codex alimentarius commission

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS
WORLD HEALTH ORGANIZATION

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Agenda Item 9 (d) **CX/PR 03/10**
March 2003

JOINT FAO/WHO FOOD STANDARDS PROGRAMME

CODEX COMMITTEE ON PESTICIDE RESIDUES

Thirty-fifth session

Rotterdam, The Netherlands, 31 March- 5 April 2003

DISCUSSION PAPER ON THE REVISION OF THE LIST OF METHODS OF ANALYSIS FOR PESTICIDE RESIDUES

prepared by The Netherlands

BACKGROUND

In CL 2002/16-PR requested Member governments and interested organizations to provide descriptions of their analytical methods together with their scope and available validation data. In previous discussions it was stressed that methods included in the list should reflect current rather that past practices in pesticide residue analysis. From the responses on CL 1998/30-PR[1] it became clear that the majority of the laboratories use modifications of methods published in either one of the following manuals: Official Methods of AOAC INTERNATIONAL; Pesticide Analytical Manual, Food and Drug Administration, USA; Manual of Pesticide Residue Analysis, Deutsche Forschungsgemeinschaft (German or English edition); or Analytical Methods for Residues of Pesticides Inspectorate for Health Protection of the Netherlands. The majority of the responses referred to pesticides amenable to gas chromatography or the analysis of carbamates by liquid chromatography with fluorescence detection. These methods cover approximately 75% of the compounds in the Codex system. The Committee could consider whether older references for these compounds can be deleted. For compounds that cannot be included in the multi-residue methods mentioned above, the committee could seek additional information targeted on commonly applied methods for this more limited set of compounds. Detailed descriptions of the methods together with the results of tests are not intended to be published as such through the official Codex channels but in a data-base that would be accessible through a data-base provided by the FAO/IAEA Training and Reference Centre for Food and Pesticide Control (TRC). This database will be linked to the Home Page of the TRC. Due to copyright issues it will not be possible to give the full description of all methods there, but summary information and details for acquiring the full texts should be found there.

COMMENTS RECEIVED

In a reaction in CL 2001/29PR Germany already submitted a number of European standardized methods and provided information on their on their scope, principle validation data and further aspects, where

[1] CX/PR 99/10

appropriate[2]. The methods submitted cover both pesticide residues as well as contaminants. The methods have therefore also been presented in the 23rd session of the CCMAS, and in agreement with the Chair of CCMAS and the Codex Procedure part of these methods also considered by CCFAC. Reference to the methods submitted by Germany is given in Table 1

Table 1: European standardized methods for pesticide residue analysis

EN 1528-1: 1996-10 (confirmed 2001)	Fatty food - Determination of pesticides and polychlorinated biphenyls (PCBs) - Part 1: General considerations	Type III
EN 1528-2: 1996-10 (confirmed 2001)	Fatty food - Determination of pesticides and polychlorinated biphenyls (PCBs) - Part 2: Extraction of fat, pesticides and PCBs and determination of fat content	Type III
EN 1528-3: 1996-10 (confirmed 2001)	Fatty food – Determination of pesticides and polychlorinated biphenyls (PCBs) - Part 3: Clean-up methods	Type III
EN 1528-4: 1996-10 (confirmed 2001)	Fatty food – Determination of pesticides and polychlorinated biphenyls (PCBs) - Part 4: Determination, confirmatory tests, Miscellaneous	Type III
EN 12393-1:1998-10	Non fatty food - Multiresidue methods for the gas chromatographic determination of pesticide residues – Part 1: General considerations	
EN 12393-2:1998-10	Non fatty food - Multiresidue methods for the gas chromatographic determination of pesticide residues – Part 2: Methods for extraction and clean-up	
EN 12393-3:1998-10	Non fatty food - Multiresidue methods for the gas chromatographic determination of pesticide residues – Part 3: Determination and confirmatory tests	
EN 12396-1:1998-10	Non fatty food - Determination of dithiocarbamate and thiuram disulfide residues - Part 1: Spectrometric method	
EN 12396-2:1998-10	Non fatty food - Determination of dithiocarbamate and thiuram disulfide residues - Part 2: Gaschromatographic method	
EN 12396-3:2000-05	Non fatty food – Determination of dithiocarbamate and thiuram disulfide residues - Part 3: UV-spectrometric xanthogenate method	
EN 13191-1:2000-04	Non fatty food - Determination of bromide residues Part 1: Determination of total bromide as inorganic bromide	
EN 13191-2:2000-04	Non fatty food - Determination of bromide residues Part 2: Determination of bromide	

CANADA

Canada submitted brief descriptions of 8 methods currently used in their country:

1. DETERMINATION OF 265 PESTICIDES IN FRUIT & VEGETABLES WITH SOLID PHASE EXTRACTION CLEAN-UP AND GC/MSD AND HPLC FLUORESCENCE DETECTION

A representative sample is blended with acetonitrile and sodium chloride and the layers are separated by centrifugation. An aliquot of the acetonitrile phase is concentrated, and cleaned up on an Envi-Carb SPE cartridge which is connected in series with an aminopropyl sep-pak. The pesticides are eluted from the cleanup column with acetonitrile : toluene 3:1. The eluant is concentrated and solvent exchanged to acetone. The sample is then split for analysis of the multiresidues by GC/MSD, and the carbamates by reverse phase HPLC with post-column derivitization and fluorescence detection.

2. DETERMINATION OF AMITRAZ IN FOOD BY GC/MSD

The sample matrix is digested under acidic conditions which serves to hydrolyze Amitraz and its metabolites to 2,4-Dimethylaniline (2,4-DMA). The matrix is then made basic and extracted with iso-octane. A portion of the extract is filtered, and the analyte is derivatized using Heptaflurobutyric Acid Anhydride, and concentrated. The instrumental analysis is performed by capillary gas-liquid chromatography with Mass Selective Detection.

