NATIONAL INSTITUTE OF PUBLIC HEALTH AND THE ENVIRONMENT

BILTHOVEN, THE NETHERLANDS

RIVM-report no. 638817014

Pesticides amenable to gas chromatography: Multi Residue Method 1.

Working Group OVR*

February 1996

Members:
R.A. Baumann, RIVM (secretary)
J.W. Dornseiffen, directie Voeding en Veiligheid van Produkten, Ministerie van VWS
W. v. d. Hoeven, IGB Utrecht
E.A. Hogendoorn, RIVM
J.T.A. Jansen, IGB Nijmegen
G. Kleter, HIGB
A. de Kok, IGB Alkmaar
J.K. Quirijns, TNO Voeding
H.A. van der Schee, IGB Amsterdam
W. Traag, RIKILT-DLO (from nov. 1st 1995)
L.G.M.Th. Tuinstra, RIKILT-DLO (till nov. 1st 1995)
W. Verwaal, IGB Amsterdam
P. van Zoonen, RIVM (chairman)

This research was carried out on behalf of the Chief Inspectorate for Health Protection from the Ministry of Health, Welfare and Sport. (Project no. 638817, OVR)

National Institute of Public Health and the Environment, P.O. Box 1, 3720 BA Bilthoven, The Netherlands
telephone ..31 30 2749111, telefax ..31 30 2742971

MAILING LIST

1	Hoofdinspecteur voor de Gezondheidsbescherming
2	Directeur Voeding en Veiligheid van Produkten van het Ministerie van Volksgezondheid, Welzijn en Sport
3	Directeur-Generaal Volksgezondheid
4 - 7	Hoofdinspectie Gezondheidsbescherming
8 - 11	Directie Voeding en Veiligheid van Produkten van het Ministerie van Volksgezondheid, Welzijn en Sport
12 - 24	Inspecties Gezondheidsbescherming te Alkmaar, Amsterdam, Enschede, 's-Gravenhage, Groningen, Goes, 's–Hertogenbosch, Leeuwarden, Maastricht, Nijmegen, Rotterdam, Utrecht en Zutphen
25	Depôt voor Nederlandse Publicaties en Nederlandse Bibliografie
26	Directie RIVM
27	Dr. H.A. van 't Klooster
28	Drs. P.R. Kootstra
29	Drs. A.K.D. Liem
30	Drs. E.G. van der Velde
31	Dr. T. Visser
32	Dr. G. Zomer
33 - 45	Auteurs
46	Hoofd Voorlichting & Public Relations
47	Bureau Rapportenregistratie
48 - 49	Bibliotheek RIVM
50 - 69	Reserve-exemplaren ten behoeve van Bureau Rapportenbeheer
70 - 89	Reserve-exemplaren

CONTENTS

ABSTRACT

In this report a multi residue method for the determination of pesticides amenable to gas chromatography in a wide variety of food items is described. The scope of the described method includes organochlorine pesticides, organophosphorous compounds, pyrethroids and nitrogen containing compounds. It updates and incorporates multi residue methods given for the separate groups of pesticides, mentioned as described in the manual "Analytical Methods for Residues of Pesticides in Foodstuffs", 5th edition (1988), supervised by the Ministry of Welfare, Public Health and Culture and published by SDU publishers (ISBN 90 12 06172 5). This manual was edited by the Working Group "Development and Improvement of Residue-analytical Methods", in which experts on pesticide analysis from regional laboratories of the Inspectorate for Health Protection and other Dutch Institutes participate.

The method as presented in this report will be incorporated in the 6th edition (1996) of the mentioned manual. This report contains information gathered from practical experience of the members of the Working Group and reflects today practice of pesticide residue analysis in The Netherlands.

SAMENVATTING

In dit rapport wordt een multiresidu methode voor de bepaling van bestrijdingsmiddelen met behulp van gaschromatografie in een grote verscheidenheid aan voedingsprodukten beschreven. De methode omvat organochloorpesticiden, organofosforverbindingen, pyrethroïden en stikstof houdende verbindingen. Het betreft een gemoderniseerde versie en omvat multiresidu methoden voor genoemde groepen bestrijdingsmiddelen zoals beschreven in het handboek "Analytical Methods for Residues of Pesticides in Foodstuffs", vijfde editie (1988), onder supervisie van het Ministerie van Welzijn, Volksgezondheid en Cultuur, gepubliceerd door SDU uitgeverij (ISBN 90 12 06172 5). Dit handboek is tot stand gekomen onder redaktie van de Werkgroep "Ontwikkeling en Verbetering van Residu-analyse methoden" (OVR), waarin experts op het gebied van de residuanalyse van bestrijdingsmiddelen werkzaam bij de Inspecties Gezondheidsbescherming en Nederlandse onderzoeksinstituten deelnemen.
De methode, zoals in dit rapport beschreven, zal in de zesde editie (1996) van boven genoemd handboek worden opgenomen. Dit rapport bevat informatie verzameld op basis van gegevens uit de praktische ervaringen van de leden van de Werkgroep OVR, en geeft een beeld van de hedendaagse praktijk van de residuanalyse van bestrijdingsmiddelen in Nederland.

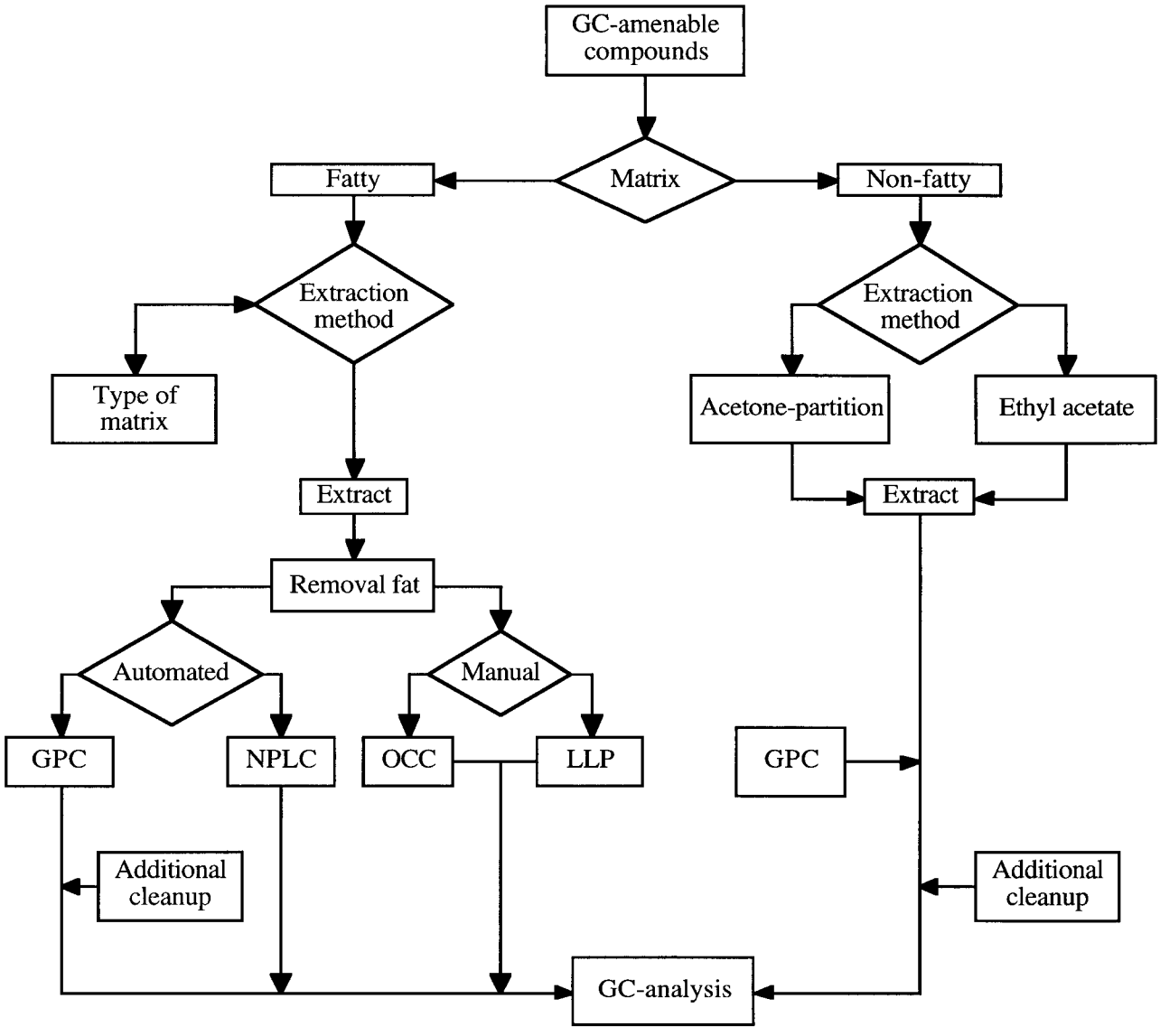
1 GENERAL INTRODUCTION

This multi-residue method (MRM 1) deals with the determination of GC-amenable compounds in a wide variety of samples. It is built up in a modular way in order to cover a wide range of pesticide/matrix combinations. Modules can be chosen depending on the specific matrix to be analysed. The scope of the method includes organochlorine pesticides, organophosphorous compounds, pyrethroids and nitrogen-containing pesticides. In the previous edition of this manual these groups were given in separate MRMs. In this edition a more unified approach is used, rendering a more harmonised methodology for a wide range of pesticides and providing a clear overview of the methodology currently used in regulatory practice in the Netherlands.
The basic structure of this MRM is presented in Fig. 1. As can be seen from this scheme, the matrix determines the methodology to be followed. Depending on the fat content of the matrix, an extraction method can be selected. The limit between "fatty" and "non-fatty" is arbitrarily set at 5%. Tables with average fat contents of a great number of products are given in Ref. 1. For fatty matrices an additional step for the removal of the fat residue prior to GC-analysis is usually required. For this purpose the techniques in use are gel permeation chromatography (GPC), liquid-liquid partition (LLP), open column chromatography (OCC) and high performance liquid chromatography (HPLC). The latter technique performed on a silica separation column in the normal phase mode (NPLC) combines fractionation and clean-up. GPC and LLP both involve a separation between analytes and fat only and, hence, an additional clean-up step will often be necessary.
For non-fatty substances, e.g. fruits and vegetables, an additional clean-up after extraction is not always required. For example, screening methods focused at relatively high MRL-levels and using selective detection, in many cases allow instrumental analysis of uncleaned (concentrated) extracts.
In The Netherlands, current GC-methodology in pesticide residue analysis makes use of capillary columns to perform separation in combination with an electron capture (ECD)-, alkali flame (NPD)-, flame photometric (FPD)- and/or a mass spectrometric detector (conventional MSD or based on the ion trap technique). Especially the use of the ion trap detector (ITD) is growing to be of increasing importance in current practice.
The scope of this MRM is summarised in Annexes A and B which give information on relative retention times and detectability of the pesticides. The information on retention in Annex A includes the relative retention times of 448 pesticides and related compounds on one or more

capillary columns.

Annex B summarises the available information on detectability of the pesticides with various GC detectors, collected through an inquiry among participants of the Working Group OVR in The Netherlands. This table also gives an indication on the number of laboratories actually analysing the pesticides listed. In Annex C information can be found on pesticide-matrix combinations which are analysed in The Netherlands using combinations of modules given in this MRM. Available performance data are listed in Annex D.

Depending on the type of investigation, the determination of the pesticides can be carried out according to a combination of one or more of the methods described below (see also Fig. 1).



Information on	
Reagents and apparatus:	Section 2
Extraction methods:	Section 3
Clean-up methods:	Section 4
Compounds retention:	Annex A
Compounds detection:	Annex B
Compounds/matrix/extraction/clean-up:	Annex C
GC-analysis:	Section 5, Annex D

Fig. 1. General scheme of MRM-1 for the determination of GC-amenable pesticides in foodstuffs.

2 REAGENTS AND APPARATUS

The procedures described in this method can be performed with the standard laboratory equipment availabe in residue laboratories. Proper safety measures must at all times be maintained in working with either toxic, inflammable or explosive chemicals. The suitability of the chemicals and the equipment used must be tested by running blank experiments. In order to avoid repetition of information on reagents and equipment used for the extraction and chromatographic methods included in MRM-1, an overview of the more generally applied chemicals and equipment is given below. Information on specific reagents, mixtures, modified chemicals and equipment related to a specific module will be given in the relevant section.

Generally applied chemicals:

- Organic solvents: acetone, ethyl acetate, cyclohexane, dichloromethane, methanol, hexane, light petroleum (b.r. 40-60°C) , acetonitrile, hexadecane, diethyl ether (peroxide free).
- Sodium sulphate, heated for 3 hours at 500 °C.
- Sodium chloride.
- Sodium oxalate.
- Phosphorous pentoxide.
- Sand, washed with hydrochloric acid and water and heated then until dry.
- Quartz wool.
- Celite 545, heated overnight at 130°C.
- Calfo E (from Johns-Manville), heated overnight at 130°C.

Generally applied equipment:

- Homogenisers, e.g. chopper, blender, Polytron and Ultra turrax.
- Centrifuge, explosion proof.
- Rotating film evaporator with water bath.
- Kuderna Danish evaporator with water bath.

- Water bath.
- Soxhlet apparatus with extraction thimbles extracted for 8 hours with a mixture of light petroleum-acetone (80:20, v/v).
- Fluted paper filter, diameter approx. 150 mm, extracted as described above for the extraction thimbles.
- Grinder.
- Ball mill.
- Chromatographic tubes, length approx. 250 mm, internal diameter approx. 6 mm with solvent reservoir.
- Chromatographic tubes, length 300 mm, internal diameter 9 mm, with solvent reservoir of at least 75 ml.
- Gas chromatograph equipped with an electron-capture, a flame-photometric, an alkali-flame or a mass spectrometric detector.

3 EXTRACTION METHODS

Introduction

For non-fatty samples two different extraction procedures are available. One method makes use of ethyl acetate and performs extraction of analytes by blending the sample with the solvent and sodium sulphate [2]. The other method originally presented by Luke [3] uses acetone for sample extraction followed by a liquid-liquid partition with another organic solvent (e.g. dichloromethane and petroleum ether). The choice of the extraction procedure can be determined by e.g. experience and equipment of the laboratory, the type of sample to be analysed and the range of target-analytes. The ethyl acetate method is more powerful than the acetone partition method for the extraction of more polar compounds. As regards selectivity, the acetone-partition procedure will be more favourable than extraction with ethyl acetate in the presence of sodium sulphate because, in general, the amount of polar co-extracted matrix interferences will be less. In the previous edition of this manual the ethyl acetate extraction procedure was advocated because of its simplicity compared to an acetone-based extraction. Recently, however miniaturised acetone-partition extraction procedures derived from the original Luke method have been developed. In these procedures manual operations as well as solvent consumption are reduced considerably, thus eliminating a large part of the drawbacks compared to ethyl acetate extraction. The miniaturised acetone-partition method can be applied for the extraction of a wide range of pesticides, including N-methylcarbamates and phenylurea herbicides (given in MRM-2) from fruits and vegetables [4]. It is used by laboratories of the Dutch Inspectorate for Health Protection.

For fatty products several extraction methods are available depending on the type of matrix. In many instances the pesticide residues in these commodities may be expressed on a fat basis. In such cases, the fat content of the sample may be based on the mass of fat "as extracted". If the residues are to be reported on a whole product basis it is necessary to determine the percentage of fat in the product. The various matrix-dependent extraction procedures are described below. Method 3.1.6 gives separate methods for the extraction of non-polar, repectively more polar compounds from meat samples.

3.1 Extraction methods for non-fatty matrices

3.1.1 Ethyl acetate for fruits and vegetables

Chop the sample. Bring an aliquot of 50 g in the cup of the blender. Add 50 g sodium sulphate and 100 ml ethyl acetate. Blend for 2-3 min. Decant the liquid through a funnel with a plug or wad of quartz-wool with some sodium sulphate added in the stem. Sometimes, it is advisable to centrifuge the macerate prior to filtration.

3.1.2 Acetone-partition for fruits, vegetables and potatoes

Chop the sample. Homogenize with an Ultra Turrax 15 g well-mixed chopped sample with 30 ml acetone in a centrifuge tube for 30 sec. Add 30 ml dichloromethane and 30 ml petroleum ether and extract by homogenizing another 60 sec. Centrifuge the tube for 2 min at 4000 rpm. Decant upper (organic extract) layer.

3.1.3 Acetone-partition for nuts, cereals, pulse, oil seeds, tropical seeds and dried fruits

Homogenize the sample very well by mixing. Transfer 25 g sample to a conical flask with stopper. Add 100 ml of acetone:dichloromethane (50:50, v/v) and allow to stand for static extraction at least overnight.

3.1.4 Acetone-partition for garlic

Disconnect the garlic cloves and homogenize them by mixing. Transfer 25 g of sample to a conical flask with stopper. Add 100 ml of acetone:dichloromethane (50:50, v/v) and allow to stand at least overnight for static extraction.

3.1.5 Acetone-partition for herbs and spices

Mix the sample very well and transfer 5 g of sample to a conical flask with stopper. Add 100 ml of acetone:dichloromethane (50:50, v/v) and allow to stand at least overnight for static extraction.

3.1.6 Non-fatty animal products (i.e.: products containing 5% fat or less)

Organochlorine pesticides and pyrethroids: Take 20-25 g sample. Add 25 g sodium sulphate and 10-15 g sand. Mix in a mortar until a free-flowing powder is obtained. Add more sodium sulphate if necessary.

Transfer the powder to an extraction thimble. Extract in a Soxhlet apparatus with light petroleum

for 8 hours (4-5 siphonings per hour).
Concentrate the extract in a Kuderna-Danish evaporator to a few milliliters. Remove the last traces of light petroleum on a water bath of 65-70°C (this procedure usually takes 2-4 hours). Dissolve the residue in light petroleum so that the solution contains 40-50 mg fat per ml.
Organophosphorus compounds: Remove inedible parts and excess fat from the sample. Mince the remainder of the sample in a meat mincer. Bring an aliquot of 25 g in a mortar and add 45 g sodium sulphate. Mix until a dry powder is obtained. Bring the powder in the cup of the blender. Add 13 ml acetone, 125 ml acetonitrile, 5 g Celite 545 and 10 g Calflo E. Blend for 2-3 min. Filter over a Buchner filter (use only partial vacuum in order to prevent clogging).
Filter again over a fluted paper filter and determine the volume of the extract. Calculate the amount of sample to which this volume corresponds. Concentrate to a few ml in a rotating film evaporator at a bath temperature of 45°C. Transfer the residue to a glass tube using acetone for rinsing and evaporate to dryness at room temperature with a gentle stream of nitrogen.

3.2 Extraction methods for fatty matrices

3.2.1 Animal products

Cut the material in cubes of approx. 1 x 1 x 1 cm. Transfer approx. 25 g to a glass funnel, diameter approx. 70 mm, which is placed on top of a glass bottle or a conical flask. Heat in a heating cabinet at approx. 65°C for 4-8 hours. Dissolve the rendered fat in light petroleum so that the solution contains 40-50 mg fat per ml.
If the pesticide content must be expressed on a product basis, it is necessary to determine the fat content of the sample under investigation from the dry-weight of an aliquot of the light petroleum extract.

3.2.2 Cheese

Cut a sample of 20-25 g in cubes of approx. 1 x 1 x 1 cm. Blend with 50 ml light petroleum. Decant over a filter with sodium sulphate. Concentrate the extract in a Kuderna-Danish evaporator to a few milliliters. Remove the last traces of light petroleum on a water bath of 65-70°C (this procedure usually takes 2-4 hours). Dissolve the residue in light petroleum so that the solution contains 40-50 mg fat per ml.

