neck round-bottomed flask, 150 mL, with ground joint

3.4 Pear-shaped flask, 250 mL, with ground joint

3.5 Rotary vacuum evaporator, water bath temperature 40 °C

3.6 Pasteur pipettes

3.7 Graduated test tubes, e.g. 12 to 15 mL, with ground stopper and graduation marks at 2.5, 5.0 and 10.0 mL

Note: Glassware cleaned with detergents must be thoroughly rinsed with water and acetone.

4 Procedure

4.1 Packing gel permeation column

Suspend 50 g of Bio-Beads in the GPC eluting mixture and allow them to swell overnight. Pour the suspension all at once into the chromatographic column (capacity approx. 180 mL). Once the gel has settled to a height of approx. 32 cm and is free from air bubbles, insert the end adapter and lower it down to the bed level. If the gel bed is compressed further after prolonged use, adjust the adapter accordingly. For further details refer to manufacturer's instructions.

4.2 Checking elution volumes

Check the elution conditions for every new gel permeation column and for a column whose separation efficiency has diminished. To do so, set the following parameters:

Dump	0 min	to discard 0 mL
Collect	2 min	to collect 10 mL

Inject 5.0 mL of the GPC test solution and elute with the GPC eluting mixture at 5.0 mL/min. Discard fractions 1 to 7. Collect the fractions 8 to 23 separately and analyze them by gas chromatography using an ECD (module D 1). From the recoveries obtained for the four analytes determine the appropriate range of elution volumes.

4.3 Cleanup of crude extracts

Inject approx. 10 ml of the filtered extract solution derived from one of the modules E into the 5-ml sample loop (5.0 mL = V_{GA}).

Elute the gel permeation column with the GPC eluting mixture at 5.0 mL/min. To do so, set the determined parameters beforehand, e.g.

Discard ("Dump")	17 min corresponding to	85 mL
Collect ("Collect")	22 min corresponding to	110 mL

The "Dump"-phase is discarded. Collect the "Collect"-fraction in a 150-mL long-neck round-bottomed flask or in a 250-mL pear-shaped flask. Concentrate it to approx. 1 mL in a rotary evaporator (rotate slowly, immerse the flask only slightly in the water bath). Pipet the remaining solution quantitatively into a ground-stoppered graduated test tube, rinse the flask with ethyl acetate, and make up to 5.0 mL (V_{GE}) with ethyl acetate.

5 Notes

During an analytical cleanup run, the flow rate must be 5.0 mL/min. For checking the flow rate, measure the volume of the eluate in a graduated cylinder.

For multiresidue analysis, a wide elution fraction is collected in order to cover a range of analytes as broad as possible. The elution volumes of the analytes to be determined are given in the Table of the Official Method L 00.00-37. For determining only some individual analytes, a smaller "Collect"-volume can be set in order to match the elution volume of the corresponding analyte.

Lipids are eluted in the volume up to approx. 100 mL. If no analytes eluting before 100 mL are to be determined, it is advisable to set the "Dump"-volume to at least 100 mL.

With high-fat materials and small "Dump"-volumes, the GPC eluate will contain more than 0.5 g of lipids. This may seriously affect the elution behaviour of the analytes when the GPC eluate is cleaned up further with modules C 1 and C 2.

6 Calculation

Calculate the dilution factor F_{GPC} using the following equation:

$$F_{GPC} = \frac{V_{GE}}{V_{GA}}$$

where:

V_{GA} is the aliquot portion of the extract volume injected onto the GPC column (5 mL)

V_{GE} is the final volume of GPC eluate after concentration (e.g. 5 mL)

Note: The dilution factor F_{GPC} is required for calculating the content of an identified analyte according to section 6.2 of the basic text.

MODULE C 1 Column chromatography on a small silica gel column (PCB residues not expected)

1 Outline

The GPC eluate is cleaned up further on a small silica gel column. This cleanup is essential for the gas chromatographic determination using an ECD (module D 1) and it is even sometimes necessary when using an NPD (module D 3). The concentrated GPC eluate is transferred onto a small silica gel column and the column is eluted with solvents or solvent mixtures of increasing polarity.

2 Reagents

2.1 Silica gel, deactivated with 1.5 % water: Heat silica gel 60, 70–230 mesh (Merck Nr. 7734) for at least 5 h at 130 °C, allow to cool in a desiccator, and store in a tightly sealed container (ground stopper and masking tape) in the desiccator. To 98,5 g dried silica gel in a 300-ml Erlenmeyer flask (with ground joint), add 1.5 ml water dropwise from a burette, with continuous swirling. Immediately stopper flask with ground stopper, 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. Check the separation efficiency of each silica gel batch according to section 4.2. The silica gel should not be kept longer than 5 days.

2.2 Sodium sulfate, p.a., anhydrous, heated at 550 °C for at least 2 h

2.3 Quartz wool

2.4 n-Hexane, for residue analysis

2.5 Isooctane, for residue analysis

2.6 Toluene, for residue analysis

2.7 Eluant 1: n-hexane + toluene mixture 65:35 (v/v)

2.8 Eluant 2: toluene

2.9 Eluant 3: toluene + acetone mixture 95:5 (v/v)

2.10 Eluant 4: toluene + acetone mixture 80:20 (v/v)

2.11 Eluant 5: acetone

2.12 Test solution in n-hexane: ρ = 0.05 µg/mL HCB, 0.1 µg/mL each of lindane, heptachlor and aldrin, 0.2 µg/mL each of cis-heptachlor epoxide, gamma-chlordane, alpha-endosulfan and dieldrin, 0.5 µg/mL each of o,p'-DDT and p,p'-DDD, 0.6 µg/mL p,p'-DDT and 1.2 µg/mL endosulfan sulfate

3 Apparatus

3.1 Long-neck round-bottomed flask, 100 mL, with ground joint

3.2 Pear-shaped flask, 25 mL, with ground joint

3.3 Chromatographic tube, length 23 cm, 7 mm i.d., with tapered outlet

3.4 Graduated test tubes, e.g. 12 to 15 mL, with ground stopper and graduation marks at 2.5, 5.0 and 10.0 mL

3.5 Rotary vacuum evaporator, water bath temperature 40 °C

3.6 Volumetric pipette, 10 mL

3.7 Pasteur pipette

3.8 Ultrasonic bath

Note: Glassware cleaned with detergents must be thoroughly rinsed with water and acetone.

4 Procedure

4.1 Preparation of column

Pack the chromatographic tube in the following order: a quartz wool plug, 1.0 g silica gel (deactivated with 1.5 % water), then a 5- to 10-mm layer of sodium sulfate. Finally insert a little quartz wool on top of the column packing. Before use, rinse the column with 5 mL n-hexane and discard the eluate.

4.2 Checking separation efficiency of silica gel

To the column pre-washed in section 4.1, add 2.0 mL of the test solution. Provided the activity of the silica gel is correctly adjusted, the added compounds should be present after elution as described in section 4.3 and gas chromatographic determination with ECD (module D 1) in the following eluates:

Eluate 1: HCB (100 %), lindane (100 %), heptachlor (100 %), aldrin (100 %), cis-heptachlor epoxide (partial fraction), gamma-chlordane (100 %), alpha-endosulfan (10 to 30 %), o,p'-DDT (100 %), p,p'-DDT (100 %), p,p'-DDD (100 %)

Eluate 2: cis-heptachlor epoxide (residual fraction), alpha-endosulfan (70 to 90%), endosulfan sulfate (95 to 100%), dieldrin (100 %)

4.3 Cleanup of sample extract

Pipet 2.5 mL (V_{CA}) of the solution derived from module GPC into a long-neck round-bottomed flask or a pear-shaped flask and add 10 mL isooctane. By rotating the flask slowly, carefully evaporate the solution to approx. 1 mL in a rotary evaporator (water bath temperature set at 30 to 40 °C). If an odour of ethyl acetate is still present, add isooctane again and repeat the evaporation. Repeat, if necessary, until no odour of ethyl acetate is present. The ethyl acetate must be completely removed (see section 5). Using a Pasteur pipette, transfer the remaining solution onto the silica gel column pre-washed in section 4.1. Allow the solution to drain to the upper surface of the column packing and then place a graduated test tube under the column.

Using a volumetric pipette, transfer 2.0 mL of eluant 1 into the flask. Immerse the flask in an ultrasonic bath and swirl carefully to dissolve the remaining residue adhering to the glass surface. Using the Pasteur pipette, transfer the solution onto the column and retain the flask to rinse it later. Allow the solution to drain to the upper surface of the column packing, then elute with a further 6.0 mL of eluant 1. After this has eluted, fill the graduated test tube up to 10.0 mL (V_{CE}) with eluant 1. Stopper the test tube and shake. This solution represents eluate 1.

Place another graduated test tube under the column. Using a volumetric pipette, add 2.0 mL of eluant 2 to the flask. Immerse and swirl the flask in the ultrasonic bath. Using the Pasteur pipette, transfer the solution onto the column and again retain the flask to rinse it later. Allow the solution to drain to the upper surface of the column packing, then elute with a further 6.0 mL eluant 2. After this has eluted, fill the graduated test tube up to 10.0 mL

(V_{CE}) with eluant 2. Stopper the test tube and shake. This solution represents eluate 2.

Continue the elution of the column as above with eluants 3 to 5 and make up eluates 3 and 4 to 10 mL (V_{CE}) with toluene and eluate 5 with acetone.

5 Notes

During preparation and storage of eluants 1, 3 and 4 make sure that the ratio of the components is correct.

The concentrated GPC eluate must not contain any traces of ethyl acetate. Otherwise the polarity of the eluants for the silica gel column will be too high, resulting in the analytes eluting much earlier (especially in eluates 1 to 3). Therefore it may be necessary to repeat the addition and evaporation of isooctane up to three times.

If the concentrated GPC eluate contains large amounts of lipids, this can also shift the analytes into other eluates. To overcome this the GPC eluate can be distributed over several silica gel columns.

If the silica gel column is eluted first with eluant 2, evaporate the GPC eluate twice and add toluene twice.

Frequently only eluates 1, 2 and 3 are needed for routine multiresidue analyses with ECD (module D 1).

The number of eluates to be collected depends on the nature of the analysis in each case.

Eluate 1 can be used for further cleanup by shaking with 1 to 2 mL concentrated sulfuric acid in order to determine such analytes which are resistant to concentrated sulfuric acid.

If the detectability of an analyte in a final eluate volume of 10 mL is not sufficient for the gas chromatographic determination, then pipet an aliquot (V_1) of the eluate V_{CE} into a 25-mL pear-shaped flask and concentrate it to approx. 0.5 mL in a rotary evaporator (bath temperature 30 to 40 °C). By rinsing the flask, transfer the remaining solution quantitatively into a graduated test tube and make up to a suitable volume (V_2). Without this concentration step, volumes V_1 and V_2 need not to be considered for the equation given in section 6.

If it is obvious that an analyte will not be detectable in a final eluate volume of 10 mL, then elute the respective fraction directly into a 25-mL pear-shaped flask and concentrate it to approx. 0.5 mL in a rotary evaporator (bath temperature 30 to 40 °C). By rinsing the flask, transfer the remaining solution quantitatively into a graduated test tube and make up to a suitable volume (V_{CE}).

On the silica gel column a fractionation of the analytes according to their polarity occurs together with the cleanup. Thus the presence of an analyte in a particular eluate gives additional information on its identity. In this respect it may be useful to clean up a GPC eluate which has already been analyzed by gas chromatography with an FPD (module D 2), NPD (module D 3) or MS (module D 4), additionally via the silica gel column. The distribution of the analytes among the eluates 1 to 5 is shown in the Table of the Official Method L 00.00-37.

6 Calculation

Calculate the dilution factor F_C using the following equation:

$$F_C = \frac{V_{CE} \cdot V_2}{V_{CA} \cdot V_1}$$

where:

- V_{CA} is the aliquot portion of the GPC eluate used, in mL (2.5 mL)
- V_{CE} is the final volume of the cleaned-up extract, in mL (e.g. 10 mL)
- V_1 is the aliquot portion of the eluate to be concentrated, in mL
- V_2 is the volume of the concentrated eluate, in mL

Note: The value for the dilution factor F_C is needed for calculating the content of an identified analyte according to section 6.2 of the basic text.

MODULE C 2 Column chromatography on a small silica gel column (PCB residues expected)

1 Outline

The GPC eluate is cleaned up further on a small silica gel column. This cleanup is essential for the gas chromatographic determination using an ECD (module D 1) and even sometimes necessary when using an NPD (module D 3). The concentrated GPC eluate is transferred onto a small silica gel column and the column is eluted with solvents or solvent mixtures of increasing polarity.

2 Reagents

2.1 Silica gel, deactivated with 1.5 % water: Heat silica gel 60, 70–230 mesh (Merck Nr. 7734) for at least 5 h at 130 °C, allow to cool in a desiccator, and store in a tightly sealed container (ground stopper and masking tape) in the desiccator. To 98,5 g dried silica gel in a 300-ml Erlenmeyer flask (with ground joint), add 1.5 ml water dropwise from a burette, with continuous swirling. Immediately stopper flask with ground stopper, 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. Check the separation efficiency of each silica gel batch according to section 4.2. The silica gel should not be kept longer than 5 days.

2.2 Sodium sulfate, p.a., anhydrous, heated at 550 °C for at least 2 h

2.3 Quartz wool

2.4 n-Hexane, for residue analysis

2.5 Isooctane, for residue analysis

2.6 Toluene, for residue analysis

2.7 Eluant 0: n-hexane

2.8 Eluant 1: n-hexane + toluene mixture 65:35 (v/v)

2.9 Eluant 2: toluene

2.10 Eluant 3: toluene + acetone mixture 95:5 (v/v)

2.11 Eluant 4: toluene + acetone mixture 80:20 (v/v)

2.12 Eluant 5: acetone

2.13 Test solution in n-hexane: ρ = 0.05 µg/mL HCB, 0.1 µg/mL each of lindane, heptachlor and aldrin, 0.2 µg/mL each of cis-heptachlor epoxide, gamma-chlordane, alpha-endosulfan and dieldrin, 0.5 µg/mL each of o,p'-DDT and p,p'-DDD, 0.6 µg/mL p,p'-DDT and 1.2 µg/mL endosulfan sulfate

3 Apparatus

3.1 Long-neck round-bottomed flask, 100 mL, with ground joint

3.2 Pear-shaped flask, 25 mL, with ground joint

3.3 Chromatographic tube, length 23 cm, 7 mm i.d., with tapered outlet

3.4 Graduated test tubes, e.g. 12 to 15 mL, with ground stopper and graduation marks at 2.5, 5.0 and 10.0 mL

3.5 Rotary vacuum evaporator, water bath temperature 40 °C

3.6 Volumetric pipette, 10 mL

3.7 Pasteur pipette

3.8 Ultrasonic bath

Note: Glassware cleaned with detergents must be thoroughly rinsed with water and acetone.

4 Procedure

4.1 Preparation of column

Pack the chromatographic tube in the following order: a quartz wool plug, 1.0 g silica gel (deactivated with 1.5 % water), then a 5- to 10-mm layer of sodium sulfate. Finally insert a little quartz wool on top of the column packing. Before use, rinse the column with 5 mL n-hexane and discard the eluate.

