

codex alimentarius commission



FOOD AND AGRICULTURE
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JOINT OFFICE: Viale delle Terme di Caracalla 00153 ROME Tel: 39 06 57051 www.codexalimentarius.net Email: codex@fao.org Facsimile: 39 06 5705 4593

Agenda Item 7 (b)

CX/PR 07/39/6

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JOINT FAO/WHO FOOD STANDARDS PROGRAMME

CODEX COMMITTEE ON PESTICIDE RESIDUES

Thirty-ninth Session

Beijing, China, 7 - 12 May 2007

PROPOSED DRAFT REVISION OF THE LIST OF METHODS FOR PESTICIDE RESIDUE ANALYSIS AT STEP 3

Governments and interested international organizations are invited to submit comments on the above subject matter at Step 3 and should do so in writing in conformity with the Uniform Procedure for the Elaboration of Codex Standards and Related Texts (see *Procedural Manual of the Codex Alimentarius Commission, Fifteenth Edition*) to: Mr Josef Brodesser, Food and Environmental Protection Section, Joint FAO/IAEA Division of Nuclear Techniques in Food and Agriculture, P.O. Box 100, Wagramer Strasse 5, Tel: +43-1-2600-26058, FAX +431 26007, or email j.brodesser@iaea.org with copies to: 1. Secretary, Codex Alimentarius Commission, Joint WHO/FAO Food Standards Programme, FAO, Viale delle Terme di Caracalla, 00100 Rome, Italy, by email codex@fao.org or fax: +39-06-5705-4593 and 2. Duang Lifang, Engineer, Institute for the Control of Agrochemicals, Ministry of Agriculture, P.R China, Fax: +0086 10 64194064, email: ccpr@agri.gov.cn by 13 April 2007.

Background

For a number of years the revision of methods for the determination of pesticide residues by the Codex Committee on Pesticide Residues (CCPR) was an ongoing activity for the *Ad Hoc* Working Group on Methods of Analysis and Sampling and the CCPR.

More in depth consideration of this issue started in 1998 when the CCPR at its 30th Session generally supported the updating of the list of methods of analysis. It was agreed by the Committee that information would be sought on which of the methods listed were still commonly used (ALINORM 99/24, paras. 94-95).

The CL 1998/30-PR invited Governments and interested international organizations to provide information on (1) which methods are used commonly in the government laboratories or other laboratories involved in the determination of MRL compliance; and (2) whether these methods in (1) meet the criteria for selection of analytical methods. From the responses to the above CL 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.

At the 31st Session of the CCPR the Committee based on a number of responses and discussion within the Working Group, the Committee agreed to the process on how to revise the List of Methods of Analysis for Pesticide residues (ALINORM 99/24A, paras 128-132).

At the subsequent CCPR sessions this issue had been considered with some progress. The 35th Session of the CCPR agreed to ask the Commission to approve new work on the revision of the list of methods (ALINORM 03/24A, para. 153) and the 26th Session of the Commission had approved it (ALINORM 03/41 and Appendix VIII).

At the 36th Session of the CCPR the Committee agreed to invite FAO/IAEA to put the list of available methods on their website in order to facilitate the update of the list of methods.

At the 37th Session the Committee welcomed the offer of the Delegation of the Netherlands to review the list of methods and to identify the pesticides for which MRLs have been set but for which no suitable methods are available; to prepare an inventory of submitted methods; and to distribute the list in a Circular Letter requesting details of additional methods. It was also **agreed** that the methods would be submitted to IAEA with a view to their publication on the IAEA Training and Reference Centre (TRC) website (ALINORM 05/28/24, para. 237).

At the last 38th Session (ALINORM 06/29/24, paras 179-181) the Chair of the Working Group provided an update of the collation of methods of analysis. The Representative of IAEA informed the Committee that the methods of analysis currently available on the IAEA website (CRD 19) had been provided by several countries and consist mostly of abstracts, method principles and literature references, as well as links to relevant external web pages.