3. DETERMINATION OF BENOMYL IN APPLES BY HPLC-UV

A representative sample is blended with ethyl acetate, filtered and concentrated. HCl is added and the acidified mixture is heated for one hour at 80°C to hydrolyze benomyl to carbendazim. After washing with hexane and ethyl acetate, the acidic aqueous phase is made basic by the addition of sodium carbonate

[2] 34th session of the CCPR, CRD5

solution. The resulting carbendazim is extracted with ethyl acetate and the ethyl acetate extract is evaporatted. The residue is dissolved in methanol and passed through a Florisil Sep Pak cartridge. Analysis is performed by high pressure liquid chromatography with UV detection.

4. DETERMINATION OF THIABENDAZOLE IN FRUITS AND VEGETABLES BY HPLC-UV AND HPLC-FLUORESCENCE

A representative sample is blended with acetonitrile and sodium chloride (NaCl). The layers are allowed to separate. A portion of the acetonitrile phase is cleaned up using an aminopropyl solid phase extraction (SPE) cartridge. The eluent is concentrated and solvent-exchanged to the mobile phase. The quantitation is performed using HPLC/UV detection or fluorescence detection, where UV interferences are observed.

5. DETERMINATION OF ETU (2-IMIDAZOLIDINETHIONE) IN FRUIT AND VEGETABLES BY GC/AED

The sample matrix is extracted using methanol . The ETU is derivatized by the alkylation of the thiocarbonyl group to form Benzylthio-2-imidazoline using benzyl chloride. The matrix is made acidic and washed with dichloromethane, then made basic and the analyte is extracted using dichloromethane. The extract is concentrated and derivatized further using Trifluroacetic Anhydride. The quantitation is performed by capillary gas-liquid chromatography with atomic emission detection (AED)using the sulphur channel.

6. DETERMINATION OF ORGANOCHLORINATED PESTICIDES AND PCBS IN EGG AND DAIRY PRODUCTS BY GC/ECD

The fat, containing the organochlorine pesticides, is extracted from the dairy sample matrix with hexane using a blender.

The egg sample matrix is extracted with dichloromethane using an chromatographic column.

The extracts are then purified using a Gel Permeation Chromatography (GPC)system, and

the quantitation is performed by capillary gas-liquid chromatography with electron capture detection.

7. DETERMINATION OF DAMINOZIDE IN APPLES BY GC-MSD

Daminozide in apples is hydrolyzed in the presence of NaOH to form unsymmetrical dimethylhydrazine (UDMH). The generated UDMH is distilled from the matrix and it reacts with salicylaldehyde to form salicylaldehyde dimethyl hydrazone which is analyzed by gas chromatography using a mass selective detector.

8. DETERMINATION OF EBDC (ETHYLENE BIS-DITHIOCARBAMATES) IN FRUITS AND VEGETABLES BY HPLC WITH FLUORESCENCE DETECTION

A representative sample is digested with hydrochloric acid and the resulting ethylenediamine is isolated with an ion exchange column, derivatized with o-phthaladehyde (OPA) and determined by HPLC/fluorescence detection.

UNITED STATES OF AMERICA

The United States of America submitted brief descriptions of the methods together with validation data utilized in their USDA Pesticide Data Program (PDP). The validation data are given in Annexes I to XII.

A. Fruit and Vegetables

The USDA PDP laboratories are analyzing fresh and processed fruit and vegetable commodities using modifications of three multi-residue methods – the California Department of Food and Agriculture (CDFA) method, the Luke multi-residue procedure, and the New York Modified Solid-Phase Extraction (SPE) method. Each laboratory independently validates their modification of the method for the particular commodity/crop combinations analyzed by their facility.

CDFA Multi-residue Method: Adaptations of the multi-residue method developed by CDFA are used by four PDP laboratories – California, Washington, Florida/Tallahassee, and Florida/Winter Haven. For California and Washington, homogenized sample is extracted by blending with acetonitrile. Extracts are cleaned up using a C-18 SPE cartridge followed by a salting out step. Aliquots are then cleaned up according to the detection system employed – no clean-up for fractions analyzed via gas chromatography (GC)/flame photometric detection (FPD); florisil SPE clean-up for samples analyzed via GC/electron-capture detection (ECD), GC/micro-ECD, or GC/electrolytic-conductivity detection (ELCD); and aminopropyl SPE clean-up for fractions analyzed via high-performance liquid chromatography (HPLC) post-column derivatization systems, GC/mass spectrometry (MS), or LC/MS.

For Florida (Tallahassee and Winter Haven), homogenized sample is extracted by shaking with acetonitrile. Extracts are cleaned up using a C-18 SPE cartridge followed by a salting out step. Aliquots are then cleaned up according to the detection system employed - SAX/PSA SPE clean-up for samples analyzed via GC/FPD or GC/MSD; florisil SPE clean-up for samples analyzed via GC/halogen-specific detection (XSD); and aminopropyl SPE clean-up for fractions analyzed via HPLC post-column derivatization systems or LC/MS (Tallahassee only).

Luke Multi-Residue Method: Adaptations of the Luke multi-residue procedure are used by three PDP laboratories – Michigan, Ohio, and Texas. Homogenized sample is extracted by blending with acetone. The extract is filtered and pesticides partitioned from aqueous acetone to an organic phase via liquid-liquid extraction. Aliquots are then cleaned up according to the detection system employed and individual laboratory practice. In Ohio, analysis by GC/ELCD, GC/FPD, GC nitrogen-phosphorus detection (NPD), and GC/MSD requires no clean-up and carbamate analysis requires a simple solvent exchange. For Texas, analysis by GC/FPD requires no clean-up; GC/ELCD requires clean-up by florisil column; GC/MSD analysis requires a C-18 SPE clean-up; and carbamate analysis requires a simple solvent exchange. In Michigan, all fractions are solvent exchanged appropriate to the detection system used, except for LC/MS analysis, where a portion of each extract is cleaned up using an ENV SPE cartridge.