3.2.3 Eggs

Separate the egg-white from the yolk (weigh egg-white and yolk separately if the results must be expressed on a whole-egg, shell-free basis). Mix the yolk with an equal amount by weight of sodium sulphate in a mortar until a free-flowing powder is obtained. Transfer the powder to an extraction thimble. Extract in a Soxhlet apparatus with light petroleum for 8 hours (4-5 siphonings per hour).
Concentrate the extract in a Kuderna-Danish evaporator to a few milliliters. Remove the last traces of light petroleum on a water bath of 65-70°C (this procedure usually takes 2-4 hours). Dissolve the residue in light petroleum so that the solution contains 40-50 mg fat per ml.

3.2.4 Butter

Heat the butter to approx. 65°C. Decant over a dry filter. Dissolve a portion of the filtrate in light petroleum so that the solution contains 40-50 mg fat per ml.

3.2.5 Avocado

Peel the avocados and cut the peels into small pieces. Mix the obtained sample and bring 25 g of sample to a conical flask with stopper. Add 100 ml of acetone:dichloromethane (50:50, v/v) and allow to stand at least overnight for static extraction.

3.2.6 Oil seeds

Grind the material in a ball-mill. Bring 20-25 g sample into an extraction thimble. Extract in a Soxhlet apparatus with light petroleum for 8 hours (4-5 siphonings per hour).
Concentrate the extract in a Kuderna-Danish evaporator to a few milliliters. Remove the last traces of light petroleum on a water bath of 65-70°C (this procedure usually takes 2-4 hours). Dissolve the residue in light petroleum so that the solution contains 40-50 mg fat per ml.

3.2.7 Vegetable oil

Prepare a solution in light petroleum which contains 40-50 mg oil per ml.

3.2.8 Milk

Method 1: Blend 50 ml milk with 140-200 ml light petroleum-acetone (50:50, v/v). Centrifuge. Take an aliquot (10-50 ml) of the upper layer. Dry by filtration over sodium sulphate. Rinse the

sodium sulphate with a minimal amount of light petroleum. Evaporate the combined filtrate and rinsings to dryness on a water bath of 65-70°C (this procedure usually takes 2-4 hours). Dissolve the residue in light petroleum so that the solution contains 40-50 mg fat per ml.
Method 2: Extraction of milk is performed according to a modified AOAC procedure [5]. An amount of 1 g sodium oxalate per 100 g sample is added before extraction. To the milk sample equal volumes of methanol, diethyl ether and light petroleum are added and extraction is performed manually for 1 min. After extraction, the organic layer is dried over sodium sulphate, evaporated with a Kuderna-Danish apparatus to a few mls and subsequently to dryness with a gentle stream of nitrogen. Finally, the fat extract is placed in an oven at 120°C for 30 min to remove residual traces of solvent. Dissolve the residue in light petroleum so that the solution contains 40-50 mg fat per ml.

3.2.9 Milk powder

Reconstitute to milk by mixing 10 g milk powder with 90 ml water. Heat to 40-50°C and shake or stir until the powder is dissolved. Proceed as described above under 3.2.8.

4 SUBSEQUENT SAMPLE PREPARATION

Introduction

This section describes the approaches available for the clean-up of extracts obtained according to section 3. No single clean-up method is able to cope with the entire pesticide/matrix range, therefore a variety of clean-up methods is presented below.

The need for a clean-up procedure prior to gas chromatographic analysis is largely dependent on the matrix to be analysed. When the MRL is not extremely low and the extract relatively clean, clean-up steps can often be omitted, especially for quick screening purposes. However, it is advisable to repeat the determination including an effective clean-up step, or by applying mass spectrometric confirmation when residues above the MRL seem to be present.

Gel permeation chromatography (GPC) is the most universally applicable clean-up method for the removal of high molecular weight compounds. It is most favourable towards the multi-matrix aspect and includes most pesticides, as shown in Annex C. GPC has its limitations in the analysis of samples with a high load of coextractives, for instance contaminated fish extracts and animal feed. Moreover, interferences are encountered in the determination of electron-captive compounds in products like onion, leek, cabbage etc. Due to the separation principle GPC does not offer selectivity with respect to interferences with low molecular weight. A selectivity gain can be obtained by the application of an additional clean-up using a small scale chromatography over silica, florisil or alumina.

If only a limited range of analytes is required, more specific clean-up methods employing open column chromatography (OCC) or HPLC may be more appropriate. For the determination of polar compounds in fatty products e.g. meat and milk, separation between fat and analytes can be achieved by liquid-liquid partitioning (LLP).

In this chapter the available sample pretreatment procedures, resp. GPC, OCC, HPLC and LLP, will be described.

4.1 Gel permeation Chromatography

Introduction

Gel permeation chromatography (GPC) has become a powerful and versatile clean-up technique in pesticide residue analysis since the publication on this subject in the 80s by Specht and Tillkes [6]. A major advantage of GPC over conventional open column chromatography is the fact that, beside the large number of GPC-amenable pesticides, the same column can be used for the clean-up of many samples, so that less handling is required and automation becomes possible. The GPC method given by Specht and Tillkes now covers more than 220 pesticides and is one of the most universal methods in use at present. However, drawbacks of this method are (i) the large volume of eluate which has to be processed and (ii) the fact that an extra clean-up step (chromatography over silica with separation in up to 7 fractions) is necessary.

The GPC method described below [7] can be combined with a wide range of extraction methods, e.g. the ethyl acetate method (3.1.1), the acetone-partition methods (3.1.2-3.1.5) and the methods given in section 3.2. In this module, a 10 mm I.D. GPC column is recommended because it is a good compromise between the loadability of fat (max. 100 mg) and fraction volumes obtained. GPC columns with similar length but with an internal diameter of 25 mm can also be applied. It offers the possibility to increase the amount of fat to be injected (up to 650 mg). However, operation must be performed at a flow rate of 5 ml/min, which results in an increase in both solvent consumption and fraction volumes. For example, for a 25 mm ID column the fraction to be discarded is approx. 100 ml and the analyte containing fraction to be collected is approx. 65 ml. In the analysis of non-fatty samples even columns with a smaller diameter can be considered because there the maximum sample amount to be injected is less limited.

Generally, no additional clean-up or separation in fractions is necessary for the more common matrix/pesticide combinations. The method is applicable for the clean-up of extracts from fatty as well as non-fatty (vegetable) products.

Reagents:

- Elution mixture consisting of 2 parts by volume of acetone with 1 part by volume of cyclohexane (Remark 1).

Apparatus:

A GPC system (Remark 2) consisting of an isocratic HPLC pump, an autosampler suitable for large volume injections (up to at least 1 ml) and equipped with a sample loop of 500 µl, a 450x10 mm I.D. GPC column packed with Bio-Beads SX-3 (Remark 3) and provided with a thermostated system for operation at constant temperature, a three-way valve with time switch and a fraction collector. Extracts containing saturated fats as for instance from eggs may pose solubility problems. In this case it is recommended to keep the GPC column at a thermostated temperature of 35 °C.

Extraction:

See methods 3.1.1-3.2.9. Prepare a final extract in the GPC eluent mixture containing a maximum amount of 200 mg fat per ml, depending on the type of fat. For non-fatty (vegetable) anhydrous extracts there is no real upper limit for the amount of sample introduced on the column. Centrifuge if the solution is turbid. If centrifuging is not sufficient, filter over a 0.2 µm filter.

Procedure:

Start the GPC-system and let it stabilise with the elution mixture during approx. 30 min at a flow rate of 0.5 ml/min. Increase the flow rate to 1.0 ml/min and inject 500 µl of the extract onto the GPC column. Discard the first eluate (approx. 16 ml) and collect the following 13-15 ml (Remark 4). Add an internal standard to the collected eluate and concentrate to an appropriate volume (Remark 5).

Remarks:

1 Although other eluents mixtures can be used, the eluent mixture acetone/cyclohexane

applied here is recommended since it forms an azeotropic mixture, hence a lower boiling point is achieved leading to lower evaporation times and minimizing loss of analytes due to volatilisation.

2 Complete GPC systems are commercially available, e.g. the GPC Autoprep 1002, marketed by ABC Laboratories Inc., or modular systems from various suppliers.

3 A 600 x 2 mm I.D. column packed with Biobeads SX3 has been applied for the determination of organochlorine pesticides in vegetables and animal fat [8]. A 20 µl injection volume combined with a flow rate of 40 µl/min yiels collection volumes of less than 1 ml; ethyl acetate-cyclohexane (50:50; v/v) was used as mobile phase.

Stationary phases with smaller particle size may also reduce the collection volume. Prelimenary experiments performed on a 300x7.5 mm I.D. column packed 5 µm PLgel 500 A (Polymer Laboratories) resulted in a seperation between vegetable fat and some pesticides (permethrin, chlorpyrifos-methyl, chlorfenvinfos and pirimifos-methyl) in less than 15 min with a collection volume of 2 ml. In this set-up, 50 µl of sample was injected with acetone-cyclohexane (2:1, v/v) as the eluent at a flow rate of 1 ml/min.

4 The exact elution volumes must be determined by experiment and are not interchangeable between different GPC eluents and/or eluents. Some separation between low-molecular weight compounds takes place on the GPC column, therefore collection volumes should always be determined for the complete range of target analytes.

After the GPC clean-up, the fat content of the eluate must not exceed 0.025 mg fat/ml , otherwise the elution times have to be adapted.

5 In order to compensate for losses during sample processing and instrumental analysis, the use of internal standards is recommended. In the analysis of organochlorine compounds using electron capture detection (i) hexabromobenzene or (ii) PCB 3 (4-chlorobiphenyl) together with PCB 198 (2,3,4,5,6-2',3',5'-octachloro-biphenyl) have been used as internal standards. When using the latter, the ratio of concentration of the two compounds between sample and standard should be at least 0.80, otherwise losses of mono-chlorobiphenyl have occurred during the evaporation step.

In general, the selection of a suitable internal standard will depend on the target analytes and the detector used. Hence, for other applications more appropriate internal standards, contaning e.g. nitrogen or phosphorous, may be chosen.

4.2 Open column chromatography

Introduction

Clean-up methods using alumina oxide or a combination of alumina oxide and silicagel have been used extensively in the past for the determination of organochlorine pesticides in fatty foods. Alumina is used for the removal of the fatty matrix, while further fractionation of the target compounds from interfering substances such as the PCBs can be accomplished by an additional clean-up step employing silica. Unfortunately, b-endosulfan cannot be recovered satisfactorily with this method. For non-fatty foods, chromatography over alumina coated with silver nitrate, which selectively reacts with sulfur, can be used in order to remove sulfur containing interferences from products such as cabbage, celery, leek, parsley and onion. However, it is known that some pesticides, e.g. captafol, captan, folpet, heptachlor and iprodione, can only partially be recovered.

For the determination of triazine herbicides a clean-up method is given using chromatography over silicagel. When cabbage extracts are under investigation or when limits of determination below 0.1 mg/kg are required, such a clean-up is necessary.

Clean-up methods using silicagel are available for the determination of pyrethroids in fatty and non-fatty products. An overview of the various clean-up procedures using open column chromatography are summarised and described in more detail in Table 1.

Table 1. Overview open column chromatography procedures

Method	Sorbent	Type of matrices	Extraction method(s)	Type of compounds	Ref.
4.2.1*	Alumina oxide	Fatty	3.2.1-3.2.9	organochlorine	9,10
4.2.2	Alumina oxide/ silver nitrate	Non-fatty	3.1.1-3.1.6	organochlorine	11,12
4.2.3*	Alumina oxide and silicagel	Fatty	3.1.6-3.2.9	organochlorine and PCBs	13
4.2.4	Silicagel	Non-fatty	3.1.2-3.1.6	triazines	14
4.2.5	Silicagel	Non-fatty	3.1.2-3.1.6	pyrethroids	15,16
4.2.6	Silicagel	Fatty	3.1.1	pyrethroids	17

* Still widely in use.

4.2.1 Chromatography over alumina oxide for the determination of organochlorine pesticides in fatty products (Remark 1)

Reagents:

- Alumina, basic, Brockmann Activity Grade I (= 1% water), for chromatography, Baker Analyzed Reagent, art. NO. 1848. *To 100 parts by weight alumina add 8.8 parts by weight water. Shake until all lumps have disappeared. Allow to stand for 24 hours. The water content of the end product should be about 9.0%. Check the activity of the product with a standard solution of b-HCH; the recovery should be 99% or more. If the recovery is lower, increase the water content of the alumina in steps of 0.2% until the recovery is satisfactory. Also check the fat retention following the procedure described below. The fat retention must be 99% or more. If the retention is lower, the alumina contains too much water, which can be removed by*

heating at 500°C for several hours. Repeat the deactivation as described above, starting with less water, and stepwise add water until the product has the required activity, both with respect to fat retention and recovery of b-HCH.

Extraction:

See methods 3.2.1-3.2.9.

Clean-up procedure:

Bring in a chromatographic tube a plug of quartz-wool and 4.0 g deactivated alumina. Tap against the wall of the tube in order to achieve an even distribution of the alumina in the tube. Bring 2 ml light petroleum solution of the extract containing 40-50 mg fat per ml onto the column (Remark 2). Rinse the inner wall of the tube with 3 x 1 ml light petroleum. Elute with 25 ml light petroleum. Collect the eluate in a Kuderna-Danish flask equipped with a calibrated tube. Concentrate the eluate on a water bath of 65-70°C to exactly 1 ml (Remark 3).

4.2.2 Chromatography over alumina oxide for the determination of organochlorine pesticides in non-fatty products

Reagents:

- Silver nitrate, A.R.
- Alumina, W 200, neutral, activity Super I, ICN. *Heat for 4 hours at 500°C. Allow to cool in an exsiccator. Add per 100 g alumina 1.0 g silver nitrate dissolved in 7.0 ml water. Mix thoroughly and store in a dark, well-closed bottle. Use within 1 week.*
- Elution mixture: light petroleum-diethyl ether (70:30, v/v)

Extraction:

See methods 3.1.1-3.1.6.

Clean-up procedure:

Evaporate an appropriate volume of extract to dryness in a rotating film evaporator at a bath temperature of 40°C. Add to the residue 5 ml of light petroleum and evaporate again to dryness. Dissolve the residue in light petroleum so that the solution contains 2.0 g of sample per ml. Bring in a chromatographic tube a plug of quartz-wool and 1.0 g silver nitrate coated alumina. Tap against the wall of the tube in order to achieve an even distribution of the alumina in the tube. Bring 1 ml extract containing 2 g of sample per 1 ml of light petroleum onto the column and rinse the inner wall of the tube with 1 ml elution mixture. Elute with 9 ml of the same mixture (Remark 4). Collect the eluate in a calibrated tube and concentrate to a suitable volume.

4.2.3 Chromatography over alumina oxide and silicagel for the determination of organochlorine pesticides in fatty products (Remark 5)

Reagents:

As for method 4.2.1; additionally:

- Silicagel, Kieselgel 60, 70-230 mesh, Merck art. no. 7754. *Bring in glass weighing bottles 5.1 g silicagel. Heat for approx. 15 hours (overnight) at 200°C. Close the bottles before taking them from the oven. Allow to cool to room temperature in an exsiccator over phosphorous pentoxide. Use immediately.*

Extraction:

See method 3.1.6 and methods 3.2.1 - 3.2.9.

Clean-up procedure:

As method 4.2.1 for fatty products, additionally:
Bring in a chromatographic tube a plug of quartz-wool, approx. 0.5 g sodium sulphate, 5 g freshly activated silicagel and again approx. 0.5 g sodium sulphate. Transfer the silicagel as quickly as possible from the weighing bottle to the tube in order to minimise contact to the moisture of the air. Tap against the wall of the tube in order to achieve an even distribution of silicagel in the tube.
Bring the concentrated eluate of the alumina clean-up onto the column, using 2 x 1 ml light petroleum for rinsing. Elute with 25-35 ml light petroleum (eluate A, see Remark 6). Continue the elution with 40-50 ml light petroleum-dichloromethane mixture (50:50, v/v) (eluate B).
Concentrate eluate A to 1 ml. In this eluate, hexachlorobenzene, aldrin, heptachlor and the PCBs are present.
Concentrate eluate B carefully to almost dry. Remove the last traces of solvent at room temperature with a gentle stream of nitrogen. Dissolve the residue in 1 ml light petroleum. In this solution, the other organochlorine compounds can be determined.

4.2.4 Chromatography over silicagel for the determination of Triazines in non-fatty foodstuffs (Remark 7).

Reagents:

- Silicagel, Kieselgel 60, 70-230 mesh, Merck art. no. 7754. *Weigh 1.1 g silicagel in a*

weighing bottle and heat for at least 8 hours at 200°C. Take the silicagel half an hour before use from the oven and allow to cool to room temperature in an exsiccator over phosphorus pentoxide.

Extraction:

See methods 3.1.2-3.1.5.

Clean-up procedure:

Evaporate an appropriate volume of extract to dryness in a rotating film evaporator at a bath temperature of 40°C. Dissolve the residue in dichloromethane so that the solution contains 5.0 g of sample per ml. Bring in a chromatographic tube a plug of quartz-wool, approx. 1 cm sodium sulphate, 1 g freshly activated silicagel and again approx. 1 cm sodium sulphate. Bring 1 ml of the dichloromethane extract onto the column. Rinse the inner wall of the tube with 2 x 1 ml dichloromethane. Elute with 15 ml dichloromethane-acetone (99.5:0.5, v/v) and discard the eluate. Continue the elution with 10 ml dichloromethane-acetone (85:15, v/v). Collect the eluate and concentrate to exactly 1 ml with a gentle stream of nitrogen.

4.2.5 Chromatography over silicagel for the determination of Pyrethroids in non-fatty foodstuffs

Reagents:

- Silicagel, Kieselgel 60, 70-230 mesh, Merck art. no. 7754.
  Activate overnight at 130°C and allow to cool in a closed conical flask in an exsiccator over phosphorous pentoxide. Add 5 parts by weight water to 95 parts by weight activated silicagel and shake until no lumps are present. Allow to stand for 24 hours before use.

- Elution mixture A: n-hexane-ethyl acetate (99.8:0.2, v/v)
- Elution mixture B: n-hexane-ethyl acetate (90:10, v/v)
- n-Decane
- Internal standard of decachlorobiphenyl (DCB)
  Prepare a solution of 1 µg DCB/ml n-hexane.

Extraction:

Add an appropriate amount of the internal standard to the extraction fluid and proceed according to method 3.1.2-3.1.5.

Clean-up procedure:

Evaporate an appropriate volume of extract to dryness in a rotating film evaporator at a bath temperature of 40°C. Dissolve the residue in n-hexane so that the solution contains 0.5 g of sample per ml n-hexane. Bring in a chromatographic tube: a plug of quartz-wool, 5 ml n-hexane and 1.0 g deactivated silicagel. Mix with a stirring rod until the mixture is homogeneous. Rinse the inner wall of the tube with 2 ml n-hexane. Drain the liquid until the meniscus just reaches the top of the silicagel. Bring 2 ml of the concentrated extract (corresponding to 1 g sample) quantitatively onto the column, using 3 x 1 ml n-hexane for rinsing. Drain again until the meniscus just reaches the top of the silicagel. Elute with 20 ml elution mixture A, collect the first 10 ml eluate (containing the internal standard) and discard the remainder of the eluate. Elute the pyrethroids with 35 ml elution mixture B and collect the eluate in a round-bottomed flask. Add the 10 ml eluate containing the internal standard and carefully evaporate to dryness. Dissolve the residue in exactly 1 ml n-decane.

4.2.6 Chromatography over silicagel for the determination of Pyrethroids in meat

Reagents:

- Silicagel, Kieselgel 60, 70-230 mesh, Merck art. no. 7754.
  Bring portions of 2 g silicagel in weighing bottles and heat overnight at 220°C. Allow to cool in an exsiccator over phosphorous pentoxide and use immediately after cooling.
- Elution mixture: light petroleum-diethyl ether (90:10, v/v)

Extraction:

See method 3.1.6.