4.2 Checking separation efficiency of silica gel

To the column pre-washed in section 4.1, add 2.0 mL of the test solution. Provided the activity of the silica gel is correctly adjusted, the added compounds should be present after elution as described in section 4.3 and gas chromatographic determination with ECD (module D 1) in the following eluates:

Eluate 1: HCB (100 %), lindane (100 %), heptachlor (100 %), aldrin (100 %), cis-heptachlor epoxide (partial fraction), gamma-chlordane (100 %), alpha-endosulfan (10 to 30 %), o,p'-DDT (100 %), p,p'-DDT (100 %), p,p'-DDD (100 %)

Eluate 2: cis-heptachlor epoxide (residual fraction), alpha-endosulfan (70 to 90%), endosulfan sulfate (95 to 100%), dieldrin (100 %)

4.3 Cleanup of sample extract

Pipet 2.5 mL (V_{CA}) of the solution derived from module GPC into a long-neck round-bottomed flask or a pear-shaped flask and add 10 mL isooctane. By rotating the flask slowly, carefully evaporate the solution to approx. 1 mL in a rotary evaporator (water bath temperature set at 30 to 40 °C). If an odour of ethyl acetate is still present, add isooctane again and repeat the evaporation. Repeat, if necessary, until no odour of ethyl acetate is present. The ethyl acetate must be completely removed (see section 5). Using a Pasteur pipette, transfer the remaining solution onto the silica gel column pre-washed in section 4.1. Allow the solution to drain to the upper surface of the column packing and then place a graduated test tube under the column.

Using a volumetric pipette, transfer 2.0 mL of eluant 0 into the flask. Immerse the flask in an ultrasonic bath and swirl carefully to dissolve the remaining residue adhering to the glass surface. Using the Pasteur pipette, transfer the solution onto the column and retain the flask to rinse it later. Allow the solution to drain to the upper surface of the column packing, then elute with a further 6.0 mL of eluant 0. After this has eluted, fill the graduated test tube up to 10.0 mL (V_{CE}) with eluant 0. Stopper the test tube and shake. This solution represents eluate 0.

Place another graduated test tube under the column. Using a volumetric pipette, add 2.0 mL of eluant 1 to the flask. Immerse and swirl the flask in the ultrasonic bath. Using the Pasteur pipette, transfer the solution onto the column and again retain the flask to rinse it later. Allow the solution to drain to the upper surface of the column packing, then elute with a further 6.0 mL eluant 1. After this has eluted, fill the graduated test tube up to 10.0 mL

(V_{CE}) with eluant 1. Stopper the test tube and shake. This solution represents eluate 1.

Repeat the elution of the column as above with eluants 2 to 5 and make up eluates 2 to 4 to 10 mL (V_{CE}) with toluene and eluate 5 with acetone.

5 Notes

This module is recommended for the determination of residues in fish. It enables the separation of polychlorinated biphenyls from polychlorinated terpenes and several other organochlorine pesticides, e.g. DDT isomers and metabolites.

During preparation and storage of eluants 1, 3 and 4 make sure that the ratio of the components is correct.

The concentrated GPC eluate must not contain any traces of ethyl acetate. Otherwise the polarity of the eluants for the silica gel column will be to high, resulting in the analytes eluting much earlier (especially in eluates 0 to 3). Therefore it may be necessary to repeat the addition and evaporation of isooctane up to three times.

If the concentrated GPC eluate contains large amounts of lipids, this can also shift the analytes into other eluates. To overcome this the GPC eluate can be distributed over several silica gel columns.

Frequently only eluates 0 to 3 are needed for routine multiresidue analyses with ECD (module D 1).

The number of eluates to be collected depends on the nature of the analysis in each case.

Eluates 0 and 1 can be used for further cleanup by shaking with 1 to 2 mL concentrated sulfuric acid in order to determine such analytes which are resistant to concentrated sulfuric acid.

If the detectability of an analyte in a final eluate volume of 10 mL is not sufficient for the gas chromatographic determination, then pipet an aliquot (V_1) of the eluate V_{CE} into a 25-mL pear-shaped flask and concentrate it to approx. 0.5 mL in a rotary evaporator (bath temperature 30 to 40 °C). By rinsing the flask, transfer the remaining solution quantitatively into a graduated test tube and make up to a suitable volume (V_2). Without this concentration step, volumes V_1 and V_2 need not to be considered for the equation given in section 6.

If it is obvious that an analyte will not be detectable in a final eluate volume of 10 mL, then elute the respective fraction directly into a 25-mL pear-shaped flask and concentrate it to approx. 0.5 mL in a rotary evaporator (bath temperature 30 to 40 °C). By rinsing the flask, transfer the remaining solution quantitatively into a graduated test tube and make up to a suitable volume (V_{CE}).

On the silica gel column a fractionation of the analytes according to their polarity occurs together with the cleanup. Thus the presence of an analyte in a particular eluate gives additional information on its identity. In this respect it may be useful to clean up a GPC eluate which has already been analyzed by gas chromatography with an FPD (module D 2), NPD (module D 3) or MS (module D 4) additionally via the silica gel column. The distribution of the analytes among the eluates 0 to 5 is shown in the Table of the Official Method L 00.00-37.

6 Calculation

Calculate the dilution factor F_C using the following equation:

$$F_C = \frac{V_{CE} \cdot V_2}{V_{CA} \cdot V_1}$$

where:

V_{CA} is the aliquot portion of the GPC eluate used, in mL (2.5 mL)

V_{CE} is the final volume of the cleaned-up extract, in mL (e.g. 10 mL)

V_1 is the aliquot portion of the eluate to be concentrated, in mL

V_2 is the volume of the concentrated eluate, in mL

Note: The value for the dilution factor F_C is needed for calculating the content of an identified analyte according to section 6.2 of the basic text.

MODULE D 1 Gas chromatography with ECD

1 Outline

Organochlorine pesticides, PCBs, synthetic pyrethroids and other compounds containing halogen atoms, nitro groups and other electronegative groups are determined by gas chromatography with an ECD.

2 Procedure

The eluates from the cleanup on a small silica gel column (module C 1 or C 2) are injected – if necessary with the addition of an internal standard – into a gas chromatograph equipped with an ECD. The determinations can be performed with different gas chromatographs and fused silica capillary columns.

3 Apparatus

The following conditions have been proved to be reliable, but they should only be considered as examples. A change in individual parameters does not mean a substantial divergence from the method.

Gas chromatograph 1

Equipment	Hewlett Packard 5890
Column	Fused silica capillary column DB-1, length 30 m, 0.25 mm i.d., film thickness 0.25 µm (J & W Scientific Nr. 123-1032)
Temperature programme	100 °C for 2 min, programmed to rise at 7 °C/min to 250 °C, isothermal for 6 min, programmed to rise at 20 °C/min to 290 °C, then isothermal for 12 min
Split ratio	1 : 10
Injector temperature	250 °C
Detector	ECD ^{63}Ni, temperature 300 °C
Carrier gas	Argon/methane (9 + 1), 1.5 mL/min
Purge gas	Argon/methane (9 + 1), 35 mL/min
Injection volume	1 µL (in split mode)

Gas chromatograph 2

Equipment	Fisons MEGA 5300
Column 1	Fused silica capillary column DB-5, length 30 m, 0.32 mm i.d., film thickness 0.25 µm (J & W Scientific Nr. 123-5032)
Column 2	Fused silica capillary column DB-1701, length 30 m, 0.32 mm i.d., film thickness 0.25 µm (J & W Scientific Nr. 123-0732)
Temperature programme	70 °C for 2 min, programmed to rise at 30 °C/min to 160 °C, at 2.5° C/min to 220 °C and at 5 °C/min to 260 °C, then isothermal for 31 min
Split ratio	1 : 20, split valve closed 90 s
Injector temperature	250 °C
Detector base	Temperature 260 °C
Detectors 1 and 2	ECD ^{63}Ni, temperature 300 °C
Carrier gas	Helium, 2.5 mL/min
Purge gas	Argon/methane (9 + 1), 30 mL/min
Injection volume	1 µL (splitless)

4 Notes

For this gas chromatographic determination, use only a sample test solution which has been adequately subjected to cleanup by silica gel column chromatography or by other means. Generally the eluates 1 to 3 (module C 1) or the eluates 0 to 3 (module C 2) are suitable. The eluates 4 and 5 frequently contain consicerable amounts of co-extractives, which may affect the evaluation of the chromatograms.

Capillary columns coated with non-polar stationary phases have proved to be particularly reliable, e.g. 100 % methyl silicone or 5 % phenyl and 95 % methyl silicone. For confirmation of positive results a polar capillary column is recommended, e.g. 50 % methyl and 50% phenyl silicone or 14 % cyanopropylphenyl and 86 % methyl silicone.

Inject standard solutions at regular intervals throughout an analytical series in order to detect more easily any changes in the detector response.

It may occur that the quantitative evaluation of a peak is affected by interfering peaks from co-extractives. In this case, compare with a sample test solution obtained from an untreated control sample which, after cleanup, was fortified with standard solutions of the analytes in question.

Deposits in the injection port and at the column inlet as well as traces of alkali in the GC vials may cause the decomposition of some analytes.

When using an integrator or computer for the evaluation, periodically check the correct integration of the peaks.

5 Evaluation

The identification and confirmation of an analyte is described in section 6.1 of the basic text.

For the quantitative evaluation measure the peak areas (or peak heights) and compare them with the peak areas (or peak heights) obtained from standard solutions with known concentration. Inject equal volumes of the sample test solutions and the standard solutions, both in the same solvent.

If the signal for the analyte detected falls within the linear range of the ECD and if the calibration line intersects the ordinate near the origin, calculate the concentration (in µg/mL) of the analyte in the sample test solution (C_A) via the standard solution using the following equation:

$$C_A = \frac{A_A \cdot C_{St} \cdot V_2}{A_{St} \cdot V_1}$$

where:

A_A is the peak area (or peak height) of the analyte in the sample test solution

A_{St} is the peak area (or peak height) of the analyte in the standard solution

C_{St} is the concentration of the analyte in the standard solution, in µg/mL

V_1 is the aliquot portion of the sample test solution to be diluted, in mL (optional, see below)

V_2 is the final volume of the diluted sample test solution, in mL (optional, see below)

If the calibration line does not intersect the ordinate near the origin, graphically plot the peak areas or peak heights of at least three standard solutions of different concentrations against the concentrations of the analyte on the abscissa. Read the concentration of the analyte in the sample test solution (C_A) from this calibration curve.

If the signal obtained for the analyte lies above the highest calibration point, dilute an aliquot (V_1) of the sample test solution with the same solvent to a suitable volume (V_2). If this is not required, leave out volumes V_1 and V_2 from the formula given above.

Note: The concentration C_A is required for calculating the content of the identified analyte in the sample according to section 6.2 of the basic text.

MODULE D 2 Gas chromatography with FPD

1 Outline

Phosphorus- and sulfur-containing compounds are determined by gas chromatography with an FPD.

2 Procedure

The GPC eluate (module GPC) or the eluates from the cleanup on a small silica gel column (module C 1 or C 2) are injected – if necessary with the addition of an internal standard – into a gas chromatograph equipped with an FPD. The determinations can be performed with different gas chromatographs and fused silica capillary columns.

3 Apparatus

The following conditions have been proved to be reliable, but they should only be considered as examples. A change in individual parameters does not mean a substantial divergence from the method.

Gas chromatograph 1

Equipment	Hewlett Packard 5890
Column	Fused silica capillary column DB-1701, length 15 m, 0.53 mm i.d., film thickness 1.0 µm (J & W Scientific Nr. 125-0712)
Temperature programme	60 °C for 2 min, programmed to rise at 10 °C/min to 260 °C, then isothermal for 10 min
Split ratio	1 : 10, split valve closed 60 s
Injector temperature	250 °C
Detector	FPD with phosphorus and sulfur filters, temperature 240 °C
Carrier gas	Helium, 8 mL/min
Detector gases	Helium, 14 mL/min Hydrogen, 75 mL/min Air, 120 mL/min
Injection volume	3 µL (splitless)

Gas chromatograph 2

Equipment	Fisons MEGA 5300
Column	Fused silica capillary column DB-17, length 30 m, 0.32 mm i.d., film thickness 0.25 µm (J & W Scientific Nr. 123-1732)
Temperature programme	70 °C for 2 min, programmed to rise at 30 °C/min to 130 °C, at 5 °C/min to 250 °C and at 1 °C/min to 260 °C, then isothermal for 12 min
Split ratio	1 : 20, split valve closed 90 s
Injector temperature	250 °C
Detector base	Temperature 260 °C
Detector	FPD with phosphorus and sulfur filters, temperature 130 °C
Carrier gas	Helium, 3 mL/min
Detector gases	Helium, 25 mL/min Hydrogen, 100 mL/min Oxygen, 25 mL/min
Injection volume	2 µL (splitless)

4 Notes

As a rule, the eluate obtained from gel permeation chromatography (module GPC) can be directly injected. Only in special cases is it recommended to use an eluate from the small silica gel column (module C 1 or C 2).

Capillary columns coated with polar stationary phases have proved to be particularly reliable, e.g. 50 % methyl and 50 % phenyl silicone or 14 % cyanopropylphenyl and 86 % methyl silicone. For confirmation of positive results a non-polar capillary column is recommended, e.g. 100 % methyl silicone or 5 % phenyl and 95 % methyl silicone.

Inject standard solutions at regular intervals throughout an analytical series in order to detect more easily any changes in the detector response.

It may occur that the quantitative evaluation of a peak is affected by interfering peaks from co-extractives. In this case, compare with a sample test solution obtained from an untreated control sample which, after cleanup, was fortified with standard solutions of the analytes in question.

Deposits in the injection port and at the column inlet as well as traces of alkali in the GC vials may cause the decomposition of some analytes.

When using an integrator or computer for the evaluation, periodically check the correct integration of the peaks.

5 Evaluation

The identification and confirmation of an analyte is described in section 6.1 of the basic text.

For the quantitative evaluation measure the peak areas (or peak heights) and compare them with the peak areas (or peak heights) obtained from standard solutions with known concentration. Inject equal volumes of the sample test solutions and the standard solutions, both in the same solvent.

If the signal for the analyte detected falls within the linear range of the FPD and if the calibration line intersects the ordinate near the origin, calculate the concentration (in µg/mL) of the analyte in the sample test solution (C_A) via the standard solution using the following equation:

$$C_A = \frac{A_A \cdot C_{St} \cdot V_2}{A_{St} \cdot V_1}$$

where:

- A_A is the peak area (or peak height) of the analyte in the sample test solution
- A_{St} is the peak area (or peak height) of the analyte in the standard solution
- C_{St} is the concentration of the analyte in the standard solution, in µg/mL
- V_1 is the aliquot portion of the sample test solution to be diluted, in mL (optional, see below)

V_2 is the final volume of the diluted sample test solution, in mL (optional, see below)

If the calibration line does not intersect the ordinate near the origin, graphically plot the peak areas or peak heights of at least three standard solutions of different concentrations against the concentrations of the analyte on the abscissa. Read the concentration of the analyte in the sample test solution (C_A) from this calibration curve.

If the signal obtained for the analyte lies above the highest calibration point, dilute an aliquot (V_1) of the sample test solution with the same solvent to a suitable volume (V_2). If this is not required, leave out volumes V_1 and V_2 from the formula given above.

Note: The concentration C_A is required for calculating the content of the identified analyte in the sample according to section 6.2 of the basic text.

MODULE D 3 Gas chromatography with NPD

1 Outline

Phosphorus- and nitrogen-containing compounds are determined by gas chromatography with an NPD.

