



JOINT FAO/IAEA DIVISION OF NUCLEAR TECHNIQUES IN FOOD AND AGRICULTURE



PROPOSED DRAFT REVISION OF THE LIST OF METHODS FOR PESTICIDE RESIDUE ANALYSIS INCLUDING METHODS OF DETERMINATION FOR DITHIOCARBAMATES

COMMONLY USED METHODS FOR PESTICIDE RESIDUE ANALYSIS IN FOOD

SUMMARY

In the following Article commonly applicable methods for the determination of residues of pesticides, including dithiocarbamates, bromide ion derived from methyl bromide and PCB, analysis in food are described. The analytical methods compiled here represent official and validated methods. Abstracts with short descriptions of the scope and applicability including the respective sources of procurement are given. Some of them are available as full methods and can be downloaded directly as pdf, as far as possible in terms of copyright protection, or download links are given to external URLs.

Updates on analytical methods were submitted by Canada, Germany, The Netherlands and the USA.

EDITOR'S NOTE

Most of the analytical methods used in pesticide residue analysis worldwide utilize similar principles of extraction, clean-up and determination. In the scientific literature a multitude of publications can be found. However, for food control laboratories there are certain practical limitations to apply methods, particularly in terms of the national and international recognition of results obtained with that. Only export certificates issued by accredited laboratories using fully validated and officially recognized methods will easily meet import requirements and can be a strong support in food trade. In that regard, IAEA's webpage and the INFOCRIS database provide a comprehensive overview about the most widely used methods to guide interested laboratories towards appropriate methods for any analytical problem related to the determination of pesticides and several pesticide metabolites, as well as other potential contaminants like PCBs.

The following gives an overview and makes reference to the original methods and literature sources. It is intended to provide a traceable path towards applicable methodologies. The information given here provides a short summary. For utilizing the detailed procedures the reader is referred to the original methods which are available from the cited references. Text and tables used here were taken from the following sources:

- CL 2005/52 – PR, December 2005, CX 4/40.2, Proposed Draft Revision of the List of Methods for Pesticide Residue Analysis at Step 3.
- CX/PR 03/10, March 2003, CODEX COMMITTEE ON PESTICIDE RESIDUES Thirty-fifth session, DISCUSSION PAPER ON THE REVISION OF THE LIST OF METHODS OF ANALYSIS FOR PESTICIDE RESIDUES, prepared by The Netherlands.
- German Comments on CL 2001/29 PR; Methods of Analysis for the Determination of Pesticide Residues.
- CX/PR 99/10¹, February 1999, CODEX COMMITTEE ON PESTICIDE RESIDUES Thirty-first Session, RECOMMENDATIONS FOR METHODS OF ANALYSIS AND SAMPLING, REVISION OF THE LIST OF METHODS OF ANALYSIS FOR

¹ For CX/PR 99/10 see (http://www-infocris.iaea.org/Download/Reprint-pr99_10e.pdf)

PESTICIDE RESIDUES AND OTHER MATTERS RELATED TO METHODS OF ANALYSIS FOR PESTICIDE RESIDUES (Prepared by The Netherlands).

In order to facilitate reading the compiled information the text and tables were edited and supplemented as necessary. It has to be noted that many of the published methods are protected by international copyright. Others can be downloaded (see URLs given on this webpage). Therefore detailed methods are not displayed here. However, with the given abstracts and descriptions a reasonable choice of methods is facilitated for interested parties.

METHODS FOR PESTICIDE RESIDUE ANALYSIS AVAILABLE TO THE CODEX COMMITTEE FOR PESTICIDE RESIDUES (CCPR)

BACKGROUND

From the responses on CL 1998/30-PR 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; published in Journal of AOAC INTERNATIONAL (JAOAC), <http://www.aoac.org/pubs/pubjaoac.html>;
- Pesticide Analytical Manual, Food and Drug Administration, USA; Vol. 1, 3rd Edition, 1994, Revised, October 1999, <http://www.cfsan.fda.gov/~frf/pami1.html>; Vol. 2, Updated January, 2002;
- Manual of Pesticide Residue Analysis, Deutsche Forschungsgemeinschaft (German or English edition); VCH² Weinheim, Vol. 1 (1987) and Vol. 2 (1992) (for details see also the European Norms referenced below);
- Analytical Methods for Residues of Pesticides, Inspectorate for Health Protection of the Netherlands, see Analytical Methods for Pesticide Residues in Foodstuffs, 6th edition (1996), Ministry of Public Health, Welfare and Sport, Rijswijk, The Netherlands Part I, Multi-Residue Methods 1-3.

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.

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 than past practices in pesticide residue analysis.