Clean-up procedure:

Evaporate 100 ml filtrate (corresponding to 25 g sample) to dryness in a rotating film evaporator at a bath temperature of 45°C. Dissolve the residue in a minimal quantity of light petroleum and transfer this with a Pasteur pipette to a calibrated tube. Rinse with minimal quantities of light petroleum and reduce the volume to 2 ml by passing a slow stream of nitrogen over the solution under gentle heating on a water bath.
Bring in a chromatographic tube: a plug of quartz-wool, approx. 1 g sodium sulphate, 2 g activated silicagel and again approx. 1 g sodium sulphate. Immediately bring 1 ml concentrated extract onto the column. Rinse with 10 ml light petroleum and elute with 10 ml elution mixture (light petroleum/ diethyl ether 9:1). Collect the eluate and reduce the volume to exactly 1 ml.

Remarks:

1 If in the chromatogram a great number of interfering peaks are found between aldrin and p.p'-DDT, PCBs can be present in the sample. Submethod 4.2.1. can be used as long as the total concentration of PCBs does not exceed 0.5 mg/kg on a fat basis. When too much interference occurs, separation according to method 4.2.3 is necessary.

2 If desired, the procedure can be scaled up to handle 200-250 mg fat (= 5 ml light petroleum solution). The amount of alumina must then be increased to 10 g and the elution volume to 75 ml. The dimensions of the chromatographic tubes must then be: length 300 mm, internal diameter 9 mm, reservoir capacity at least 75 ml.

3 If undue losses of hexachlorobenzene occur, it is advisable to add a "holder" (e.g. 2,2,4-trimethyl pentane) prior to the final evaporation step.

4 Chlorothalonil is found to decompose during column chromatography. This problem can be alleviated somewhat by applying a slight over-pressure on the column during the elution. The elution time should not exceed 1-2 min

5 Method 4.2.3 must be used for the determination of the compounds mentioned in method 4.2.1 in fat isolated from vegetable or animal material when interference from PCBs occurs (i.e. when the total concentration of PCBs significantly exceeds 0.5 mg/kg on a fat basis). The determination of the PCBs itself is outside the scope of this manual.

6 The exact elution volumes must be determined by experiment for each new batch of silicagel or light petroleum. Traces of benzene or acetone in the light petroleum significantly influence the elution pattern. Especially the separation of p.p'-DDE from the PCBs is critical.

7 Method 4.2.4 must be used when cabbage extracts are under investigation, or when limits of determination below 0.1 mg/kg are required.

4.3 Clean-up method using HPLC

This method has been applied for the determination of organochlorine pesticides in vegetable oil, fish oil, milk fat (Remark 1), animal fat and herbs.

Introduction

Normal-phase column liquid chromatography (NPLC) is a good alternative for the automated clean-up of fatty samples compared to open column chromatographic methods based on florisil, alumina or silica. Hogendoorn et al. [18] published a method for the clean-up of organochlorine pesticides (OCs) and PCBs in fatty samples based on a column switching NPLC system. In the fat clean-up step on the first column dieldrin was the last eluting OC pesticide which can be recovered before the elution of the fatty matrix. The column switching step is used to separate the PCBs from the early eluting OCs to avoid PCB interferences during GC/ECD analysis. If PCB interferences do not play an important role a more simple single column system is recommended.

Method development in LC clean-up of fatty samples depends on several variables: sensitivity, fat solubility and separation capacity. The amount of sample used in the clean-up step is of major influence on the sensitivity of the overall method. In the GC-ECD determination of OCs in a sample, a convenient amount to analyse is about 10 picogram injected per OC-pesticide. Therefore at least an amount of sample extract equivalent to 0.2 mg of fat should be injected into the GC in order to lead to lower quantification levels of 10 µg/kg, which is sufficient for most applications.

The fat is extracted from the sample and dissolved in hexane, which is compatible with the LC clean-up step. The maximum solubility of fat in hexane is approximately 45 mg fat/ml.

In NPLC the elution volume of the OCs is strongly influenced by the amount of matrix brought onto the LC column because large amounts of triglycerides deactivate the active silica surface, reducing the capacity of the column. However, this effect can be used beneficially in order to achieve a reduction of the volume of the fraction to be collected. In this way the total number of fractions to be collected can be reduced to one. Furthermore, this fraction can be injected into the GC without any further manual evaporation/concentration steps.

The method is also applicable to the clean-up of non-fatty samples, in this case separation of the

matrix from the analytes is less critical. The method has been applied to tea, animal feed and herbs.

Apparatus:

- HPLC-system consisting of an autosampler equipped with an injection loop of 600 µl, a pump suited for the delivery of n-hexane, a pump suited for the delivery of dichloromethane, a high-pressure 6-way valve and a low-pressure 3-way valve, a UV detector operated at a wavelength of 214 nm, a fraction collector and a programmable logic controller for the time based switching of the two LC valves. The instrumental set-up of the LC equipment is depicted in Figure 2.

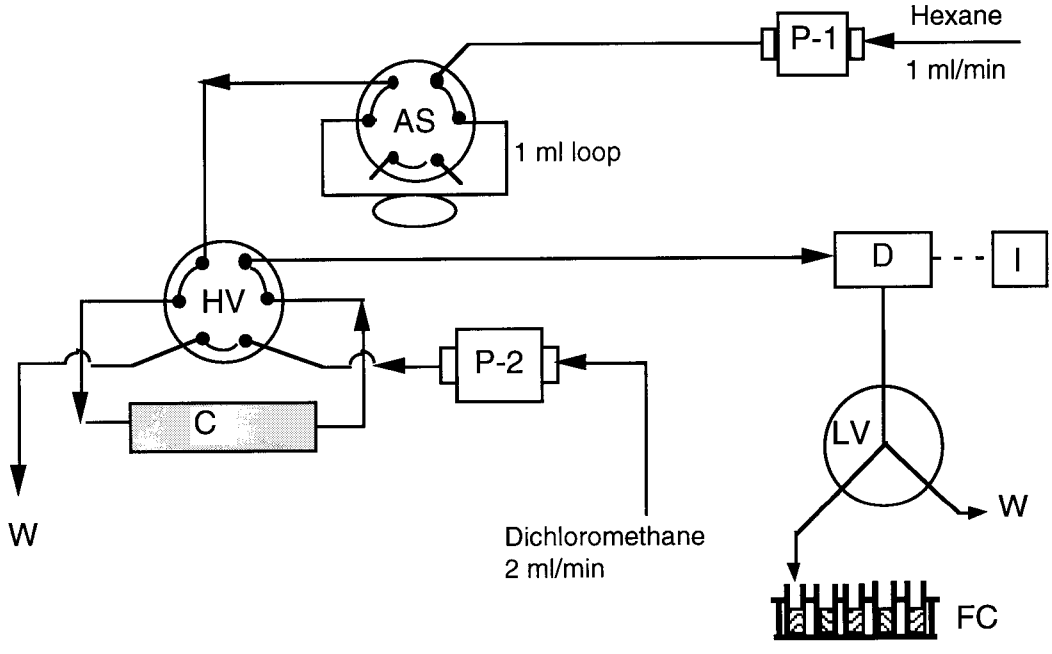


Fig 2. Schematic representation of the equipment used in the normal-phase LC clean-up of fatty samples. P-1, LC-pump (n-hexane); P-2, LC-pump (dichloromethane); AS, autosampler; HV, high-pressure 6 way valves; LV, low pressure 3-way valve; FC: fraction collector; C, LC-column ; D, UV-detector; I, Integrator; W, Waste.

Extraction:

See methods 3.2.1-3.2.9

Clean-up procedure:

The HPLC sample clean-up procedure is performed as follows: an aliquot (typically 600 µl) of the extracted fat (or oil) dissolved in n-hexane at a 45 mg/ml concentration is injected onto the LC column. After fraction collection, the fat retaining on the LC column is removed by a backflush step with 10 ml dichloromethane at a flow rate of 2 ml/min. The system is cleaned from dichloromethane. Prior to the next injection, the LC column is reconditioned during 15 min with n-hexane at a flow of 1.0 ml/min. Fat clean-up is performed automatically by means of the autosampler which activates the programmable logic controller used for the time based switching of the two valves and the pump with dichloromethane (Fig. 2).
A typical HPLC column is 50 x 4.6 mm I.D. packed with Chromspher 3 µm from Chrompack (Remark 2).
In order to determine the fraction volume to be collected after LC clean-up, the fat solution is spiked with dieldrin at a level of approx. 0.1 µg/ml. This solution is used to check the reproducibility of the LC system by monitoring the UV-chromatogram.
For extracts of non-fatty foods the same method can be followed, contrary to the fat clean-up there is no sharp upper limit of the sample load on the HPLC column. In order to obtain a lower elution volume polarity modifiers, e.g. a small amount if isopropylalcohol, may be used.

Remarks:

1 The application of NPLC clean-up in the analysis of PCBs in fatty matrices was performed analog to the clean-up procedure used for the OCs [9]. PCB analysis in milk samples was performed in the same hexane extract as applied for the OC-pesticide clean-up. Due to their similar chemical structure all the PCBs elute on silica in a small fraction, this in

contrast with the OCs which cover a wider polarity range.

2 The main purpose of the described clean-up method is the removal of the fatty matrix from the OCs to be analysed. Hence, complete separation of the fat matrix from the last eluting OC-pesticide, dieldrin is of major importance. As shown in experiments performed by Hogendoorn et al., maximal fat capacity on a column of 60 x 4.6 mm I.D. packed with 10 µm silica is approx. 45 mg fat. With this column, increase of injection volume only resulted in loss of separation between dieldrin and the first eluting glycerides. This constraint is caused by both the capacity of the column and the injection band-broadening, which in turn is governed by the solubility of fat in hexane. More recently an NPLC column of 50 x 4.6 mm I.D. packed with 3 µm Chromspher Si-particles proved to be more suitable in its performance and showed a total fraction volume of 10 ml for the OCs when an aliquot of 600 µl, corresponding to 27 mg fat sample, is injected. The application of this column enabled a higher sample throughput since elution times were reduced by a factor of at least three compared to the column used by Hogendoorn et al.

4.4 Clean-up method using liquid-liquid partitioning

This method has been applied for the determination of organophosphorous compounds in milk [19] and meat [20].

Extraction:

See methods 3.1.6 (meat) and 3.2.8 (milk).

Clean-up procedure milk:

Dissolve the residue in 10 ml n-hexane and extract with 2 x 25 ml acetonitrile which has been saturated beforehand with n-hexane. Combine the acetonitrile phases and evaporate to dryness in a rotating film evaporator at a bath temperature of 45 °C. Dissolve the residue in 2 ml ethyl acetate.

Clean-up procedure meat:

Dissolve the residue in 2.0 ml n-hexane which has been saturated beforehand with acetonitrile. Add 2.0 ml acetonitrile which has been saturated beforehand with n-hexane. Shake vigorously for 2 min. Allow the phases to separate. Use the lower (acetonitrile) phase for the gas chromatographic determination.

5 GAS CHROMATOGRAPHIC ANALYSIS

Introduction

This section deals with the final analysis of extracts by means of gas chromatography. In this section also the overall information on analytical procedures used for the analysis of pesticide residues in the Netherlands is summarised.

For the set-up of a GC-based multi-residue-method for a certain pesticide-matrix combination information is needed on GC-retention and detectability of the analytes, also the need for a clean-up procedure must be evaluated. With the approach presented here such a method is obtained by selecting modules given in Sections 2-5 and Annexes 1-3. GC-retention information is given in Annex A, while Annex B informs on suitable detectors for the specific analytes. Annex C gives a general idea on the applicability of the method for a certain pesticide. The performance that can be achieved using the methodologies given in this MRM is given in Annex D.

5.1 Chromatography

Relative retention data on pesticides and related compounds are given in Annex A. As far as possible the data are given under standardized conditions on a 30 m x 0.25 mm I.D. capillary column

In laboratory practice, other dimensions may be used. In general, the nature of the analytes determines the choice of the stationary phase. For example, for the separation of organochlorine and pyrethroid pesticides a non-polar stationary phase like DB-1 (or OV-1) and DB-5 (or BPX-5) is recommended. For the separation of somewhat more polar compounds, like organophosphorous compounds, OV-17 (or DB-1701) can be applied , and even highly recommended when using FPD. In addition, for confirmation purposes using two columns, a distinct difference in stationary phase polarity, e.g. a DB-1 and a DB-1701 is certainly required. A polar stationary phase e.g. DB-wax is suitable for the more polar compounds such as methamidofos, but its application to some detection modes is limited due to stationary phase bleeding.

5.2 Detection

The conventional sensitive and specific GC-detectors such as ECD, NPD and FPD, are still widely used in pesticide residue analysis. In recent years mass spectrometric detection is becoming more and more important. The equipment used in modern residue laboratories can be based on two different types of mass analysers. On the one hand there are detectors based on quadrupole analysers on the other hand more recently detectors based on the ion trap principle became available.

For most compounds the information on the m/z fragments listed in Annex B were obtained with a quadropole instrument. Nowadays mass-spectrometric detection offers a sensitivity similar to NPD or FPD detection. It should be mentioned however, that the sensitivity of quadrupole instruments must be enhanced by means of limited mass range scanning or selected ion monitoring, while ion trap instruments offer a fair sensitivity with simultaneous monitoring of the complete m/z range. It is for that reason that, nowadays, ITD-based methods are commonly used in the Dutch laboratories covering the analysis of more then 300 pesticides in fruits and vegetables.

5.3 Methods

The pesticide-matrix combinations covered by the specific combinations of the modules given in MRM-1, are presented in Annex C. This information is gathered from practical experience of the members of the Working Group OVR. The indication **none** in the last column of Annex C shows that the residue analysis of pesticides in fruits and vegetables, can usually be performed without a clean-up. However, most compounds are amenable for GPC, which has the advantage of producing a cleaner extract, thus increasing the life-time of the GC-column and injector parts. Compounds for which no GPC information was available from the literature or from our own experience are indicated by an **R**. If uncleaned extracts are analysed, quantitation should preferably be performed by use of standards added to blank matrix extract.

Fruits and vegetables are amongst the most widely analysed samples for pesticide residues, typical concentration factors employing the acetone-partition method given in modules 3.1.2 and 3.1.3 are given in Table 2. The total volume of the liquid obtained after the extraction will depend on the water content of sample. Hence, when using these acetone-based extraction methods one must apply a small correction due to volume contraction in the calculation of the amount of residue. On the basis of practical experience, the average correction factor for fruits and

vegetables is 87/90. The exact correction factor should be determined experimentally.

Table 2. GC-methods for pesticides in non fatty-foodstuffs using an acetone-partition procedure without a clean-up method.

Compounds	Matrices	Sample processing	Detector
P- and S-containing pesticides	Cereals	Evaporate 25 ml of extract to dryness. Redissolve residue into 5 ml iso-octane/toluene (90:10). Inject 0.8 µl of extract	FPD, 526 nm (P) 394 nm (S)
P- and S-containing pesticides	Fruits, vegetables	Evaporate 25 ml of extract to dryness. Redissolve residue into 5 ml iso-octane/toluene (90:10). Inject 0.8 µl of extract.	FPD, 526 nm (P) 394 nm (S)
OCs, pyrethroids	Fruits, vegetables, cereals	Transfer 200 µl of extract to an autosampler vial and remove solvent by open air contact. Redissolve residue into 1 ml iso-octane/toluene (90:10). Inject 0.8 µl of extract.	ECD
N-and P-containing pesticides	Fruits, vegetables, cereals	Evaporate 25 ml of extract to dryness. Redissolve residue into 5 ml iso-octane/toluene (90:10). Inject 0.8 µl of extract.	NPD
All types	Fruits, vegetables, cereals	Evaporate 25 ml of extract to dryness*. Redissolve residue into 5 ml iso-octane/toluene (90:10). Inject 1.5 µl of extract	ITD

*Waterbath at 65 °C untill nearly dry; evaporate to dryness by air contact. During these steps, n-decane may be added as a holder.

Using the ethyl acetate method given in module 3.1.1, an aliquot of the filtrate can usually directly be injected in the gas chromatograph equipped with a suitable detector. When the

sensitivity of the detector is not sufficient, concentration of the filtrate in a rotating film evaporator at a bath temperature of 45°C is recommended.

5.4 Performance and validation

Summary information on recovery and limit of determination for various pesticide-matrix combinations is given in Table 3 on the next page. It must be stressed that these data are indicative and may depend on the type of matrix to be analysed.
The amount of effort allocated with the validation of a method composed from the modules given in this MRM will vary considerably, depending on the ultimate goal of the analysis. However satisfactory performance should be demonstrated initially and thereafter checked regularly at all times. Guidelines for method validation on the determination of residues of pesticides in foodstuffs in regulatory practice as applied by the Dutch Inspectorate for Health Protection are given elsewhere. Validation usually involves the analyses of blank samples and samples spiked at two concentration levels analysed on different days providing information on limit of determination, repeatability and reproducibility.

Annex B gives an indication on the applicability of this MRM to the analysis of specific pesticides. The indication +++ shows that the pesticide is analysed by several laboratories in The Netherlands. The indication ++ shows that the pesticide is analysed by at least one laboratory in The Netherlands, and that the performance of the method is checked. The indication + is used when a compound has been found in some occasions, however, without additional validation data.
For several years now regulatory analysis have been performed by laboratories of the Dutch Inspectorate for Health protection applying the acetone-partition extraction method followed by direct GC analysis (see Overview above). This method has a wide scope in terms of both analytes and matrices. Repeatability and reproducibility (intra-laboratory) achievable with this method are given in Annex D.

Table 3. Ranges recovery and limit of determination for various pesticide-matrix combinations.

Type of compounds	Type of matrices	Clean-up method	Recovery (%)	Limit of determination (mg/kg)	Ref.
Organophos-phorous	Non-fatty	None (ethyl acetate extraction)	> 80	0.01 - 0.05	2
Various	Non-fatty	None (acetone-partition)	80 - 100	< 0.1	5
Various	Fatty, non-fatty	GPC (4.1)	> 80	0.001 - 0.1	8
Organochlorine	Fatty	OCC (4.2.1)	> 95	0.01 - 0.05	9,10
Organochlorine	None-fatty	OCC (4.2.2)	> 80	0.01 - 0.5	11,12
Organochlorine	Fatty	OCC (4.2.3)	> 80	0.05 - 0.1	13
Triazines	Non-fatty	OCC (4.2.4)	80 - 120	0.01	14
Pyrethroids	Non-fatty	OCC (4.2.5)	85 - 110	0.01 - 0.3	15,16
Pyrethroids	Fatty	OCC (4.2.6)	85 - 110	0.02	17
Organochlorine	Fatty	HPLC (4.3)	80 - 110	0.002 - 0.05	18
Organophos-phorous	Fatty	LLP (4.4)	65 -105	0.01 - 0.04	19,20

5.5 Confirmation

In regulatory practice it is of importance that confirmatory tests are carried out before reporting adversely on samples containing residues of pesticides not normally associated with the commodity analysed or where MRLs appear to have been exceeded. A guideline on confirmatory tests is given in reference [21]. Confirmatory tests for GC based methods using ECD, FPD or NPD may involve the analysis on alternative gas chromatographic columns. Residue data obtained by mass spectrometry can represent more definite evidence, in this case additional confirmation of the presence of a certain residue can also be obtained by the use of an alternative GC column, but also by the use of an alternative ionisation technique (e.g. chemical ionization); by monitoring further reaction products of selected ions by tandem mass spectrometry; or by monitoring selected ions at increased mass resolution. The approach followed will depend on the specific equipment available.

For quantification, the ions monitored should be those which are the most specific to the analyte, or which are subject to a minimum of interference, thus providing good signal-to-noise ratios (cf Annex B).

6 REFERENCES

1 Pesticide Analytical Manual, Food and Drug Administation, Vol. I, section 201, 3rd edition 1994, , Washington D.C., U.S.A.