2 Procedure

The GPC eluate (module GPC) or the eluates from the cleanup on a small silica gel column (module C 1 or C 2) are injected – if necessary with the addition of an internal standard – into a gas chromatograph equipped with an NPD. The determinations can be performed with different gas chromatographs and fused silica capillary columns.

3 Apparatus

The following conditions have been proved to be reliable, but they should only be considered as examples. A change in individual parameters does not mean a substantial divergence from the method.

Gas chromatograph 1

Equipment	Hewlett Packard 5890
Column	Fused silica capillary column DB-5, length 30 m, 0.53 mm i.d., film thickness 1.5 µm (J & W Scientific Nr. 125-5032)
Temperature programme	100 °C for 2 min, programmed to rise at 10 °C/min to 250 °C, then isothermal for 25 min
Split ratio	1 : 10, split valve closed 60 s
Injector temperature	250 °C
Detector	NPD, temperature 270 °C
Carrier gas	Helium, 5 mL/min
Detector gases	Helium, 30 mL/min Hydrogen, 3 mL/min Air, 120 mL/min
Injection volume	3 µL (splitless)

Gas chromatograph 2

Equipment	Fisons MEGA 5300
Column 1	Fused silica capillary column DB-5 MS, length 30 m, 0.32 mm i.d., film thickness 0.25 µm (J & W Scientific Nr. 123-5532)
Column 2	Fused silica capillary column DB-17, length 30 m, 0.32 mm i.d., film thickness 0.25 µm (J & W Scientific Nr. 123-1732)
Temperature programme	70 °C for 2 min, programmed to rise at 30 °C/min to 100 °C and at 7 °C/min to 250 °C, isothermal for 15 min, programmed to rise at 1 °C/min to 260 °C, then isothermal for 5 min
Split ratio	1 : 20, split valve closed 90 s
Injector temperature	250 °C
Detector base	Temperature 260 °C
Detectors 1 and 2	NPD
Carrier gas	Helium, 2.5 mL/min
Detector gases	Nitrogen, 19 mL/min
Detector 1	Hydrogen, 1.8 mL/min Air, 100 mL/min
Injection volume	2 µL (splitless)

4 Notes

As a rule, the eluate obtained from gel permeation chromatography (module GPC) can be directly injected. Only in special cases is it recommended to use an eluate from the small silica gel column (module C 1 or C 2).

Capillary columns coated with polar stationary phases have proved to be particularly reliable, e.g. 50 % methyl and 50 % phenyl silicone or 14 % cyanopropylphenyl and 86 % methyl silicone. For confirmation of positive results a non-polar capillary column is recommended, e.g. 100 % methyl silicone or 5 % phenyl and 95 % methyl silicone.

Inject standard solutions at regular intervals throughout an analytical series in order to detect more easily any changes in the detector response.

It may occur that the quantitative evaluation of a peak is affected by interfering peaks from co-extractives. In this case, compare with a sample test solution obtained from an untreated control sample which, after cleanup, was fortified with standard solutions of the analytes in question.

Deposits in the injection port and at the column inlet as well as traces of alkali in the GC vials may cause the decomposition of some analytes.

When using an integrator or computer for the evaluation, periodically check the correct integration of the peaks.

5 Evaluation

The identification and confirmation of an analyte is described in section 6.1 of the basic text.

For the quantitative evaluation measure the peak areas (or peak heights) and compare them with the peak areas (or peak heights) obtained from standard solutions with known concentration. Inject equal volumes of the sample test solutions and the standard solutions, both in the same solvent.

If the signal for the analyte detected falls within the linear range of the NPD and if the calibration line intersects the ordinate near the origin, calculate the concentration (in µg/mL) of the analyte in the sample test solution (C_A) via the standard solution using the following equation:

$$C_A = \frac{A_A \cdot C_{St} \cdot V_2}{A_{St} \cdot V_1}$$

where:

A_A is the peak area (or peak height) of the analyte in the sample test solution

A_{St} is the peak area (or peak height) of the analyte in the standard solution

C_{St} is the concentration of the analyte in the standard solution, in µg/mL

V_1 is the aliquot portion of the sample test solution to be diluted, in mL (optional, see below)

V_2 is the final volume of the diluted sample test solution, in mL (optional, see below)

If the calibration line does not intersect the ordinate near the origin, graphically plot the peak areas or peak heights of at least three standard solutions of different concentrations against the concentrations of the analyte on the abscissa. Read the concentration of the analyte in the sample test solution (C_A) from this calibration curve.

If the signal obtained for the analyte lies above the highest calibration point, dilute an aliquot (V_1) of the sample test solution with the same solvent to a suitable volume (V_2). If this is not required, leave out volumes V_1 and V_2 from the formula given above.

Note: The concentration C_A is required for calculating the content of the identified analyte in the sample according to section 6.2 of the basic text.

MODULE D 4 Gas chromatography with MS

1 Outline

Analytes which are not detected by an ECD (module D 1), an FPD (module D 2) or an NPD (module D 3), or at best with minor sensitivity, are determined by gas chromatography with a mass spectrometric detector (MS). This technique is suitable for confirming the identity of an analyte as well.

2 Procedure

The GPC eluate (module GPC) or the eluates from the cleanup on a small silica gel column (module C 1 or C 2) are injected – if necessary with the addition of an internal standard – into a gas chromatograph equipped with an MS. The determinations can be performed with different gas chromatographs and fused silica capillary columns.

3 Apparatus

The following conditions have been proved to be reliable, but they should only be considered as examples. A change in individual parameters does not mean a substantial divergence from the method.

Equipment	Hewlett Packard 5890
Column	Fused silica capillary column HP-5 MS, length 30 m, 0.25 mm i.d., film thickness 0.25 µm (Hewlett Packard Nr. 190915-433)
Temperature programme	60 °C for 2 min, programmed to rise at 40 °C/min to 100 °C and at 10 °C/min to 250 °C, then isothermal for 15 min
Split ratio	1 : 10, split valve closed 60 s
Injector temperature	250 °C
Interface temperature	280 °C
Detector	MSD 5972
Carrier gas	Helium, 1 mL/min
Injection volume	1 µL (splitless)

4 Notes

As a rule, the eluate obtained from gel permeation chromatography (module GPC) can be directly injected. Only in special cases is it recommended to use an eluate from the small silica gel column (module C 1 or C 2).

Capillary columns coated with non-polar stationary phases have proved to be particularly reliable, e.g. 100 % methyl silicone or 5 % phenyl and 95 % methyl silicone. For confirmation of positive results a polar capillary column is recommended, e.g. 50 % methyl and 50 % phenyl silicone or 14 % cyanopropylphenyl and 86 % methyl silicone.

For detecting an analyte, selected ion monitoring (SIM mode) is more sensitive than scanning the full mass range. Select at least two, preferably three, characteristic mass ions of the analyte to ensure a reliable detection. In order to outline the chromatogram accurately under these conditions, adjust the scan rate to the selected number of ions and their scan times. Make sure that the retention time and the peak form as well as the intensity ratios of the selected ions from the sample test solution do correspond with the parameters and the intensity ratios of these ions from the standard solution. Do not use any peak of undefined shape for quantitative evaluation.

The MS is a particularly suitable tool for confirming the identity of an analyte which has been detected with an ECD (module D 1), an FPD (module D 2) or an NPD (module D 3). Confirmation of identity should be performed particularly in those cases in which it would appear that a maximum residue level (MRL) has been exceeded or in which a compound seems to be present, which is not expected in the sample analyzed. In this case the scan mode is used in order to identify the compound by means of its mass spectrum.

Inject standard solutions at regular intervals throughout an analytical series in order to detect more easily any changes in the detector response.

It may occur that the quantitative evaluation of a peak is affected by interfering peaks from co-extractives. In this case, compare with a sample test solution obtained from an untreated control sample which, after cleanup, was fortified with standard solutions of the analytes in question.

Deposits in the injection port and at the column inlet as well as traces of alkali in the GC vials may cause the decomposition of some analytes.

When using an integrator or computer for the evaluation, periodically check the correct integration of the peaks.

5 Evaluation

The identification and confirmation of an analyte is described in section 6.1 of the basic text.

For the quantitative evaluation measure the peak areas (or peak heights) and compare them with the peak areas (or peak heights) obtained from standard solutions with known concentration. Inject equal volumes of the sample test solutions and the standard solutions, both in the same solvent.

If the signal for the analyte detected falls within the linear range of the MS and if the calibration line intersects the ordinate near the origin, calculate the concentration (in µg/mL) of the analyte in the sample test solution (C_A) via the standard solution using the following equation:

$$C_A = \frac{A_A \cdot C_{St} \cdot V_2}{A_{St} \cdot V_1}$$

where:

- A_A is the peak area (or peak height) of the analyte in the sample test solution
- A_{St} is the peak area (or peak height) of the analyte in the standard solution
- C_{St} is the concentration of the analyte in the standard solution, in µg/mL
- V_1 is the aliquot portion of the sample test solution to be diluted, in mL (optional, see below)
- V_2 is the final volume of the diluted sample test solution, in mL (optional, see below)

If the calibration line does not intersect the ordinate near the origin, graphically plot the peak areas or peak heights of at least three standard solutions of different concentrations against the concentrations of the analyte on the abscissa. Read the concentration of the analyte in the sample test solution (C_A) from this calibration curve.

If the signal obtained for the analyte lies above the highest calibration point, dilute an aliquot (V_1) of the sample test solution with the same solvent to a suitable volume (V_2). If this is not required, leave out volumes V_1 and V_2 from the formula given above.

Note: The concentration C_A is required for calculating the content of the identified analyte in the sample according to section 6.2 of the basic text.

Table A 1: Average water content of crops and foodstuffs and calculated amounts of water to be added to 100 g of sample material for modules E 1 to E 5

Group	Crop and foodstuff	Average water content g/100 g	Water to be added to 100 g of sample material
Fruits			
Citrus fruits	Grapefruit	90	10
	Lemons	90	10
	Mandarins	90	10
	Orange peels	75	25
	Oranges	85	15
	Citrus juices	90	10
Pome fruits	Apples	85	15
	Pears	85	15
	Quinces	85	15
	Apples, dried	30	70
	Apple sauce	80	20
	Apple juice	90	10
Stone-fruits	Apricots	85	15
	Cherries	85	15
	Nectarines	85	15
	Peaches	90	10
	Plums	85	15
	Yellow plums	80	20
	Apricots, dried	30	70
	Peaches, dried	20	80
	Plums, dried	20	80
	Apricot nectar	85	15
Berries and small fruits	Blackberries	85	15
	Blueberries	85	15
	Elderberries	80	20
	Gooseberries	90	10
	Grapes	80	20
	Raisins	20	80
	Raspberries	85	15
	Red/black currants	85	15
	Strawberries	90	10
Other fruits	Bananas	75	25
	Figs, dried	20	80
	Kiwis	85	15
	Mangoes	80	20
	Papayas	90	10
	Pineapples	85	15

(continued)

Table A 1 (continued)

Group	Crop and foodstuff	Average water content g/100 g	Water to be added to 100 g of sample material
Vegetables			
Root and tubercules	Carrots	90	10
	Celeriac	90	10
	Horseradish	75	25
	Parsley roots	90	10
	Radishes	95	5
	Red turnips	90	10
	Shallots	80	20
	Viper's grass	80	20
	White radishes	95	5
Bulbs	Garlic	85	40
	Onions	85	10
Fruit vegetables	Aubergines	90	10
	Cucumbers	95	5
	Melons	90	10
	Paprika	90	10
	Pumpkins	95	5
	Tomatoes	95	5
	Zucchinis	95	5
Brassica	Broccoli	90	10
	Brussels sprouts	85	15
	Cauliflower	90	10
	Chinese cabbage	95	5
	Kale	90	10
	Kohlrabi	90	10
	Red cabbage	90	10
	Savoy cabbage	90	10
	White cabbage	90	10
Leafy vegetables and fresh herbs	Chicory	95	5
	Chives	85	15
	Cress	90	10
	Endive	95	5
	Iceberg lettuce	95	5
	Lamb's lettuce	85	15
	Lettuce	95	5
	Parsley	80	20
	Spinach	90	10
Shoot vegetables	Artichokes	85	15
	Asparagus	95	5
	Celery	95	5
	Leek	85	15
	Rhubarb	95	5
Pulse	Beans	90	10
	Peas (pods)	80	20

(continued)

Table A 1 (concluded)

Group	Crop and foodstuff	Average water content g/100 g	Water to be added to 100 g of sample material
Pulse (dry)	Beans, lentils, peas	10	[a]
Mushrooms		90	10
4.3 Diverse			
Potatoes		80	20
Cereals	(Grain, flakes, semolina, flour)	10	[a]
Spices		10	[a]
Coffee (raw)		10	[a]
Tea		10	[a]
Tea products		10	[a]
Beer		90	10
Must		90	10
Wine		90	10

[a] depending on weight (10–50 g) 95–99 g of water are necessary

Table A 2: Crops, for which the choice of extraction is determined by their fat content

Foodstuff	Fat (%)	Water (%)		Foodstuff	Fat (%)	Water (%)
Almonds (sweet)	54	6		Olives	36	41
Apricot stones	51	8		Peach stones	51	8
Avocado	24	70		Peanuts	48	5
Beechnuts	50	7		Pine nuts	51	6
Brazil nuts	67	4		Pistachios	52	6
Cashew nuts	42	4		Poppy seed	42	6
Coconut flesh	37	45		Pumpkin seeds	46	2
Coconuts	37	45		Sesame seeds	50	5
Corn	4	12		Soya beans	6	68
Cotton seed	19	7		Soya meal	20	9
Hazelnuts	62	5		Sunflower seeds	49	6
Linseed	31	6		Sweet chestnuts	11	45
Millet	4	11		Unripe spelt grain	3	13
Nuts	48	5		Walnuts	63	4
Oats	7	13				

Table A 3: Results from fortification trials

Analyte	Matrix [a]	Module used		Fortification level [mg/kg]	Recovery [b]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Acephate	W	E1	—	0.05–0.10	45	71	16	5
Acephate	W	E4	—	0.10	37		2	1
Acephate	T	E2	—	0.20	36	26	8	4
Acephate	T	E5	—	0.20	92		2	1
Acephate	T	E9	—	0.05–0.25	59	11	6	2
Aclonifen	F, W	E1	—	0.10–0.30	89	20	8	1
Aclonifen	T	E2	—	0.40	87	11	6	1
Acrinathrin	T	E9	C1	0.02	80	8	4	1
Aldicarb sulfone	W	E1	—	0.20	24		2	1
Aldrin	W	E1	—	0.05–0.20	87	10	12	2
Aldrin	W	E1	C1	0.02	89	11	9	3
Aldrin	W	E4	C1	0.02	62		2	1
Aldrin	T	E2	C1	0.04	78	17	5	2
Aldrin	T	E2	—	0.04	84	9	6	2
Aldrin	T	E5	—	0.04	76		2	1
Ametryn	W	E1	—	0.05–0.10	81	33	10	1
Anilazine	W	E1	C1	0.20	88		2	1
Atrazine	W	E1	—	0.11	89	15	10	4
Atrazine	T	E2	—	0.22	93	6	8	4
Atrazine	T	E5	—	0.22	100		2	1
Azinphos-ethyl	F, W	E1	—	0.01–1.00	93	16	10	1
Azinphos-ethyl	T	E2	—	0.10–0.20	134		2	1
Azinphos-ethyl	T	E9	—	0.05–0.20	98	19	6	2
Azinphos-methyl	W	E1	—	0.05–0.40	94	23	19	5
Azinphos-methyl	W	E1	C2	0.05–1.00	98	5	6	1
Azinphos-methyl	W	E4	C2	0.05–1.00	108	6	6	1
Azinphos-methyl	W	E4	—	0.40	102		2	1
Azinphos-methyl	T	E2	—	0.80	95	6	10	4
Azinphos-methyl	T	E5	—	0.80	101		2	1
Azinphos-methyl	T	E9	—	0.05–0.10	89	28	6	2
Azoxystrobin	F, W	E1	—	0.01–1.00	95	17	24	2
Azoxystrobin	T	E2	—	0.01–2.00	88	14	22	2
Benalaxyl	W	E1	—	0.05–0.30	87	18	19	2
Benalaxyl	W	E4	—	0.05–0.50	73	21	19	1
Bendiocarb	W	E1	—	0.05–1.00	114	20	32	2
Bendiocarb	T	E2	—	0.12–1.00	97	11	10	2
Bifenox	W	E1	—	0.05–0.10	86	22	10	1
Bifenthrin	W	E1	C1	0.03	84	18	6	3
Bifenthrin	W	E1	—	0.03	96		2	1
Bifenthrin	W	E4	—	0.03	75		2	1
Bifenthrin	T	E2	C1	0.06	87	10	6	3