New York Modified SPE Method: This method is based on the Agriculture and Agri-Food Canada SPE method with some improvements based on the Luke extraction. It is applicable for extracting organochlorine, organophosphate, carbamate, and other pesticides from fruit, vegetables, and milk. For fruit and vegetables, homogenized sample is extracted by blending with 5% ethanol in acetonitrile. Extracts are salted out with sodium chloride, followed by sodium sulfate, and an aliquot cleaned up using SPE (Envi-carb, SAX, and PSA). Portions of each extract are exchanged into appropriate solvents for analysis via GC (selective detectors and MS-MS) or LC (HPLC post-column derivatization for carbamates, LC/MS, or LC/MS-MS).

DATA

PDP fruit and vegetable method performance data for various commodities are provided in Anexes I to III. Compounds included are those pesticides in the Codex Alimentarius system designated as marker pesticides by the analytical laboratory. Marker pesticides are used by PDP to collect routine recovery data following extensive initial method validation procedures. Many of the PDP laboratories also spike additional compounds to monitor performance – data for these analytes, if included in the Codex Alimentarius system, are also provided in the attached table. Recoveries shown were performed at (or about) twice the limit of quantitation (LOQ). Parameters provided include: compound; LOQ range[3]; spike amount range[4]; recovery range; and recovery statistics [count of results, mean, standard deviation, and percent Coefficient of Variation (%CV)].

B Grain products

PDP has analyzed wheat, soybeans, oats, peanut butter, and rice for selected multi-residue compounds. PDP is currently sampling and testing rice and barley; however, barley data are undergoing final quality assurance review and are not available for release at this time. Analysis of grain and processed grain samples is performed by the USDA Grain Inspection, Packers and Stockyards Administration laboratory, Kansas City, Missouri. Wheat, soybean, and oat samples were extracted using supercritical fluid extraction (SFE) coupled with a C-18/aminopropyl SPE clean-up. Sample extracts were analyzed via (GC/ MS or HPLC post-column derivatization systems. Rice and peanut butter samples were extracted with acetonitrile and cleaned up via SPE. Analysis for multi-residue compounds in rice and peanut butter was accomplished using GC/MSD and HPLC/post-column derivatization systems.

[3] LOQs may have been modified at some time during the study so that more than one limit of determination was reported.

[4] Spike amounts may vary as limits of determination were modified or spike mixture preparation necessitated changes.

Table 2: Sampling dates, analytical method, and method performance data timeframe for grain/processed grain commodities.

Commodity	Sampling Dates	Analytical Method	Timeframe for Method Performance Data Presented
Wheat	Feb 1995 – Jan 1998	SFE and SPE	1997
Soybeans	Dec 1996 – Feb 1998	SFE and SPE	1997
Oats	Jul 1999 – Apr 2000	SFE and SPE	1999
Peanut butter	Jan 2000 – Dec 2000	Acetonitrile extraction and SPE clean up	2000
Rice	Oct 2000 – present	Acetonitrile extraction and SPE clean up	2001

DATA

PDP method performance data for a selected, representative year for each type of grain/processed grain product are provided in Annexes IV to VIII. Compounds included are those pesticides in the Codex Alimentarius system designated as marker pesticides by the analytical laboratory. Marker pesticides are used by PDP to collect routine recovery data following extensive initial method validation procedures. Most of the recoveries shown were performed at (or about) twice the LOQ. Parameters provided include: compound; LOQ range; spike amount range; recovery range; and recovery statistics (count of results, mean, standard deviation, and %CV).

C. Meat Products

PDP sampled and tested poultry (young chickens) adipose, liver, and muscle tissues for selected multi-residue compounds and their metabolites April 1, 2000 through March 31, 2001. Beef (cattle) adipose, liver, and muscle tissues were sampled and tested June 26, 2001 through June 30, 2002. Two analytical methods were used by the Agricultural Marketing Service National Science Laboratory for testing meat products – one for GC analysis of selected compounds and metabolites in adipose, liver, and muscle tissues and one for HPLC analysis of carbamates in liver.

GC Analysis of Adipose, Liver, and Muscle Tissues: Poultry and beef adipose, liver, and muscle tissues were extracted and analyzed for organohalogen, organophosphate, and other types of pesticides. The methodology initially involved extraction with ethyl acetate followed by gel permeation chromatography (GPC) sample clean-up. During 2001, the extraction procedure was modified to include microwave digestion and liquid-liquid separation followed by GPC clean-up. Quantitative analysis was performed by GC coupled with selective detectors or MS. Confirmation was performed either by dual column or MS techniques.

Carbamates in Poultry and Beef Liver: The methodology for determining the presence of n-methyl carbamates is applicable only to liver tissues. Samples are homogenized with dry ice followed by extraction with acetonitrile and water. Fats and oils are separated from the sample by partitioning with hexane while sugars and other water-soluble materials are removed by partitioning with dichloromethane and saltwater. SPE and Envirocarb (Florisil) cartridges are used to clean-up sample extracts prior to analysis via HPLC post-column derivatization systems.

DATA

PDP poultry and beef method performance data for fat and muscle[5] are provided in Annexes IX to XII. Compounds included are those pesticides in the Codex Alimentarius system designated as marker pesticides by the analytical laboratory. Marker pesticides are used by PDP to collect routine recovery data following extensive initial method validation procedures. Recoveries shown were performed at (or about) twice the LOQ. Parameters provided include: compound; LOQ; recovery range; and recovery statistics (count of results, mean, standard deviation, and %CV).

[5] No MRLs are established for poultry or chicken liver so no data are presented for this tissue. For beef liver, no PDP marker pesticides monitored for QA purposes have established MRLs so no beef liver data are presented.

CONCLUSION

From the responses on this and previous Circular Letters[6] is clear that the majority of the laboratories use similar procedures modified to their own specific needs. With the information that got available through the last 3 Circular Letters concerning methods of analysis some 80% of the pesticides currently covered by the Codex System is covered by well documented methods. The amount of validation available, however, varies considerably. The Committee could consider the methods available now for their suitability to enforce Codex MRLs. Methods should be assessed in the framework of guidelines previously developed by the Committee[7].