2 W. Krijgsman and C.G. van de Kamp, Analysis of organophosphorous pesticides by gas chromatography with flame photometric detection, J. Chromatogr. 177 (1976) 201.

3 M. A. Luke, J.E. Forberg and H.T. Masumoto, Extraction and clean-up of organophosphorous, organonitrogen and organochlorine pesticides in procedure using flame photometric and electrolytic conductivity detectors, J. Assoc. Off. Anal. Chem. 58 (1975) 1020.

4 A. de Kok and M. Hiemstra, Optimization, automation, and validation of the solid-phase extraction clean-up and on-line liquid chromatographic determination of N-methylcarbamate pesticides in fruits and vegetables, Journal of AOAC International 75 (1992) 1063.

5 K. Helrich (ed.), Official Methods of Analysis of the AOAC, 15the edition, Arlington, VA (1990) Vol. 1, 274.

6 W. Specht and M. Tillkes, Gas-chromatographische bestimmung von Rückständen an Pflanzenbehandlungsmitteln nach Clean-up über Gel-chromatographie und Mini-kieselgel-saülen-chromatographie, Fresenius Z. Anal. Chem. 322 (1985) 443.

7 A.H. Roos, A.J. van Munsteren, F.M. Nab and L.G.M.Th. Tuinstra, Universal extraction/clean-up procedure for screening of pesticides by extraction with ethyl acetate and size exclusion chromatography, Anal. Chim. Acta 196 (1987) 95.

8 J.A. van Rhijn and L.G.M.Th. Tuinstra, Miniaturisation of size-exclusion chromatography as a powerful clean-up tool in residue analysis, J. Chromatogr. 552 (1991) 517.

9 P.A. Greve and W.B.F. Grevenstuk, A convenient small-scale clean-up method for extracts of fatty samples with basic alumina before GLC-analysis on organochlorine pesticides residues, Meded. Fac. Landbouww. Rijksuniv. Gent 40 (1975) 1115.

10 P.A. Greve and W.B.F. Grevenstuk, Resultaten verkregen uit een collaboratief onderzoek van monsters varkensvet en koemelk op organochloorbestrijdingsmiddelen, RIV, Report 111/75 (1975).

11 P.A. Greve and H.A.G. Heusinkveld, Comparison of different silver nitrate/alumina columns for the clean-up of plant extracts prior to gas chromatographic analysis with electron-capture detection, Meded. Fac. Landbouww. Rijksuniv. Gent 46 (1981) 316.

12 P.A. Greve and G.E. Janssen, Onderzoek naar het voorkomen van electroncaptieve verbindingen in ui-, wortel-, kool-, en preimonsters, RIV, Report 638210003 (1984).

13 P.A. Greve and W.B.F. Grevenstuk, Screening of food-stuffs and human tissues for PCBs by the perchlorination method, Meded. Fac. Landbouww. Rijksuniv. Gent 42 (1972) 1795.

14 H. Rosenboom and H.A. Herbold, Determination of triazine herbicides in various crops by capillary gas chromatography with thermionic detection, J. Chromatogr. 202 (1980) 431.

15 G.H. Tjan, J.T.A. Jansen, Th. Konter and E. Tissen, Gaschromatografische bepaling van bioresmethrin, cypermethrin, deltamethrin, fenothrin, fenvalerate en permethrin, RKvW Nijmegen, Report P 10 (1986).

16 J.M. van der Poll, O. de Wilde and P.D.A. Olthof, Gaschromatografische bepaling van permethrin, cypermethrin, decamethrin, fenvaleraat, bioallethrin en bioresmethrin, CIVO-TNO, Report PRA 84/1 (1984).

17 P.A. Greve and E.A. Hogendoorn, De bepaling van synthetische pyrethroiden in vlees, RIVM, Report 638201005 (1984).

18 E.A. Hogendoorn, G.R. van der Hoff and P. van Zoonen, Automated sample clean-up and fractionation of organochlorine pesticides and polychlorinated biphenyls in human milk using NP-HPLC with column switching, HRC & GC 12 (1989) 784.

19 G.F. Ernst and F.A. van Ramshorst-Steenblik, KvW Utrecht, Reports IR/48/08/77/R20 (1977) and IR/71/08/79/R49 (1979).

20 P.A. Greve and H.A.G. Heusinkveld, Bepaling van enkele organofosforbestrijdingsmiddelen in vlees, RIV, Report 637702012 (1983).

21 Supplement one to volume two of the Codex Alimentarius on Pesticide residues in food, section 4.2. FAO, Rome 1993.

ANNEX A Relative retention data of pesticides and related compounds (relative to paration-ethyl), obtained on 4 GC columns.

COMPOUND	DB-1	DB-5	DB-1701	DB-wax
Acephate	0.62	0.64	0.70	
Alachlor	0.95	0.95	0.91	0.68
Aldrin	1.01	0.99	0.89	0.61
Allethrin I	1.07	1.04	1.03	0.71
Allethrin II	1.07	1.04	1.04	0.71
Ametryn		0.90[b]		
Amidithion	0.97	0.96	1.04	
Aminocarb			0.83	
Amitraz			2.30	
Anilazine	1.05	1.03		
Aniline	0.26	0.26	0.28	
Antraquinone		0.97[c]		
Atrazine	0.84	0.85	0.84	0.80
Azaconazole			1.37	
Azamethiphos	1.27	1.32	1.60	
Azinphos-ethyl	1.86	2.02	2.68	
Azinphos-methyl	1.64	1.78	2.42	
Aziprotryne		0.78[b]		
Azolamide (isocarbomid)		0.73[b]		
Barban	1.13	1.15	1.26	
Benalaxyl		1.41[b]		
Benazolin		0.87[b]		
Bendiocarb	0.78	0.78	0.79	0.76
Benfuracarb		1.76[b]		
Benodanil	1.24	1.32	1.53	
Bensulide	2.22			
Bentazone			1.36	
Benzenesulphonamide	0.68	0.71	0.82	
Benzoximate		0.46[b]		
Benzoylprop-ethyl		1.54[b]		
Bicyclohexyl	0.55	0.52		
Bifenox	1.59	1.75	1.99	
Bifenthrin		1.83	1.53	
Binapacryl		1.21	1.31	
Bioallethrin I and II		1.13[b]		
Bioresmethrin	1.46	1.52	1.44	1.46
Bitertanol I	2.10	2.29	2.68	
Bitertanol II	2.14	2.34	2.83	
Branam	1.00	0.99	0.98	1.03
Bromacil	0.97	0.96	1.14	>2.4
Bromfenvinphos	1.13	1.12	1.13	1.21
2-Bromo-4-chloro-6-methylaniline	0.68	0.68	0.66	0.54
4-Bromo-2,6-dimethylaniline	0.66	0.67	0.66	0.54
Bromophos	1.03	1.00	0.96	
Bromophos-ethyl	1.10	1.10	1.04	0.84
Bromopropylate	1.56	1.59	1.70	>2.4
Bufencarb 1			0.81	
Bufencarb 2			0.84	
Buminafos		0.38[b]		
Bupirimate		1.18	1.24	
Buprofezin		1.26[b]		
Butocarboxim		0.48[b]		
Butonate	0.83	0.82	0.81	0.59
Butoxycarboxim			0.69	
Butralin		1.01[b]		

COMPOUND	DB-1	DB-5	DB-1701	DB-wax
Butylate			0.55	
Captafol	1.41	1.46		
Captan	1.04	1.04	1.10	0.83
Carbaryl	0.94	0.94	0.98	0.84
Carbetamide	1.00	0.99	1.14	0.44
Carbofuran	0.83	0.82	0.84	0.82
Carbophenothion	1.32	1.33	1.43	1.73
Carbosulfan			1.68	
Carboxin			1.37	
Chinomethionat	1.08	1.07	1.05	1.08
Chlofentezin		1.31[b]		
Chlorbenside	1.08	1.07	1.03	1.09
Chlorbromuron	1.05	1.03		
Chlorbufam	0.84	0.82	0.84	1.00
trans-Chlordane	1.09	1.08	1.02	0.85
Chlordecone	1.32	1.31	1.19	
Chlordimeform	0.79	0.77	0.76	0.54
Chlorfenprop-methyl		0.68[c]		
Chlorfenson	1.11	1.14	1.16	1.70
Chlorfenvinphos-E	1.04	1.05	1.04	0.91
Chlorfenvinphos-Z	1.06	1.05	1.06	1.00
Chlorfluazuron I		0.98[b]		
Chlorfluazuron II		1.25[b]		
Chloridazon	1.28	1.39	2.16	
Chlormephos	0.63	0.61	0.60	0.44
3-Chloroaniline	0.43	0.43	0.47	0.47
4-Chloroaniline	0.43	0.43	0.47	
Chlorobenzilate		1.37	1.27	
Chloropropylate		1.29		
Chlorothalonil	0.88	0.88	0.91	
Chlorotoluron			0.44	
Chloroxuron			0.88	
Chlorpropham	0.79	0.76	0.78	0.66
Chlorpyrifos-ethyl	1.00	0.98	0.91	0.72
Chlorpyrifos-methyl	0.94	0.92	0.89	0.73
Chlorthal-dimethyl			0.96	
Chlorthiamid	0.90	0.92	1.01	>2.4
Chlorthion	1.01	0.99	1.01	
Chlorthiophos I		1.24	1.27	
Chlorthiophos II		1.27	1.13	
Chlorthiophos III	1.27	1.29	1.38	1.40
Chlorthiophos-sulphone	1.63	1.75		
Chlorthiophos-sulphoxide	1.51	1.63	1.80	
Chlozolinate		1.08		
Cinerin I	1.19	1.20	1.16	0.83
Cinerin II	1.76	1.89	2.03	
Coumaphos	2.18	2.46	2.66	
m-Cresol	0.34	0.34	0.34	0.44
o-Cresol	0.32	0.31	0.38	0.41
p-Cresol	0.34	0.34	0.40	0.43
Crimidine	0.68	0.67	0.70	0.52
Crotoxyphos	1.06	1.06	1.10	1.35
Crufomate	1.01	1.00	1.03	1.25
Cyanazine	0.98	0.98	1.11	0.84
Cyanofenphos	1.31	1.35	1.58	>2.4
Cyanophos	0.86	0.86	0.86	0.88
Cycloate		0.53[b]		
Cycloxydim*			1.61	
Cyfluthrin I	2.50	2.92	3.33	
Cyfluthrin II	2.56	3.01	3.46	

COMPOUND	DB-1	DB-5	DB-1701	DB-wax
Cyfluthrin III	2.61	3.06	3.49	
Cyfluthrin IV	2.65	3.12	3.56	
Cyhalothrin I			2.56	
Cyhalothrin II			2.78	
Cymoxanil*		0.52[b]	1.27	
Cypermethrin I	2.68	3.12	3.49	
Cypermethrin II	2.76	3.24	3.56	
Cypermethrin III	2.81	3.29	3.58	
Cypermethrin IV	2.85	3.35	3.63	
Cyproconazole*			1.18	
Cyprofuran		1.35[b]		
Cyromazine		1.35[b]		
Dazomet		0.66[b]		
o,p'-DDD	1.17	1.19	1.20	1.28
p,p'-DDD	1.24	1.26	1.33	1.76
o,p'-DDE	1.10	1.11	1.01	0.91
p,p'-DDE	1.16	1.15	1.10	1.02
o,p'-DDT	1.27	1.29	1.20	1.24
p,p'-DDT	1.36	1.38	1.36	1.70
Decachlorobiphenyl	3.05	3.29	2.9	>2.4
Deltamethrin	3.93	4.10	>4.1	
Demephion	0.70	0.70	0.71	0.57
Demephion-sulphon	0.88	0.89	1.02	
Demephion-sulphoxide	0.38	0.38	0.44	
Demeton PO	0.82	0.81	0.80	0.58
Demeton PS	0.75	0.74	0.71	0.58
Demeton-S-methyl	0.75	0.76	0.77	0.58
Demeton-S-methyl sulphone	0.94	0.96	1.08	
Desmethylpirimicarb			0.88	
Desmetryn	0.92	0.90	0.90	0.99
Dialifos	1.92	2.15	2.74	
Diallate I	0.82	0.79	0.75	0.49
Diallate II	0.82	0.80	0.77	0.50
Diazinon	0.88	0.86	0.80	0.54
2,6-Dibromo-4-chloroaniline	0.75	0.74	0.70	0.57
2,6-Dibromo-3-chloro-4-methoxyaniline	0.92	0.90	0.89	0.90
2,6-Dibromo-3-chloro-4-methylaniline	0.85	0.85	0.79	0.66
2,6-Dibromo-3,4-dichloroaniline	0.90	0.90	0.85	0.79
2,6-Dibromo-4-isopropylaniline	0.80	0.80	0.74	0.54
Dicamba			0.82	
Dicamba-methyl (Disugran)			0.65	
Dichlobenil	0.54	0.54	0.57	0.46
Dichlofenthion	0.93	0.93	0.86	0.63
Dichlofluanid	0.98	0.96	0.99	
p,p'-Dichlorbenzophenon		1.04[c]		
3,4-Dichloroaniline	0.61	0.60	0.66	0.62
3,5-Dichloroaniline		0.59	0.63	
Dichlorvos	0.47	0.47	0.50	0.39
Diclobutrazole		1.26[b]		
Dicloran	0.82	0.82	0.85	
Dicofol	1.58	1.62	1.64	
Dicrotophos	0.78	0.78	0.81	0.70
Dicyclohexyltin dimethyl	0.84	0.79	0.73	
Dieldrin	1.17	1.16	1.11	1.04
Dienochlor		1.21		
Diethatyl-ethyl		1.19[b]		
Diethofencarb		0.99[b]		
Diethyleneglycol	0.26	0.27	0.32	0.39
Difenoconazole I		2.59[b]		
Difenoconazole II		2.60[b]		

COMPOUND	DB-1	DB-5	DB-1701	DB-wax
Difenoxuron			0.93	
Diflufenican*		1.02[b]	1.21	
Dimefox	0.29	0.30	0.35	0.27
Dimethachlor	0.93	0.92	0.91	0.73
Dimethipin	0.92			
Dimethirimol	0.91	0.89	0.92	0.86
Dimethoate	0.82	0.82	0.86	
2,4-Dimethylaniline		0.40	0.43	
2,6-Dimethylaniline			0.41	
Dimetilan	0.94	0.92	0.94	0.96
Diniconazole		1.34[b]		
Dinobuton		1.10[b]	1.14	
Dinocap I	1.46	1.52	1.58	
Dinocap II	1.51	1.58	1.66	
Dinocap III	1.56	1.64	1.77	
Dinocap IV	1.62	1.72	1.82	
Dinoseb	0.89	0.88	0.86	
Dinoseb-acetate			0.96	
Dinoterb			0.83	
Dioxacarb			0.94	
Dioxathion	0.85	0.84	0.84	0.66
Diphenylamine			0.71	
Diphenyltin dimethyl	0.83	0.81	.	0.49
Disulfoton	0.89	0.86	0.84	0.59
Ditalimfos	1.10	1.11	1.15	1.56
DNOC	0.74	0.75	0.77	
Dodemorph	1.04	1.00	0.90	0.52
Edifenphos	1.31	1.35	1.44	
a-Endosulfan	1.12	1.12	1.02	0.89
ß-Endosulfan	1.22	1.25	1.28	1.69
Endosulfan-ether	0.92	0.89	0.86	0.63
Endosulfan-lacton	1.03	1.03	1.12	1.44
Endosulfansulphate	1.32	1.35	1.50	
Endothion	1.10	1.13	1.43	
Endrin	1.21	1.23	1.17	1.12
EPN		1.59[b]		
EPTC		0.26[b]		
Etaconazole		1.34[b]		
Ethidimuron			1.55	
Ethiofencarb	0.90	0.91	0.92	
Ethion	1.26	1.28	1.34	1.37
Ethirimol			1.10	
Ethofumesate		0.93[c]		
Ethoprophos	0.77	0.76	0.74	0.49
Ethoxyquin	0.77	0.65[b]		
Ethylenethioureum (ETU)		0.48[b]		
Etridiazole	0.64	0.63	0.61	0.43
Etrimfos	0.90	0.88	0.82	0.61
Fenamiphos	1.12	1.12	1.20	1.52
Fenarimol	1.85	1.99	2.26	
Fenchlorphos	0.96	0.95	0.90	0.72
Fenfuram		0.78[b]		
Fenitrothion	0.97	0.97	0.96	1.00
Fenoxycarb			2.05	
Fenpropathrin	1.60	1.71	1.77	>2.4
Fenpropimorph			0.87	
Fenson	1.01	0.99	1.03	1.28
Fensulfothion	1.21	1.24	1.50	
Fenthion	0.99	0.98	0.96	0.96
Fenthionsulfoxide		1.35[b]		

COMPOUND	DB-1	DB-5	DB-1701	DB-wax
Fenvalerate I	3.38	3.77	3.88	
Fenvalerate II	3.59	3.88	3.98	
Flamprop-isopropyl		1.46[b]		
Flamprop-methyl		1.33[b]		
Fluazifop-butyl		1.31[b]		
Flubenzimine	1.28			
Fluchloralin		0.77[b]		
Flucythrinate I*			2.28	
Flucythrinate II*			2.39	
Fluometuron	0.77	0.76		
Fluorchloridone		1.04[b]		
Flusilazole		1.27[b]		
Flutriafol		1.20[b]		
Fluvalinate I		3.86		
Fluvalinate II		3.95		
Folpet	1.05	1.08	1.10	
Fonofos	0.87	0.85	0.80	0.60
Formothion	0.90	0.89	0.95	
Fuberidazole	0.93	0.95	1.01	
Furalaxyl		1.11[b]	1.11	
Furathiocarb		1.65[b]	1.42	
a-HCH	0.81	0.80	0.79	0.58
ß-HCH	0.83	0.83	0.92	0.88
d-HCH	0.86	0.87	0.94	0.53
Heptachlor	0.96	0.95	0.86	0.60
Heptachlor epoxide (isomer A)	1.06	1.06	1.01	0.89
Heptachlor epoxide (isomer B)	1.06	1.05	1.00	
Heptenophos	0.73	0.71	0.71	0.53
Hexachlorobenzene	0.84	0.83	0.74	0.49
Hexaconazole*			1.09	
Hexaflumuron		0.52[b]		
Hexazinone		1.39		
3-Hydroxycarbofuran			1.01	
Imazalil		1.13	1.21	
Ioxynil	0.96	0.95		
Iprodione	1.49	1.58	2.03	
Isocyanuric acid*			0.93	
Isodrin			0.93	
Isofenphos	1.06	1.04	1.06	0.85
Isoprocarb			0.68	
Jasmolin I	1.29	1.30	1.25	0.90
Jasmolin II	2.01	2.18	2.33	
Jodfenphos	1.13	1.13	1.13	
3-Ketocarbofuran			0.89	
Lenacil	1.30	1.43	1.84	
Leptophos	1.73	1.82	1.74	
Leptophos-oxon	1.52	1.60		
Lindane (gamma-HCH)	0.85	0.86	0.84	0.66
Linuron	0.98	0.96		
Malaoxon (*malathion oxon*)	0.93	0.94	0.94	0.87
Malathion	0.98	0.98	0.96	0.86
Mecarbam	1.06	1.05	1.09	1.01
Mefosfolan		1.13[b]		
Menazon*			1.60	
Metalaxyl	0.96	0.93	0.93	0.78
Metazachlor	1.04	1.05	1.06	1.20
Methacrifos	0.68	0.66	0.65	0.48
Methamidophos	0.45	0.46	0.55	0.59
Methidathion	1.08	1.08	1.14	
Methiocarb	0.96	0.95	0.97	1.23