[a] Abbreviations for matrix type: W = high water content; T = low water content; F = high fat content

[b] Abbreviations for recovery: x = mean recovery; V = relative standard deviation ; n = number of individual results

(continued)

Table A 3 (continued)

Analyte	Matrix [a)]	Module used		Fortification level [mg/kg]	Recovery [b)]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Bifenthrin	T	E2	—	0.06	93		2	1
Bifenthrin	T	E5	—	0.06	89		2	1
Bifenthrin	T	E9	C1	0.02	103	2	4	1
Binapacryl	T	E9	C1	0.02	112		2	1
Bitertanol	W	E1	—	0.05–0.21	92	23	18	5
Bitertanol	W	E4	—	0.21	105	1	2	1
Bitertanol	T	E2	—	0.41–0.50	88	12	9	4
Bitertanol	T	E5	—	0.41	107		2	1
Bromacil	W	E1	—	0.10	85	25	8	4
Bromacil	W	E1	C1	0.40	80		2	1
Bromacil	W	E4	—	0.10	105		2	1
Bromacil	T	E2	—	0.19	82	16	4	4
Bromacil	T	E5	—	0.19	74		2	1
Bromophos	F, W	E1	—	0.05–1.00	91	15	20	1
Bromophos	T	E2	—	0.10–0.20	94		2	1
Bromophos	T	E9	—	0.05–0.10	105	13	6	2
Bromophos	T	E9	—	0.10	119		2	1
Bromopropylate	W	E1	—	0.04–0.10	88	22	14	1
Bromopropylate	W	E1	C1	0.04	94	7	16	3
Bromopropylate	W	E4	—	0.04	79	12	4	1
Bromuconazole	F, W	E1	—	0.10–0.30	83	19	8	1
Bromuconazole	T	E2	—	0.40	83	11	6	1
Bupirimate	W	E1	—	0.05–0.20	91	27	21	5
Bupirimate	W	E4	—	0.05	84		2	1
Bupirimate	T	E2	—	0.10	92	7	8	4
Bupirimate	T	E5	—	0.10	106		2	1
Buprofezin	F, W	E1	—	0.10–0.30	82	21	18	5
Buprofezin	W	E4	—	0.10	89		2	1
Buprofezin	T	E2	—	0.19–0.40	90	16	12	5
Buprofezin	T	E5	—	0.19	105		2	1
Buturon	W	E1	—	1.00	77		2	1
Captafol	W	E1	—	0.05–0.10	77	23	10	1
Captan	W	E1	—	0.04–0.10	67	35	12	2
Captan	W	E1	C1	0.04	84	45	9	3
Captan	W	E4	C1	0.04	70		2	1
Captan	T	E2	C1	0.08	92	13	4	2
Captan	T	E2	—	0.08	61	29	4	2
Captan	T	E5	—	0.08	8		2	1
Carbaryl	W	E1	—	0.05–0.40	91	22	24	5
Carbaryl	F, W	E1	C2	0.05–0.60	98	9	4	1
Carbaryl	W	E4	—	0.21	123		2	1
Carbaryl	T	E2	—	0.21–0.41	100	17	8	4
Carbaryl	T	E5	—	0.41	125		2	1
Carbofuran	T	E2	—	0.42	83	35	6	4

(continued)

Table A 3 (continued)

Analyte	Matrix [a]	Module used		Fortification level [mg/kg]	Recovery [b]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Carbofuran	T	E5	—	0.42	111		2	1
Carbofuran	W	E1	—	0.20–0.50	82	19	9	4
Carbofuran	W	E4	—	0.21	91		2	1
Carbosulfan	W	E1	—	0.10	51	18	3	1
Chinomethionat	W	E1	C1	0.20	79		1	1
Chlorbenside	W	E1	C1	0.20	56		1	1
Chlordane, gamma	T	E9	C1	0.02	101	3	4	1
Chlorfenson	T	E9	C1	0.02	100	4	4	1
Chlorfenvinphos	W	E1	—	0.05–0.20	89	18	21	5
Chlorfenvinphos	W	E4	—	0.10	102		2	1
Chlorfenvinphos	T	E2	—	0.20	107	18	8	4
Chlorfenvinphos	T	E5	—	0.20	102		2	1
Chlorfenvinphos	T	E9	—	0.13	97		2	1
Chloridazon	T	E2	—	0.73	83	14	8	4
Chloridazon	T	E5	—	0.73	106		2	1
Chloridazon	W	E1	—	0.37	94	9	8	4
Chloridazon	W	E4	—	0.37	108		2	1
Chlormephos	T	E9	—	0.10	120		2	1
Chloroneb	T	E9	C1	0.02	100	6	4	1
Chloropropylate	T	E2	C1	0.66	87	7	4	2
Chloropropylate	T	E2	—	0.66	91	9	6	2
Chloropropylate	T	E5	—	0.66	87		2	1
Chloropropylate	W	E1	C1	0.33	84	22	9	3
Chloropropylate	W	E1	—	0.33	104		2	1
Chloropropylate	W	E4	C1	0.33	94		2	1
Chlorothalonil	T	E2	C1	0.04	74	14	4	2
Chlorothalonil	T	E2	—	0.04	32	55	4	1
Chlorothalonil	T	E5	—	0.04	46		2	1
Chlorothalonil	W	E1	C1	0.02	85	10	6	3
Chlorothalonil	W	E1	—	0.05–0.10	40	77	8	1
Chlorothalonil	W	E4	C1	0.02	80		2	1
Chlorothalonil	T	E9	C1	0.02	106	7	4	1
Chlorotoluron	W	E1	—	1.00	67		2	1
Chlorpropham	T	E2	—	0.19	90	14	8	4
Chlorpropham	T	E5	—	0.19	112		2	1
Chlorpropham	W	E1	—	0.10–0.20	97	26	10	4
Chlorpropham	W	E4	—	0.10	108		2	1
Chlorpyrifos	W	E1	—	0.05–0.10	88	13	19	5
Chlorpyrifos	W	E4	—	0.10	99		2	1
Chlorpyrifos	T	E2	—	0.20	93	4	8	4
Chlorpyrifos	T	E5	—	0.20	90		2	1
Chlorpyrifos	T	E9	—	0.10	118		2	1
Chlorpyrifos-methyl	F, W	E1	—	0.05–1.00	88	22	26	2
Chlorpyrifos-methyl	T	E2	—	0.10–0.20	76		2	1

(continued)

Table A 3 (continued)

Analyte	Matrix [a]	Module used		Fortification level [mg/kg]	Recovery [b]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Chlorpyrifos-methyl	T	E9	—	0.10	119		2	1
Chlorthal-dimethyl	W	E1	C1	0.20	92		1	1
Chlorthal-dimethyl	T	E9	C1	0.02	97	8	4	1
Chlozolinate	W	E1	C1	0.20	69		2	1
Chlozolinate	W	E1	—	0.20–0.40	86	17	13	4
Chlozolinate	W	E1	C1	0.10–1.00	103		2	1
Chlozolinate	W	E4	—	0.38	106		2	1
Chlozolinate	T	E2	C1	0.20	81		2	1
Chlozolinate	T	E2	—	0.75	98	10	8	4
Chlozolinate	T	E5	—	0.75	103		2	1
Cyanazine	W	E1	—	0.20	43		2	1
Cyanofenphos	W	E1	—	0.20	89		1	1
Cyanofenphos	T	E9	—	0.10	110		2	1
Cycloate	W	E1	C1	0.10–0.20	76	27	4	1
Cycloate	W	E1	—	0.05–0.20	91	12	12	4
Cycloate	W	E4	—	0.05	109		2	1
Cycloate	T	E2	C1	0.20	91		2	1
Cycloate	T	E2	—	0.10	97	12	8	4
Cycloate	T	E5	—	0.10	108		2	1
Cyfluthrin	W	E1	—	0.05–0.30	90	21	14	2
Cyfluthrin	W	E1	C1	0.10–0.30	85	10	22	3
Cyfluthrin	W	E4	—	0.30	80	12	4	1
Cyfluthrin	T	E9	C1	0.02	102	7	4	1
Cyhalothrin, lambda	W	E1	—	0.05–0.10	84	27	10	1
Cyhalothrin, lambda	W	E1	C1	0.20	91		1	1
Cyhalothrin, lambda	T	E9	C1	0.02	103	6	4	1
Cyhalothrin	W	E1	C1	0.10	66	38	14	3
Cyhalothrin	W	E1	—	0.10	85	12	4	1
Cyhalothrin	W	E4	—	0.10	72	17	4	1
Cypermethrin	W	E1	—	0.05–0.30	91	30	12	1
Cypermethrin	W	E1	C1	0.30	90	3	6	3
Cypermethrin	W	E4	—	0.30	80		2	1
Cypermethrin	T	E2	C1	0.60	92	3	6	3
Cypermethrin	T	E2	—	0.60	102		2	1
Cypermethrin	T	E5	—	0.60	86		2	1
Cypermethrin	T	E9	C1	0.02–2.50	103	11	10	2
Cyproconazole	F, W	E1	—	0.10–0.30	77	20	9	1
Cyproconazole	T	E2	—	0.40	80	9	6	1
DDD, p,p'-	T	E2	C1	0.08	85	15	5	2
DDD, p,p'-	T	E2	—	0.08	92	16	6	2
DDD, p,p'-	T	E5	—	0.08	79		2	1
DDD, p,p'-	W	E1	C1	0.04	90	10	9	3
DDD, p,p'-	W	E1	—	0.04	97		2	1
DDD, p,p'-	W	E4	C1	0.04	94		2	1

(continued)

Table A 3 (continued)

Analyte	Matrix [a]	Module used		Fortification level [mg/kg]	Recovery [b]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
DDE, p,p'-	T	E2	C1	0.04	91	8	6	3
DDE, p,p'-	T	E2	—	0.04	87		2	1
DDE, p,p'-	T	E5	—	0.04	78		2	1
DDE, p,p'-	T	E9	C1	0.02	101	4	4	1
DDE, p,p'-	W	E1	C1	0.02	87	10	6	3
DDE, p,p'-	W	E1	—	0.02	99		2	1
DDE, p,p'-	W	E4	—	0.02	77		2	1
DDT, p,p'-	W	E1	—	0.04	82	8	4	1
DDT, p,p'-	W	E1	C1	0.04	84	18	16	3
DDT, p,p'-	W	E4	—	0.04	120	29	4	1
DDT, p,p'-	T	E9	C1	0.02	104	3	4	1
Deltamethrin	W	E1	—	0.05–0.10	82	23	14	2
Deltamethrin	W	E1	C1	0.10	92	6	16	3
Deltamethrin	W	E4	—	0.10	90	12	4	1
Deltamethrin	T	E9	C1	0.02	100	2	4	1
Demeton-S-methyl	W	E1	—	0.05–0.10	46	38	10	1
Demeton-S-methyl	T	E9	—	0.05–0.13	80	12	6	2
Demeton-S-methyl sulfone	W	E1	—	0.05–0.10	75	33	10	1
Demeton-S-methyl sulfone	T	E9	—	0.25	78		2	1
Diazinon	W	E1	—	0.05–0.10	89	14	20	5
Diazinon	W	E4	—	0.10	99		2	1
Diazinon	T	E2	—	0.20	93	5	8	4
Diazinon	T	E5	—	0.20	96		2	1
Diazinon	T	E9	—	0.20	121		2	1
Dichlobenil	T	E2	—	0.39	90	9	8	4
Dichlobenil	T	E5	—	0.39	104		2	1
Dichlobenil	W	E1	—	0.19	92	14	8	4
Dichlobenil	W	E4	—	0.19	98		2	1
Dichlofluanid	W	E1	—	0.04–0.10	83	23	12	1
Dichlofluanid	W	E1	C1	0.04–0.20	82	12	10	3
Dichlofluanid	W	E4	C1	0.04	87		2	1
Dichlofluanid	T	E2	—	0.08	53	92	4	1
Dichlofluanid	T	E2	C1	0.08	72	26	5	3
Dichlofluanid	T	E5	—	0.08	3	0	1	1
Dichlorvos	W	E1	—	0.05–0.20	81	17	20	5
Dichlorvos	W	E4	—	0.10	86		2	1
Dichlorvos	T	E2	—	0.20	83	11	10	4
Dichlorvos	T	E4	—	0.20	84		2	1
Dichlorvos	T	E9	—	0.05–0.10	91	5	6	2
Dicloran	T	E2	C1	0.04	87	7	4	2
Dicloran	T	E2	—	0.04	71	19	6	2
Dicloran	T	E5	—	0.04	72		2	1

(continued)

Table A 3 (continued)