[6] CL 98-30 PR, 2001-29PR and 2002-16PR

[7] ALINORM 03/24 Appendices V and VI

Annex I Data on CDFA MRM
(Apples, Bananas, Broccoli, Carrots, Celery, Cherries, Green Beans, Lettuce, Mushrooms, Nectarines, Oranges, Pineapples, Potatoes, Peas, Sweet Corn, and Tomato Paste in California, Florida and Washington Laboratories)

Compound	LOQ Minimum (mg/kg)	LOQ Maximum (mg/kg)	Spike Amount Minimum (mg/kg)	Spike Amount Maximum (mg/kg)	Percent Recovery Minimum	Percent Recovery Maximum	n	Mean	Standard Deviation	%CV
Acephate	0,015	0,025	0,030	0,050	48	98	24	61	12	20
Aldicarb	0,067	0,067	0,163	0,163	58	133	60	96	17	18
Aldicarb sulfone (Aldoxycarb)	0,072	0,072	0,170	0,171	51	120	60	88	17	19
Aldicarb sulfoxide	0,010	0,089	0,020	0,176	46	102	117	70	12	16
Aldrin	0,005	0,005	0,010	0,010	92	104	3	98	6	6
Dieldrin	0,003	0,033	0,010	0,020	70	110	20	84	10	12
Anilazine	0,037	0,037	0,074	0,075	67	96	6	87	11	13
Azinphos methyl	0,020	0,040	0,014	0,080	49	192	225	107	21	19
Bifenthrin	0,027	0,037	0,055	0,075	85	104	4	94	10	11
Buprofezin	0,015	0,020	0,030	0,040	81	128	22	110	15	13
Captan	0,013	0,025	0,026	0,050	61	129	32	90	14	15
Tetrahydrophthalimide (THPI)	0,015	0,015	0,030	0,030	66	123	6	92	19	20
Carbaryl	0,010	0,089	0,020	0,167	61	147	253	99	12	13
Carbofuran	0,110	0,110	0,253	0,254	69	134	60	97	17	17
3-Hydroxycarbofuran	0,058	0,058	0,123	0,123	53	136	60	93	19	21
Chlordane cis	0,004	0,033	0,008	0,010	57	113	27	89	11	13
Chlordane trans	0,004	0,033	0,008	0,010	55	107	27	88	11	12
Chlorothalonil	0,003	0,015	0,008	0,030	54	113	33	85	12	14
Chlorpyrifos	0,007	0,050	0,014	0,030	55	145	158	96	16	17
Chlorpyrifos methyl	0,007	0,027	0,030	0,075	60	134	220	95	14	15
Cyfluthrin	0,077	0,150	0,150	0,300	72	123	48	96	12	12
Cypermethrin	0,053	0,077	0,110	0,150	112	123	4	118	6	5
DDT p,p'	0,010	0,015	0,020	0,030	57	130	27	93	15	16
DDE p,p'	0,003	0,067	0,008	0,046	44	141	256	90	15	17
DDD p,p'	0,003	0,015	0,008	0,030	80	126	27	96	11	11
Deltamethrin	0,037	0,075	0,075	0,150	72	133	27	99	15	16
Diazinon	0,007	0,016	0,007	0,037	72	142	270	107	12	12
Dichlorvos	0,003	0,020	0,008	0,050	34	118	68	67	16	25
Dicloran	0,007	0,026	0,014	0,051	55	148	158	102	16	16
Dicofol p,p'	0,043	0,100	0,088	0,200	48	143	57	94	21	22
Dimethoate	0,003	0,020	0,006	5,000	59	194	204	108	19	18
Diphenylamine	0,015	0,015	0,030	0,030	102	151	6	123	19	16
Disulfoton	0,013	0,025	0,025	0,050	74	129	21	88	13	14
Disulfoton sulfone	0,013	0,025	0,025	0,050	77	152	21	95	16	17
Endosulfan I	0,003	0,033	0,008	0,034	59	145	220	95	13	14
Endosulfan II	0,003	0,033	0,008	0,025	70	113	35	91	11	12
Endosulfan sulfate	0,003	0,013	0,008	0,025	69	119	35	95	12	12
Ethion	0,003	0,017	0,008	0,047	74	143	117	108	13	12
Fenamiphos	0,005	0,013	0,010	0,040	46	175	44	112	26	23
Fenamiphos sulfone	0,005	0,030	0,008	0,060	81	157	28	108	18	17
Fenbuconazole	0,053	0,053	0,110	0,110	53	125	13	91	22	24
Fenpropathrin	0,015	0,033	0,030	0,070	34	167	34	106	27	25
Fenthion	0,005	0,025	0,050	0,050	94	115	4	102	10	10
Fenvalerate	0,050	0,200	0,087	0,400	65	130	61	99	12	12
Folpet	0,050	0,050	0,100	0,100	59	102	20	80	12	15
Heptachlor	0,003	0,020	0,005	0,040	54	110	27	84	13	16
Heptachlor epoxide	0,003	0,010	0,008	0,020	65	120	59	89	11	12
Imazalil	0,005	0,010	0,010	0,020	70	162	27	112	22	19