COMPOUND	DB-1	DB-5	DB-1701	DB-wax
Methiocarb-sulphone			1.27	
Methiocarb-sulphoxide			1.11	
Methomyl	0.70	0.72	0.79	
Methoprotryne			1.25	
Methoxychlor		1.85[b]		
3-Methylaniline	0.33	0.33		
Methyl isothiocyanate			0.14	
Metobromuron	0.91	0.89		
Metolachlor	1.00	0.99	0.97	
Metolcarb	0.65			
Metribuzin	0.92	0.92	0.93	
Mevinphos-cis	0.62	0.61	0.62	0.49
Mevinphos-trans	0.61	0.61	0.66	0.51
Mirex	1.80	1.81	1.55	1.85
Monalide*			0.91	
Monocrotophos	0.79	0.80	0.85	1.13
Monolinuron	0.84	0.82		
Myclobutanil		1.17		
Naled	0.78	0.78	0.47	
p-Nitroanisol			0.60	
Nitrofen		1.31[b]		
Nitrothal-isopropyl		1.02[b]		
Norflurazon		1.45[b]		
Nuarimol		1.50[b]		
Omethoate	0.73	0.74	0.80	
Oxadixyl	1.22	1.27	1.62	>2.4
Oxamyl	0.69	0.68	0.77	
Oxycarboxim*			1.60	
Oxychlordane		1.12[b]		
Oxydemeton-methyl	0.38	0.38	0.41	
Paclobutrazol		1.16[b]		
Para-oxon	0.95	0.93	0.96	1.02
Para-oxon-methyl	0.88	0.87	0.90	
PARATHION-ETHYL	1.00	1.00	1.00	1.00
Parathion-methyl	0.93	0.94	0.94	1.12
Penconazole	1.05	1.03	1.07	
Pencycuron	0.81	0.78	0.74	
Pendimethalin		1.05[b]		
Pentachloroaniline		0.80[b]		
Pentachloroanisole		0.69[b]		
Pentachlorobenzene		0.53[b]		
Pentachlorophenol (PCP)	0.85	0.85	0.84	
Pentachlorophenyl acetate (PCP-acetate)	0.90	0.91	0.82	
Pentachlorothioanisole		0.95[b]		
Pentanochlor		0.96[b]		
Permethrin I	2.16	2.42	2.37	>2.4
Permethrin II	2.23	2.52	2.50	>2.4
Phenkapton	1.58	1.64	1.78	
Phenothrin I	1.67	1.79	1.69	1.93
Phenothrin II	1.71	1.84	1.72	1.97
Phenthoate	1.06	1.05	1.06	
o-Phenylphenol	0.68	0.68		
Phorate	0.81	0.79	0.76	0.53
Phosalone	1.69	1.79	2.38	
Phosmet	1.48	1.57	2.00	
Phosphamidon I	0.88	0.86	0.88	0.71
Phosphamidon II	0.92	0.91	0.94	0.85
Piperonyl butoxide	1.46	1.47	1.48	1.45
Pirimicarb		0.91	0.91	
Pirimiphos-ethyl	1.03	1.01	0.99	0.69

COMPOUND	DB-1	DB-5	DB-1701	DB-wax
Pirimiphos-methyl	0.98	0.95	0.90	0.70
Plifenate	0.95	0.94	0.87	
Prochloraz		2.85	3.14	
Proclonol	1.24	1.24	1.33	2.20
Procymidone	1.08	1.06	1.15	1.12
Profenofos	1.15	1.14	1.15	1.12
Promecarb			0.76	
Prometryn			0.89	
Propachlor	0.75	0.74	0.75	0.54
Propargite	1.43	1.51	1.46	
Propazine	0.85	0.83	0.84	0.70
Propetamphos	0.86	0.84	0.84	0.66
Propham	0.64	0.63	0.64	
Propiconazole I	1.33	1.41	1.47	
Propiconazole II	1.35	1.44	1.49	
Propoxur	0.76	0.74	0.77	0.62
Propyzamide		0.85	0.87	
Prothiofos	1.15	1.14	1.08	0.93
Prothoate	0.93	0.91	0.94	0.82
Pyracarbolide			1.11	
Pyrazophos	1.94	2.12	2.39	
Pyrethrin I	1.32	1.35	1.32	
Pyrethrin II	2.01	2.20	2.44	
Pyridaben		1.97[b]		
Pyridafenthion		1.62[b]		
Pyrifenox I			1.02	
Pyrifenox II			1.08	
Pyrimethanil		0.78[b]		
Quinalphos	1.06	1.05	1.04	1.06
Quintozene	0.87	0.85	0.82	0.55
Quizalofop-ethyl		1.21		
Sethoxydim		1.51[b]		
Simazine	0.83	0.84	0.84	0.91
Sulfanilamide		1.08	1.34	
Sulfotep	0.80	0.78	0.76	0.52
Sulphur	1.02	1.04	0.97	
Sulprofos	1.29	1.32	1.35	1.55
T 824 (metabolite of Imazalil)		1.33	1.46	
p,p'-TDE		1.12[c]		
Tebuconazole		1.49[b]		
Tebuthiuron		0.42[b]		
Tecnazene	0.75	0.73	0.70	0.50
Telodrin	1.03	1.00	0.91	0.65
Temephos	4.56			
TEPP	0.71	0.71	0.74	0.54
Terbacil		0.79[b]		
Terbufos	0.87	0.84	0.80	0.53
Terbuthylazine	0.86	0.86	0.88	
Terbutryn	0.97	0.96	0.94	
Tetrachloroanizole		0.56[c]		
2,3,4,5-Tetrachlorophenol		0.67[c]		
2,3,5,6-Tetrachlorophenol		0.69[c]		
Tetrachlorvinphos-E	1.08	1.06	1.10	1.12
Tetradifon	1.64	1.73	2.14	>2.4
Tetramethrin I	1.50	1.57	1.73	2.06
Tetramethrin II	1.54	1.62	1.77	2.15
Tetrasul	1.28	1.28	1.22	1.30
Thanite	0.90	0.90	0.92	
Thiabendazole	1.04	1.04	1.14	
Thiobencarb		0.97[b]		

COMPOUND	DB-1	DB-5	DB-1701	DB-wax
Thiofanox	0.51	0.49	0.49	0.44
Thiometon	0.82	0.80	0.76	0.60
Thiometon-sulphone	1.02	1.02	1.22	
Thionazin	0.74	0.73	0.71	0.54
Tolclofos-methyl	0.94	0.92	0.90	0.77
p-Toluenesulphonamide	0.77	0.78	0.86	2.30
Tolylfluanid	1.05	1.04	1.08	1.03
Triadimefon	1.01	0.99	1.00	0.97
Triadimenol	1.07	1.05	1.10	1.55
Tri-allate		0.79[b]		
Triamiphos	1.25	1.27	1.39	>2.4
Triazophos	1.26	1.31	1.54	
2,4,6-Tribromoaniline	0.82	0.82	0.76	0.65
2,4,6-Tribromo-3-chloroaniline	0.97	0.97	0.91	1.00
2,4,6-Tribromo-3-methylaniline	0.91	0.91	0.84	0.74
2,4,6-Tribromo-3-trifluoromethylaniline	0.86	0.84	0.80	0.68
Tributyl phosphate		0.78	0.74	
Tributyltin methyl	0.65	0.61	0.52	0.20
Trichlophenidin*			1.91	
Trichlorfon			0.67	
Trichloronate	1.03	1.00	0.97	0.70
Tricyclohexyltin methyl	1.26	1.21	1.04	0.55
Tridemorph	0.94	0.88	0.82	0.42
Trietazine		0.71[b]		
Trifenmorph		1.72[b]		
Triflumizole		1.12[b]		
Trifluralin	0.81	0.78	0.76	0.46
2,3,5-Trimethacarb		0.56[b]	0.76	
3,4,5-Trimethacarb		0.56[b]	0.80	
Triphenyltin methyl	1.22	1.26		1.07
Vamidothion	1.08	1.09	1.26	
Vernolate		0.33[b]		
Vinclozolin	0.94	0.92	0.91	0.74

[a] Data from the Inspectorate for Health Protection Amsterdam using a 30 m x 0.25 mm ID column, a 0.25 µm film thickness of stationary phase and a temperature programme of 60°C(1 min)-280°C(10°C/min)-280°C(17 min)-40 min or, indicated by *, 80°C(2 min)-150°C(25°C/min)-280°C(10°C/min)-280°C(22.2 min)-40 min.

[b] Data from the Inspectorate for Health Protection Alkmaar using a temperature programme of 80°C(1 min)-180°C(25°C/min)-280°C(5°C/min)-10 min.

[c] Data from Rikilt DLO Wageningen on a 50 m L column using a temperature programme of 90°C(2 min)-280°C(10°C/min)-300°C(3°C/min)-2.7 min.

ANNEX B Status of analytical performance for pesticides and related compounds, obtained for different GC detectors[a].

COMPOUND	ECD[a]	NPD[a]	ITD[a]	m/z fragments
Acephate		+++	++	94, 136, 142, 183
Alachlor	+	+	+++	160, 188, 237, 269-271
Aldrin	+++		++	260-270, 290-300
Allethrin I	++			107, 123, 136, 168
Allethrin II	++			107, 123, 136, 168
Ametryn			++	170, 184, 212, 227
Amidithion				171, 199, 215, 273
Aminocarb		+		
Amitraz		+		
Aniliazine			++	178-180, 239-243, 274-278
Aniline				65, 66, 92-94
Anthraquinone			++	152, 180, 208
Atrazine		+++	++	173-175, 200-202, 215-217
Azamethiphos		+		155,184, 215-217, 324-326
Azinphos-ethyl		+++	++	105, 129, 132, 160
Azinphos-methyl		+++	+++	105, 125, 132, 160
Aziprotryne		+	++	157, 184, 199
Azolamide (isocarbomid)		+	++	130, 142
Barban				153-155, 222-224, 257-261
Benalaxyl		+	++	148, 176, 206
Benazolin		+		
Bendiocarb		++	++	126, 151, 166, 223
Benfucarb		++	++	135, 144, 163, 190
Benodanil		+	++	196, 203, 231, 323
Bensulide				141, 170, 215, 256
Benzenesulphonamide				93, 141, 157
Benzoximate		+	++	170, 198, 213
Benzoyl-prop-ethyl		+	++	77, 105
Bifenox		+	++	173, 189, 310, 341-345
Bifenthrin	++		++	165, 166, 181, 182
Binapacryl		+	++	83
Biphenyl			++	152-154
Bioallethrin	+++			
Bioresmethrin	+++			
Bitertanol I and II	+++	++	++	141, 168, 170, 337
Bromacil		+	++	205-207, 231-233, 260-262
Bromfenvinphos				267-271, 295-299, 323-327
2-Bromo-4-chloro-6-methylaniline				184, 186, 218-224
4-Bromo-2,6-dimethylaniline				184, 186, 198-202
Bromophos		+++	+++	125, 211-215, 329-333
Bromophos-ethyl		+++	+++	301-305, 329-333, 357-361
Bromopropylate	+++		++	155, 183, 185, 339-343
Buminafos		+		
Bupirimate		+++	++	193, 208, 273, 316
Buprofezin	++	+	++	105, 175, 249
Butonate				111, 152, 180, 221
Butralin		+		
Butylate		+	++	146, 156, 174, 188
Captafol	+++		++	79, 150, 167, 183
Captan	+++		+++	79, 117, 149, 264-266
Carbaryl		++	+++	115, 116, 144, 201
Carbetamide				93, 119, 120, 236
Carbofuran		+++	+++	131, 149, 164, 221
Carbophenothion		+++	++	157-159, 199, 342-344
Carbosulfan		+		

COMPOUND	ECD[a]	NPD[a]	ITD[a]	m/z fragments
Carboxin		+	++	143, 235
Chinomethionat		++	++	148, 174, 206, 234
Chlofentezin		+		
Chlorbenside	++		++	125, 127, 143, 268-270
Chlorbromuron		++	++	124-128, 203-209, 231-235
Chlorbufam		++	+	127-129, 164-166, 171-173, 223-225
trans-Chlordane	+++		+++	235-241, 270-278, 371-379
Chlordecone	+		+	235-241, 270-278, 353-359
Chlordimeform			+	152,154, 181-183, 196-198
Chlorfenprop-methyl			+	125, 165, 196
Chlorfenson	+++		++	111-113, 175-177, 302-306
Chlorfenvinphos-E		+++	+++	267-271, 295-299, 323-327
Chlorfenvinphos-Z		+++	+++	267-271, 295-299, 323-327
Chlorfluazuron I and II	+			
Chloridazon				77, 105, 130, 220-224
Chlormephos		+	++	97, 121, 154, 234-236
3-Chloroaniline		++		92, 100, 127, 129
Chlorobenzilate	+++		+++	111-113, 139-141, 251-255
Chloropropylate				111-113, 139-141, 251-255
Chlorothalonil	+++		+++	264, 266, 268, 270
Chlorpropham		+++	+++	127-129,153, 171, 213-215
Chlorpyrifos-ethyl		+++	+++	197-201, 258-262, 314-318
Chlorpyrifos-methyl		+++	+++	125, 197-201, 286-290
Chlorthal-dimethyl	+		++	299, 301, 303, 332
Chlorthiamid	+			170-176, 189-193, 205-209
Chlorthion				109, 125, 297, 299
Chlorthiophos		+++	++	269-271, 297-299, 325-327, 360-364
Chlorthiophos-sulphone		+		301-303, 329-331, 357-359
Chlorthiophos-sulphoxide				285-287,313-315, 341-343, 360-364
Chlozolinate	+		++	187, 188, 259, 331
Cinerin I				123, 150, 168, 316
Cinerin II				212, 167, 212, 329
Coumaphos		+++	+++	210-212,226-228, 334-336, 362-364
Crimidine				142-144, 156-158, 171-173
Crotoxyphos				105, 127, 166, 193
Crufomate		++	++	182-184, 256, 276-278, 291-293
Cyanazine		+++	++	198-200, 212-214, 225-227, 240-242
Cyanofenphos		+++		157, 169, 185, 303
Cyanophos				109, 125, 180, 243
Cycloate		+	++	83, 154
Cyfluthrin I-IV	++		++	163-167, 199, 206, 226-228
Cyhalothrin I and II	++			
Cymoxanil		+		
Cypermethrin I-IV	+++		++	163-167, 181, 206-210
Cyproconazole		+		
Cyprofuran		+	++	69, 211, 279
Cyromazine		++		
o,p'- and p,p'-DDD	+++			165, 199, 212, 235-239
o,p'-and p,p'-DDE	+++		++	176, 210-212, 246-250, 316-320
o,p'-and p,p'-DDT	+++		++	165,199, 212-214, 235-239
Decachlorobiphenyl	++			354-360, 424-432, 494-504
Deltamethrin	+++			
Demephion				109, 125, 142, 216
Demephion-sulphone				109, 125, 142, 169
Demephion-sulphoxide				109, 110, 142, 168

COMPOUND	ECD[a]	NPD[a]	ITD[a]	m/z fragments
Demeton-S		+	+	88, 143, 170, 171
Demeton-O-sulfoxide		++		
Demeton-S-methyl		+++	++	88, 109, 142, 230
Demeton-S-methyl sulphone		+++	++	109, 125, 142, 169
Demeton-S-methyl sulphoxide		+++		
Desmethylpirimicarb				72, 152, 179, 224
Desmetryn		+++	++	156,171, 198, 213
Dialifos		+++		173, 208, 210, 357
Diallate I and II	+		++	128, 152, 192, 234-238
Diazinon		+++	+++	179, 199, 276, 304
Dichlobenil	++	+	+++	100, 136-138, 171-175
Dichlofenthion		+++	+	162, 223, 251-253,279-281
Dichlofluanid	+++		+++	123, 167, 224, 332
3,4-Dichloroaniline		++	++	126, 161, 163
3,5-Dichloroaniline		+		
Dichlorvos		+++	+++	109,145, 185-187, 220-224
Dicloran	+++	+	++	124, 160-164, 176-180, 206-210
Dicofol	+++		++	111-113, 139-141, 199-201, 250-255
Diclobutrazool		+		
Dicrotophos		+		109, 127, 193, 237
Dicyclohexyltin dimethyl				150, 229-237, 312-320
Dieldrin	+++		++	261-267, 275-283, 378-384
Dienochlor	+++			235-241, 330-336, 470-478
Diethatyl-ethyl		+	++	160, 188, 238, 262
Diethofencarb		+++	++	168, 196, 225, 267
Difenoconazole I and II	++	+		
Diflubenzuron	+			113, 125-129, 141,153-157
Diflufenican	+		++	266, 267, 394
Dimefox				110, 111, 153, 154
Dimethachlor		+	+++	134, 148, 197-199,210-212
Dimethirimol		+	++	166, 167 180, 209
Dimethoate		+++	+++	93, 125, 143, 229
Diniconazole		+		
Dinobuton		+	++	163, 205, 211
Dinoseb		+	++	147, 163, 211, 240
Dinoterb		+	++	131, 177, 225
Dioxathion		+++	++	125, 153, 197, 270
Diphenylamine		++	+++	167-169
Disulfoton		+++		
Disulfoton-sulphone		+		
Ditalimfos		+++	++	130, 148, 243, 299
DNOC		+	++	121, 152, 168, 198
Dodemorph		+	++	154, 238, 252, 281
Edifenphos		+		109, 173, 201, 310
a-and b-Endosulfan	+++		+++	235-243, 270-274, 337-343
Endosulfan-ether				235-245, 270-280, 340-346
Endosulfan-lacton				235-245, 270-280, 319-325
Endosulfansulphate	+++		++	235-245, 270-278, 385-391
Endothion				138, 156, 171, 280
Endrin I-III	+++		++	243-247, 261-267, 343-349
EPN		+		
EPTC		+	++	128, 132, 190
Etaconazole		+		
Ethidimuron		+		
Ethiofencarb		++		107, 108, 168, 225
Ethion		+++	+++	125, 153, 231, 384
Ethirimol				138, 166, 194, 209
Ethofumesate			++	79, 137, 161
Ethoprophos		+++	+++	139, 158, 200, 242

COMPOUND	ECD[a]	NPD[a]	ITD[a]	m/z fragments
Ethoxyquin		++	++	174, 202
Ethylenethioureum (ETU)		++		
Etridiazole	++	+	++	183-187, 211-215, 246-250
Etrimfos		+++	++	153, 181, 277, 292
Fenamiphos		+++	+++	154, 217, 260, 303
Fenarimol	++	+	++	219-223, 251-255, 330-334
Fenchlorphos		+++	++	125, 167-171, 285-289
Fenfuram		+	++	
Fenitrothion		+++	+++	109, 125, 260, 277
Fenoxycarb		+		
Fenpropathrin	+++		++	181, 209, 265, 349
Fenpropimorph		+++	+++	110, 128
Fenson				127, 141, 268-270
Fensulfothion		+++		125, 141, 293, 308
Fenthion		+++	+++	125, 153, 169, 278
Fenthion-sulphoxide		++		
Fenvalerate I and II	+++		++	167, 181, 225, 419-421
Flamprop-isopropyl	+			
Flamprop-methyl	+		++	77, 105, 230
Fluazifop-butyl		+	++	254, 282, 383
Fluchloralin	+		++	264, 306, 326
Flucythrinate I and II	++		++	157, 199, 225
Fluometuron				159, 168, 187, 232
Fluorochloridone		+		
Flusilazole		+	++	179, 206, 233
Flutriafol		+	++	123, 164, 219
Fluvalinate I and II	++		++	181, 250, 252
Folpet	+++	+++	++	232-236, 260-264, 295-299
Fonofos		+++	++	109, 137, 174, 246
Formothion		+++		125, 170, 224, 257
Fuberidazole		+	++	129, 155, 156, 184
Furalaxyl		+++	++	95, 152, 242
Furathiocarb		+		
Furmecyclax		+		
a- and b-HCH	+++		+++	145-151, 181-187, 217-223
d-HCH	+		++	145-151, 181-187, 217-223
Heptachlor	+++		+++	235-241, 270-278, 370-376
Heptachlor epoxide (isomer A)	+			183-187, 235-234, 351-359
Heptachlor epoxide (isomer B)	+++		+++	235-243, 351-359, 386-394
Heptenophos		+++	+++	124, 200, 215, 250-252
Hexachlorobenzene	+++		+++	282, 284, 286, 288
Hexaconazole		+	++	82, 175, 214, 216
Hexaflumuron		+		
Hexazinone		+	++	83, 171, 253
3-Hydroxycarbofuran		++		
Imazalil	+	+++	+++	173-177, 215-219, 296-300
Ioxynil				117, 127, 216, 371
Iprodione	+++	+	+++	124, 187-191, 244-248
Isofenphos		+++		121, 185, 213, 255
Isoprocarb		+		
Jodfenphos		+++	++	125, 250-254, 377-381
Lenacil		+		136, 153, 154, 234
Leptophos				155, 171, 211-215,375-379
Leptophos-oxon				155, 211-215, 240-246, 359-363
Lindane (gamma-HCH)	+++		+++	181-187, 217-223, 252-258
Linuron	++			159-164, 187-191, 248-252
Malaoxon (*malathion oxon*)		+		127, 195, 239, 268
Malathion		+++	+++	125, 158, 173, 256
Mecarbam		+++	++	131, 159, 296, 329
Mefosfolan		+		