Analyte	Matrix [a)]	Module used		Fortification level [mg/kg]	Recovery [b)]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Dicloran	W	E1	C1	0.02	74	35	9	3
Dicloran	W	E1	—	0.02–0.10	90	15	12	2
Dicloran	W	E4	—	0.02	87		2	1
Dicofol, p,p'-	W	E1	—	0.05–0.10	88	53	12	2
Dicofol, p,p'-	W	E1	C1	0.05–0.50	84	10	7	3
Dicofol, p,p'-	W	E4	—	0.05	99		2	1
Dicofol, p,p'-	T	E2	C1	0.10	88	11	6	3
Dicofol, p,p'-	T	E2	—	0.10	76		2	1
Dicofol, p,p'-	T	E5	—	0.10	103		2	1
Dicofol	T	E9	C1	0.02–2.50	98	17	8	2
Dieldrin	W	E1	—	0.02–0.10	87	19	14	2
Dieldrin	W	E1	C1	0.02	85	13	16	3
Dieldrin	W	E4	—	0.02	68	15	4	1
Dieldrin	T	E9	C1	0.02	89	14	4	1
Difenoconazole	F, W	E1	—	0.10–0.30	79	18	7	1
Difenoconazole	T	E2	—	0.40	86	11	6	1
Dimefox	T	E9	—	0.05	83	1	4	1
Dimethenamid	F, W	E1	—	0.10–0.30	82	16	9	1
Dimethenamid	T	E2	—	0.40	83	12	6	1
Dimethoate	W	E1	—	0.05–0.10	95	29	19	5
Dimethoate	W	E4	—	0.10	110		2	1
Dimethoate	T	E2	—	0.20	93	12	10	4
Dimethoate	T	E5	—	0.20	113		2	1
Dimethoate	T	E9	—	0.25	91		2	1
Diniconazole	F, W	E1	—	0.10–0.30	81	15	9	1
Diniconazole	T	E2	—	0.40	81	9	6	1
Dioxathion	W	E1	—	0.05–0.10	76	42	10	1
Dioxathion	T	E9	—	0.25	104		2	1
Diphenylamine	W	E1	—	0.20	57		2	1
Disulfoton	W	E1	—	0.05–0.10	72	40	16	5
Disulfoton	W	E4	—	0.10	90		2	1
Disulfoton	T	E2	—	0.20	53	72	6	4
Disulfoton	T	E5	—	0.20	54		2	1
Disulfoton	T	E9	—	0.05–0.25	95	9	6	2
Diuron	W	E1	—	1.00	49	9	2	1
Endosulfan, alpha	W	E1	—	0.02–0.10	94	34	12	2
Endosulfan, alpha	W	E1	C1	0.02	89	10	12	3
Endosulfan, alpha	W	E4	—	0.02	82		2	1
Endosulfan, alpha	T	E2	C1	0.04	88	14	6	3
Endosulfan, alpha	T	E2	—	0.04	82		2	1
Endosulfan, alpha	T	E5	—	0.04	79		2	1
Endosulfan, beta	T	E2	C1	0.04	92	7	6	3
Endosulfan, beta	T	E2	—	0.04	84		2	1
Endosulfan, beta	T	E5	—	0.04	77		2	1

(continued)

Table A 3 (continued)

Analyte	Matrix [a)]	Module used		Fortification level [mg/kg]	Recovery [b)]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Endosulfan, beta	T	E9	C1	0.02	95	5	4	1
Endosulfan, beta	W	E1	C1	0.02–0.03	92	13	12	3
Endosulfan, beta	W	E1	—	0.02–0.10	91	34	12	2
Endosulfan, beta	W	E4	—	0.02	79		2	1
Endosulfan sulfate	W	E1	—	0.02–0.10	89	24	12	2
Endosulfan sulfate	W	E1	C1	0.02–0.04	97	9	12	3
Endosulfan sulfate	W	E4	—	0.02	90		2	1
Endosulfan sulfate	T	E2	C1	0.04	82	9	6	3
Endosulfan sulfate	T	E2	—	0.04	91		2	1
Endosulfan sulfate	T	E5	—	0.04	88		2	1
Endosulfan sulfate	T	E9	C1	0.02	96	6	4	1
Endrin	T	E2	C1	0.04	85	9	5	2
Endrin	T	E2	—	0.04	82	14	6	2
Endrin	T	E5	—	0.04	82		2	1
Endrin	W	E1	C1	0.02	83	8	9	3
Endrin	W	E1	—	0.02	92		2	2
Endrin	W	E4	C1	0.02	92		2	1
EPN	T	E9	—	0.05	95	2	4	1
Epoxiconazole	W	E1	—	0.10–0.30	83	18	8	1
Epoxiconazole	T	E2	—	0.40	84	12	6	1
Ethidimuron	W	E1	—	1.00	72		2	1
Ethion	T	E2	—	0.20	93	6	8	4
Ethion	T	E5	—	0.20	99		2	1
Ethion	T	E9	—	0.05	99	4	4	1
Ethion	W	E1	—	0.05–0.10	90	16	21	5
Ethion	W	E4	—	0.10	96		2	1
Ethion	T	E9	—	0.05	110		2	1
Ethoprophos	F, W	E1	—	0.05–0.30	80	19	20	2
Ethoprophos	T	E2	—	0.20	79	12	5	1
Ethoxyquin	W	E1	—	0.40	27		2	1
Etrimfos	W	E1	—	0.05–0.10	87	13	11	1
Etrimfos	T	E9	—	0.05	114		2	1
Fenamiphos	W	E1	—	0.05–0.10	68	22	10	1
Fenamiphos	T	E9	—	0.13	109		2	1
Fenarimol	W	E1	—	0.05–0.21	79	29	20	5
Fenarimol	W	E4	—	0.21	84		2	1
Fenarimol	T	E2	—	0.42	93	28	8	4
Fenarimol	T	E5	—	0.42	105		2	1
Fenbuconazole	F, W	E1	—	0.10–0.30	61	80	9	1
Fenbuconazole	T	E2	—	0.40	80	10	6	1
Fenfluthrin	T	E9	C1	0.02	102	4	4	1
Fenitrothion	W	E1	—	0.05–0.10	86	15	10	1
Fenitrothion	T	E9	—	0.05–0.13	96	3	6	2
Fenpropathrin	W	E1	—	0.05–0.10	94	49	10	1

(continued)

Table A 3 (continued)

Analyte	Matrix [a]	Module used		Fortification level [mg/kg]	Recovery [b]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Fenpropathrin	T	E9	C1	0.02	90	7	4	1
Fenpropidin	F, W	E1	—	0.10–0.30	17	107	6	1
Fenpropidin	T	E2	—	0.40	23	130	6	1
Fenpropimorph	W	E1	—	0.05–1.00	90	23	48	6
Fenpropimorph	W	E4	—	0.21	91		2	1
Fenpropimorph	T	E2	—	0.14–1.00	97	12	16	4
Fenpropimorph	T	E5	—	0.41	110		2	1
Fensulfothion	F, W	E1	—	0.10–0.30	81	14	10	2
Fensulfothion	T	E2	—	0.20	65	14	5	1
Fensulfothion	T	E9	—	0.10	108		2	1
Fenthion	F, W	E1	—	0.05–0.10	77	14	16	1
Fenthion	T	E9	—	0.25	97		2	1
Fenthion sulfoxide	W	E1	—	0.05–0.10	95	28	10	1
Fenthion sulfoxide	T	E9	—	0.13	104		2	1
Fenvalerate	W	E1	—	0.05–0.20	87	27	14	2
Fenvalerate	W	E1	C1	0.20	89	12	17	3
Fenvalerate	W	E4	—	0.20	80	6	4	1
Fenvalerate	T	E9	C1	0.02	94	6	4	1
Flucythrinate	W	E1	—	0.05–0.20	85	27	14	2
Flucythrinate	W	E1	C1	0.20	76	30	16	3
Flucythrinate	W	E4	—	0.20	77	11	4	1
Flucythrinate	T	E9	C1	0.02	60	32	4	1
Flumetralin	T	E9	C1	0.02	89	14	4	1
Fluorodifen	W	E1	—	0.20	88		1	1
Flurtamone	F, W	E1	—	0.10–0.30	81	12	9	1
Flurtamone	T	E2	—	0.40	66	14	6	1
Flusilazole	W	E1	—	0.05–1.00	100	20	41	6
Flusilazole	T	E2	—	0.10–1.00	95	10	18	6
Flusilazole	W	E4	—	0.005–0.05	123	23	6	2
Flusilazole	T	E5	—	0.01–0.50	122	21	6	2
Fluvalinate	W	E1	C1	0.20	57	60	16	3
Fluvalinate	W	E1	—	0.20	81	11	4	1
Fluvalinate	W	E4	—	0.20	78	21	4	1
Fluvalinate	T	E9	C1	0.02	103		2	1
Fluvalinate, tau	W	E1	—	0.05–0.10	79	37	10	1
Folpet	W	E1	—	0.02–0.10	79	27	12	2
Folpet	W	E1	C1	0.02	72	19	9	3
Folpet	W	E4	C1	0.02	65		2	1
Folpet	T	E2	—	0.04	70	54	4	2
Folpet	T	E2	C1	0.04	78	19	5	2
Folpet	T	E5	—	0.04	55		2	1
Fonofos	W	E1	—	0.10	83		1	1
Formothion	F, W	E1	—	0.05–0.20	77	16	10	2
Formothion	T	E2	—	0.10	73	16	5	1

(continued)

Table A 3 (continued)

Analyte	Matrix [a]	Module used		Fortification level [mg/kg]	Recovery [b]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Formothion	T	E9	—	0.10	100		2	1
Fuberidazole	W	E1	—	0.20	63		1	1
HCH, alpha	W	E1	C1	0.02	90	6	16	3
HCH, alpha	W	E1	—	0.02	88	5	4	1
HCH, alpha	W	E4	—	0.02	98	7	4	1
HCH, alpha	T	E9	C1	0.02	101	4	4	1
HCH, beta	W	E1	—	0.03	91	5	4	1
HCH, beta	W	E1	C1	0.03	90	11	16	3
HCH, beta	W	E4	—	0.03	94	9	4	1
Heptachlor	T	E2	C1	0.04	79	12	5	2
Heptachlor	T	E2	—	0.04	87	8	6	2
Heptachlor	T	E5	—	0.04	75		2	1
Heptachlor	W	E1	C1	0.02	86	9	9	3
Heptachlor	W	E1	—	0.02	91		2	1
Heptachlor	W	E4	C1	0.02	74		2	1
Heptachlor	T	E9	C1	0.02	102	4	4	1
Heptachlor epoxide, cis	W	E1	—	0.02	91	5	4	1
Heptachlor epoxide, cis	W	E4	—	0.02	79	7	4	1
Heptachlor epoxide, cis	W	E1	C1	0.02	90	12	16	3
Heptenophos	T	E9	—	0.20	114		2	1
Hexachlorobenzene	T	E2	C1	0.02	88	11	6	3
Hexachlorobenzene	T	E2	—	0.02	101		2	1
Hexachlorobenzene	T	E5	—	0.02	100		2	1
Hexachlorobenzene	T	E9	C1	0.02	97	4	4	1
Hexachlorobenzene	W	E1	C1	0.01	85	10	6	3
Hexachlorobenzene	W	E1	—	0.01	85		2	1
Hexachlorobenzene	W	E4	—	0.01	105		2	1
Hexaconazole	T	E2	—	0.19	93	11	6	3
Hexaconazole	T	E5	—	0.19	99		2	1
Hexaconazole	W	E1	—	0.10–0.20	83	33	12	4
Hexaconazole	W	E4	—	0.10	102		2	1
Imazalil	W	E1	—	0.20	32		2	1
Iodofenphos	T	E2	—	0.20	95	4	8	4
Iodofenphos	T	E5	—	0.20	99		2	1
Iodofenphos	T	E9	—	0.25	37		2	1
Iodofenphos	W	E1	—	0.10	91	9	11	4
Iodofenphos	W	E4	—	0.10	103		2	4
Iprobenfos	T	E9	—	0.05	97	5	4	1
Iprodione	W	E1	—	0.05–0.29	87	80	12	2
Iprodione	W	E1	C1	0.29–0.50	94	23	10	3
Iprodione	W	E4	C1	0.29	87		2	1
Iprodione	T	E2	C1	0.58	92	6	5	2
Iprodione	T	E2	—	0.58	84	11	6	2
Iprodione	T	E5	—	0.58	94		2	1

(continued)

Table A 3 (continued)

Analyte	Matrix [a]	Module used		Fortification level [mg/kg]	Recovery [b]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Isobumeton	W	E1	—	0.20	81		2	1
Isofenphos	W	E1	—	0.05–0.10	85	14	10	1
Isofenphos	T	E9	—	0.25	101		2	1
Isofenphos oxone	T	E9	—	0.13	95		2	1
Lindane	W	E1	—	0.02–0.10	87	11	14	2
Lindane	W	E1	C1	0.02–0.05	92	9	20	3
Lindane	W	E4	—	0.02	99	7	4	1
Lindane	T	E9	C1	0.02	108	6	4	1
Linuron	W	E1	—	1.00	84		2	1
Malaoxon	F, W	E1	—	0.05–1.00	88	37	19	1
Malaoxon	T	E2	—	0.10–0.20	109		2	1
Malaoxon	T	E9	—	0.13	101		2	1
Malathion	W	E1	—	0.05–0.10	87	14	20	5
Malathion	W	E4	—	0.10	111		2	1
Malathion	T	E2	—	0.20	98	6	8	4
Malathion	T	E5	—	0.20	107		2	1
Malathion	T	E9	—	0.25	107		1	1
Mecarbam	W	E1	—	0.05–0.10	87	20	21	5
Mecarbam	W	E4	—	0.10	108		2	1
Mecarbam	T	E2	—	0.20	96	5	8	4
Mecarbam	T	E5	—	0.20	102		2	1
Mecarbam	T	E9	—	0.05	116		2	1
Metalaxyl	W	E1	—	0.05–0.20	89	19	22	5
Metalaxyl	W	E4	—	0.10	108		2	1
Metalaxyl	T	E2	—	0.19	95	7	8	4
Metalaxyl	T	E5	—	0.19	119		2	1
Metazachlor	W	E1	—	0.05–0.10	96	22	18	5
Metazachlor	W	E1	C1	0.20	82	7	3	1
Metazachlor	W	E4	—	0.10	107		2	1
Metazachlor	T	E´2	—	0.19	95	12	8	4
Metazachlor	T	E5	—	0.19	111		2	1
Metconazole	F, W	E1	—	0.10–0.30	80	15	9	1
Metconazole	T	E2	—	0.40	81	10	6	1
Methabenzthiazuron	T	E2	—	0.20	100	11	8	4
Methabenzthiazuron	T	E5	—	0.20	113		2	1
Methabenzthiazuron	W	E1	—	0.10–0.40	103	12	10	4
Methabenzthiazuron	W	E4	—	0.10	110		2	1
Methacrifos	F, W	E1	—	0.01–1.00	82	12	25	3
Methacrifos	T	E2	—	0.10–0.23	78	16	4	2
Methacrifos	T	E9	—	0.05–0.10	105	12	6	2
Methamidophos	W	E1	—	0.05–0.10	50	76	20	5
Methamidophos	W	E4	—	0.05	72		2	1
Methamidophos	T	E2	—	0.10	36	34	10	4
Methamidophos	T	E5	—	0.10	78		2	1

(continued)

Table A 3 (continued)