Iprodione	0,020	0,081	0,040	0,165	38	125	165	87	21	24
Lambda cyhalothrin (R ester)	0,033	0,050	0,070	0,100	70	119	22	94	13	14
Lindane (BHC gamma)	0,003	0,010	0,008	0,020	71	117	58	89	11	12
Malathion	0,007	0,017	0,014	0,035	77	133	59	99	12	12
Metalaxyl	0,010	0,033	0,020	0,070	55	147	62	94	21	22
Methamidophos	0,006	0,033	0,010	0,070	35	164	171	85	26	30
Methidathion	0,007	0,013	0,014	0,025	70	117	39	100	10	10
Methiocarb	0,140	0,140	0,349	0,350	67	142	60	99	15	15
Methomyl	0,010	0,050	0,020	0,100	57	134	232	94	11	12
Mevinphos (total)	0,003	0,027	0,008	0,055	69	131	46	96	12	13
Monocrotophos	0,005	0,033	0,020	0,050	74	102	21	84	8	10
Myclobutanil	0,026	0,077	0,056	0,150	54	126	34	85	17	20
O-Phenylphenol	0,010	0,020	0,020	0,040	61	167	60	103	22	22
Oxamyl	0,010	0,066	0,020	0,165	52	132	102	89	15	17
Parathion ethyl	0,007	0,025	0,014	0,050	75	135	56	103	11	11
Parathion methyl	0,007	0,013	0,014	0,025	75	128	40	100	10	10
Permethrin cis	0,038	0,050	0,076	0,101	35	146	113	93	20	21
Permethrin trans	0,040	0,050	0,079	0,100	41	147	113	98	22	22
Permethrin (total)	0,050	0,130	0,100	0,250	69	131	48	99	14	15
Phosalone	0,050	0,050	0,100	0,100	114	121	3	117	4	3
Phosmet	0,007	0,025	0,014	0,050	64	127	42	102	13	12
Phosphamidon	0,007	0,050	0,014	0,100	80	147	26	104	13	13
Procymidone	0,015	0,015	0,030	0,030	82	102	3	95	11	12
Propargite	0,010	0,083	0,020	0,161	51	166	154	99	24	25
Propiconazole	0,005	0,005	0,010	0,080	81	131	25	101	14	14
Propoxur	0,010	0,050	0,020	0,100	68	138	66	97	12	12
Quintozene (PCNB)	0,003	0,010	0,007	0,020	53	140	153	96	15	15
Pentachloroaniline (PCA)	0,015	0,015	0,030	0,030	62	110	24	84	12	14
Tebuconazole	0,028	0,077	0,056	0,150	77	123	19	100	10	10
Tebufenozide	0,010	0,010	0,020	0,020	73	112	5	96	16	16
Tecnazene	0,004	0,004	0,008	0,008	108	143	6	126	12	10
Thiabendazole	0,010	0,100	0,020	0,200	53	164	131	105	21	20
Triadimefon	0,020	0,037	0,040	0,075	86	121	16	101	11	11
Vinclozolin	0,007	0,010	0,014	0,020	69	117	16	97	13	13

Annex II, data on Luke MRM

Compound	LOQ Minimum (mg/kg)	LOQ aximum (mg/kg)	Spike Amount Minimum (mg/kg)	Spike Amount Maximum (mg/kg)	Percent Recovery Minimum	Percent Recovery Maximum	n	Mean	Standard Deviation	%CV
Acephate	0,005	0,016	0,010	0,032	62	151	49	101	19	19
Aldicarb	0,068	0,068	0,136	0,136	84	171	24	110	20	18
Aldicarb sulfoxide	0,013	0,125	0,027	0,250	51	176	48	110	28	25
Azinphos methyl	0,020	0,043	0,040	0,085	61	150	159	99	14	14
Bifenthrin	0,054	0,054	0,108	0,108	51	90	6	67	14	21
Carbaryl	0,005	0,033	0,010	0,066	46	193	209	98	22	23
Carbofuran	0,010	0,028	0,020	0,056	64	159	47	123	20	16
3-Hydroxycarbofuran	0,010	0,040	0,020	0,080	51	166	47	119	22	18
Chlorothalonil	0,009	0,066	0,018	0,048	34	199	42	61	28	46
Chlorpyrifos	0,007	0,013	0,013	0,026	76	166	52	108	16	15
Diazinon	0,003	0,037	0,007	0,082	73	127	212	97	9	10
Dicloran	0,010	0,032	0,028	0,064	54	134	150	90	15	17
Dicofol o,p'	0,050	0,051	0,101	0,101	75	96	3	88	11	13
Dicofol p,p'	0,050	0,060	0,100	0,120	43	173	46	103	21	20
Dieldrin	0,026	0,060	0,053	0,120	55	136	10	90	21	23

Dimethoate	0,003	0,030	0,007	0,060	67	168	158	99	13	13
Disulfoton	0,003	0,024	0,007	0,048	58	133	52	104	14	14
Disulfoton sulfone	0,013	0,030	0,027	0,060	83	164	10	125	29	23
Endosulfan I	0,013	0,024	0,028	0,048	57	138	212	89	14	15
Endosulfan II	0,020	0,024	0,040	0,048	52	127	51	94	14	15
Endosulfan sulfate	0,024	0,034	0,048	0,067	53	164	52	85	20	23
Ethoprop	0,003	0,054	0,007	0,108	82	103	10	93	7	7
Fenamiphos	0,007	0,020	0,013	0,040	84	164	46	108	16	14
Fenamiphos sulfone	0,011	0,017	0,022	0,022	89	112	4	102	10	9
Fenvalerate	0,063	0,140	0,280	0,317	59	144	51	112	20	18
Heptachlor	0,012	0,012	0,024	0,024	58	144	41	105	21	20
Heptachlor epoxide	0,012	0,017	0,024	0,034	58	129	51	98	16	16
Imazalil	0,100	0,100	0,200	0,200	57	192	40	105	25	23
Iprodione	0,028	0,070	0,056	0,093	50	137	155	84	15	18
Lambda cyhalothrin (total)	0,054	0,054	0,108	0,108	56	81	6	72	9	12
Lindane (BHC gamma)	0,013	0,020	0,026	0,040	51	143	51	92	16	18
Malathion	0,007	0,024	0,013	0,048	78	124	51	103	11	10
Metalaxyl	0,027	0,040	0,054	0,080	86	135	10	105	16	16
Methamidophos	0,003	0,012	0,007	0,024	51	158	91	84	20	24
Methidathion	0,003	0,032	0,007	0,064	77	158	46	107	14	13
Methomyl	0,002	0,083	0,026	0,166	52	156	162	98	16	16
Mevinphos E	0,010	0,010	0,194	0,201	73	113	4	93	17	18
Mevinphos Z	0,010	0,010	0,020	0,020	101	117	4	109	7	6
Mevinphos (total)	0,040	0,040	0,080	0,080	72	129	47	98	13	13
Myclobutanil	0,028	0,028	0,056	0,056	56	189	48	113	24	21
Oxamyl	0,017	0,028	0,033	0,056	66	191	40	123	24	19
Parathion ethyl	0,003	0,020	0,007	0,040	74	127	51	103	10	10
Parathion methyl	0,003	0,020	0,007	0,040	63	130	46	99	17	17
Permethrin cis	0,068	0,068	0,171	0,313	69	116	48	88	10	12
Permethrin trans	0,068	0,068	0,136	0,173	69	106	48	90	8	9
Permethrin (total)	0,095	0,095	0,190	0,190	61	147	47	103	17	17
Phorate	0,003	0,040	0,007	0,080	73	136	51	103	13	13
Phorate sulfone	0,007	0,040	0,013	0,080	60	105	10	94	13	14
Phosmet	0,018	0,040	0,035	0,080	82	149	52	105	14	14
Phosphamidon	0,096	0,096	0,190	0,190	84	154	41	110	15	13
Pirimiphos methyl	0,054	0,054	0,108	0,108	56	87	6	76	11	14
Propargite	0,027	0,130	0,047	0,280	60	148	140	94	16	17
Propiconazole	0,054	0,073	0,108	0,143	77	106	7	92	10	11
Quintozene (PCNB)	0,013	0,017	0,026	0,034	53	148	90	95	17	17
Thiabendazole	0,100	0,150	0,200	0,300	67	187	111	103	23	22
Vinclozolin	0,023	0,048	0,047	0,096	54	149	46	114	21	18

