codex alimentarius commission

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

WORLD HEALTH ORGANIZATION

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Agenda Item 7(b) **CX/PR 99/10**

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JOINT FAO/WHO FOOD STANDARDS PROGRAMME

CODEX COMMITTEE ON PESTICIDE RESIDUES
Thirty-first Session
The Hague, The Netherlands, 12 - 17 April 1999

RECOMMENDATIONS FOR METHODS OF ANALYSIS AND SAMPLING

REVISION OF THE LIST OF METHODS OF ANALYSIS FOR PESTICIDE RESIDUES AND OTHER MATTERS RELATED TO METHODS OF ANALYSIS FOR PESTICIDE RESIDUES

(Prepared by The Netherlands)

BACKGROUND

1. In September 1998 a Codex Circular Letter, CL 1998/30-PR, was distributed to Member countries requesting to provide information on (1) which methods are commonly used in government laboratories or other laboratories involved in the determination of MRL compliance; and (2) whether these methods meet the criteria contained in the present list in Volume 2 of the *Codex Alimentarius* and those contained in the *Codex Alimentarius Commission Procedural Manual*. The contents of the present list will be evaluated against the information provided. The Committee at its 31st Session should consider the above matters based on the following.

COMPILATION OF GOVERNMENT COMMENTS

2. The governments of Algeria, Austria, Canada, Denmark, Germany, the Netherlands, Nigeria, Paraguay, Peru, Poland, the Slovak Republic and the United States of America submitted information as summarised below.

3. **Algeria** refers to various manuals (reference 1, (12th and 13th edition); reference 2 (2nd edition); reference 3 and reference 5). Individual methods are rendered from references 9 and 11. Furthermore, complete multi-residue methods are utilized as issued by the Pesticide Laboratory, Food Production and Inspection Branch, Agriculture Canada:

N°: Pest-Res-DFV-1 01 February 1988
N°: P-RE-023-90(3)-DFV 01 August 1990
N°: P-RE-023-92(4)-DFV 12 April 1992

There is no experience on the analysis of N-methylcarbamates in Algeria. Residues of organochlorine products in egg and egg products are analyzed by:

N°: LSD P-RE-001-88-EGG 10 September 1988

It is stated that the methods listed above comply with the criteria given in Annex I to CL 1998/30-PR.

4. **Austria** informs the Committee that for fruits, vegetables and honey, multi-residue method 1 of reference 9 is applied; for benomyl (69), carbendazim (72) and thiabendazole (65) in the same matrices also the method from reference 1 is used. Dithiocarbamates are analyzed according to method S-15 of reference 4. Fatty foods of animal or plant origin are analyzed with method S-19 of reference 4. All methods are subject to in-house validation prior to use.

5. **Canada** in its reply refers to the methods employed by CFIA and PMRA Lab services, none of these methods at present comply with the criterion that the method should be available in open literature. In general the methods do comply with the criteria (iii) to (v) and (b) to (e) of Annex I to the above Circular Letter.

6. In **Denmark** the current monitoring of pesticide residues is based on three multi-residue methods and some single-residue methods. None of these are directly included in the present list, however, the methods are based on similar principles as used by other nations and described in the manuals listed in paragraph 3.2 of Annex II to the Circular Letter. The laboratories carrying out the analytical work are accredited in accordance with EN-45001. **Denmark** proposes the entry of the new method for chlormequat (15) in the list. The method has not been elaborated by an international organization nor validated by intercomparison tests, but meets the other criteria contained in Annex I. The method is referenced as: Analysis of Chlormequat Residues in Grains Using Liquid Chromatography-Mass Spectrometry (LC-MS/MS); Vahl M., Graven A. and Juhler R.K., *Fres. J. Anal. Chem.* **1998**, 361, 817-820.

7. **Germany** provided a revised and updated list of methods of analysis currently used in their country. The majority of the methods were originated from reference 4 and 7, but it should be noted that the original multi-residue method S-19 is gradually replaced by a modified gel permeation method using ethyl acetate/cyclohexane instead of dichloromethane: W. Specht, S. Pelz and W. Gilsbach: *Fres. J. Anal. Chem.* **1995**, 353, (1995). This method now determines more than 70 pesticides. Germany proposes to include 6 references for individual or smaller groups of compounds.

8. In **the Netherlands** pesticide residues are analyzed according to reference 9. The criteria for selection of methods for this manual comply with those given in Annex I of the Circular Letter. It is however stressed that any laboratory using these methods must perform a thorough in-house validation prior to use. In general this requirement is fulfilled in laboratories with EN-45000 accreditation.

9. The criteria that **Nigeria** uses for the selection of methods are (I) and (iii) to (v) from section A of Annex I to the Circular Letter. The literature relied on in the choice of methods were references 1 and 2, while background information is used from section 3.1 of Annex II to the Circular Letter.

10. **Paraguay** uses gas chromatography with alumina columns for analysis of pesticide residues presently at the national level.