Analyte	Matrix [a]	Module used		Fortification level [mg/kg]	Recovery [b]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Methamidophos	T	E9	—	0.05–0.25	56	19	6	2
Methidathion	W	E1	—	0.05–0.10	95	17	21	5
Methidathion	W	E4	—	0.10	96		2	1
Methidathion	T	E2	—	0.20	96	4	8	4
Methidathion	T	E5	—	0.20	87		2	1
Methidathion	T	E9	—	0.05	110		2	1
Methiocarb	W	E1	—	0.40	111		2	1
Methomyl	F, W	E1	C2	0.10–0.60	92	12	4	1
Methomyl	W	E1	—	0.20	58		2	1
Methoxychlor	W	E1	—	0.05–0.10	86	22	12	2
Methoxychlor	W	E1	C1	0.05	81	9	9	3
Methoxychlor	W	E4	C1	0.05	91		2	1
Methoxychlor	T	E2	C1	0.10	89	5	5	2
Methoxychlor	T	E2	—	0.10	95	10	6	2
Methoxychlor	T	E5	—	0.10	88		2	1
Methoxychlor	T	E9	C1	0.02	86	14	4	1
Metobromuron	W	E1	—	1.00	87		2	1
Metolachlor	T	E2	—	0.19	96	7	8	4
Metolachlor	T	E5	—	0.19	98		2	1
Metolachlor	W	E1	—	0.10	90	13	10	4
Metolachlor	W	E4	—	0.10	97		2	1
Metoxuron	W	E1	—	1.00	49		2	1
Mevinphos	W	E1	—	0.05–0.10	86	10	19	5
Mevinphos	W	E4	—	0.10	96		2	1
Mevinphos	T	E2	—	0.20	89	14	10	4
Mevinphos	T	E5	—	0.20	85		2	1
Mevinphos	T	E9	—	0.10	104		2	1
Monocrotophos	T	E9	—	0.05	74	10	4	1
Monolinuron	W	E1	—	1.00	79		2	1
Myclobutanil	F, W	E1	—	0.05–1.00	84	21	27	2
Myclobutanil	T	E2	—	0.10	72	18	5	1
Nuarimol	W	E1	—	0.05–0.10	86	49	10	1
Nuarimol	W	E1	C1	0.20	52		1	1
Omethoate	W	E1	—	0.05–0.10	44	50	19	5
Omethoate	W	E4	—	0.10	107		2	1
Omethoate	T	E2	—	0.20	50	45	10	4
Omethoate	T	E5	—	0.20	102		2	1
Omethoate	T	E9	—	0.25	58		2	1
Oxadixyl	W	E1	—	0.05–1.00	95	15	42	3
Oxadixyl	T	E2	—	0.12–1.00	91	10	6	1
Oxamyl	F, W	E1	—	0.05–0.60	68	30	17	2
Oxamyl	T	E2	—	0.20–0.40	57	36	7	2
Oxydemeton-methyl	W	E1	—	0.10–1.00	28	77	4	1
Oxydemeton-methyl	T	E2	—	0.10–0.20	66		2	1

(continued)

Table A 3 (continued)

Analyte	Matrix [a]	Module used		Fortification. level [mg/kg]	Recovery [b]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Oxydemeton-methyl	T	E9	—	0.25	78		2	1
Paraoxon	W	E1	—	0.05–0.10	81	38	10	1
Paraoxon	T	E9	—	0.25	106		2	1
Paraoxon-methyl	W	E1	—	0.05–0.10	81	15	10	1
Paraoxon-methyl	T	E9	—	0.13	115		2	1
Parathion	W, F	E1	—	0.05–1.00	92	12	30	5
Parathion	W	E4	—	0.10	101		2	1
Parathion	T	E2	—	0.10–0.20	90	12	12	5
Parathion	T	E5	—	0.20	101		2	1
Parathion	T	E9	—	0.05	105	10	6	2
Parathion-methyl	W	E1	—	0.05–0.10	91	17	21	5
Parathion-methyl	W	E4	—	0.10	106		2	1
Parathion-methyl	T	E2	—	0.20	98	8	8	4
Parathion-methyl	T	E5	—	0.20	97		2	1
Parathion-methyl	T	E9	—	0.05	117		2	1
PCB 138	T	E2	C1	0.04	92	13	6	3
PCB 138	T	E2	—	0.04	89		2	1
PCB 138	T	E5	—	0.04	79		2	1
PCB 138	T	E9	C1	0.02	101	5	4	1
PCB 138	W	E1	C1	0.02	86	16	6	3
PCB 138	W	E1	—	0.02	106		2	1
PCB 138	W	E4	—	0.02	83		2	1
PCB 28	T	E2	C1	0.04	89	6	6	3
PCB 28	T	E2	—	0.04	89		2	1
PCB 28	T	E5	—	0.04	112		2	1
PCB 28	W	E1	C1	0.02	83	13	6	3
PCB 28	W	E1	—	0.02	93		2	1
PCB 28	W	E4	—	0.02	103		2	1
Penconazole	F, W	E1	—	0.05–0.30	85	21	18	1
Penconazole	W	E1	C1	0.10–0.20	75	20	4	1
Penconazole	T	E2	C1	0.20	88		2	1
Penconazole	T	E2	—	0.40	85	10	6	1
Pendimethalin	W	E1	—	0.05–0.10	84	15	12	2
Pendimethalin	W	E1	C1	0.05	86	15	9	3
Pendimethalin	W	E4	C1	0.05	89		2	1
Pendimethalin	T	E2	C1	0.10	90	8	5	2
Pendimethalin	T	E2	—	0.10	96	12	6	2
Pendimethalin	T	E5	—	0.10	107		2	1
Permethrin	W	E1	—	0.05–0.10	89	24	12	2
Permethrin	W	E1	C1	0.10–0.20	91	10	10	3
Permethrin	W	E4	C1	0.10	97		2	1
Permethrin	T	E2	C1	0.20	88	6	5	2
Permethrin	T	E2	—	0.20	90	12	6	2
Permethrin	T	E5	—	0.20	82		2	1

(continued)

Table A 3 (continued)

Analyte	Matrix [a)]	Module used		Fortification level [mg/kg]	Recovery [b)]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Permethrin	T	E9	C1	0.02	101	4	4	1
Phenkapton	T	E9	—	0.05	91	4	4	1
Phorate	W	E1	—	0.05–0.10	77	13	10	1
Phorate	F, W	E1	—	0.05	61	37	6	1
Phorate	T	E9	—	0.25	98		2	1
Phosalone	F, W	E1	—	0.05–1.00	104	28	20	1
Phosalone	T	E2	—	0.10–0.20	130		2	1
Phosalone	T	E9	—	0.05–0.20	104	15	6	2
Phosmet	F, W	E1	—	0.01–1.00	99	31	26	2
Phosmet	W	E1	C1	0.10–0.20	70	16	4	1
Phosmet	T	E2	—	0.10–0.21	104	23	4	2
Phosmet	T	E2	C1	0.20	105		2	1
Phosmet	T	E9	—	0.10	112		2	1
Phosphamidon	W	E1	—	0.05–0.30	78	27	20	5
Phosphamidon	W	E4	—	0.30	80		2	1
Phosphamidon	T	E2	—	0.60	81	27	8	1
Phosphamidon	T	E5	—	0.60	91		2	1
Phosphamidon	T	E9	—	0.13	112		2	1
Pirimicarb	W	E1	—	0.05–0.10	83	41	18	5
Pirimicarb	W	E4	—	0.05	119		2	1
Pirimicarb	T	E2	—	0.10	94	16	8	4
Pirimicarb	T	E5	—	0.10	105		2	1
Pirimiphos-ethyl	F, W	E1	—	0.01–1.00	90	9	10	1
Pirimiphos-ethyl	T	E2	—	0.10–0.20	91		2	1
Pirimiphos-ethyl	T	E9	—	0.10	121		2	1
Pirimiphos-methyl	W	E1	—	0.05–0.10	88	14	20	1
Pirimiphos-methyl	W	E4	—	0.10	96		2	1
Pirimiphos-methyl	T	E2	—	0.20	98	9	8	1
Pirimiphos-methyl	T	E5	—	0.20	117		2	1
Pirimiphos-methyl	T	E9	—	0.05–0.10	105	14	6	2
Prochloraz	F, W	E1	—	0.05–0.15	72	9	9	1
Prochloraz	T	E2	—	0.10	68	21	5	1
Procymidone	W	E1	—	0.05–0.53	90	20	12	2
Procymidone	W	E1	C1	0.53	87	10	9	3
Procymidone	W	E4	C1	0.53	90		2	1
Procymidone	T	E2	C1	1.06	89	3	5	2
Procymidone	T	E2	—	1.06	90	7	6	2
Procymidone	T	E5	—	1.06	98		2	1
Profenofos	W	E1	—	0.05–0.10	91	22	20	5
Profenofos	W	E4	—	0.10	92		2	1
Profenofos	T	E2	—	0.20	92	4	8	4
Profenofos	T	E5	—	0.20	99		2	1
Profenofos	T	E9	—	0.05–0.20	108	10	6	2
Propamocarb	W	E1	—	0.20–1.20	56		2	1

(continued)

Table A 3 (continued)

Analyte	Matrix [a]	Module used		Fortification level [mg/kg]	Recovery [b]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Propham	T	E2	—	0.22	96	11	8	4
Propham	T	E5	—	0.22	108		2	1
Propham	W	E1	—	0.11–0.20	97	25	12	4
Propham	W	E4	—	0.11	106		2	1
Propiconazole	W	E1	—	0.05–0.21	83	29	20	5
Propiconazole	W	E1	C1	0.20–0.40	70	6	3	1
Propiconazole	W	E4	—	0.21	100		2	1
Propiconazole	T	E2	—	0.41	90	18	8	4
Propiconazole	T	E5	—	0.41	102		2	1
Propoxur	F, W	E1	—	0.05–1.00	84	20	20	2
Propoxur	T	E2	—	0.10	75	14	5	1
Propyzamide	W	E1	—	0.05–0.10	86	18	10	1
Prothiofos	W	E1	—	0.05–0.10	84	15	10	1
Prothiofos	F, W	E1	—	0.01–1.00	95	9	10	1
Prothiofos	T	E2	—	0.10–0.20	99		2	1
Prothiofos	T	E9	—	0.05	103	6	4	1
Pyrazophos	W	E1	—	0.05–0.20	88	18	21	5
Pyrazophos	W	E4	—	0.20	83		2	1
Pyrazophos	T	E2	—	0.40	94	5	8	4
Pyrazophos	T	E5	—	0.40	95		2	1
Pyrazophos	T	E9	—	0.05–0.10	95	18	6	2
Pyridaphenthion	W	E1	—	0.10	76	11	3	1
Pyridaphenthion	T	E9	—	0.50	105		2	1
Pyrifenox	W	E1	—	0.60	63		2	1
Quinalphos	W	E1	—	0.05–0.10	87	15	20	5
Quinalphos	W	E4	—	0.10	97		2	1
Quinalphos	T	E2	—	0.20	96	3	8	4
Quinalphos	T	E5	—	0.20	97		2	1
Quinalphos	T	E9	—	0.05–0.10	108	12	6	2
Quinoclamine	F, W	E1	—	0.10–0.30	69	17	8	1
Quinoclamine	T	E2	—	0.40	80	12	6	1
Quintozene	W	E1	—	0.02–0.10	86	17	12	2
Quintozene	W	E1	C1	0.02	90	11	9	3
Quintozene	W	E4	C1	0.02	73		2	1
Quintozene	T	E2	C1	0.04	82	12	5	2
Quintozene	T	E2	—	0.04	89	16	6	2
Quintozene	T	E5	—	0.04	73		2	1
Quizalofop-ethyl	W	E1	—	0.60	71		2	1
Simazine	T	E2	—	0.19	95	21	6	4
Simazine	T	E5	—	0.19	103		2	1
Simazine	W	E1	—	0.10	107	20	6	4
Simazine	W	E4	—	0.10	114		2	1
Sulfotep	W	E1	—	0.05–0.10	88	10	19	5
Sulfotep	W	E4	—	0.10	91		2	1

(continued)

Table A 3 (continued)

Analyte	Matrix [a]	Module used		Fortification level [mg/kg]	Recovery [b]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Sulfotep	T	E2	—	0.20	87	12	10	4
Sulfotep	T	E5	—	0.20	98		2	1
Sulfotep	T	E9	—	0.10	121		2	1
Sulprofos	W	E1	—	0.10	71		2	1
Sulprofos	T	E9	—	0.13	103		2	1
Tebuconazole	W	E1	—	0.05–1.00	91	21	44	6
Tebuconazole	W	E4	—	0.10	106		2	1
Tebuconazole	T	E2	—	0.19–2.00	97	11	26	5
Tebuconazole	T	E5		0.19	110		2	1
Tebutam	W	E1	C1	0.10–0.20	75	20	4	1
Tebutam	W	E1	—	0.10	97	10	10	4
Tebutam	W	E4	—	0.10	109		2	1
Tebutam	T	E2	—	0.19	99	10	8	4
Tebutam	T	E5	—	0.19	109		2	1
Tebutam	T	E2	C1	0.20	88		2	1
Tefluthrin	T	E9	C1	0.02	101	5	4	1
Terbacil	T	E2	—	0.41	101	9	8	4
Terbacil	T	E5	—	0.41	96		2	1
Terbacil	W	E1	—	0.21	97	16	10	4
Terbacil	W	E4	—	0.21	81		2	1
Terbufos	W	E1	—	0.05–0.10	82	12	10	1
Terbufos	T	E9	—	0.25	101		2	1
Terbuthylazine	W	E1	—	0.05–0.10	99	20	23	6
Terbuthylazine	W	E4	—	0.10	107		2	1
Terbuthylazine	T	E2	—	0.19–0.20	103	10	8	5
Terbuthylazine	T	E5	—	0.19	105		2	1
Terbuthylazine	W	E4	C2	0.002–0.10	101	10	6	1
Tetrachlorvinphos	W	E1	—	0.20	124		1	1
Tetrachlorvinphos	T	E9	—	0.10	113		2	1
Tetraconazole	F, W	E1	—	0.10–0.30	85	19	8	1
Tetraconazole	T	E2	—	0.40	85	11	6	1
Tetradifon	W	E1	—	0.03–0.10	85	20	12	2
Tetradifon	W	E1	C1	0.03	83	23	6	3
Tetradifon	W	E4	—	0.03	92		2	1
Tetradifon	T	E2	C1	0.06	87	7	6	3
Tetradifon	T	E2	—	0.06	94		2	1
Tetradifon	T	E5	—	0.06	91		2	1
Tetradifon	T	E9	C1	0.02	99	6	4	1
Tetramethrin	W	E1	C1	0.20	93		1	1
Thiabendazole	W	E1	—	0.05–0.21	71	50	8	1
Thiabendazole	T	E2	—	0.21	80		2	1
Tolclofos-methyl	W	E1	—	0.05–0.10	88	14	20	5
Tolclofos-methyl	W	E4	—	0.10	98		2	1
Tolclofos-methyl	T	E2	—	0.20	95	6	8	4

(continued)

Table A 3 (continued)

Analyte	Matrix [a)]	Module used		Fortification level [mg/kg]	Recovery [b)]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Tolclofos-methyl	T	E5	—	0.20	104		2	1
Tolclofos-methyl	T	E9	—	0.25	107		2	1
Tolylfluanid	W	E1	—	0.05–0.10	84	25	10	1
Triadimefon	W	E1	—	0.05–0.10	86	25	20	5
Triadimefon	W	E4	—	0.10	110		2	1
Triadimefon	T	E2	—	0.19	97	8	8	4
Triadimefon	T	E5	—	0.19	106		2	1
Triadimenol	W	E1	—	0.05–0.10	84	24	20	5
Triadimenol	W	E4	—	0.10	108		2	1
Triadimenol	T	E2	—	0.19	95	7	8	4
Triadimenol	T	E5	—	0.19	104		2	1
Tri-allate	T	E2	C1	0.10	90	4	5	2
Tri-allate	T	E2	—	0.10	90	6	6	2
Tri-allate	T	E5	—	0.10	82		2	1
Tri-allate	W	E1	C1	0.05	85	11	9	3
Tri-allate	W	E1	—	0.05	94		2	1
Tri-allate	W	E4	C1	0.05	89		2	1
Triamiphos	T	E9	—	0.50	95		2	1
Triazophos	W	E1	—	0.05–0.20	87	19	21	5
Triazophos	W	E4	—	0.10	92		2	1
Triazophos	T	E2	—	0.20	98	9	8	4
Triazophos	T	E5	—	0.20	103		2	1
Triazophos	T	E9	—	0.05–0.10	101	12	8	2
Trichloronat	W	E1	—	0.02	91		2	1
Trichloronat	W	E1	C1	0.02	85	11	9	3
Trichloronat	W	E4	C1	0.02	79		2	1
Trichloronat	T	E2	—	0.04	86	12	6	2
Trichloronat	T	E2	C1	0.04	80	12	5	2
Trichloronat	T	E5	—	0.04	84		2	1
Trifluralin	W	E1	—	0.03–0.10	87	9	12	2
Trifluralin	W	E1	C1	0.03–0.50	83	9	13	3
Trifluralin	W	E4	C1	0.03	78		2	1
Trifluralin	T	E2	C1	0.06	82	13	5	2
Trifluralin	T	E2	—	0.06	69	30	6	2
Trifluralin	T	E5	—	0.06	80		2	1
Trifluralin	T	E9	C1	0.02	111	7	4	1
Triticonazole	F, W	E1	—	0.10–0.30	88	19	8	1
Triticonazole	T	E2	—	0.40	77	13	6	1
Vamidothion	W	E1	—	0.05–1.00	67	63	8	2
Vamidothion	T	E2	—	0.10–0.21	47	116	4	2
Vamidothion	T	E9	—	0.13	107		2	1
Vinclozolin	W	E1	—	0.03–0.10	87	12	14	1
Vinclozolin	W	E1	C1	0.03–0.20	90	11	17	3
Vinclozolin	W	E4	—	0.03	95	6	4	1