Annex III, data on New York modified MRM										
Compound	LOQ Minimum (mg/kg)	LOQ Maximum (mg/kg)	Spike Amount Minimum (mg/kg)	Spike Amount Maximum (mg/kg)	Percent Recovery Minimum	Percent Recovery Maximum	n	Mean	Standard Deviation	%CV
Azinphos methyl	0,010	0,010	0,020	0,020	53	133	29	89	19	21
Captan	0,064	0,064	0,128	0,128	33	128	44	82	21	25
Tetrahydrophthalimide (THPI)	0,066	0,066	0,133	0,133	42	139	18	83	22	26
Carbaryl	0,004	0,013	0,008	0,008	48	161	64	80	19	24
Carbofuran	0,006	0,020	0,012	0,012	41	124	69	80	17	21
3-Hydroxycarbofuran	0,006	0,020	0,012	0,012	50	123	65	89	16	18
Chlordane cis	0,002	0,002	0,005	0,005	54	127	35	92	17	18
Chlordane trans	0,002	0,002	0,005	0,005	58	119	33	89	16	19

Oxychlordane	0,008	0,008	0,016	0,016	55	136	39	93	19	20
Chlorfenvinphos beta	0,004	0,004	0,007	0,007	75	136	28	98	11	12
Chlorpyrifos	0,004	0,005	0,008	0,010	45	139	60	93	17	19
Chlorpyrifos methyl	0,010	0,010	0,050	0,050	66	115	63	94	11	11
Cypermethrin	0,077	0,256	0,154	0,154	44	139	43	88	21	24
DDT o,p'	0,003	0,003	0,006	0,006	45	106	38	85	12	14
DDT p,p'	0,006	0,006	0,013	0,013	42	118	40	84	15	18
DDE p,p'	0,006	0,006	0,013	0,013	59	130	39	91	16	18
DDD o,p'	0,003	0,003	0,006	0,006	56	141	41	93	17	19
DDD p,p'	0,003	0,003	0,006	0,006	44	127	35	87	16	19
Deltamethrin	0,064	0,064	0,128	0,128	55	128	40	84	17	21
Diazinon	0,006	0,006	0,012	0,012	70	103	27	88	8	9
Dichlorvos	0,005	0,005	0,010	0,010	33	108	28	62	16	26
Dicloran	0,006	0,006	0,013	0,013	43	109	42	82	14	17
Dicofol o,p'	0,009	0,010	0,019	0,019	53	146	40	85	18	21
Dicofol p,p'	0,010	0,010	0,019	0,019	44	101	37	76	12	16
Dieldrin	0,016	0,016	0,032	0,032	43	107	38	82	12	15
Diflubenzuron	0,022	0,022	0,045	0,045	69	117	3	88	26	29
Dimethoate	0,004	0,004	0,008	0,008	69	118	26	92	11	12
Disulfoton	0,005	0,005	0,010	0,010	51	115	27	86	18	20
Disulfoton sulfone	0,003	0,003	0,006	0,006	70	150	29	97	16	16
Endosulfan I	0,020	0,020	0,040	0,040	47	108	39	81	13	16
Endosulfan II	0,020	0,020	0,040	0,040	34	128	40	90	18	21
Endosulfan sulfate	0,032	0,032	0,064	0,064	46	173	40	106	33	31
Fenamiphos	0,003	0,003	0,006	0,006	60	118	30	92	13	15
Fenamiphos sulfone	0,003	0,003	0,006	0,006	53	125	28	93	17	18
Fenamiphos sulfoxide	0,003	0,003	0,006	0,006	58	143	25	96	16	17
Fenarimol	0,032	0,032	0,064	0,064	49	121	36	90	18	20
Fenbuconazole	0,048	0,048	0,096	0,096	54	127	38	89	18	21
Fenitrothion	0,003	0,003	0,006	0,006	67	133	27	95	14	14
Fenthion	0,005	0,005	0,010	0,010	74	107	26	92	9	10
Fenvalerate	0,018	0,018	0,035	0,035	44	153	43	94	25	27
Iprodione	0,028	0,028	0,056	0,056	44	180	42	82	22	27
Lindane (BHC gamma)	0,010	0,010	0,019	0,019	52	156	41	86	19	23
Malathion	0,005	0,005	0,010	0,010	56	112	27	88	13	14
Metalaxyl	0,020	0,020	0,040	0,040	40	109	44	80	13	16
Methidathion	0,004	0,004	0,008	0,008	74	109	29	93	9	10
Methomyl	0,004	0,013	0,008	0,008	53	154	66	85	17	21
Methoprene	0,075	0,075	0,045	0,045	81	127	5	107	17	16
Myclobutanil	0,010	0,032	0,019	0,019	45	104	47	80	13	17
Oxamyl	0,006	0,020	0,012	0,012	41	146	57	80	18	22
Parathion ethyl	0,006	0,006	0,012	0,012	78	106	27	93	8	8
Parathion methyl	0,004	0,004	0,008	0,008	56	110	27	90	12	14
Permethrin cis	0,002	0,007	0,004	0,004	45	105	38	81	12	15
Permethrin trans	0,002	0,006	0,004	0,004	42	119	37	82	15	19
Phosmet	0,004	0,004	0,008	0,008	53	126	29	85	17	19
Phosphamidon	0,004	0,004	0,008	0,018	80	106	20	93	7	7
Pirimicarb	0,032	0,032	0,064	0,064	54	134	38	90	21	23
Pirimiphos methyl	0,004	0,004	0,008	0,008	73	101	26	91	8	9
Propargite	0,082	0,082	0,163	0,163	64	130	42	91	17	18
Propiconazole	0,048	0,048	0,096	0,096	41	141	42	81	19	24
Propoxur	0,010	0,010	0,050	0,050	45	141	105	85	19	23
Tebuconazole	0,064	0,064	0,128	0,128	59	140	40	92	20	22
Vinclozolin	0,012	0,012	0,024	0,024	44	107	38	79	12	15