11. **Peru** informs the committee that on the national level thin-layer chromatography is widely used as a screening technique. Furthermore method 970.52 of reference 1 is used. Electron-capture and flame ionization are used as detection techniques in gas chromatography. At present analytical methods for organophosphorus pesticides and pyrethroids are implemented, requiring other detection modes in GC and the introduction of HPLC.

12. **Poland** uses modified methods originating from reference 4. Other references relied on are: Ambrus, A. et al., *JAOAC*, **1981,** 64, 733-768; General method for determination of pesticide residues in samples of plant origin, soil, and water, *Becker, G., Schug, P., Deutsche Lebensm. Rundschau* **1990,** 86, 239-242; Eine miniaturmethode zur schnellen Bestimmung von Pestizidrückständen in pflanzlichen Lebensmitteln, and Kadenczki, L., *et al., JAOAC* **1992,** 75, 53-61; Column extraction of residues of several pesticides from fruits and vegetables: a simple multi-residue analysis method. The recovery rates vary from 70-120% with a standard deviation of less than 15%. Limits of detection are generally below MRL, with the exception of some pesticide matrix combinations where LODs are reported at the MRL.

13. **The Slovak Republic** refers to reference 1 for a number of compounds, while for other compounds, methods supplied by the Centre of Technical Information for Food Industry (Prague) or the Research Institute for Veterinary Medicine are used. It is not clear whether these methods are available in open literature.

14. **The United States of America** categorized the methods in references 1 and 2 in four classes:

A) in use, meet criteria
B) not in routine use, but might be used to determine particular residues targeted by the method. Most of these methods are single residue methods and few have been collaborated; thus they do not meet all the criteria.

C) nor in routine use, and would require additional testing before application
D) obsolete, deletion from the list is proposed.

	A	B	C	D
Method references	1(o), 2(a) [identical with 1(a,b &n)]; 2(b); 2(d) [identical to 1(p)]; 2(g)[identical to 1(q)] and 2(h)	1(k); Daft (1983), Gilvydis and Walters (1984), Heikes (1985) and Krause and August (two references 1983)	2(e)	1(d-j); 1(l,m); 2(c); 2(f) and Pomerantz and Ross (1968)

15. The **United States** also suggests that the reference to the second edition of PAM (reference 2) should be deleted. In addition, the a description of the methods employed in the United States Pesticide Data Program as used in Federal and State laboratories was provided. In brief, this information is summarized as follows:

- Multi-Residue Screen Methods for Fruits and Vegetables

Lab*	extraction solvent	Cleanup
1	acetonitrile	organochlorine compounds: florisil (SPE), carbamates: aminopropyl (SPE) organophosphorus compounds: none
2	acetone, dichlormethane/petroleum ether	organochlorine compounds: florisil (SPE), carbamates: aminopropyl (SPE) organophosphorus compounds: none
3	acetone, dichlormethane/petroleum ether	solvent exchange
4	acetone, SPE-C18, dichloromethane	prepartition on C-18 Sep-Pak post-partition on SAX(SPE)
5	acetone, dichlormethane/hexane	organochlorine compounds: precipitation carbamates: C-18(SPE) organophosphorus compounds: none
6	acetone/dichloromethane	Florisil column chromatography
7	acetonitrile	organochlorine compounds: Sep-Pak (SPE), carbamates: aminopropyl (SPE) organophosphorus compounds: none

* 1 California Department of Food and Agriculture
2 Florida Department of Agriculture and Consumer Services
3 Michigan Department of Agriculture
4 New York Department of Agriculture and Markets
5 Ohio Department of Agriculture
6 Texas Department of Agriculture
7 Washington Department of Agriculture

- Multi-Residue Screen methods* for Soybeans and Wheat using SFE

extraction solvent	Cleanup
acetonitrile/CO_2/ SFE	Liquid partition and SPE on C-18 and aminopropyl

*United States Department of Agriculture Laboratory (GIPSA-FGIS)

- Multi-Residue Analysis of Milk*

extraction solvent	Cleanup
Na_2SO_4/EtOH-EtAc(5:95)	organochlorine compounds: florisil (SPE), carbamates: aminopropyl (SPE) organophosphorus compounds: none

*California Department of Food & Agriculture

Note: All methods above apply GC with selective detection for organochlorine organophosphorus and organonitrogen compounds and HPLC with fluorescence detection for the carbamate pesticides

- Immunoassay Method of United States Department of Agriculture Laboratory (AMS) for Analyzing Benomyl/Carbendazim in Milk

- Immunoassay Method of United States Department of Agriculture Laboratory (APHIS) for Analyzing Benomyl/Carbendazim and Thiabendazole in Fruits and Vegetables

STATUS OF THE LIST OF [RECOMMENDED] METHODS OF ANALYSIS FOR PESTICIDE RESIDUES

16. The status of the methods given in the list was discussed in some detail at previous sessions of the CCPR. The Committee at its 30th session generally supported the updating of the list of methods of analysis. It was also agreed that information would be sought on which of the methods listed are still commonly used.