Supplement to Table A 3: Additional results from fortification trials

Analyte	Matrix [a]	Module used		Fortification level [mg/kg]	Recovery [b]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Aclonifen	W	E1	C1	0.05–0.50	94	18	15	4
Aclonifen	W	E1	–	0.05–0.50	85	18	18	2
Aclonifen	W	E4	C1	0.05–0.50	87	10	9	2
Aclonifen	S	E1	–	0.05–0.50	80	19	18	2
Aclonifen	S	E1	C1	0.05–0.50	78	13	15	4
Aclonifen	S	E4	C1	0.05–0.50	86	14	12	3
Aclonifen	T	E2	C1	0.05–0.50	85	21	30	4
Aclonifen	T	E2	–	0.05–0.50	81	22	36	2
Aclonifen	T	E5	C1	0.05–0.50	88	14	23	3
Aclonifen	F	E1	C1	0.05–0.50	83	19	8	3
Aclonifen	F	E1	–	0.05–0.50	77	40	18	2
Aclonifen	F	E4	C1	0.05–0.50	77	16	12	3
Azoxystrobin	W	E1	–	0.05–0.50	75	20	18	2
Azoxystrobin	W	E1	C1	0.05–0.50	96	22	7	2
Azoxystrobin	W	E4	C1	0.05–0.50	85	13	12	3
Azoxystrobin	S	E1	–	0.05–0.50	73	36	18	2
Azoxystrobin	S	E1	C1	0.05–0.50	77	18	12	4
Azoxystrobin	S	E4	C1	0.05–0.50	93	6	3	2
Azoxystrobin	T	E2	–	0.05–0.50	77	23	24	2
Azoxystrobin	T	E2	C1	0.05–0.50	76	23	30	4
Azoxystrobin	T	E5	C1	0.05–0.50	119	33	12	2
Azoxystrobin	F	E1	C1	0.05–0.50	78	15	9	3
Azoxystrobin	F	E1	–	0.05–0.50	77	36	14	2
Azoxystrobin	F	E4	C1	0.05–0.50	99	12	12	3
Clodinafop-propargyl	W	E1	–	0.05–0.50	62	51	9	2
Clodinafop-propargyl	W	E1	C1	0.05–0.50	67	35	3	1
Clodinafop-propargyl	W	E4	C1	0.05–0.50	83	27	9	3
Clodinafop-propargyl	S	E1	–	0.05–0.50	87	11	9	2
Clodinafop-propargyl	S	E1	C1	0.05–0.50	98	7	3	1
Clodinafop-propargyl	S	E4	C1	0.05–0.50	92	22	9	3
Clodinafop-propargyl	T	E2	–	0.05–0.50	80	20	18	2
Clodinafop-propargyl	T	E2	C1	0.05–0.50	91	15	6	1
Clodinafop-propargyl	T	E5	C1	0.05–0.50	93	23	18	3
Clodinafop-propargyl	F	E1	–	0.05–0.50	90	32	8	2
Clodinafop-propargyl	F	E1	C1	0.05–0.50	100	20	3	1
Clodinafop-propargyl	F	E4	C1	0.05–0.50	88	43	6	2
Cloquintocet-mexyl	W	E1	–	0.05–0.50	89	10	9	2
Cloquintocet-mexyl	W	E1	C1	0.05–0.50	95	5	3	1
Cloquintocet-mexyl	W	E4	C1	0.05–0.50	73	22	9	3

[a] Abbreviations for matrix type: W = high water content; T = low water content; F = high fat content
S = high acid content

[b] Abbreviations for recovery: x = mean recovery; V = relative standard deviation ;
n = number of individual results

(continued)

Supplement to Table A 3 (continued)

Analyte	Matrix [a)]	Module used		Fortification level [mg/kg]	Recovery [b)]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Cloquintocet-mexyl	S	E1	–	0.05–0.50	86	12	9	2
Cloquintocet-mexyl	S	E1	C1	0.05–0.50	89	7	3	1
Cloquintocet-mexyl	S	E4	C1	0.05–0.50	79	21	9	3
Cloquintocet-mexyl	T	E2	–	0.05–0.50	83	20	18	2
Cloquintocet-mexyl	T	E2	C1	0.05–0.50	99	9	6	1
Cloquintocet-mexyl	T	E5	C1	0.05–0.50	80	28	18	3
Cloquintocet-mexyl	F	E1	–	0.05–0.50	74	24	9	2
Cloquintocet-mexyl	F	E1	C1	0.05–0.50	98	12	3	1
Cloquintocet-mexyl *)	F	E4	C1	0.05–0.50	99	47	6	2
Cyprodinil	W	E1	C1	0.05–0.50	97	15	12	4
Cyprodinil	W	E1	–	0.05–0.50	81	17	18	2
Cyprodinil	W	E4	C1	0.05–0.50	95	21	12	3
Cyprodinil	S	E1	C1	0.05–0.50	76	22	12	4
Cyprodinil	S	E1	–	0.05–0.50	76	23	18	2
Cyprodinil	S	E4	C1	0.05–0.50	90	23	12	3
Cyprodinil	T	E2	C1	0.05–0.50	84	14	24	4
Cyprodinil	T	E2	–	0.05–0.50	77	24	36	2
Cyprodinil	T	E5	C1	0.05–0.50	86	22	24	3
Cyprodinil	F	E1	C1	0.05–0.50	70	8	9	3
Cyprodinil	F	E1	–	0.05–0.50	68	33	14	2
Cyprodinil	F	E4	C1	0.05–0.50	100	18	12	4
Diethofencarb	W	E1	–	0.05–0.50	89	8	9	2
Diethofencarb	W	E1	C1	0.05–0.50	89	18	3	1
Diethofencarb	W	E4	C1	0.05–0.50	94	12	9	3
Diethofencarb	S	E1	–	0.05–0.50	89	9	9	2
Diethofencarb	S	E1	C1	0.05–0.50	92	7	3	1
Diethofencarb	S	E4	C1	0.05–0.50	77	18	9	3
Diethofencarb	T	E2	–	0.05–0.50	84	9	15	2
Diethofencarb	T	E2	C1	0.05–0.50	99	29	6	1
Diethofencarb	T	E5	C1	0.05–0.50	84	27	18	3
Diethofencarb	F	E1	–	0.05–0.50	86	13	9	2
Diethofencarb	F	E1	C1	0.05–0.50	92	15	3	1
Diethofencarb	F	E4	C1	0.05–0.50	80	36	8	3
Difenoconazole	W	E1	C1	0.05–0.50	89	14	15	4
Difenoconazole	W	E1	–	0.05–0.50	74	20	18	2
Difenoconazole	W	E4	C1	0.05–0.50	115	37	10	3
Difenoconazole	S	E1	C1	0.05–0.50	81	13	15	4
Difenoconazole	S	E1	–	0.05–0.50	84	32	18	2
Difenoconazole	S	E4	C1	0.05–0.50	126	34	8	3
Difenoconazole	T	E2	C1	0.05–0.50	83	22	30	4
Difenoconazole	T	E2	–	0.05–0.50	73	20	36	2
Difenoconazole	T	E5	C1	0.05–0.50	115	31	15	3
Difenoconazole	F	E1	C1	0.05–0.50	86	29	9	3

(continued)

Supplement to Table A 3 (continued)

Analyte	Matrix [a)]	Module used		Fortification level [mg/kg]	Recovery [b)]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Difenoconazole	F	E1	–	0.05–0.50	99	37	14	2
Difenoconazole	F	E4	C1	0.05–0.50	99	21	10	3
Diphenylamine	W	E1	C1	0.05–0.50	81	25	10	4
Diphenylamine	W	E1	–	0.05–0.50	71	23	18	2
Diphenylamine	W	E4	C1	0.05–0.50	76	13	11	3
Diphenylamine	S	E1	C1	0.05–0.50	69	25	11	4
Diphenylamine	S	E1	–	0.05–0.50	65	27	18	2
Diphenylamine	S	E4	C1	0.05–0.50	100	30	12	3
Diphenylamine	T	E2	C1	0.05–0.50	75	33	17	3
Diphenylamine	T	E2	–	0.05–0.50	73	34	24	2
Diphenylamine	T	E5	C1	0.05–0.50	68	31	18	3
Diphenylamine	F	E1	C1	0.05–0.50	71	34	6	2
Diphenylamine	F	E1	–	0.05–0.50	68	35	18	2
Diphenylamine	F	E4	C1	0.05–0.50	85	15	6	3
Fenpiclonil	W	E1	–	0.05–0.50	86	11	9	2
Fenpiclonil	W	E1	C1	0.05–0.50	94	5	3	1
Fenpiclonil	W	E4	C1	0.05–0.50	76	40	9	3
Fenpiclonil	S	E1	–	0.05–0.50	84	13	9	2
Fenpiclonil	S	E1	C1	0.05–0.50	94	5	3	1
Fenpiclonil	S	E4	C1	0.05–0.50	68	33	7	3
Fenpiclonil	T	E2	–	0.05–0.50	76	16	18	2
Fenpiclonil	T	E2	C1	0.05–0.50	98	13	6	1
Fenpiclonil	T	E5	C1	0.05–0.50	88	29	17	3
Fenpiclonil	F	E1	–	0.05–0.50	67	33	9	2
Fenpiclonil	F	E1	C1	0.05–0.50	96	7	3	1
Fenpiclonil *)	F	E4	C1	0.05–0.50	90	58	4	2
Fludioxonil	W	E1	–	0.05–0.50	93	9	9	2
Fludioxonil	W	E1	C1	0.05–0.50	93	10	3	1
Fludioxonil	W	E4	C1	0.05–0.50	78	30	9	3
Fludioxonil	S	E1	–	0.05–0.50	95	15	9	2
Fludioxonil	S	E1	C1	0.05–0.50	74	16	3	1
Fludioxonil	S	E4	C1	0.05–0.50	59	41	9	3
Fludioxonil	T	E2	–	0.05–0.50	80	17	18	2
Fludioxonil	T	E2	C1	0.05–0.50	98	12	6	1
Fludioxonil	T	E5	C1	0.05–0.50	76	43	17	3
Fludioxonil	F	E1	–	0.05–0.50	79	19	9	2
Fludioxonil	F	E1	C1	0.05–0.50	98	13	3	1
Fludioxonil *)	F	E4	C1	0.05–0.50	62	62	6	2
Fluoroglycofen-ethyl	W	E1	–	0.05–0.50	87	13	9	2
Fluoroglycofen-ethyl	W	E1	C1	0.05–0.50	92	5	3	1
Fluoroglycofen-ethyl	W	E4	C1	0.05–0.50	106	18	9	3
Fluoroglycofen-ethyl	T	E2	–	0.05–0.50	81	17	18	2
Fluoroglycofen-ethyl	T	E2	C1	0.05–0.50	102	19	6	1

(continued)

Supplement to Table A 3 (continued)

Analyte	Matrix [a)]	Module used		Fortification level [mg/kg]	Recovery [b)]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Fluoroglycofen-ethyl	T	E5	C1	0.05–0.50	85	34	16	3
Fluoroglycofen-ethyl	F	E1	–	0.05–0.50	94	33	7	2
Fluoroglycofen-ethyl	F	E1	C1	0.05–0.50	107	19	3	1
Fluoroglycofen-ethyl	F	E4	C1	0.05–0.50	100	38	7	3
Fluquinconazole	W	E1	C1	0.05–0.50	89	12	15	4
Fluquinconazole	W	E1	–	0.05–0.50	71	20	18	2
Fluquinconazole	W	E4	C1	0.05–0.50	100	22	11	3
Fluquinconazole	S	E1	C1	0.05–0.50	76	20	15	4
Fluquinconazole	S	E1	–	0.05–0.50	72	29	18	2
Fluquinconazole	S	E4	C1	0.05–0.50	92	13	12	3
Fluquinconazole	T	E2	C1	0.05–0.50	85	15	30	4
Fluquinconazole	T	E2	–	0.05–0.50	73	22	36	2
Fluquinconazole	T	E5	C1	0.05–0.50	85	19	23	3
Fluquinconazole	F	E1	C1	0.05–0.50	70	20	12	3
Fluquinconazole	F	E1	–	0.05–0.50	69	45	16	2
Fluquinconazole	F	E4	C1	0.05–0.50	86	21	12	3
Flutriafol	W	E1	–	0.05–0.50	91	9	9	2
Flutriafol	W	E1	C1	0.05–0.50	91	4	3	1
Flutriafol	W	E4	C1	0.05–0.50	67	33	9	3
Flutriafol	S	E1	–	0.05–0.50	87	12	9	2
Flutriafol	S	E1	C1	0.05–0.50	114	4	3	1
Flutriafol	S	E4	C1	0.05–0.50	60	53	9	3
Flutriafol	T	E2	–	0.05–0.50	85	11	16	2
Flutriafol	T	E2	C1	0.05–0.50	90	13	4	1
Flutriafol	T	E5	C1	0.05–0.50	82	40	16	3
Flutriafol	F	E1	–	0.05–0.50	80	14	9	2
Flutriafol	F	E1	C1	0.05–0.50	80	17	3	1
Flutriafol	F	E4	C1	0.05–0.50	75	49	7	3
Kresoxim-methyl	W	E1	C1	0.05–0.50	89	11	15	4
Kresoxim-methyl	W	E1	–	0.05–0.50	74	20	18	2
Kresoxim-methyl	W	E4	C1	0.05–0.50	90	7	12	3
Kresoxim-methyl	S	E1	C1	0.05–0.50	78	17	15	4
Kresoxim-methyl	S	E1	–	0.05–0.50	73	22	18	2
Kresoxim-methyl	S	E4	C1	0.05–0.50	88	11	12	3
Kresoxim-methyl	T	E2	C1	0.05–0.50	86	15	28	4
Kresoxim-methyl	T	E2	–	0.05–0.50	70	21	36	2
Kresoxim-methyl	T	E5	C1	0.05–0.50	84	14	24	3
Kresoxim-methyl	F	E1	C1	0.05–0.50	81	25	10	4
Kresoxim-methyl	F	E1	–	0.05–0.50	60	44	9	2
Kresoxim-methyl	F	E4	C1	0.05–0.50	85	17	9	3
Metconazole	W	E1	C1	0.05–0.50	86	15	12	4
Metconazole	W	E1	–	0.05–0.50	73	20	18	2
Metconazole	W	E4	C1	0.05–0.50	90	14	12	3