The responses to CL 2002/16-PR yielded more recent information on validated methods that are currently in use³. Moreover in its 35th session the Committee was informed by the Delegation of Germany on a new LC/MS multi-method⁴ that covers many pesticides that were not covered by multi-residue methods before. The Committee decided that older references for these compounds are to be deleted. The Delegation of The Netherlands offered to review the list of methods and to identify the pesticides for which MRLs have been set but for which no suitable methods were made available to the Committee during the last 5 years.

² Books cannot be ordered anymore. Methods and supplements are now integrated in "Lebensmittel-, Bedarfsgegenstaende- und Futtermittelgesetzbuch (LFGB), Amtliche Sammlung von Untersuchungsverfahren nach Paragraph 64" (*Official collection of test procedures according to paragraph 64 LFGB for food surveillance and testing institution*), method collection available from Beuth Verlag, Berlin, Germany, <http://www.beuth.de>. However, some of the "old" multi-residue and single methods can be downloaded at <http://www.bfr.bund.de/cd/1637> and <http://www.bfr.bund.de/cd/1652>

³ CX/PR 03/10

⁴ J. Klein and L. Alder: Application of Gradient Liquid Chromatography with Tandem Mass Spectrometry to the Simultaneous Screening for About 100 Pesticides in Crops. J. Assoc. Off. Anal. Int. 86 (2003) 1015. For the abstract see in (<http://www-infocris.iaea.org/Download/Germany-EN-Methods.pdf>)

SUMMARY OF METHODS AVAILABLE TO THE COMMITTEE AT PRESENT

Analytical methods for the determination of pesticides, including dithiocarbamates, bromide ion derived from methyl bromide and PCBs. The procedures are summarized and referenced below. In addition to the abstracts complete methods are provided for downloading, as far as possible with regard to copyright protection.

CANADA

Canada submitted descriptions of ten methods currently used in their country. These methods were also made available for downloading. References to, abstracts and download addresses of the methods as submitted by Canada are given in (<http://www-infocris.iaea.org/Download/Canada-Methods.pdf>).

GERMANY

Germany submitted a number of European standardized methods and provided information on their scope, principle validation data and further aspects, where appropriate⁵. The methods submitted cover both pesticide residues as well as contaminants.

The resulting European Standards were elaborated by CEN/TC 275 "Food analysis - Horizontal methods" as proposed by the German delegation to be endorsed as CODEX-methods by the CCFAC.

References to and abstracts of the methods as submitted by Germany are given in (<http://www-infocris.iaea.org/Download/Germany-EN-Methods.pdf>).

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)

<http://www.ams.usda.gov/Science/pdp/quick.htm>. References to and abstracts of the methods as submitted by the USA are given in (<http://www-infocris.iaea.org/Download/USA-Methods.pdf>).

THE NETHERLANDS

The Netherlands submitted brief descriptions of methods. References to and a brief listing of the methods as submitted by The Netherlands are given in (<http://www-infocris.iaea.org/Download/Dutch-Methods.pdf>).

PREVIOUS INPUTS FOR ANALYTICAL METHODS TO CCPR

Inputs to Codex provided by other countries are from 1999. As this information needs updating it was not listed here. The country information provided for the 31st session of the CCPR can be found under http://www-infocris.iaea.org/Download/Reprint-pr99_10e.pdf.

PESTICIDES FOR WHICH NO METHODS ARE AVAILABLE TO THE CCPR YET

Governments and International Organizations are invited to submit information on methods of analysis and their performance characteristics on the following pesticides:

⁵ 34th session of the CCPR, CRD5

abamectine (177), amitraz (122), anilazine (163), azocyclotin (129), benalaxyl (155), benomyl (69), bentazone (172), bioresmethrin (93), bitertanol (144), buprofezin (173), cadusofos (174), cartap (97), chinomethionat (80), chlormequat (15), ciprodinil (207), clofentezine (165), cycloxydim (179), cyhexatin (67), cyromazine (169), dimethipin (151), diquat (31), dithianon (180), dodine (84), esfenvalerate (204), ethephon (106), ethoxyquin (35), etofenprox (184), etrimfos (123), famoxadone (208), fenbutatin oxide (109), fenpyroximate (193), fentin (40), fipronil (202), flusilazole (165), flutolanil (205), glufosinate ammonium (175), glyphosate (158), guazatine (114), hexaconazole (170), hexathiazox (176), hydrogen phosphide (46), maleic hydrazide (102), methacrifos (125), methoprene (147), methoxyfenozide (209), methyl bromide (52), metiram (186), paclobutrazol (161), paraquat (57), penconazole (182), phentoate (128), 2-phenylphenol (56), pyraclostrobin (210), piperonyl butoxide (62), procloraz, (142), spinozad (203), thiophanate-methyl (77), trifloxystrobin (213) and triforine (116).

Furthermore governments and international organizations are invited to give information on validated methods for the determination of individual dithiocarbamates⁶.