17. The current List does contain criteria for inclusion of methods in the List. The question remains whether these specific criteria are in line with the general criteria given in the *Codex Alimentarius Commission Procedural Manual* (Tenth edition pp. 57-58; Annex I (B) of CL 1998/30-PR). Both sets of criteria allow some degrees of freedom because the wording used is of general nature, such as "preference should be given to" or "wherever possible the following criteria where applied when selecting methods". From this point of view both sets of criteria can be seen as equivalent. The Committee should evaluate whether the present set of criteria still meet the Codex requirements, whether they can be redrafted or expanded in order to characterize the methods more appropriately. One of the additional criteria to be considered by the Committee is whether obsolete methods that fulfil the criteria should still be included in the List.

18. From the responses on the Circular Letter it is 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 include approximately 75% of the compounds listed in the present List. 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.

REFERENCES

(1) Official Methods of AOAC INTERNATIONAL, 16th edition (1995)

(a)	970.52	(j)	978.16	(n)	983.21
(b)	976.23	(k)	977.19	(o)	984.21
(d)	977.18	(l)	960.43	(p)	985.22
(e)	975.40	(m)	963.24	(q)	985.23

(2) Pesticide Analytical Manual, Food and Drug Administration, Washington, D.C., USA

		2nd edition	3rd edition
(a)	Vol. I,	Table 201-A and sections, 211.1, 212.1, 231.1, 232.1 and 252	nonfat foods: Section 303 fatty foods: Section 304, E1-E5+C1-C4
(b)	Vol. I,	Table 201-D and section 221.1	Section 402
(c)	Vol. I,	Table 201-H and section 232.3	[method not in PAM I 3rd edition]
(d)	Vol. I,	Table 201-I and section 232.4	Section 302 E1-E4, no cleanup
(e)	Vol. II,	Method under compound name (when in this reference several methods have been given, they are generally listed in order of preference)	
(f)	Vol. I,	Table 651-A and sections 650 and 651	[not in PAM I 3rd edition]

(g) Vol. I, Table 242.2-1 and section 242.2 Section 401
(h) Vol. I, Section 242.3 Section 404

(3) Manual on Analytical Methods for Pesticide Residues in Foods, Health Protection Branch, Health and Welfare Canada, Ottawa, Ont., Canada (1985) (available in English and French)

(4) Methodensammlung zur Rückstandsanalytik von Pflanzenschutzmitteln, 1.- 11. Lieferung, VCH Verlagsgesellschaft, Weinheim, FRG (1991) (the numbers in parentheses refer to the numbers of the methods in this manual; methods preceded by "S" are multi-residue methods; the manual is also available in English, see ref. 7).

(5) Laboratory Manual for Pesticide Residues Analysis in Agricultural Products, compiled by R.B. Maybury, Pesticide Laboratory, Food Production and Inspection Branch, Agriculture Canada, Ottawa, Ont., Canada (1984) (available in English and French).

(6) Zweig, G. (edit.), Analytical Methods for Pesticides, Plant Growth Regulators , Academic Press, New York - San Francisco - London

(a) Vol. VII (1974)
(b) Vol. VIII (1976)
(c) Vol. IX (1977)
(d) Vol. X (1978)
(e) Vol. XI (1980)
(f) Vol. XII (1982) (Lawrence J.F. Editor)
(g) Vol. XIII (1984) (Zweig, G. and Sherma, J. Editors)
(h) Vol. XVI (1988) (Sherma, J. Editor)

(7) Manual of Pesticide Residue Analysis, Deutsche Forschungsgemeinschaft, VCH Verlagsgesellschaft, Weinheim, FRG (1987) (English translation of ref. 4)

(a) Vol. I, Section Clean-up Methods (the numbers in parentheses refer to the numbers of the clean-up methods in this volume)
(b) Vol. I, Section Individual Pesticide Residue Analytical Methods
(c) Vol. I, Section Multiple Pesticide Residue Analytical Methods (the numbers in parentheses refer to the numbers of the multi-residue methods in this volume)
(d) Vol. II (1992).

(8) Chemistry Laboratory Guidebook, United States Department of Agriculture, Food Safety and Inspection Service, Science Program, Washington, D.C., USA

(a) Section 5.001
(b) Section 5.002
(c) Section 5.003
(d) Section 5.004
(e) Section 5.006
(f) Section 5.005
(g) Section 5.050

(9) Analytical Methods for Pesticides Residues in Foodstuffs, P. van Zoonen (edit.), 6th edition, The Inspectorate for Health Protection, Ministry of Public Health, Welfare and Sport, Drukkerij T.O. Offset B.V, Maasstricht, The Netherlands (1996).

(a) Part I: Multi-residue Methods (the numbers in parentheses refer to numbers of the multi-residue methods in this volume)
(b) Part II: Special Methods (methods given under compound name)

(10) Materials and Methods Used for Pesticide Residues Monitoring in Sweden, Vår Föda, 38, Suppl.2, 79-136 (1986)

(11) Comprehensive Analytical Profiles of Important Pesticides (Modern methods for pesticides analysis) e.d. J. Sherma & T Cairns 1992.