(continued)

Supplement to Table A 3 (continued)

Analyte	Matrix [a)]	Module used		Fortification level [mg/kg]	Recovery [b)]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Metconazole	S	E1	C1	0.05–0.50	73	27	12	4
Metconazole	S	E1	–	0.05–0.50	67	28	18	2
Metconazole	S	E4	C1	0.05–0.50	83	13	12	3
Metconazole	T	E2	C1	0.05–0.50	80	20	24	4
Metconazole	T	E2	–	0.05–0.50	68	21	36	2
Metconazole	T	E5	C1	0.05–0.50	89	23	19	3
Metconazole	F	E1	C1	0.05–0.50	83	20	8	3
Metconazole	F	E1	–	0.05–0.50	66	41	10	2
Metconazole	F	E4	C1	0.05–0.50	102	33	10	3
Nuarimol	W	E1	C1	0.05–0.50	85	10	15	4
Nuarimol	W	E1	–	0.05–0.50	80	16	12	2
Nuarimol	W	E4	C1	0.05–0.50	95	11	11	3
Nuarimol	S	E1	C1	0.05–0.50	70	18	15	4
Nuarimol	S	E1	–	0.05–0.50	65	37	18	2
Nuarimol	S	E4	C1	0.05–0.50	86	17	9	3
Nuarimol	T	E2	C1	0.05–0.50	83	20	30	4
Nuarimol	T	E2	–	0.05–0.50	70	17	36	2
Nuarimol	T	E5	C1	0.05–0.50	87	16	24	3
Nuarimol	F	E1	C1	0.05–0.50	91	22	12	3
Nuarimol	F	E1	–	0.05–0.50	70	40	12	2
Nuarimol	F	E4	C1	0.05–0.50	91	12	12	3
Prosulfocarb	W	E1	–	0.05–0.50	93	10	9	2
Prosulfocarb	W	E1	C1	0.05–0.50	87	11	3	1
Prosulfocarb	W	E4	C1	0.05–0.50	82	19	9	3
Prosulfocarb	S	E1	–	0.05–0.50	93	5	9	2
Prosulfocarb	S	E1	C1	0.05–0.50	95	9	3	1
Prosulfocarb	S	E4	C1	0.05–0.50	70	26	8	3
Prosulfocarb	T	E2	–	0.05–0.50	84	15	16	2
Prosulfocarb	T	E2	C1	0.05–0.50	87	15	6	1
Prosulfocarb	T	E5	C1	0.05–0.50	69	32	18	3
Prosulfocarb	F	E1	–	0.05–0.50	83	5	7	2
Prosulfocarb	F	E1	C1	0.05–0.50	97	10	3	1
Prosulfocarb	F	E4	C1	0.05–0.50	71	45	9	3
Pyrifenox1	W	E1	–	0.05–0.50	79	11	9	2
Pyrifenox1	W	E1	C1	0.05–0.50	77	16	3	1
Pyrifenox1	W	E4	C1	0.05–0.50	55	46	9	3
Pyrifenox1	S	E1	–	0.05–0.50	74	19	9	2
Pyrifenox1	S	E1	C1	0.05–0.50	87	2	3	1
Pyrifenox1	S	E4	C1	0.05–0.50	47	64	9	3
Pyrifenox1	T	E2	–	0.05–0.50	84	10	18	2
Pyrifenox1	T	E2	C1	0.05–0.50	81	8	6	1
Pyrifenox1	T	E5	C1	0.05–0.50	76	34	18	3
Pyrifenox1	F	E1	–	0.05–0.50	76	13	9	2

(continued)

Supplement to Table A 3 (concluded)

Analyte	Matrix [a)]	Module used		Fortification level [mg/kg]	Recovery [b)]			Lab.
		Extraction	Clean-up (incl. of GPC)		x	V	n	
Pyrifenox1	F	E1	C1	0.05–0.50	96	4	3	1
Pyrifenox1	F	E4	C1	0.05–0.50	57	62	9	3
Pyrifenox2	W	E4	C1	0.05–0.50	74	30	6	1
Pyrifenox2	S	E4	C1	0.05–0.50	87	28	6	1
Pyrifenox2	T	E5	C1	0.05–0.50	103	36	12	2
Pyrifenox2	F	E4	C1	0.05–0.50	20	48	6	1
Triflumizole	W	E1	–	0.05–0.50	49	57	9	2
Triflumizole	W	E1	C1	0.05–0.50	57	22	3	1
Triflumizole	W	E4	C1	0.05–0.50	20	83	7	3
Triflumizole	S	E1	–	0.05–0.50	55	48	9	2
Triflumizole	S	E1	C1	0.05–0.50	84	8	3	1
Triflumizole	S	E4	C1	0.05–0.50	33	17	9	3
Triflumizole	T	E2	–	0.05–0.50	77	48	18	2
Triflumizole	T	E2	C1	0.05–0.50	76	16	6	1
Triflumizole	T	E5	C1	0.05–0.50	69	46	18	3
Triflumizole	F	E1	–	0.05–0.50	77	12	9	2
Triflumizole	F	E1	C1	0.05–0.50	83	20	3	1
Triflumizole	F	E4	C1	0.05–0.50	60	37	9	3
Triticonazole	W	E1	C1	0.05–0.50	81	22	15	3
Triticonazole	W	E1	–	0.05–0.50	85	7	6	1
Triticonazole	W	E4	C1	0.05–0.50	105	21	11	3
Triticonazole	S	E1	C1	0.05–0.50	69	37	9	3
Triticonazole	S	E1	–	0.05–0.50	88	10	6	1
Triticonazole	S	E4	C1	0.05–0.50	85	23	10	3
Triticonazole	T	E2	C1	0.05–0.50	85	12	30	4
Triticonazole	T	E2	–	0.05–0.50	66	26	42	2
Triticonazole	T	E5	C1	0.05–0.50	90	34	20	3
Triticonazole	F	E1	C1	0.05–0.50	78	25	6	2
Triticonazole	F	E1	–	0.05–0.50	63	49	12	2
Triticonazole	F	E4	C1	0.05–0.50	79	35	9	3

*) Strong matrix interferences observed in one laboratory

Table A 4: Summarized data obtained within the EU-Project SMT4-CT-95-2030; 1998 [10] by using detection modules D 1 to D 4

Matrix: Strawberries								
Pesticide or metabolite	Bupirimate		Chlorpyrifos		Dichlofluanid		Iprodione	
Modules used Fortification level (mg/kg)	E1+GPC 0.54	E4+GPC 0.54	E1+GPC 0.40	E4+GPC 0.40	E1+GPC 3.07	E4+GPC 3.07	E1+GPC 2.89	E4+GPC 2.89
Number of laboratories after eliminating outliers	5	7	8	8	6	7	6	8
Number of laboratories not considered	0	0	0	0	1	0	1	0
Number of accepted results	40	56	64	64	48	56	48	64
Mean value $\bar{X}$ (mg/kg)	0.42	0.50	0.35	0.37	2.78	2.57	2.73	2.79
Standard deviation s_R (mg/kg)	0.06	0.07	0.03	0.09	0.22	0.44	0.16	0.64
Reproducibility relative standard deviation RSD_R (%)	14	13	8	24	8	17	6	23
Reproducibility limit R (mg/kg)	0.17	0.18	0.08	0.25	0.63	1.24	0.46	1.82
Horrat value (RSD_R observed / RSD_R expected)	0.77	0.73	0.43	1.29	0.58	1.22	0.44	1.68

Matrix: Spinach										
Pesticide or metabolite	Bifenthrin		Dimethoate		Metalaxyl		Omethoate		Permethrin	
Modules used Fortification level (mg/kg)	E1+GPC 0.36	E4+GPC 0.36	E1+GPC 0.72	E4+GPC 0.72	E1+GPC 1.08	E4+GPC 1.08	E1+GPC 0.15	E4+GPC 0.15	E1+GPC 0.54	E4+GPC 0.54
Number of laboratories after eliminating outliers	8	7	9	8	7	7	8	7	8	8
Number of laboratories not considered	0	1	0	0	0	1	0	1	0	0
Number of accepted results	64	56	72	64	56	56	64	56	64	64
Mean value $\bar{X}$ (mg/kg)	0.3	0.31	0.64	0.68	1.06	1.03	0.07	0.09	0.48	0.48
Standard deviation s_R (mg/kg)	0.05	0.02	0.05	0.08	0.06	0.08	0.03	0.02	0.06	0.04
Reproducibility relative standard deviation RSD_R (%)	15	7	8	12	6	8	36	20	13	8
Reproducibility limit R (mg/kg)	0.13	0.06	0.14	0.23	0.18	0.23	0.07	0.05	0.18	0.11
Horrat value (RSD_R observed / RSD_R expected)	0.78	0.37	0.47	0.71	0.38	0.50	1.51	0.87	0.73	0.45

(continued)

Table A 4 (continued)

Matrix: Carrots												
Pesticide or metabolite	Chlorfenvinphos		Cypermethrin		Dimethoate		Metalaxyl		Omethoate		Triazophos	
Modules used Fortification level (mg/kg)	E1+GPC 0.47	E4+GPC 0.47	E1+GPC 0.07	E4+GPC 0.07	E1+GPC 0.62	E4+GPC 0.62	E1+GPC 0.04	E4+GPC 0.04	E1+GPC 0.06	E4+GPC 0.06	E1+GPC 0.54	E4+GPC 0.54
Number of laboratories after eliminating outliers	8	7	8	7	7	7	5	6	5	6	7	7
Number of laboratories not considered	0	0	0	0	1	0	0	0	0	0	1	0
Number of accepted results	64	56	64	56	56	56	40	48	40	48	56	56
Mean value $\bar{X}$ (mg/kg)	0.42	0.45	0.07	0.07	0.56	0.56	0.03	0.03	0.04	0.04	0.53	0.56
Standard deviation s_R (mg/kg)	0.03	0.10	0.01	0.01	0.03	0.10	0.00	0.01	0.01	0.01	0.05	0.11
Reproducibility relative standard deviation RSD_R (%)	7	23	16	19	6	18	10	19	25	27	10	20
Reproducibility limit R (mg/kg)	0.08	0.29	0.03	0.04	0.10	0.29	0.01	0.02	0.03	0.03	0.15	0.32
Horrat value (RSD_R observed / RSD_R expected)	0.38	1.27	0.67	0.80	0.34	1.03	0.37	0.70	0.96	1.04	0.57	1.15

Matrix: Tomatoes														
Pesticide or metabolite	Bupirimate		Chlorothalonil		α-Endosulfan		β-Endosulfan		Endosulfan sulfate		Tetradifon		Tolylfluanid	
Modules used Fortification level (mg/kg)	E1+GPC 0.63	E4+GPC 0.63	E1+GPC 1.08	E4+GPC 1.08	E1+GPC 0.58	E4+GPC 0.58	E1+GPC 0.58	E4+GPC 0.58	E1+GPC 0.29	E4+GPC 0.29	E1+GPC 0.11	E4+GPC 0.11	E1+GPC 1.17	E4+GPC 1.17
Number of laboratories after eliminating outliers	7	8	8	8	8	8	8	8	8	8	8	8	8	8
Number of laboratories not considered	1	0	0	0	0	0	0	0	0	0	0	0	0	0
Number of accepted results	56	64	64	64	64	64	64	64	64	64	64	64	64	64
Mean value $\bar{X}$ (mg/kg)	0.58	0.50	1.04	0.93	0.54	0.52	0.55	0.50	0.27	0.27	0.10	0.10	1.05	1.00
Standard deviation s_R (mg/kg)	0.05	0.22	0.07	0.13	0.03	0.08	0.03	0.07	0.02	0.04	0.01	0.02	0.15	0.15
Reproducibility relative standard deviation RSD_R (%)	9	43	7	14	6	16	6	13	6	16	6	15	14	15
Reproducibility limit R (mg/kg)	0.15	0.61	0.21	0.37	0.09	0.24	0.09	0.18	0.05	0.12	0.02	0.04	0.42	0.42
Horrat value (RSD_R observed / RSD_R expected)	0.52	2.42	0.44	0.87	0.34	0.91	0.34	0.73	0.31	0.82	0.27	0.66	0.88	0.94

(continued)

Table A 4 (concluded)

Matrix: Apples										
Pesticide or metabolite	Bromopropylate		Captan		Fenoxycarb		Phosalone		Thiabendazole	
Modules used Fortification level (mg/kg)	E1+GPC 1.17	E4+GPC 1.17	E1+GPC 1.44	E4+GPC 1.44	E1+GPC 1.62	E4+GPC 1.62	E1+GPC 1.08	E4+GPC 1.08	E1+GPC 3.24	E4+GPC 3.24
Number of laboratories after eliminating outliers	7	6	8	7	7	6	8	7	6	7
Number of laboratories not considered	1	1	0	0	0	1	0	0	0	0
Number of accepted results	56	48	64	56	56	48	64	56	48	56
Mean value $\bar{X}$ (mg/kg)	1.06	1.04	1.27	1.32	1.44	1.52	0.95	0.96	1.35	1.94
Standard deviation s_R (mg/kg)	0.05	0.06	0.19	0.28	0.12	0.11	0.10	0.16	0.93	1.05
Reproducibility relative standard deviation RSD_R (%)	5	6	15	21	8	7	11	17	69	54
Reproducibility limit R (mg/kg)	0.15	0.18	0.54	0.78	0.33	0.30	0.30	0.46	2.64	2.96
Horrat value (RSD_R observed / RSD_R expected)	0.32	0.38	0.97	1.37	0.53	0.47	0.68	1.06	4.51	3.73
Matrix: Wheat grain										
Pesticide or metabolite	Chlorpyrifos-methyl		Deltamethrin		Lindane		Permethrin		Pirimiphos-methyl	
Modules used Fortification level (mg/kg)	E1+GPC 1.62	E4+GPC 1.62	E1+GPC 0.64	E4+GPC 0.64	E1+GPC 0.12	E4+GPC 0.12	E1+GPC 1.50	E4+GPC 1.50	E1+GPC 1.54	E4+GPC 1.54
Number of laboratories after eliminating outliers	9	8	8	8	8	8	8	8	9	7
Number of laboratories not considered	0	0	0	0	0	0	0	0	0	1
Number of accepted results	72	64	64	64	64	64	64	64	72	56
Mean value $\bar{X}$ (mg/kg)	1.39	1.58	0.54	0.62	0.09	0.11	1.19	1.38	1.25	1.34
Standard deviation s_R (mg/kg)	0.15	0.30	0.09	0.14	0.02	0.03	0.11	0.30	0.15	0.16
Reproducibility relative standard deviation RSD_R (%)	11	19	16	22	17	25	9	22	12	12
Reproducibility limit R (mg/kg)	0.43	0.85	0.24	0.39	0.04	0.08	0.30	0.86	0.42	0.46
Horrat value (RSD_R observed / RSD_R expected)	0.72	1.27	0.91	1.28	0.74	1.12	0.58	1.44	0.78	0.78