Annex IV PDP data on wheat

Compound	LOQ Minimum (mg/kg)	LOQ Maximum (mg/kg)	Spike Amount Minimum (mg/kg)	Spike Amount Maximum (mg/kg)	Percent Recovery Minimum	Percent Recovery Maximum	n	Mean	Standard Deviation	%CV
Aldicarb	0,017	0,017	0,033	0,033	41	107	22	76	13	17
Aldicarb sulfone (Aldoxycarb)	0,017	0,017	0,033	0,033	58	117	21	80	13	16
Carbaryl	0,008	0,008	0,017	0,017	44	97	24	78	12	16
Carbofuran	0,017	0,017	0,033	0,033	40	105	23	79	15	19
3-Hydroxycarbofuran	0,017	0,017	0,033	0,033	51	108	22	75	12	16
Chlorpyrifos methyl	0,004	0,004	0,008	0,008	56	187	23	106	29	28
Dichlorvos[1,2]	0,009	0,009	0,018	0,018	34	64	17	47	9	20
Fenitrothion[2]	0,010	0,010	0,020	0,020	67	160	28	107	22	21
Imazalil	0,020	0,020	0,041	0,041	67	199	22	106	31	30
Malathion[2]	0,011	0,011	0,022	0,023	59	153	20	102	25	24
Methomyl	0,017	0,017	0,033	0,033	58	120	21	79	13	17
Phorate	0,007	0,009	0,014	0,017	59	123	20	83	15	19
Phorate sulfone	0,016	0,016	0,033	0,033	72	117	24	92	12	13
Pirimiphos methyl[2]	0,008	0,008	0,016	0,016	61	121	22	90	14	16

1. Did not meet initial or ongoing QA criteria. Reported as "laboratory's best effort".

2. MRL for bran/flour/germ/wholemeal

Annex V PDP data on soybean

Compound	LOQ Minimum (mg/kg)	LOQ Maximum (mg/kg)	Spike Amount Minimum (mg/kg)	Spike Amount Maximum (mg/kg)	Percent Recovery Minimum	Percent Recovery Maximum	n	Mean	Standard Deviation	%CV
Aldicarb	0,017	0,017	0,033	0,033	40	86	7	68	15	23
Aldicarb sulfone (Aldoxycarb)	0,017	0,023	0,033	0,047	38	110	8	77	22	28
Azinphos methyl	0,018	0,018	0,035	0,035	74	197	6	106	46	44
Carbaryl	0,008	0,009	0,017	0,017	54	83	6	69	11	16
Carbofuran	0,017	0,020	0,033	0,040	61	97	8	76	13	17
3-Hydroxycarbofuran	0,017	0,025	0,033	0,050	33	118	8	71	26	37
Fenamiphos	0,005	0,005	0,011	0,011	67	105	4	88	16	18
Fenvalerate	0,039	0,039	0,077	0,077	51	123	7	88	26	30
Methomyl	0,017	0,020	0,033	0,040	33	83	7	65	18	28
Oxamyl	0,017	0,021	0,033	0,042	45	87	8	68	15	22
Parathion ethyl	0,035	0,035	0,070	0,070	61	110	7	85	16	19
Permethrins	0,014	0,014	0,028	0,028	36	64	4	46	13	27
Phorate	0,007	0,007	0,014	0,014	57	114	6	92	21	23

Annex VI PDP data on oats

Compound	LOQ Minimum (mg/kg)	LOQ Maximum (mg/kg)	Spike Amount Minimum (mg/kg)	Spike Amount Maximum (mg/kg)	Percent Recovery Minimum	Percent Recovery Maximum	n	Mean	Standard Deviation	%CV
Aldrin	0,011	0,011	0,023	0,023	44	79	9	61	12	20
Dieldrin	0,011	0,011	0,023	0,023	61	92	7	75	11	14
Carbaryl	0,008	0,008	0,017	0,017	59	95	14	79	12	16
Carbofuran	0,017	0,017	0,033	0,033	62	102	15	81	12	14

3-Hydroxycarbofuran	0,017	0,017	0,033	0,033	39	91	15	67	15	22
DDT p,p'	0,015	0,015	0,030	0,030	64	100	10	84	12	14
DDE p,p'	0,011	0,011	0,023	0,023	48	79	6	66	11	16
DDD p,p'	0,011	0,011	0,023	0,023	61	87	7	74	9	13
Dichlorvos[1]	0,008	0,009	0,018	0,018	40	69	7	54	10	18
Heptachlor	0,006	0,006	0,012	0,012	43	157	7	103	41	40
Heptachlor epoxide[1]	0,006	0,006	0,012	0,012	43	87	5	68	17	25
Methomyl	0,017	0,017	0,033	0,033	43	92	15	71	13	18
Propiconazole	0,018	0,018	0,035	0,035	77	151	13	113	21	19
Tebuconazole	0,018	0,018	0,035	0,035	68	168	13	110	33	30
Triadimenol	0,026	0,260	0,053	0,053	61	146	15	108	24	22