The Delegation of Australia stated that the list of methods should be considered as a resource list and was not a list of preferred or obligatory methods for Codex purposes. Some delegations indicated that they would provide relevant methods to the Committee or that their methods were available free of charge on the internet.

The Committee agreed that a Circular Letter would be sent requesting information on methods for the determination of pesticide residues, to be addressed to the Codex Secretariat and the IAEA, for further consideration at the next session.

In response to the CL 2006/9-PR requesting information on methods for determination of pesticide residues some countries provided their data.

The List of Methods for determination of pesticide residues is attached and also available from the following IAEA website:

<http://www-infocris.iaea.org/Download/Methods-Main.pdf>

Member governments and interested international organizations are invited to provide their comments on the attached List to addresses indicated above by 15 April 2007.

Appendix

PROPOSED DRAFT LIST OF METHODS FOR PESTICIDE RESIDUE ANALYSIS**CANADA methods of analysis**

1. DETERMINATION OF 265 PESTICIDES IN FRUIT & VEGETABLES WITH SOLID PHASE EXTRACTION CLEAN-UP AND GC/MSD AND HPLC FLUORESCENCE DETECTION
2. DETERMINATION OF AMITRAZ IN FOOD BY GC/MSD
3. DETERMINATION OF BENOMYL IN APPLES BY HPLC-UV
4. DETERMINATION OF THIABENDAZOLE IN FRUITS AND VEGETABLES BY HPLC-UV AND HPLC-FLUORESCENCE
5. DETERMINATION OF ETU (AS 2-IMIDAZOLIDINETHIONE) IN FRUIT AND VEGETABLES BY GC/AED
6. DETERMINATION OF ORGANOCHLORINATED PESTICIDES AND PCBs IN EGG AND DAIRY PRODUCTS BY GC/ECD
7. DETERMINATION OF DAMINOZIDE IN APPLES BY GC-MSD
8. DETERMINATION OF EBDC (ETHYLENE BIS-DITHIOCARBAMATES) IN FRUITS AND VEGETABLES BY HPLC WITH FLUORESCENCE DETECTION
9. DETERMINATION OF FORMETANATE IN FRUITS BY HPLC
10. DETERMINATION OF ABAMECTIN IN FRUITS AND VEGETABLES USING HPLC WITH FLUORESCENCE DETECTION

EUROPEAN STANDARDS elaborated by CEN/TC 275 “Food analysis – Horizontal methods” proposed by the German delegation

Determination of pesticides and PCBs

EN 1528-1: 1996-10 (confirmed 2001)	Fatty food – Determination of pesticides and polychlorinated biphenyls (PCBs). Part 1: General considerations.
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.
EN 1528-3: 1996-10 (confirmed 2001)	Fatty food – Determination of pesticides and polychlorinated biphenyls (PCBs). Part 3: Clean-up methods.
EN 1528-4: 1996-10 (confirmed 2001)	Fatty food – Determination of pesticides and polychlorinated biphenyls (PCBs). Part 4: Determination, confirmatory tests, Miscellaneous.
EN 12393-1:1998-10	Non fatty food – Multi-residue methods for the gas chromatographic determination of pesticide residues. Part 1: General considerations.
EN 12393-2:1998-10	Non fatty food – Multi-residue 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 – Multi-residue 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: Gas chromatographic 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.

Notes:

All methods listed above are Type III methods (Alternative Approved Methods).

It was notified by **GERMANY** in Codex document **CX/PR 06/38/9-Add.1** that an internationally validated LC/MS method exists for Chloromequat and Mepiquat in food. Further on notifications were made on the extension of the scope of LC/MS methodology for more than 150 active substances.

It was notified by the **UK** in Codex document **CX/PR 06/38/9-Add.1** that there are several European standard methods which are not included in the EN methods list provided by Germany. These are:

BS EN 14185-1:2004 Determination of N-methyl carbamate residues,

- Part 1: HPLC method with SPE clean up.