Note: Some of the above listed active ingredients may be found in one of the tables shown elsewhere. However, this compilation reflects the current state regarding active ingredients for which analytical methods were available. Further inputs and new methods to be submitted should minimize this list in the future.

ACKNOWLEDGEMENTS

The input of Dr. Piet van Zoonen of the National Institute of Public Health and the Environment, Bilthoven, The Netherlands, who compiled the information to the present state (March 2006) is appreciated. Many thanks for providing analytical methods also to Donna J. Grant, Calgary Laboratory - Canadian Food Inspection Agency, Steven Lehotay, USDA Agricultural Research Service Eastern Regional Research Center, and Lutz Alder, BFR, Berlin, Germany.

Descriptions of further methods should also be submitted to IAEA for publication on the IAEA Training and Reference Centre (TRC) website: <mailto:Josef.Brodesser@iaea.org>, [FAO/IAEA Joint Division for Food and Environmental Protection \(http://www-naweb.iaea.org/nafa/fep/index.html\)](http://www-naweb.iaea.org/nafa/fep/index.html).

⁶ such as: H. van Lieshaut, W. Schwack: Selective Trace Determination of Dithiocarbamate Fungicides in Fruits and Vegetables by Reversed-Phase Ion-Pair Liquid Chromatography with Ultraviolet and Electrochemical Detection. Journal of AOAC International , Vol. 83 (2000), 720-727

PESTICIDES WITH REFERENCE TO THEIR METHODS OF ANALYSIS

The following table makes references to the respective methods of analyses discussed in the documents linked to German and USA methods. Canadian methods and references are covered in a separate listing (see <http://www-infocris.iaea.org/Download/Canada-Methods.pdf>).

No	Active ingredient	EN 1528	EN 12393	EN 12396 EN 13191	CFDA	PDP	LCMS
177	Abamectine						
95	Acephate		X		X	X	X
117	Aldicarb				X		X
1	Aldrin and Dieldrin	X	X		X	X	
134	Aminocarb						
122	Amitraz						
79	Amitrole						
163	Anilazine				X		
68	Azinphos-ethyl		X				
2	Azinphos-methyl		X		X	X	
129	Azocyclotin						
155	Benalaxyl						
137	Bendiocarb						X*
69	Benomyl						
172	Bentazone						
178	Bifentrin		X		X		
3	Binapacryl						
93	Bioresmethrin						
144	Bitertanol						
47	Bromide ion			EN 13191			
4	Bromophos	X	X				
5	Bromophos-ethyl	X	X				
70	Bromopropylate		X				
173	Buprofezin						
139	Butocarboxim						
174	Cadusofos						
71	Camphechlor	X					
6	Captafol		X				
7	Captan		X		X	X	
8	Carbaryl				X	X	X
72	Carbendazim						X*
96	Carbofuran					X	X*
9	Carbon disulfide						
10	Carbon tetrachloride						
11	Carbophenothion	X	X				
145	Carbosulfan						
97	Cartap						
80	Chinomethionat						

No	Active ingredient	EN 1528	EN 12393	EN 12396 EN 13191	CFDA	PDP	LCMS
12	Chlordane	X			X		
13	Chlordimeform						
14	Chlorfenvinphos	X	X				
15	Chlormequat						
16	Chlorobenzilate		X				
81	Chlorothalonil		X		X		
201	Chlorpropopham		X				
17	Chlorpyrifos	X	X		X		
90	Chlorpyrifos-methyl	X	X		X	X	
207	Ciprodinil						
187	Clethodim						X
156	Clofentezine						
18	Coumaphos		X				
19	Crufomate						
91	Cyanofenphos		X				
179	Cycloxydim						
157	Cyfluthrin		X		X		
146	Cyhalothrin		X		X		
67	Cyhexatin						
118	Cypermethrin		X				
207	Cyprodinil						X*
169	Cyromazine						
104	Daminozide						X*
20	2,4-D						X*
21	DDT	X	X		X	X	
135	Deltamethrin		X		X		
92	Demeton		X				X
73	Demeton-S-methyl		X				X
164	Demeton-S-methylsulphon		X				X
98	Dialofos		X				
22	Diazinon	X	X		X		
23	1,2-Dibromoethane						
82	Dichlofluanid		X				
24	1,2-Dichloroethane						
25	Dichlorvos	X	X		X	X	
83	Dicloran		X				
26	Dicofol		X		X		
130	Diflubenzuron						X*
151	Dimethipin						
27	Dimethoate		X		X		X
87	Dinocap						
28	Dioxathion		X				
29	Diphenyl						