1. Did not meet initial or ongoing QA criteria. Reported as "laboratory's best effort".

Annex VII PDP data on peanut butter

Compound	LOQ Minimum (mg/kg)	LOQ Maximum (mg/kg)	Spike Amount Minimum (mg/kg)	Spike Amount Maximum (mg/kg)	Percent Recovery Minimum	Percent Recovery Maximum	n	Mea n	Standard Deviation	%CV
Aldicarb	0,033	0,033	0,067	0,067	70	112	17	88	10	11
Aldicarb sulfone (Aldoxycarb)	0,046	0,046	0,093	0,093	50	102	25	80	13	16
Aldicarb sulfoxide	0,040	0,040	0,080	0,080	53	100	25	78	13	16
Carbaryl	0,017	0,017	0,035	0,035	55	110	21	95	12	12
Disulfoton	0,018	0,049	0,037	0,098	59	189	27	102	31	30
Disulfoton sulfone	0,084	0,084	0,168	0,168	87	161	29	116	19	17
Ethoprop	0,009	0,009	0,018	0,018	66	134	25	93	16	17
Fenamiphos	0,010	0,010	0,021	0,021	56	193	33	109	35	32
Fenamiphos sulfone	0,077	0,077	0,154	0,154	39	145	27	91	29	32
Fenvalerate	0,049	0,049	0,100	0,100	39	189	29	94	35	38
Metalaxyl	0,025	0,025	0,049	0,049	89	159	25	111	17	15
Methomyl	0,033	0,033	0,067	0,067	69	109	20	89	11	12
Monocrotophos	0,009	0,009	0,018	0,018	88	197	28	133	26	20
Oxamyl	0,041	0,041	0,083	0,083	64	113	23	91	12	13
Phorate	0,014	0,014	0,028	0,028	66	142	27	104	18	17
Phorate sulfone	0,032	0,032	0,065	0,065	87	139	27	108	14	13
Propargite	0,042	0,042	0,084	0,084	34	134	27	88	24	27
Propiconazole	0,035	0,035	0,070	0,070	50	185	31	111	26	23
Quintozene (PCNB)	0,014	0,014	0,028	0,028	47	138	26	84	21	25
Pentachloroaniline (PCA)	0,009	0,009	0,018	0,018	57	103	22	75	12	16
Tebuconazole	0,035	0,035	0,070	0,070	79	183	28	125	27	22

Annex VIII PDP data on rice

Compound	LOQ Minimum (mg/kg)	LOQ Maximum (mg/kg)	Spike Amount Minimum (mg/kg)	Spike Amount Maximum (mg/kg)	Percent Recovery Minimum	Percent Recovery Maximum	n	Mean	Standard Deviation	%CV
Carbaryl	0,019	0,019	0,039	0,039	33	115	21	75	25	33
Carbofuran	0,041	0,041	0,082	0,082	71	121	27	93	13	14
3-Hydroxycarbofuran	0,043	0,043	0,087	0,087	50	124	27	86	18	21
Chlorpyrifos methyl	0,006	0,006	0,013	0,013	66	104	22	88	11	13
DDE p,p'	0,013	0,013	0,026	0,026	75	108	20	94	8	9
Dieldrin	0,025	0,025	0,051	0,051	79	111	22	96	8	8

Disulfoton	0,013	0,013	0,027	0,027	41	95	23	75	15	20
Disulfoton sulfone	0,043	0,043	0,085	0,085	72	167	26	103	18	17
Heptachlor epoxide	0,013	0,013	0,026	0,026	70	110	23	93	10	10
Iprodione	0,033	0,033	0,067	0,067	73	117	24	96	10	11
Propoxur	0,012	0,012	0,060	0,060	66	106	21	90	10	11

Annex IX PDP data on poultry adipose tissue

Compound	LOQ (mg/kg)	Percent Recovery Minimum	Percent Recovery Maximum	n	Mean	Standard Deviation	%CV
Methidathion	0,035	47	96	11	77	13	17

Annex X PDP data om Poultry muscle

Compound	LOQ (mg/kg)	Percent Recovery Minimum	Percent Recovery Maximum	n	Mean	Standard Deviation	%CV
Bifenthrin	0,002	65	100	12	81	10	12
Chlorpyrifos	0,033	60	138	12	103	28	27
Diazinon	0,031	54	90	12	75	13	18
Dicofol p,p'	0,005	80	137	12	105	16	15
Fenpropathrin	0,002	78	117	12	97	12	12
Methidathion	0,035	67	112	12	86	13	15
Myclobutanil	0,005	87	135	12	112	16	14
Permethrin cis	0,007	72	128	12	102	16	16
Propargite	0,110	86	166	12	119	29	25
Propiconazole	0,003	74	117	12	97	15	15
Triadimenol	0,048	98	154	9	116	18	16

Annex XI PDP data on beef adipose tissue

Compound	LOQ (mg/kg)	Percent Recovery Minimum	Percent Recovery Maximum	n	Mean	Standard Deviation	%CV
Carbofuran	0,080	58	105	22	83	10	12
3-Hydroxycarbofuran	0,080	50	84	22	69	9	12
Methidathion	0,009	51	118	24		14	21

Annex XII PDP data on beef muscle

Compound	LOQ (mg/kg)	Percent Recovery Minimum	Percent Recovery Maximum	n	Mean	Standard Deviation	%CV
Carbaryl	0,012	50	126	22	86	18	22

Carbofuran	0,020	50	103	22	81	15	19
3-Hydroxycarbofuran	0,020	47	88	22	66	10	16
Chlorpyrifos	0,009	60	112	24	90	15	17
Diazinon	0,006	51	92	24	74	11	15
Fenthion sulfone	0,007	52	146	24	73	22	30
Methidathion	0,009	59	100	24	73	12	17
Methomyl	0,011	46	97	22	74	14	19
Phorate sulfoxide	0,067	52	99	24	71	13	18
Profenofos	0,008	50	119	24	75	17	23
Propargite	0,029	52	199	24	89	27	31
Propiconazole	0,002	55	146	24	109	27	24