BS EN 14333:2004 Determination of benzimidazole fungicides carbendazim, thiabendazole and benomyl (as carbendazim),

- Part 1: HPLC method - with solid phase extraction clean-up,
- Part 2: - - - with gel permeation chromatography,
- Part 3: - - - with liquid/liquid clean up.

Analytical Methods for Pesticide Residues in Foodstuffs, General Inspectorate for Health Inspection, Ministry of Public Health, Water and Sport, THE NETHERLANDS, Sixth Edition, June 1996

The full methods of the compendium were made available by The Netherlands. The method collection consists of four parts:

- Part I – Multi-residue methods (MRM)
 - MRM-1: Pesticides amenable to gas chromatography
 - MRM-2: Pesticides analyzed with HPLC-procedures
 - MRM-3: Carboxylic acids
 - MRM-4: Derivatives of Aromatic Amines
 - MRM-5: Dithiocarbamates
- Part II – Special methods
 - Methods for the determination of individual compounds, e.g. abamectin, amitraz, amitrole, etc, altogether more than 60 compounds/ groups
- Part III – Literature methods
 - Methods from the literature are given as references including descriptions and scope
- Part IV – Screening methods

- Submethod 1 informs about the application of cholinesterase inhibitors for screening of a multitude of individual compounds

Residue methods proposed by the USA

- USDA PDP Analytical Methods Information Summary (California MRM; Modified Luke MRM; New York Modified SPE; QuEChERS MRM; Analytical Methods for Meat Products; Analytical Methods for Dairy Products).
- Method, limit of determination, precision and accuracy for 73 pesticides in/on grapes, grapefruit, pears, strawberries, sweet potato, and watermelon.
- Method, limit of determination, precision and accuracy for various pesticide/commodity combinations.
- Method, limit of determination, precision and accuracy for various pesticides in meat and poultry.
- Method, limit of determination, precision and accuracy for various pesticides in milk.
- Modified Luke: Method, limit of determination, and precision and accuracy for various pesticide/commodity combinations.
- SPE: Method, limit of determination, precision and accuracy for apples, bell peppers, cauliflower, and lettuce.
- FDA Laboratory Bulletin No. 4178 on a MRM using SPE without methylene chloride.
- FDA Laboratory Bulletin No. 4320 on a rapid SPE clean-up procedure for Luke extracts.
- FDA Laboratory Bulletin No. 4304 on a MRM for the determination of halogenated pesticides by GC/MSD.
- FDA Laboratory Bulletin No. 4308 on a MRM for the determination of pesticides containing nitrogen, oxygen and/or sulfur by GC/MSD.

Métodos aplicados en ARGENTINA

DETERMINACION DE PLAGUICIDAS ORGANOCOLORADOS Y PCB's EN GRASA POR CROMATOGRAFÍA GASEOSA CON DETECCIÓN POR CAPTURA DE ELECTRONES (GC-ECD)

- METODO: PCP-ME N° 001; REFERENCIA: FSIS, Versión Julio Método CHC2
- METODO: MA 15/9; REFERENCIA: FSIS CHC2 mod. *FSIS CHC3 mod.

DETERMINACION DE PLAGUICIDAS ORGANOCOLORADOS Y PCB's EN LECHE POR CROMATOGRAFÍA GASEOSA CON DETECCIÓN POR CAPTURA DE ELECTRONES (GC-ECD)

- METODO: PCP-ME N° 012; REFERENCIA: FSIS, Versión Julio Método CHC2
- METODO: PCP-ME N° 021; REFERENCIA: Intern. J. Environ Anal Chem, Vol 57, pp. 63-71, 1994, Veterinary Drug Residues Second Edition. J. Chromatogr., 624, 353-367, 1992.

DETERMINACION DE PLAGUICIDAS ORGANOFOSFORADOS EN GRASA POR CROMATOGRAFÍA GASEOSA CON DETECCIÓN ESPECIFICA PARA FÓSFORO (GC-FPD)

- METODO: PCP-ME N° 022; REFERENCIA: FSIS. Versión 1991, ORP 1.1-16.
- METODO: MA 05/09; REFERENCIA: AOAC N° 970.52

DETERMINACION DE PLAGUICIDAS ORGANOFOSFORADOS EN HIGADO POR CROMATOGRAFÍA GASEOSA CON DETECCIÓN ESPECIFICA PARA FÓSFORO (GC-FPD)

- METODO: PCP-ME N° 002; REFERENCIA: FSIS. Versión 1991, ORP 1.1-16.