COMPOUND	ECD[a]	NPD[a]	ITD[a]	m/z fragments
Menazon		+++		
Metalaxyl		+++	++	206, 220, 249, 279
Metazachlor		+	++	132-135, 160, 209-211
Methabenzthiazuron		+		135, 136, 163, 164
Methacrifos		+		180, 193, 208, 240
Methamidophos		+++	++	94, 95, 126, 141
Methidathion		+++	+++	125, 145, 157, 302
Methiocarb		+++	+++	109, 153, 168, 225
Methiocarb-sulphoxide		+		
Methomyl				88, 105, 115, 162
Methoprotryne		+++	++	213, 226, 256, 271
Methoxychlor	+++		+++	227, 228, 274-276,344-348
Metobromuron	++			169-172, 197-199, 258-260
Metolachlor		+	+++	162, 211-213, 238-240
Metribuzin		+	+	171, 182, 198, 214
Mevinphos-cis and trans		+++	+++	127, 164, 192, 224
Mirex	+		++	235-243, 270-278, 400-408
Monocrotophos		+++	+++	109, 127, 192, 223
Monolinuron		+	++	125-128, 153-155, 214-216
Myclobutanil	+	+++	++	150, 152, 179, 181
Naled		+++	++	109, 145, 185-191
Neburon			++	124-128, 159-165, 187-191
p-Nitroanisol				92, 123, 137, 153
Nitrofen		+	++	108, 202, 253, 283
Nitrothal-isopropyl	++	+	++	194, 212, 236, 254
Nonachlor-cis and trans		+		
Norflurazon			++	102, 145, 303
Nuarimol		+		
Omethoate		+++	++	110, 141, 156, 213
Oxadixyl				132, 163, 233, 278
Oxamyl		++		98, 115, 145, 162
Oxychlordane	++		++	115, 149, 185, 389
Oxydemeton-methyl		+++		109, 110, 142, 168
Paclobutrazol		+		
Para-oxon				220, 232, 247, 275
Para-oxon-methyl				186, 200, 230, 247
Parathion-ethyl		+++	+++	155, 186, 235, 291
Parathion-methyl		+++	+++	109, 125, 246, 263
Penconazole	++	++	++	159-163, 213-215, 248-250
Pencycuron		+	++	125, 166, 180-182, 209-211
Pendimethalin		+	++	252, 162, 191, 208
Pentachloroaniline (PCA)	+++		++	263, 265, 267, 269
Pentachloroanisole	++		+++	246, 263, 296, 298
Pentachlorobenzene	+++			
Pentachlorophenol (PCP)			+	200-204, 228-232, 264-272
Pentachlorophenyl-acetate	++			165-169, 264-270, 306-312
Pentachlorothioanisole	+++			244-250, 261-267, 294-302
Pentanochlor	++		++	141, 197
Permethrin I and II	+++		++	127, 163-167, 183
Phenkapton		++		153, 191,341-345, 376-380
Phenothrin I and II	+++			123, 168, 183, 350
Phenthoate		+	++	91, 246, 274
o-Phenylphenol			+++	115, 141, 169, 170
Phorate		+++	++	121, 199, 231, 260
Phosalone		+++	+++	121, 154, 182-184, 367-369
Phosmet		+++	+++	93, 133, 160, 161
Phosphamidon		+++	++	127, 193, 227-229, 264
Phoxim		+++		
Piperonyl butoxide			++	176, 177, 193, 338
Pirimicarb		+++	+++	72, 138, 166, 238

COMPOUND	ECD[a]	NPD[a]	ITD[a]	m/z fragments
Pirimiphos-ethyl		+++	+	290, 304, 318, 333
Pirimiphos-methyl		+++	+++	233, 276, 290, 305
Plifenate				175, 217, 334-340
Prochloraz	++	++	++	180, 266-270, 308-312
Proclonol	+++			139-141, 251-255, 264-268
Procymidone	+++	+++	++	212-214, 255-259, 283-287
Profenofos		+++	++	206-210, 337-339, 372-376
Prometryn		+++	++	184, 226, 241
Propachlor	+++	+	+++	169, 176, 196, 211-213
Propanil		+		
Propargite	+++		++	173, 201, 231, 350
Propazine		+++	+++	172-174, 214-216, 229-231
Propetamphos		+		138, 194, 222, 236
Propham		++	++	93, 120, 137, 179
Propiconazole I and II		++	++	173-177, 191-195, 259-263
Propoxur		+++	+++	81, 110, 152, 209
Propyzamide	+++	++	+++	145-249, 173-177, 254-259
Prothiofos		+	+++	239-243, 267-269, 309-311
Prothoate		+++		115, 208, 252, 285
Pyracarbolide		+		
Pyrazophos		+++	++	221, 232, 265, 373
Pyrethrin I	+			123, 133, 160, 162
Pyrethrin II	+			107, 133, 160, 167
Pyrethrin III and IV	+			
Pyridaben	++		++	117, 147, 309
Pyridafenthion		++	++	188, 199, 340
Pyrifenox I and II	+	+++		
Pyrimethanil			++	198, 199
Quinalphos		+++	+++	146, 241, 270, 298
Quintozene	+++		+++	235-241, 247-253, 293-299
Quizalofop-ethyl		+	++	299, 372
Resmethrin				123, 128, 143, 171
Sethoxydim		+		
Simazine		+++	++	173-175, 186-188, 201-203
Sulfanilamide				92, 108, 156, 172
Sulfotep		+++	+++	202, 238, 266, 322
Sulphur	++			128, 160, 192, 256
Sulprofos		+		140, 156, 280, 322
p,p'-TDE	++		++	165, 235, 237
Tebuconazole		++	++	70, 125, 250
Tebuthiuron		+	++	156, 171
Tecnazene	+++		+++	201-207, 213-219, 259-265
Telodrin				235-234, 309-317, 373-381
Temephos		+++		125, 171, 203, 466
TEPP		+++		161, 179, 263, 290
Terbacil		+	++	117, 160, 161
Terbufos		+	+	153, 186, 231, 288
Terbumeton		+		
Terbuthylazine		+++	++	173-175, 214-216, 229-231
Terbutryn		+++	++	170, 185, 226, 241
2,3,4,5-Tetrachlorophenol			+	137, 194, 232
2,3,5,6-Tetrachlorophenol			+	137, 194, 232
Tetrachlorvinphos-E and Z		+++	++	109, 238-242, 329-333
Tetradifon	+++		+++	159-161, 227-231, 354-358
Tetramethrin I and II	+		+	123, 135, 164, 165
Tetrasul				252-256, 286-290, 322-328
Thanite				95, 110, 121, 136
Thiabendazole		++	++	129, 174, 201-203
Thiobencarb		+	++	117, 160, 161
Thiofanox				83, 115, 144, 161

COMPOUND	ECD[a]	NPD[a]	ITD[a]	m/z fragments
Thiometon		+++	+	125, 158, 185, 246
Thiometon-sulphone				125, 157, 169, 185
Thionazin				143, 175, 192, 248
Tolclofos-methyl		+++	+++	125, 250-252, 265-267
p-Toluenesulphonamide				107, 155, 171
Tolylfluanid	+++	+	+++	137, 181, 238-242
Triadimefon		+++	++	128-130, 181-183, 208-210, 293
Triadimenol	+++	+++	++	112, 128-130, 168, 169
Tri-allate	+		++	86, 268, 270
Triamiphos		+++		135, 160, 251, 294
Triazophos		+++	+++	161, 257, 285, 313
2,4,6-Tribromoaniline				168-172, 248-252, 327-333
2,4,6-Tribromo-3-chloroaniline				202-207, 282-286, 316-367
2,4,6-Tribromo-3-methylaniline				181-185, 262-266, 341-347
2,4,6-Tribromo-3-trifluoromethyl-aniline				236-240, 316-321, 395-401
Tributyl phosphate				99, 125, 155, 211
Tributyltin methyl				137, 189-197, 245-253
Trichlorfon		+++		109, 145-147, 185-187, 221-223
Trichloronate		+++		
2,4,5-Trichlorophenol			+	
Tridemorph				84, 115, 128, 129
Trietazine		+		
Trifenmorph		+		
Triflumizole		+		
Trifluralin		+	+++	264, 290, 306, 335
Trimethacarb		++		
Vamidothion		+++		87, 109, 145, 169
Vernolate		++		
Vinclozolin	+++	+	+++	198-202, 212-216, 285-289

[a]+++, ++ and +, status on performance instrumental analysis; for further explanation see Text in section 5.4.

ANNEX C Information on matrices, extraction and clean-up for pesticides and related compounds.

COMPOUND	Matrix[a]	Extraction method	Clean-up method[B]
Acephate	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Alachlor	NF	3.1.2-3.1.5	none
Aldrin	NF	3.1.2-3.1.6	none, 4.2.2
	F	3.2.1-3.2.9	4.1, 4.2.3, 4.3
Allethrin I and II	NF	3.1.2-3.1.5	none, R
Ametryn	NF	3.1.2-3.1.5	none, R
Aminocarb	NF	3.1.2-3.1.5	none, R
Amitraz	NF	3.1.2-3.1.5	none
Anilazine	NF	3.1.2-3.1.5	none
Anthraquinone	NF	3.1.2-3.1.5	none
Atrazine	NF	3.1.2-3.1.6	none, 4.2.4
Azamethiphos	NF	3.1.2-3.1.5	none
Azinphos-ethyl	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
	milk	3.2.8	4.4
Azinphos-methyl	NF	3.1.2-3.1.6	none
	F	3.2.1-3.2.9	4.1
Aziprotryne	NF	3.1.2-3.1.5	none, R
Azolamide (isocarbomid)	NF	3.1.2-3.1.5	none, R
Benalaxyl	NF	3.1.2-3.1.5	none
Benazolin	NF	3.1.2-3.1.5	none
Bendiocarb	NF	3.1.2-3.1.5	none
Benfuracarb	NF	3.1.2-3.1.5	none, R
Benodanil	NF	3.1.2-3.1.5	none
Benzoximate	NF	3.1.2-3.1.5	none, R
Benzoylprop-ethyl	NF	3.1.2-3.1.5	none
Bifenox	NF	3.1.2-3.1.5	none
Bifenthrin	NF	3.1.2-3.1.5	none
Binapacryl	NF	3.1.2-3.1.6	none
Bioallethrin I and II	NF	3.1.2-3.1.6	none
	NF	3.1.2-3.1.6	4.2.5
Bioresmethrin	NF	3.1.2-3.1.6	4.2.5
Biphenyl	NF	3.1.2-3.1.5	none, R
Bitertanol I and II	NF	3.1.2-3.1.6	none
	F	3.2.1-3.2.9	4.1
Bromacil	NF	3.1.2-3.1.5	none
Bromophos	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
	meat	3.1.6	4.4
Bromophos-ethyl	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Bromopropylate	NF	3.1.2-3.1.5	none, 4.2.2
	F	3.2.1-3.2.9	4.1
Buminafos	NF	3.1.2-3.1.5	none, R
Bupirimate	NF	3.1.2-3.1.6	none
Buprofezin	NF	3.1.2-3.1.5	none
Butralin	NF	3.1.2-3.1.5	none, R
Butylate	NF	3.1.2-3.1.5	none, R
Captafol	NF	3.1.1-3.1.5	none
	F	3.1.1-3.2.9	4.1
Captan	NF	3.1.1-3.1.5	none
	F	3.1.1-3.2.9	4.1
Carbaryl	NF	3.1.2-3.1.5	none
Carbofuran	NF	3.1.2-3.1.5	none

COMPOUND	Matrix[a]	Extraction method	Clean-up method[B]
Carbophenothion	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Carbosulfan	NF	3.1.2-3.1.5	none
Carboxin	NF	3.1.2-3.1.5	none
Chinomethionat	NF	3.1.2-3.1.6	none
Chlofentezin	NF	3.1.2-3.1.6	none
Chlorbenside	NF	3.1.2-3.1.5	none
Chlorbromuron	NF	3.1.2-3.1.5	none
Chlorbufam	NF	3.1.2-3.1.5	none
trans-Chlordane	NF	3.1.2-3.1.6	none
	F	3.2.1-3.2.9	4.1, 4.2.3, 4.3
Chlordecone	NF	3.1.2-3.1.5	none
Chlorfenson	NF	3.1.2-3.1.5	none
Chlorfenvinphos E and Z	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Chlorfluazuron I and II	NF	3.1.2-3.1.5	none
Chlormephos	NF	3.1.2-3.1.6	none
3-Chloroaniline	NF	3.1.2-3.1.5	none, R
Chlorobenzilate	NF	3.1.2-3.1.6	none
Chlorothalonil	NF	3.1.2-3.1.6	none, 4.2.2
	F	3.2.1-3.2.9	4.1
Chlorpropham	NF	3.1.2-3.1.6	none
Chlorpyrifos-ethyl and -methyl	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Chlorthal-dimethyl	NF	3.1.2-3.1.5	none
Chlorthiamid	NF	3.1.2-3.1.5	none
Chlorthiophos	NF	3.1.1-3.1.6	none
Chlorthiophos-sulphone	NF	3.1.2-3.1.5	none, R
Chlozolinate	NF	3.1.2-3.1.5	none, R
Coumaphos	NF	3.1.1-3.1.6	none
	meat	3.1.6	4.4
Crufomate	NF	3.1.2-3.1.5	none
Cyanazine	NF	3.1.2-3.1.5	none, 4.2.4
Cyanofenphos	NF	3.1.1	none
Cycloate	NF	3.1.2-3.1.6	none
Cyfluthrin I-IV	NF	3.1.2-3.1.6	none
Cyhalothrin I and II	NF	3.1.2-3.1.5	none
Cymoxanil	NF	3.1.2-3.1.5	none
Cypermethrin I-IV	NF	3.1.2-3.1.6	none, 4.2.5
	meat	3.1.1	4.2.6
Cyproconazole	NF	3.1.2-3.1.5	none
Cyprofuran	NF	3.1.2-3.1.5	none
Cyromazine	NF	3.1.2-3.1.5	none, R
o,p'- and p,p'-DDD	NF	3.1.2-3.1.5	none
o,p'-and p,p'-DDE	NF	3.1.2-3.1.6	none
p,p'-DDE	F	3.2.1-3.2.9	4.3
o,p'-and p,p'-DDT	NF	3.1.1-3.1.6	none, 4.2.2
	F	3.2.1-3.2.9	4.1, 4.2.3, 4.3
Decachlorobiphenyl	NF	3.1.2-3.1.5	none, R
Deltamethrin	NF	3.1.2-3.1.6	none, 4.2.5
	F	3.2.1-3.2.9	4.1
	meat	3.1.1	4.2.6
Demeton-O and -S	NF	3.1.2-3.1.5	none
Demeton-O-sulfoxide	NF	3.1.2-3.1.5	none
Demeton-S-methyl	NF	3.1.1-3.2.5	none
Demeton-S-methyl sulphone	NF	3.1.1	none
Demeton-S-methyl sulphoxide	NF	3.1.2-3.1.5	none
Desmetryn	NF	3.1.2-3.1.5	none, 4.2.4
Dialifos	NF	3.1.1	none
Diallate I and II	NF	3.1.2-3.1.5	none

COMPOUND	Matrix[a]	Extraction method	Clean-up method[B]
Diazinon	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
	meat and milk	3.1.6 and 3.2.8	4.4
Dichlobenil	NF	3.1.1-3.1.5	none
	F	3.2.1-3.2.9	4.1
Dichlofenthion	NF	3.1.1	none
	F	3.2.1-3.2.9	4.1
Dichlofluanid	NF	3.1.2-3.1.6	none, 4.2.2
	F	3.2.1-3.2.9	4.1
3,4-Dichloroaniline	NF	3.1.2-3.1.5	none
Dichlorvos	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
	meat and milk	3.1.6 and 3.2.8	4.4
Dicofol	NF	3.1.1-3.1.5	none, 4.2.2
	F	3.2.1-3.2.9	4.1
Diclobutrazool	NF	3.1.2-3.1.5	none, R
Dicloran	NF	3.1.2-3.1.5	none, 4.2.2
Dicrotophos	NF	3.1.2-3.1.5	none, R
Dieldirin	NF	3.1.1-3.1.5	none, 4.2.2
	F	3.2.1-3.2.9	4.1, 4.3
Dienochlor	NF	3.1.2-3.1.5	none
Diethatyl-ethyl	NF	3.1.2-3.1.5	none, R
Diethofencarb	NF	3.1.2-3.1.5	none, R
Difenoconazole I and II	NF	3.1.2-3.1.5	none
Diflubenzuron	NF	3.1.2-3.1.5	none
Diflufenican	NF	3.1.2-3.1.5	none, R
Dimethachlor	NF	3.1.2-3.1.5	none
Dimethirimol	NF	3.1.2-3.1.5	none, R
Dimethoate	NF	3.1.1-3.1.5	none
	F	3.2.1-3.2.9	4.1
	meat and milk	3.1.6 and 3.2.8	4.4
Diniconazole	NF	3.1.2-3.1.5	none, R
Dinobuton	NF	3.1.2-3.1.5	none
Dinoseb	NF	3.1.2-3.1.5	none
Dinoterb	NF	3.1.2-3.1.5	none
Dioxathion cis and trans	NF	3.1.1	none
	F	3.2.1-3.2.9	4.1
Diphenylamine	NF	3.1.2-3.1.5	none
Disulfoton	NF	3.1.1-3.1.6	none
Disulfoton-sulphone	NF	3.1.2-3.1.5	none, R
Ditalimfos	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Dodemorph	NF	3.1.2-3.1.5	none, R
Edifenphos	NF	3.1.2-3.1.6	none
a- and b-Endosulfan	NF	3.1.2-3.1.6	none, 4.2.2
	F	3.2.1-3.2.9	4.1, 4.2.3, 4.3
Endosulfan-sulphate	NF	3.1.2-3.1.6	none
Endrin	NF	3.1.2-3.1.6	none, 4.2.2
	F	3.2.1-3.2.9	4.1, 4.2.3, 4.3
EPN	NF	3.1.2-3.1.6	none, R
EPTC	NF	3.1.2-3.1.5	none
Etaconazole	NF	3.1.2-3.1.5	none, R
Ethidimuron	NF	3.1.2-3.1.5	none
Ethiofencarb	NF	3.1.2-3.1.5	none
Ethion	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
	milk	3.2.8	4.4
Ethofumesate	NF	3.1.2-3.1.5	none
Ethoprophos	NF	3.1.1-3.1.6	none
Ethoxyquin	NF	3.1.2-3.1.5	none