No	Active ingredient	EN 1528	EN 12393	EN 12396 EN 13191	CFDA	PDP	LCMS
30	Diphenylamine				X		
31	Diquat						
74	Disulfoton		X		X	X	
180	Dithianon						
105	Dithiocarbamates			EN 12396			
84	Dodine						
99	Edifenphos						
32	Endosulfan	X	X		X		
33	Endrin	X	X				
204	Esfenvalerate						
106	Ethephon						
107	Ethiofencarb						X
34	Ethion	X	X		X		
149	Ethropophos		X				
35	Ethoxyquin						
108	Ethylenethiourea (ETU)						
184	Etofenprox						
123	Etrimfos						
208	Famoxadone						
85	Fenamiphos		X		X	X	
192	Fenarimol		X				
109	Fenbutatin oxide						
36	Fenchlorphos	X	X				
37	Fenitrothion		X			X	
185	Fenpropathrin		X		X		
188	Fenpropimorph						X*
193	Fenproximate						
38	Fensulfothion		X				
39	Fenthion	X	X		X		
40	Fentin						
119	Fenvalerate		X		X	X	
202	Fipronil						
152	Flucythrinate		X				
211	Fludioxonil						X*
165	Flusilazole						
205	Flutolanil						
41	Folpet		X		X		
42	Formothion		X				
175	Glufosinate- ammonium						
158	Glyphosate						
114	Guazatine						
194	Haloxypop						X*

No	Active ingredient	EN 1528	EN 12393	EN 12396 EN 13191	CFDA	PDP	LCMS
43	Heptachlor	X	X		X	X	
44	Hexachlorobenzene	X	X				
170	Hexaconazole						
176	Hexathiazox						
45	Hydrogen cyanide						
46	Hydrogen phosphide						
110	Imazalil				X	X	X
206	Imidaclopride						X
111	Iprodione		X		X	X	
131	Isophenphos		X				
88	Leptophos						
48	Lindane	X	X		X		
49	Malathion	X	X		X	X	
102	Maleic hydrazide						
50	Mancozeb						
124	Mecarbam		X		X		
138	Metalaxyl		X			X	X
212	Metalaxyl-M						
125	Methacrifos						
100	Methamidophos		X		X	X	X
51	Methidathion		X		X		
132	Methiocarb				X		X
94	Methomyl				X	X	X
147	Methoprene						
209	Methoxyfenozide						
52	Methyl bromide						
186	Metiram						
53	Mevinphos		X		X		
54	Monocrotophos		X		X	X	X
181	Myclobutanil				X		
140	Nitrofen		X				
55	Omethoate		X				X
126	Oxamyl				X	X	X
166	Oxydemeton-methyl		X				
161	Paclobutrazol						
57	Paraquat						
58	Parathion	X	X		X	X	
59	Parathion-methyl	X	X		X		
182	Penconazole						
120	Permethrin		X		X	X	
128	Phenthoate						
56	2-Phenylphenol						
112	Phorate		X			X	

No	Active ingredient	EN 1528	EN 12393	EN 12396 EN 13191	CFDA	PDP	LCMS
60	Phosalone		X		X		
102	Phosmet	X	X		X		
61	Phosphamidon		X		X		
141	Phoxim		X				
210	Pyraclostrobin						
62	Piperonyl butoxide						
101	Pirimicarb						X
86	Pirimiphos-methyl	X	X			X	
142	Prochloraz						
136	Procymidone		X		X		
171	Profenofos		X				
148	Propamocarb						X*
113	Propargite				X		
183	Propham		X				
160	Propiconazole				X	X	
75	Propoxur				X	X	X
150	Propylenethiourea (PTU)						
153	Pyrazophos		X				
63	Pyrethrins		X				
64	Quintozene		X		X	X	
89	Sec-butylamine						
203	Spinozad						
121	2,4,5-T						
189	Tebuconazole				X	X	X
196	Tebufenozide				X		X
115	Tecnazene		X		X		
190	Teflubenzuron						X*
167	Terbufos		X				
65	Thiabendazole				X		X
154	Thiodicarb						X
76	Thiometon		X				
77	Thiophanate-methyl						
191	Tolcophos-methyl		X				
162	Tolyfluanid		X				
133	Triadimefon		X				
168	Triadimenol					X	
143	Triazophos		X				
66	Trichlorfon		X				
213	Trifloxystrobin						
116	Triforine						
78	Vamidotion		X				X*
159	Vinclozolin		X		X		

Glossary:

PDP – USDA Pesticide Data Program (<http://www.ams.usda.gov/Science/pdp/quick.htm>)

CDFA – California Department of Food and Agriculture (<http://www-infocris.iaea.org/Download/USA-Methods.pdf>).

LCMS – Liquid Chromatography Mass Spectrometry (<http://www-infocris.iaea.org/Download/Germany-EN-Methods.pdf>).

EN 1528, EN 12393, EN 12396 (<http://www-infocris.iaea.org/Download/Germany-EN-Methods.pdf>).