DETERMINACION DE PIRETROIDES EN GRASA POR CROMATOGRAFÍA GASEOSA CON DETECCIÓN ESPECÍFICA PARA FÓSFORO (GC-ECD)

- METODO: MA 18/09 REFERENCIA: FSIS. Versión 1991 modif.

DETERMINACION DE CARBAMATOS EN TEJIDOPOR CROMATOGRAFÍA LIQUIDA DE ALTA RESOLUCIÓN GASEOSA CON DETECCIÓN DE FLUORESCENCIA (HPLC-FLD)

- METODO: MA 40/09; REFERENCIA: FSIS. Versión 1991.

DETERMINACION DE AMITRAZ EN GRASA Y MIEL POR CROMATOGRAFÍA GASEOSA CON DETECTOR DE ESPECTROMETRIA DE MASAS (GC-MS)

- METODO: MA 42/09; REFERENCIA: Det.Total Amitraz Residue in Honey by GC/ ECD. Council Regulatory EEC Nro. 2377/90 PAM-VOL II y Analyst 1993 GC-MS Methods for the simultaneous det. Amitraz, Coumaphos, Cymazole, Fluvalinate in honey

DETERMINACION DE ABAMECTINA EN HIGADO, MÚSCULO Y LECHE POR CROMATOGRFÍA LIQUIDA DE ALTA RESOLUCIÓN CON DETECCIÓN DE FLUORESCENCIA (HPLC-FLD)

- METODO: MA 48/09; REFERENCIA: Journal of AOAC vol. 83 N° 1 (2000) .Simultaneous det. of Eprinomectin, Abamectin, Doramectin and Ivermectin in beef liver by HPLC-FLD

DETERMINACIÓN DE PLAGUICIDAS EN FRUTAS Y HORTALIZAS CON PURIFICACIÓN POR EXTRACCIÓN EN FASE SÓLIDA Y CROMATOGRFÍA DE GASES CON DETECTORES ECD, FID Y FTD.

- METODO: LCQ-FH N° 001; REFERENCIA Official Methods de AOAC INTERNATIONAL; Pesticide Analytical Manual, Administración de Alimentos y Medicamentos (FDA) EE.UU.; Manual of Pesticide Residue Análisis

DETERMINACIÓN DE 2,4 D EN CÍTRICOS CON PURIFICACIÓN POR EXTRACCIÓN EN FASE SÓLIDA Y CROMATOGRFÍA GASEOSA CON DETECTOR ECD

- METODO: LCQ-CI N° 002; REFERENCIA Official Methods de AOAC INTERNATIONAL; Pesticida Analytical Manual, Administración de Alimentos y Medicamentos (FDA) EE.UU.; Manual of Pesticide Residue Análisis

DETERMINACION DE PLAGUICIDAS HEXATIAZOL Y MICROBUTANIL EN FRUTILLA POR CROMATOGRFÍA GASEOSA CON DETECCIÓN POR CAPTURA DE ELECTRONES (GC-ECD)

- METODO: LRQ-FR N° 003; REFERENCIA Official Methods de AOAC INTERNATIONAL; Pesticide Analytical Manual, Administración de Alimentos y Medicamentos (FDA) EE.UU.; Manual of Pesticida Residue Análisis

DETERMINACION DE PLAGUICIDAS GUAZATINA, PROCLORAZ E IMAZALIL EN CITRICOS POR CROMATOGRFÍA GASEOSA CON DETECCIÓN POR CAPTURA DE ELECTRONES (GC-ECD)