COMPOUND	Matrix[a]	Extraction method	Clean-up method[B]
Ethylenethioureum	NF	3.1.2-3.1.5	none, R
Etridiazole	NF	3.1.2-3.1.5	none
Etrimfos	NF	3.1.1-3.1.6	none
Fenamiphos	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Fenarimol	NF	3.1.2-3.1.5	none
Fenchlorphos	NF	3.1.1-3.1.6	none
	meat	3.1.6	4.4
Fenfuram	NF	3.1.2-3.1.5	none
Fenitrothion	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
	meat and milk	3.1.6 and 3.2.8	4.4
Fenoxycarb	NF	3.1.2-3.1.5	none
Fenpropathrin	NF	3.1.2-3.1.6	none, 4.2.5
Fenpropimorph	NF	3.1.2-3.1.5	none
Fensulfothion	NF	3.1.1-3.1.6	none
Fenthion	NF	3.1.1	none
	meat	3.1.6	4.4
Fenthion-sulphoxide	NF	3.1.2-3.1.5	none, R
Fenvalerate I and II	NF	3.1.2-3.1.6	none, 4.2.5
	meat	3.1.1	4.2.6
Flamprop-isopropyl	NF	3.1.2-3.1.5	none, R
Flamprop-methyl	NF	3.1.2-3.1.5	none, R
Fluazifop-butyl	NF	3.1.2-3.1.5	none
Fluchloralin	NF	3.1.2-3.1.5	none, R
Flucythrinate	NF	3.1.2-3.1.5	none, R
	meat	3.1.1	4.2.6
Fluorochloridone	NF	3.1.2-3.1.5	none
Flusilazole	NF	3.1.2-3.1.5	none
Flutriafol	NF	3.1.2-3.1.5	none, R
Fluvalinate I and II	NF	3.1.2-3.1.5	none
Folpet	NF	3.1.1-3.1.5	none
	F	3.2.1-3.2.9	4.1
Fonofos	NF	3.1.1-3.1.6	none
Formothion	NF	3.1.1	none
	F	3.2.1-3.2.9	4.1
Fuberidazole	NF	3.1.2-3.1.5	none
Furalaxyl	NF	3.1.2-3.1.6	none
Furathiocarb	NF	3.1.2-3.1.5	none, R
Furmecyclax	NF	3.1.2-3.1.5	none, R
a- and b-HCH	NF	3.1.2-3.1.6	none, 4.2.2
	F	3.2.1-3.2.9	4.1, 4.2.3, 4.3
Heptachlor	NF	3.1.1-3.1.5	none, 4.2.2
	F	3.2.1-3.2.9	4.1, 4.2.3, 4.3
b-Heptachlor epoxide	NF	3.1.1-3.1.6	none, 4.2.2
	F	3.2.1-3.2.9	4.1, 4.2.3, 4.3
Heptenophos	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Hexachlorobenzene	NF	3.1.1-3.1.6	none, 4.2.2
	F	3.2.1-3.2.9	4.1, 4.2.3, 4.3
Hexaconazole	NF	3.1.2-3.1.5	none
Hexaflumuron	NF	3.1.2-3.1.5	none, R
Hexazinone	NF	3.1.2-3.1.5	none
3-Hydroxycarbofuran	NF	3.1.2-3.1.5	none, R
Imazalil	NF	3.1.2-3.1.6	none
Iprodione	NF	3.1.2-3.1.6	none
	F	3.2.1-3.2.9	4.1
Isofenphos	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Isoprocarb	NF	3.1.2-3.1.5	none, R

COMPOUND	Matrix[a]	Extraction method	Clean-up method[B]
Jodfenphos	NF	3.1.2-3.1.6	none
	F	3.2.1-3.2.9	4.1
	meat	3.1.6	4.4
Lenacil	NF	3.1.2-3.1.5	none
Leptophos	NF	3.1.2-3.1.6	none, R
Lindane (gamma-HCH)	NF	3.1.2-3.1.6	none, 4.2.2, 4.2.4
	F	3.2.1-3.2.9	4.1, 4.2.3, 4.3
Malaoxon (malathion oxon)	NF	3.1.2-3.1.5	none, R
Malathion	NF	3.1.1-3.1.6	none
	F	3.2.1-4.1.9	4.1
	meat and milk	3.1.6 and 3.2.8	4.4
Mecarbam	NF	3.1.2-3.1.6	none
Mefosfolan	NF	3.1.2-3.1.5	none, R
Menazon	NF	3.1.1	none, R
Metalaxyl	NF	3.1.2-3.1.6	none
Metazachlor	NF	3.1.2-3.1.5	none
Methabenzthiazuron	NF	3.1.2-3.1.5	none
Methacrifos	NF	3.1.2-3.1.5	none, R
Methamidophos	NF	3.1.1-3.1.5	none
Methidathion	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Methiocarb	NF	3.1.2-3.1.5	none
Methiocarb-sulphoxide	NF	3.1.2-3.1.5	none, R
Methoprotryne	NF	3.1.2-3.1.5	none, 4.2.4
Methoxychlor	NF	3.1.2-3.1.6	none, 4.2.2
	F	3.2.1-3.2.9	4.1, 4.2.3
Metolachlor	NF	3.1.2-3.1.5	none
Metribuzin	NF	3.1.2-3.1.5	none
Mevinphos-cis and trans	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
	milk	3.2.8	4.4
Mirex	NF	3.1.2-3.1.6	none, R
Monocrotophos	NF	3.1.1-3.1.5	none
Monolinuron	NF	3.1.2-3.1.5	none
Myclobutanil	NF	3.1.2-3.1.5	none
Naled	NF	3.1.1	none
Nitrofen	NF	3.1.2-3.1.5	none
Nitrothal-isopropyl	NF	3.1.2-3.1.5	none
Nonachlor- trans	F	3.2.1-3.2.9	4.3
Norflurazon	NF	3.1.2-3.1.5	none, R
Nuarimol	NF	3.1.2-3.1.5	none
Omethoate	NF	3.1.1-3.1.5	none
Oxychlordane	NF	3.1.2-3.1.5	none, 4.2.2
	F	3.2.1-3.2.9	4.2.3, 4.3
Oxydemeton-methyl	NF	3.1.1	none
Paclobutrazol	NF	3.1.2-3.1.5	none, R
Parathion-ethyl and -methyl	NF	3.1.1-3.16	none
	F	3.2.1-3.2.9	4.1
	milk	3.2.8	4.4
Penconazole	NF	3.1.2-3.1.5	none
Pencycuron	NF	3.1.2-3.1.5	none
Pendimethalin	NF	3.1.2-3.1.5	none
Pentachloroaniline (PCA)	NF	3.1.1-3.1.6	none, 4.2.2
	F	3.1.1-3.2.9	4.1, 4.2.3
Pentachloroanisole	NF	3.1.2-3.1.5	none, R
Pentachlorobenzene	NF	3.1.2-3.1.6	none, R
Pentachlorothioanisole	NF	3.1.2-3.1.5	none, R, 4.2.2
	F	3.1.6-3.2.9	4.2.3
Pentanochlor	NF	3.1.2-3.1.5	none, R
Permethrin I and II	NF	3.1.2-3.1.6	none, 4.2.2, 4.2.5

COMPOUND	Matrix[a]	Extraction method	Clean-up method[B]
Permethrin I and II	F	3.2.1-3.2.9	4.1
	meat	3.1.1	4.2.6
Phenkapton	NF	3.1.2-3.1.6	none, R
Phenothrin I and II	NF	3.1.2-3.1.6	none, 4.2.5
Phenthoate	NF	3.1.2-3.1.6	none
Phorate	NF	3.1.1-3.1.6	none
Phosalone	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Phosmet	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Phosphamidon	NF	3.1.1	none
	F	3.2.1-3.2.9	4.1
Phoxim	NF	3.1.1	none
Piperonyl butoxide	NF	3.1.2-3.1.5	none
Pirimicarb	NF	3.1.2-3.1.5	none
Pirimiphos-ethyl	NF	3.1.1-3.1.6	none
Pirimiphos-methyl	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Prochloraz	NF	3.1.2-3.1.5	none
Procymidone	NF	3.1.2-3.1.6	none
	F	3.2.1-3.2.9	4.1
Profenofos	NF	3.1.2-3.1.6	none
Prometryn	NF	3.1.2-3.1.5	none, 4.2.4
Propachlor	NF	3.1.2-3.1.5	none, 4.2.2
Propanil	NF	3.1.2-3.1.5	none, R
Propargite	NF	3.1.2-3.1.5	none
Propazine	NF	3.1.2-3.1.5	none, 4.2.4
Propetamphos	NF	3.1.2-3.1.6	none
Propham	NF	3.1.2-3.1.6	none
Propiconazole I and II	NF	3.1.2-3.1.5	none
Propoxur	NF	3.1.2-3.1.5	none
Propyzamide	NF	3.1.2-3.1.5	none
Prothiofos	NF	3.1.2-3.1.6	none
Prothoate	NF	3.1.1	none
	F	3.2.1-3.2.9	4.1
Pyracarbolide	NF	3.1.2-3.1.5	none, R
Pyrazophos	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Pyrethrin I-IV	NF	3.1.2-3.1.6	none
Pyrifenox I and II	NF	3.1.2-3.1.5	none, R
Pyridaben	NF	3.1.2-3.1.5	none, R
Pyridafenthion	NF	3.1.2-3.1.5	none, R
Pyrimethanil	NF	3.1.2-3.1.5	none
Quinalphos	NF	3.1.2-3.1.6	none
Quintozene	NF	3.1.2-3.1.6	none, 4.2.2
	F, NF	3.1.6-3.2.9	4.1, 4.2.3
Quizalofop-ethyl	NF	3.1.2-3.1.5	none
Sethoxydim	NF	3.1.2-3.1.5	none, R
Simazine	NF	3.1.2-3.1.5	none, 4.2.4
Sulfotep	NF	3.1.1-3.1.6	none
Sulphur	NF	3.1.2-3.1.5	none
Sulprofos	NF	3.1.2-3.1.6	none, R
p,p'-TDE	F	3.2.1-3.2.9	4.3
Tebuconazole	NF	3.1.2-3.1.5	none, R
Tebuthiuron	NF	3.1.2-3.1.5	none, R
Tecnazene	NF	3.1.2-3.1.6	none, 4.2.2
	F	3.2.1-3.2.9	4.1, 4.2.3
Temephos	NF	3.1.1	none, R
TEPP	NF	3.1.1	none, R
Terbacil	NF	3.1.2-3.1.5	none, R

COMPOUND	Matrix[a]	Extraction method	Clean-up method[b]
Terbufos	NF	3.1.2-3.1.6	none
Terbumeton	NF	3.1.2-3.1.5	none, R
Terbuthylazine	NF	3.1.2-3.1.5	none, 4.2.4
Terbutryn	NF	3.1.2-3.1.5	none, 4.2.4
Tetrachlorvinphos E and Z	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
	meat	2.1.6	4.4
Tetradifon	NF	3.1.2-3.1.5	none
Tetramethrin I and II	NF	3.1.2-3.1.6	none
Thiabendazole	NF	3.1.2-3.1.5	none
Thiobencarb	NF	3.1.2-3.1.5	none, R
Thiometon	NF	3.1.1-3.1.6	none
	F	3.2.1-3.2.9	4.1
Tolclofos-methyl	NF	3.1.1-3.1.6	none
Tolylfluanid	NF	3.1.2-3.1.6	none, 4.2.4
	F	3.2.1-3.2.9	4.1
Triadimefon	NF	3.1.2-3.1.6	none
Tridadimenol	NF	3.1.1-3.1.5	none, R
Triadimenol	F	3.2.1-3.2.9	4.1
Tri-allate	NF	3.1.2-3.1.5	none
Triamiphos	NF	3.1.1	none
	F	3.2.1-3.2.9	4.1
Triazophos	NF	3.1.1-3.1.6	none
Trichlorfon	NF	3.1.1	none
	F	3.2.1-3.2.9	4.1
	meat and milk	3.1.6 and 3.2.8	4.4
Trichloronate	NF	3.1.1-3.1.6	none
Trietazine	NF	3.1.2-3.1.5	none, R
Trifenmorph	NF	3.1.2-3.1.5	none, R
Triflumizole	NF	3.1.2-3.1.5	none, R
Trifluralin	NF	3.1.2-3.1.5	none
Trimethacarb	NF	3.1.2-3.1.5	none, R
Vamidothion	NF	3.1.1	none
Vernolate	NF	3.1.2-3.1.5	none, R
Vinclozolin	NF	3.1.2-3.1.6	none, 4.2.2
	F	3.2.1-3.2.9	4.1

[a] NF, non-fatty; F, fatty.

[b] R indicates that no information on additional clean-up with GPC is available, for all other compounds an additional GPC clean-up is possible.

ANNEX D Method validation on compounds analysed in fruits and vegetables[a.]

COMPOUND	Matrix	Spiked level (mg/kg)	n	Rec. (%)	RSD (%)[b] r	RSD (%)[b] R	Detector
Acephate	lettuce	0.12	10	n.d.			ITD
	lettuce	0.58	10	31	6.2		ITD
	various	0.58	8	31		27	ITD
Alachlor	various	0.29	10	88	6.0		ITD
Aldrin	lettuce	0.02	10	100	9.0		ECD
	lettuce	0.20	10	99	4.3		ECD
	various	0.13	30	99		6.7	ECD
	lettuce	0.02	10	106	9.5		ITD
	lettuce	0.12	10	102	4.5		ITD
	various	0.12	8	98		7.3	ITD
Ametryn	various	0.29	10	94	8.2		ITD
Anilazine	various	0.29	10	95	12.7		ITD
Atrazine	various	0.29	10	81	9.6		ITD
Azinphos-ethyl	lettuce	0.10	10	96	2.9		NPD
	lettuce	0.52	10	105	2.9		NPD
	various	0.35	10	103		6.6	NPD
	lettuce	0.07	10	99	7.7		ITD
	lettuce	0.35	10	105	1.9		ITD
	various	0.35	8	102		5.5	ITD
Azinphos-methyl	lettuce	0.10	10	99	4.7		NPD
	lettuce	0.52	10	107	3.9		NPD
	various	0.35	10	106		7.8	NPD
	lettuce	0.07	10	83	10.2		ITD
	lettuce	0.35	10	107	5.4		ITD
	various	0.35	8	101		7.9	ITD
Aziprotryne	various	0.29	10	104	12.2		ITD
Azolamide (isocarbomid)	various	0.29	10	90	12.4		ITD
Benalaxyl	various	0.29	10	91	5.9		ITD
Benfuracarb	various	0.29	10	90	4.8		ITD
Benodanil	various	0.29	10	88	6.6		ITD
Benzoximate degradation	various	0.29	10	93	13.1		ITD
Benzoylprop-ethyl	various	0.29	10	91	5.6		ITD
Bifenox	various	0.29	10	98	4.2		ITD
Bifenthrin	various	0.67	10	91	5.8		ITD
Binapacryl	various	0.29	10	89	7.9		ITD
Biphenyl	lettuce	0.02	10	83	9.4		ITD
	lettuce	0.12	10	76	4.8		ITD
	various	0.12	8	86		14	ITD
Bitertanol	lettuce	0.35	10	87	5.7		ITD
	lettuce	1.74	10	79	2.4		ITD
	various	1.74	8	101		4.3	ITD
Bromacil	various	0.29	10	86	6.1		ITD
Bromophos-ethyl	lettuce	0.05	10	110	9.2		ITD
	lettuce	0.23	10	112	3.5		ITD
	various	0.23	8	104		5.3	ITD
Bromophos-methyl	lettuce	0.05	10	105	3.9		ITD
	lettuce	0.23	10	110	2.6		ITD
	various	0.23	8	104		5.0	ITD
Bromopropylate	lettuce	0.10	10	104	14.5		ECD
	lettuce	1.0	10	100	3.0		ECD
	various	0.67	30	101		6.6	ECD
	lettuce	0.12	10	102	4.2		ITD
	lettuce	0.58	10	100	1.9		ITD
	various	0.58	8	103		8.3	ITD
Bupirimate	lettuce	0.03	10	88	7.1		ITD
	lettuce	0.17	10	102	4.5		ITD

COMPOUND	Matrix	Spiked level (mg/kg)	n	Rec. (%)	RSD (%)[b] r	R	Detector
Bupirimate	various	0.17	8	100		5.1	ITD
Buprofezin	various	0.29	10	98	7.2		ITD
Butylate	various	0.29	10	94	5.0		ITD
Captafol	various	0.29	10	93	15.5		ITD
Captan	various	0.29	10	101	4.6		ITD
Carbaryl	lettuce	0.02	10	100	8.8		ITD
	lettuce	0.12	10	98	3.5		ITD
	various	0.12	8	101		6.0	ITD
Carbofuran	lettuce	0.02	10	113	4.6		ITD
	lettuce	0.12	10	105	3.1		ITD
	various	0.12	8	102		8.7	ITD
Carbophenothion	lettuce	0.05	10	99	7.0		ITD
	lettuce	0.23	10	106	2.9		ITD
	various	0.23	8	99		3.5	ITD
Carboxin	various	0.29	10	63	13.5		ITD
Chinomethionat	lettuce	0.12	10	81	8.9		ITD
	lettuce	0.58	10	87	3.1		ITD
	various	0.58	8	105	6.9		ITD
Chlofentezin	various	0.29	10	81	12		ITD
Chlorbenside	various	0.29	10	92	11.2		ITD
Chlorbromuron	various	0.67	10	94	6.2		ITD
Chlorfenson	lettuce	0.04	10	104	12.7		ECD
	lettuce	0.40	10	99	5.0		ECD
	various	0.27	30	103		8.9	ECD
	lettuce	0.05	10	110	10.6		ITD
	lettuce	0.23	10	98	2.4		ITD
	various	0.23	8	103		7.5	ITD
Chlorfenvinphos-E	lettuce	0.07	10	103	4.1		ITD
	lettuce	0.35	10	100	2.0		ITD
	various	0.35	8	103		7.2	ITD
Chlorfenvinphos-Z	lettuce	0.07	10	101	4.4		ITD
	lettuce	0.35	10	96	2.6		ITD
	various	0.35	8	106		4.4	ITD
Chloroaniline	various	0.29	10	65	12		ITD
Chlorobenzilate	lettuce	0.40	10	102	15.3		ECD
	lettuce	4.0	10	100	2.7		ECD
	various	2.7	30	100		6.2	ECD
	lettuce	0.46	10	102	1.3		ITD
	lettuce	2.32	10	103	1.4		ITD
	various	2.32	8	102		3.9	ITD
Chlorothalonil	lettuce	0.02	10	104	11.9		ECD
	lettuce	0.20	10	98	3.8		ECD
	various	0.13	30	102		8.1	ECD
	lettuce	0.02	10	89	7.3		ITD
	lettuce	0.12	10	101	4.5		ITD
	various	0.12	8	103		9.2	ITD
Chlorpropham	lettuce	0.12	10	105	3.7		ITD
	lettuce	0.58	10	104	4.0		ITD
	various	0.58	8	104		7.3	ITD
Chlorpyrifos-ethyl	lettuce	0.030	10	103	8.5		ITD
	lettuce	0.17	10	111	3.5		ITD
	various	0.17	8	103		4.5	ITD
Chlorpyrifos-metyl	lettuce	0.03	10	105	5.0		ITD
	lettuce	0.17	10	107	2.0		ITD
	various	0.17	8	105		5.1	ITD
Chlorthal-dimethyl	various	0.29	10	76	36		ITD
Coumaphos	lettuce	0.10	10	97	3.3		NPD
	lettuce	0.52	10	103	3.4		NPD
	various	0.35	10	100		6.5	NPD