- METODO: LRQ-CI N° 004; REFERENCIA Official Methods de AOAC INTERNATIONAL; Pesticide Analytical Manual, Administración de Alimentos y Medicamentos (FDA) EE.UU.; Manual of Pesticide Residue Análisis

DETERMINACION DE PLAGUICIDAS ORGANOCOLORADOS, ORGANOFOSFORADOS Y PIRETROIDES EN ACEITES ESENCIALES EN CITRICOS POR CROMATOGRFÍA GASEOSA CON DETECCIÓN POR CAPTURA DE ELECTRONES (GC-ECD) Y DETECTOR DE IONIZACIÓN POR FLAMA (GC-FID)

- METODO: LRQ-AC N° 005; REFERENCIA Official Methods de AOAC INTERNATIONAL; Pesticide Analytical Manual, Administración de Alimentos y Medicamentos (FDA) EE.UU.; Manual of Pesticide Residue Análisis

DETERMINACION DE PLAGUICIDAS ORGANOCOLORADOS, ORGANOFOSFORADOS Y PIRETROIDES EN TOMATE POR CROMATOGRFÍA GASEOSA CON DETECCIÓN POR CAPTURA DE ELECTRONES (GC-ECD) Y DETECTOR DE IONIZACIÓN POR FLAMA (GC-FID)

- METODO: LRQ-TO N° 006; REFERENCIA Official Methods de AOAC INTERNATIONAL; Pesticide Analytical Manual, Administración de Alimentos y Medicamentos (FDA) EE.UU.; Manual of Pesticide Residue Análisis

DETERMINACION DE PLAGUICIDAS ORGANOCOLORADOS, ORGANOFOSFORADOS Y PIRETROIDES EN ACEITE DE SOJA POR CROMATOGRFÍA GASEOSA CON DETECCIÓN POR CAPTURA DE ELECTRONES (GC-ECD) Y EL DETECTOR DE IONIZACIÓN POR FLAMA (GC-FID)

- METODO: LRQ -AS N° 007; REFERENCIA Official Methods de AOAC INTERNATIONAL; Pesticide Analytical Manual, Administración de Alimentos y Medicamentos (FDA) EE.UU.; Manual of Pesticide Residue Análisis

DETERMINACION DE PLAGUICIDAS ORGANOCOLORADOS Y PCB's EN MIEL POR CROMATOGRFÍA GASEOSA CON DETECCIÓN POR CAPTURA DE ELECTRONES (GC-ECD)

- METODO: LRQ-MI N° 007; REFERENCIA: Intern. J. Environ Anal Chem, Vol 57, pp. 63-71, 1994, Veterinary Drug Residues Second Edition. J. Chromatogr., 624, 353-367, 1992.

DETERMINACION DE DISTINTAS SUSTANCIAS EN ALIMENTOS DE ORIGEN VEGETAL**DETERMINACION DE PLAGUICIDAS y OTROS COMPUESTOS ORGANOFOSFORADOS GCMS O GC- FTIR****COSTA RICA**

El laboratorio de residuos del Ministerio de Agricultura y Ganadería (MAG) analiza, en frutas y vegetales frescos, plaguicidas organoclorados, organofosforados, carbamatos y ditiocarbamatos, utilizando principalmente métodos para residuos múltiples. Se utilizan los métodos de análisis modificados de la FDA (Food and Drug Administration), publicados en el manual "Pesticide Analytical Manual" (PAM). Se utiliza el Manual of Pesticide Residue Analysis-Deutsche Forschungsgemeinschaft, VCH Verlagsgesellschaft-Weinheim, FRG para la determinación de ditiocarbamatos.

Further Methods

More method descriptions not listed here in detail were given by other countries in CX/PR 06/38/9/-Add.1. Those were not discussed here explicitly nor put on the IAEA web site since they are not peer validated yet, or references/ abstracts/ details of methods were not available as yet, i.e.:

- Republic of Korea e.g. provided HPLC methods for determining individual dithiocarbamates, partly involving derivatization steps.
- Denmark provided an extended list of substances which can be analysed by a GC/MS/MS multi method in fruit and vegetables.