COMPOUND	Matrix	Spiked level (mg/kg)	n	Rec. (%)	RSD (%)[b] r	R	Detector
Coumaphos	lettuce	0.07	10	104	3.6		ITD
	lettuce	0.35	10	102	3.6		ITD
	various	0.35	8	103		5.6	ITD
Cyanazine	various	0.29	10	97	7.3		ITD
Cycloate	various	0.29	10	89	12.3		ITD
Cyfluthrin	various	0.29	10	104	7.7		ITD
Cypermethrin	lettuce	0.30	10	100	8.3		ECD
	lettuce	3.0	10	99	4.3		ECD
	various	2.0	30	101		6.4	ECD
	lettuce	0.35	10	106	5.4		ITD
	lettuce	1.74	10	108	2.5		ITD
	various	1.74	8	102		6.7	ITD
Cyprofuran	various	0.29	10	108	10.6		ITD
p,p'-DDE	various	0.29	10	96	4.2		ITD
p,p'-DDT	various	0.29	10	99	6.0		ITD
Demeton-S-methyl	various	0.29	10	79	6.0		ITD
Desmetryn	various	0.29	10	92	10.6		ITD
Diallate	various	0.29	10	87	12		ITD
Diazinon	lettuce	0.034	10	93	2.7		NPD
	lettuce	0.17	10	99	5.2		NPD
	various	0.12	10	96		7.0	NPD
	lettuce	0.02	10	108	7.3		ITD
	lettuce	0.12	10	102	3.9		ITD
	various	0.12	8	103		5.2	ITD
Dichlobenil	various	0.29	10	64	12.2		ITD
Dichlofluanid	lettuce	0.04	10	104	14.2		ECD
	lettuce	0.40	10	95	8.0		ECD
	various	0.27	30	99		10.3	ECD
	lettuce	0.05	10	100	5.5		ITD
	lettuce	0.23	10	104	3.6		ITD
	various	0.23	8	103		17	ITD
Dichlone?	various	0.29	10	172	164		ITD
Dichloran	various	0.67	10	98	7.8		ITD
3,4-Dichloroaniline	various	0.29	10	63	7.5		ITD
Dichlorvos	lettuce	0.03	10	55	8.3		NPD
	lettuce	0.17	10	56	10.1		NPD
	various	0.12	10	61		24	NPD
	lettuce	0.020	10	96	18.4		ITD
	lettuce	0.12	10	81	11.9		ITD
	various	0.12	8	95		13.5	ITD
Dicofol	various	0.29	10	83	14.6		ITD
Dieldrin	lettuce	0.02	10	102	9.4		ECD
	lettuce	0.20	10	99	4.5		ECD
	various	0.13	30	102		6.5	ECD
	lettuce	0.02	10	n.d.			ITD
	lettuce	0.12	10	105	4.5		ITD
Diethatyl-ethyl	various	0.29	10	99	11.8		ITD
Diethofencarb	various	0.29	10	100	3.4		ITD
Diflufenican	various	0.29	10	90	6.5		ITD
Dimethachlor	various	0.29	10	101	9.1		ITD
Dimethirimol	various	0.29	10	74	12.3		ITD
Dimethoate	lettuce	0.07	10	112	3.8		NPD
	lettuce	0.34	10	120	6.8		NPD
	various	0.23	10	113		12.3	NPD
	lettuce	0.05	10	98	11.3		ITD
	lettuce	0.23	10	90	3.2		ITD
	various	0.23	8	97		9.1	ITD
Dinobuton	various	0.29	10	101	9.1		ITD
Dinoseb	various	0.29	10	100	10.1		ITD

COMPOUND	Matrix	Spiked level (mg/kg)	n	Rec. (%)	RSD (%)[b] r	R	Detector
Dinoterb	various	0.29	10	93	13.7		ITD
Diphenylamine	lettuce	0.12	10	78	10.2		ITD
	lettuce	0.58	10	76	9.6		ITD
	various	0.58	8	97		7.5	ITD
DNOC	various	0.29	10	89	10.6		ITD
Dodemorph	various	0.29	10	86	12.0		ITD
a-Endosulfan	lettuce	0.02	10	108	12.6		ECD
	lettuce	0.20	10	99	3.5		ECD
	various	0.13	30	101		6.3	ECD
	lettuce	0.02	10	n.d.			ITD
	lettuce	0.12	10	114	10.1		ITD
b-Endosulfan	lettuce	0.04	10	104	12.2		ECD
	lettuce	0.40	10	99	3.2		ECD
	various	0.27	30	99		6.1	ECD
	lettuce	0.05	10	n.d.			ITD
	lettuce	0.23	10	113	6.6		ITD
	various	0.23	8	103		15	ITD
Endosulfan-sulphate	lettuce	0.04	10	102	14.8		ECD
	lettuce	0.40	10	99	3.2		ECD
	various	0.27	30	99		5.9	ECD
	lettuce	0.05	10	108	12		ITD
	lettuce	0.23	10	109	2.9		ITD
	various	0.23	8	103		14	ITD
Endrin	various	0.29	10	89	13.6		ITD
EPTC	various	0.29	10	59	16.8		ITD
Ethion	lettuce	0.03	10	96	2.5		NPD
	lettuce	0.17	10	101	3.6		NPD
	various	0.12	10	98		6.6	NPD
	lettuce	0.02	10	110	8.5		ITD
	lettuce	0.12	10	107	4.0		ITD
	various	0.12	8	104		8.8	ITD
Ethoprophos	lettuce	0.02	10	110	9.7		ITD
	lettuce	0.12	10	102	3.6		ITD
	various	0.12	8	94		8.6	ITD
Ethoxyquin	various	0.29	10	70	5.1		ITD
Etridiazole	various	0.29	10	63	10.0		ITD
Fenamiphos	lettuce	0.07	10	55	22		ITD
	lettuce	0.35	10	70	8.5		ITD
	various	0.35	8	100		4.3	ITD
Fenarimol	various	0.29	10	105	3.5		ITD
Fenfuram	various	0.29	10	91	10.3		ITD
Fenitrothion	lettuce	0.03	10	102	8.9		ITD
	lettuce	0.17	10	109	3.1		ITD
	various	0.17	8	105		6.1	ITD
Fenoxycarb	various	0.29	10	96	10.2		ITD
Fenpicionil	various	0.29	10	90	7.4		ITD
Fenpropathrin	various	0.29	10	100	3.8		ITD
Fenpropimorph	various	0.29	10	98	7.8		ITD
Fenthion	various	0.29	10	101	4.2		ITD
Fenthion-sulphoxide							
Fenvalerate	various	0.67	10	92	5.8		ITD
Flamprop-isopropyl	various	0.29	10	92	5.6		ITD
Flamprop-methyl	various	0.29	10	90	6.0		ITD
Fluazifop-butyl	various	0.29	10	98	10.7		ITD
Fluchloralin	various	0.29	10	95	7.1		ITD
Flucythrinate	various	0.29	10	100	5.6		ITD
Flusilazole	various	0.29	10	104	4.1		ITD
Flutriafol	various	0.29	10	99	8.0		ITD
Fluvalinate	various	0.67	10	90	6.8		ITD

COMPOUND	Matrix	Spiked level (mg/kg)	n	Rec. (%)	RSD (%)[b] r	R	Detector
Folpet	various	0.29	10	101	5.2		ITD
Fuberidazole	various	0.29	10	83	13.6		ITD
Furalaxyl	lettuce	0.12	10	94	3.7		ITD
	lettuce	0.58	10	94	4.7		ITD
	various	0.58	8	104		5.2	ITD
Furathiocarb	various	0.29	10	100	10.6		ITD
a-HCH	various	0.29	10	86	3.6		ITD
b-HCH	various	0.29	10	85	7.0		ITD
Heptachlor	various	0.29	10	90	5.9		ITD
b-Heptachlor epoxide (trans)	various	0.29	10	95	8.3		ITD
Heptenophos	lettuce	0.09	10	87	3.8		NPD
	lettuce	0.43	10	96	5.5		NPD
	various	0.29	10	97		12.3	NPD
	lettuce	0.06	10	107	5.6		ITD
	lettuce	0.29	10	100	4.4		ITD
	various	0.29	8	100		8.3	ITD
Hexachlorobenzene (HCB)	lettuce	0.01	10	91	8.2		ECD
	lettuce	0.10	10	97	3.5		ECD
	various	0.07	30	91		10.5	ECD
	lettuce	0.01	10	103	8.8		ITD
	lettuce	0.06	10	100	5.1		ITD
	various	0.06	8	101		8.2	ITD
Hexaconazole	various	0.29	10	99	10.4		ITD
Hexazinone	various	0.29	10	93	8.6		ITD
Imazalil	lettuce	0.35	10	88	23.6		ITD
	lettuce	1.74	10	93	3.6		ITD
	various	1.74	8	102		13	ITD
Iprodione	lettuce	0.30	10	103	13.2		ECD
	lettuce	3.0	10	100	3.4		ECD
	various	2.0	30	105		7.8	ECD
	lettuce	0.35	10	107	4.1		ITD
	lettuce	1.74	10	106	2.6		ITD
	various	1.74	8	103		6.0	ITD
Lindane (gamma-HCH)	lettuce	0.01	10	104	12.6		ECD
	lettuce	0.10	10	99	4.5		ECD
	various	0.07	30	98		8.1	ECD
	lettuce	0.01	10	91	11.9		ITD
	lettuce	0.06	10	112	5.3		ITD
	various	0.06	8	100		8.9	ITD
Malathion	lettuce	0.07	10	97	1.8		NPD
	lettuce	0.34	10	103	4.1		NPD
	various	0.23	10	104		5.0	NPD
	lettuce	0.05	10	102	9.1		ITD
	lettuce	0.23	10	106	4.2		ITD
	various	0.23	8	111		20	ITD
Mecarbam	lettuce	0.05	10	105	7.3		ITD
	lettuce	0.25	10	103	3.8		ITD
	various	0.25	8	102		6.6	ITD
Metalaxyl	lettuce	0.17	10	99	2.8		ITD
	lettuce	0.87	10	108	3.5		ITD
	various	0.87	8	104		5.1	ITD
Metazachlor	various	0.29	10	100	10.7		ITD
Methamidophos	lettuce	0.07	10	n.a.			ITD
	lettuce	0.35	10	16	10.4		ITD
	various	0.35	8	28		23	ITD
Methidathion	lettuce	0.09	10	100	2.1		NPD
	lettuce	0.43	10	104	3.5		NPD
	various	0.29	10	103		6.7	NPD
	lettuce	0.06	10	101	3.8		ITD

COMPOUND	Matrix	Spiked level (mg/kg)	n	Rec. (%)	RSD (%)[b] r	R	Detector
Methidathion	lettuce	0.29	10	102	2.3		ITD
	various	0.29	8	101		5.3	ITD
Methiocarb	lettuce	0.02	10	116	4.9		ITD
	lettuce	0.12	10	97	2.0		ITD
	various	0.12	8	101		11	ITD
Methoprotryne	various	0.29	10	101	9.6		ITD
Methoxychlor	various	0.29	10	72	48		ITD
Metolachlor	various	0.29	10	99	11.3		ITD
Mevinphos-trans	lettuce	0.09	10	88	5.8		NPD
	lettuce	0.43	10	94	4.9		NPD
	various	0.29	10	190?		12.3	NPD
	lettuce	0.12	10	96	3.2		ITD
	lettuce	0.58	10	96	3.9		ITD
	various	0.58	8	97		6.8	ITD
Mirex							
Monocrotophos	lettuce	0.12	10	47	9.2		ITD
	lettuce	0.58	10	44	8.9		ITD
	various	0.58	8	56		22	ITD
Myclobutanil	various	0.29	10	107	5.2		ITD
Nitrofen	various	0.29	10	96	7.8		ITD
Nitrothal-isopropyl	various	0.29	10	97	5.9		ITD
Norflurazon	various	0.29	10	63	10.0		ITD
Omethoate	lettuce	0.12	10	n.d.			ITD
	lettuce	0.58	10	28	10.5		ITD
	various	0.58	8	30	29		ITD
Oxychlordane	various	0.29	10	95	9.1		ITD
Parathion-ethyl	lettuce	0.05	10	96	2.4		NPD
	lettuce	0.26	10	102	4.6		NPD
	various	0.17	10	105		7.3	NPD
	lettuce	0.03	10	106	5.9		ITD
	lettuce	0.17	10	110	4.4		ITD
	various	0.17	8	104		4.6	ITD
Parathion-methyl	lettuce	0.03	10	118	4.8		ITD
	lettuce	0.17	10	107	3.5		ITD
	various	0.17	8	101		8.7	ITD
Penconazole	lettuce	0.12	10	101	3.6		ITD
	lettuce	0.58	10	95	2.6		ITD
	various	0.58	8	102		6.5	ITD
Pencycuron	various	0.29	10	101	5.5		ITD
Pendimethalin	various	0.29	10	93	11.2		ITD
Pentachloroaniline (PCA)	various	0.29	10	92	8.2		ITD
Pentachlorothioanisole	various	0.29	10	91	8.0		ITD
Pentanochlor	various	0.29	10	99	12.4		ITD
Permethrin cis	various	0.67	10	88	5.9		ITD
Permethrin trans	various	0.67	10	94	5.0		ITD
Perthane	various	0.29	10	90	6.6		ITD
Piperonylbutoxide	various	0.29	10	98	4.5		ITD
Phenthoate	various	0.29	10	91	5.0		ITD
o-Phenylphenol	lettuce	0.02	10	80	13.9		ITD
	lettuce	0.12	10	95	3.2		ITD
	various	0.12	10	99		6.9	ITD
Phosalone	lettuce	0.07	10	96	5.1		ITD
	lettuce	0.35	10	105	2.8		ITD
	various	0.35	8	104		6.6	ITD
Phosmet	lettuce	0.10	10	98	3.9		NPD
	lettuce	0.52	10	106	4.0		NPD
	various	0.35	10	103		7.8	NPD
	lettuce	0.07	10	95	3.2		ITD
	lettuce	0.35	10	96	2.9		ITD

COMPOUND	Matrix	Spiked level (mg/kg)	n	Rec. (%)	RSD (%)[b] r	R	Detector
Phosmet	various	0.35	8	105		5.4	ITD
Pirimicarb	lettuce	0.03	10	71	10.2		ITD
	lettuce	0.17	10	81	7.4		ITD
	various	0.17	8	105		17	ITD
Pirimiphos-methyl	lettuce	0.05	10	96	2.0		NPD
	lettuce	0.26	10	100	3.8		NPD
	various	0.15	10	99		7.8	NPD
	lettuce	0.03	10	107	5.2		ITD
	lettuce	0.15	10	106	2.4		ITD
	various	0.15	8	103		5.4	ITD
Prochloraz	lettuce	0.35	10	n.d.			ITD
	lettuce	1.74	10	114	12.5		ITD
	various	1.74	8	116		21	ITD
Procymidone	lettuce	0.10	10	106	17.2		ECD
	lettuce	1.0	10	98	3.3		ECD
	various	0.67	30	100		5.6	ECD
	lettuce	0.12	10	99	6.2		ITD
	lettuce	0.58	10	111	2.9		ITD
	various	0.58	8	102		5.5	ITD
Profenofos	lettuce	0.07	10	112	7.0		ITD
	lettuce	0.35	10	109	3.5		ITD
	various	0.35	8	103		5.8	ITD
Prometryn	various	0.29	10	98	10.3		ITD
Propachlor	various	0.29	10	92	8.3		ITD
Propargite	lettuce	0.02	10	n.d.			ITD
	lettuce	0.12	10	93	7.8		ITD
	various	0.12	8	112		27	ITD
Propazine	various	0.29	10	100	8.1		ITD
Propham	lettuce	0.12	10	103	6.4		ITD
	lettuce	0.58	10	101	5.7		ITD
	various	0.58	8	97		6.1	ITD
Propiconazole	various	0.29	10	109	13.9		ITD
Propoxur	lettuce	0.02	10	98	12		ITD
	lettuce	0.12	10	106	6.0		ITD
	various	0.12	8	103		10	ITD
Propyzamide	various	0.29	10	103	4.8		ITD
Prothiofos	various	0.29	10	100	3.2		ITD
Pyracarbolide	various	0.29	10	96	7.6		ITD
Pyrazophos	lettuce	0.07	10	92	4.3		ITD
	lettuce	0.35	10	98	2.4		ITD
	various	0.35	8	102		6.3	ITD
Pyridaben	various	0.29	10	99	2.7		ITD
Pyridafenthion	lettuce	0.05	10	98	7.3		ITD
	lettuce	0.23	10	103	2.8		ITD
	various	0.23	8	102		7.4	ITD
Pyrifenox	various	0.67	10	105	8.8		ITD
Pyrimethanil	various	0.29	10	97	2.4		ITD
Quinalphos	lettuce	0.05	10	98	2.7		NPD
	lettuce	0.26	10	103	4.3		NPD
	various	0.17	10	103		6.6	NPD
	lettuce	0.03	10	97	9.5		ITD
	lettuce	0.17	10	106	3.1		ITD
	various	0.17	8	101		7.0	ITD
Quintozene	various	0.67	10	90	5.4		ITD
Quizalofop-ethyl	various	0.29	10	99	9.7		ITD
Simazine	various	0.29	10	92	7.9		ITD
Sulfotep	lettuce	0.02	10	115	8.8		ITD
	lettuce	0.12	10	109	4.4		ITD
	various	0.12	8	101		10	ITD

COMPOUND	Matrix	Spiked level (mg/kg)	n	Rec. (%)	RSD (%)[b] r	R	Detector
Tebuconazole	lettuce	0.12	10	95	8.6		ITD
	lettuce	0.58	10	88	4.0		ITD
	various	0.58	8	103		7.6	ITD
Tebuthiuron	various	0.29	10	90	10.4		ITD
Tecnazene	various	0.29	10	81	12.9		ITD
Terbacil	various	0.29	10	110	10.1		ITD
Terbuthylazine	various	0.29	10	99	12.3		ITD
Tetradifon	lettuce	0.06	10	102	13.8		ECD
	lettuce	0.60	10	99	3.6		ECD
	various	0.40	30	101		5.0	ECD
	lettuce	0.07	10	107	10.5		ITD
	lettuce	0.35	10	105	1.9		ITD
	various	0.35	8	101		4.2	ITD
Thiabendazole	lettuce	0.23	10	57	22		ITD
	lettuce	1.16	10	83	11.2		ITD
Thiobencarb	various	0.29	10	97	10.7		ITD
Tolclofos-methyl	lettuce	0.05	10	95	2.6		NPD
	lettuce	0.26	10	100	4.8		NPD
	various	0.17	10	102		6.4	NPD
	lettuce	0.03	10	100	5.6		ITD
	lettuce	0.17	10	94	4.1		ITD
	various	0.17	8	103		4.4	ITD
Tolylfluanid	lettuce	0.04	10	104	14.2		ECD
	lettuce	0.40	10	97	4.1		ECD
	various	0.27	30	94		8.5	ECD
	lettuce	0.05	10	106	5.4		ITD
	lettuce	0.23	10	111	2.7		ITD
	various	0.23	8	104		20	ITD
Triadimefon	various	0.67	10	91	5.1		ITD
Triadimenol	various	0.29	10	106	5.7		ITD
Tri-allate	various	0.29	10	87	7.0		ITD
Triazophos	lettuce	0.10	10	98	4.2		NPD
	lettuce	0.52	10	106	4.2		NPD
	various	0.35	10	103		7.8	NPD
	lettuce	0.07	10	98	7.3		ITD
	lettuce	0.35	10	104	3.2		ITD
	various	0.35	8	102		7.1	ITD
Trifluralin	various	0.29	10	92	9.7		ITD
Vinclozolin	lettuce	0.02	10	105	9.7		ECD
	lettuce	0.20	10	98	3.2		ECD
	various	0.13	30	102		5.9	ECD
	lettuce	0.02	10	97	7.9		ITD
	lettuce	0.12	10	107	2.7		ITD
	various	0.12	8	100		7.5	ITD

[a] Extracted with the acetone-partition method (3.1.2-3.1.5) and analysed without clean-up.

[b] r, repeatability; R, reproducibility (intra-laboratory).