SLOVENSKI STANDARD
SIST-TP CEN/TR 16468:2013

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Analiza živil - Določevanje ostankov pesticidov z uporabo GC-MS - Retenzijski časi, parametri masne spektrometrije in informacije odziva detektorja

Food analysis - Determination of pesticide residues by GC-MS - Retention times, mass spectrometric parameters and detector response information

Lebensmitteluntersuchung - Bestimmung von Pestizidrückständen mit GC-MS - Retentionszeiten, Parameter für die Massenspektrometrie und Detektionsempfindlichkeit

Analyse des produits alimentaires - Détermination des résidus de pesticides par CG-SM - Temps de rétention, paramètres de spectrométrie de masse et information sur la réponse des détecteurs

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67.050	Splošne preskusne in analizne metode za živilske proizvode	General methods of tests and analysis for food products

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Food analysis - Determination of pesticide residues by GC-MS - Retention times, mass spectrometric parameters and detector response information

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This Technical Report was approved by CEN on 3 December 2012. It has been drawn up by the Technical Committee CEN/TC 275.

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Management Centre: Avenue Marnix 17, B-1000 Brussels

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Foreword

This document (CEN/TR 16468:2013) has been prepared by Technical Committee CEN/TC 275 “Food analysis - Horizontal methods”, the secretariat of which is held by DIN.

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Introduction

Pesticide residue analysis employs multiple methods involving extraction of residues from foods and clean-up of the extract to obtain as many analytes as possible in the purified extracts. Afterwards the extracts can be analysed by different kinds of instruments.

The hyphenation of gas chromatography (GC) and mass spectrometry (MS) is one of the most often used universal and selective analysis techniques for identification and quantification of pesticide residues in food extracts.

For the ionisation of the analytes (pesticides and/or their metabolites) in GC-MS, electron impact ionisation (EI) is most commonly used. If the typical electron energy of 70 eV is used, very often molecular ions (cation radicals) and several fragment ions are formed simultaneously.

The selective determination of each target analyte is performed by simultaneous aquisition of typically three ions formed by the analyte in the selected ion monitoring (SIM) mode. The diagnostic value of an ion depends on its mass. Usually even-numbered, high mass ions are less frequently formed and their recording results in more specific chromatograms. A reduction of selectivity may be caused by background ions formed during ‘column bleeding’ or by sample matrix (e.g. typical ions from fatty of fruit acids or hydrocarbons).

1 Scope

This Technical Report lists mass spectrometric parameters which are useful for the application of European Standards for the determination of pesticide residues in foods that use GC-MS, such as the following standards:

— EN 1528 (all parts), *Fatty food — Determination of pesticides and polychlorinated biphenyls (PCBs)*;

— EN 12393 (all parts), *Foods of plant origin — Multiresidue methods for the gas chromatographic determination of pesticide residues*;

— EN 15662, *Foods of plant origin — Determination of pesticide residues using GC-MS and/or LC-MS/MS following acetonitrile extraction/partitioning and clean-up by dispersive SPE — QuEChERS-method*.

To facilitate the determination of pesticides and/or metabolites using GC-MS, Table 1 specifies the diagnostic ions suitable for quantification, which can be used.

2 Analyte specific parameters for gas chromatographic determination of pesticides

2.1 General

All values indicated in Table 1 were acquired using GC-MS, GC-ECD or GC-NPD systems under the experimental conditions as outlined in 2.2. Comparative investigations showed that these parameters can be transferred simply on instruments of other types of the same or other manufacturers [1].

2.2 GC-MS, GC-ECD and GC-NPD Parameters

The following GC operating conditions have been proven to be satisfactory. This is an example for appropriate experimental conditions. Equivalent conditions may be used if they can be shown to lead to the same results.

Gas chromatograph	Agilent model 6890
Carrier gas	Helium, constant flow 1,0 ml/min (typical pressure at 70 °C is 61 kPa)
Injection technique	Pulsed splitless, 200 kPa; Pulse time 1,0 min
Injector temperature	240 °C
Injection liner	single taper, splitless (Agilent 5181-3316)
Injection volume	1 µl or 2 µl
Purge Gas	Helium; purge flow to split vent 50 ml/min; Purge time 1,5 min
Column	Fused silica capillary column HP-5MS, length 30 m, inner diameter 0,25 mm, film thickness 0,25 µm (Agilent Nr. 19091S-433)
Temperature programme	2 min 70 °C, programmed to rise at 25 °C/min to 170 °C, at 3 °C/min to 210 °C, at 30 °C/min to 290 °C, then isothermal for 9 min
Transfer Line Temperatur	280 °C
Mass spectrometer	Agilent MSD 5973N inert
MS temperatures	Quadrupole 150 °C; Source 230 °C;
Ionisation	Electron impact 70 eV
Solvent Delay	4,0 min
Retention time of parathion	15,85 min (parathion is used for calculation of relative retention times)

As an alternative to the abovementioned fused silica capillary column HP-5MS a column DB-35MS can be used. This column requires some slightly changed conditions.

Column	Fused silica capillary column DB-35MS, length 30 m, inner diameter 0,25 mm, film thickness 0,25 µm (Agilent Nr. 122-3832)
Carrier gas/MS detection	Hydrogen, constant flow 1,1 ml/min (typical pressure at 80 °C is 15,9 kPa)
Carrier gas/NPD and ECD detection	Hydrogen, constant flow 1,9 ml/min (typical pressure at 80 °C is 88,3 kPa)
Temperature programme	1,8 min 80 °C, programmed to rise at 30 °C/min to 190 °C, at 6 °C/min to 240 °C, at 30 °C/min to 290 °C, then isothermal for 12 min
Injection technique/MS detection	Pulsed splitless, 80 kPa; Pulse time 1,5 min
Injection technique/NPD and ECD, parallel detection	Pulsed splitless, 172 kPa; Pulse time 1,5 min
Injector temperature	240 °C
Injection liner	single taper, splitless (Agilent 5181-3316)
Injection volume	2 µl
Purge Gas	nitrogen; purge flow to split vent 35 ml/min; Purge time 2,0 min
Detector split ratio	1:5 (ECD:NPD; post column)
Detector temperature (NPD)	280 °C
Detector temperature (ECD)	300 °C
Transfer line temperature (MS)	280 °C
Mass spectrometer	Agilent MSD 5973N
MS temperatures	Quadrupole 150 °C; Source 230 °C;
Ionisation	Electron impact 70 eV
Solvent Delay/MS	4,0 min
Retention time of parathion	14,69 min (RT parathion with GC NPD/ECD is used for calculation of relative retention times)

As slight fluctuations in the measurement conditions influence the retention time, usually relative retention times (RRT), related to a standard substance, are compared. The standard substance for the calculation of the RRT values in the tables was parathion (RRT = 1,000).

2.3 Analyte specific retention times and MS parameters

The analyte specific parameters for selected ion monitoring (SIM) of pesticides by GC-MS with EI ionisation are listed in Table 1. These data are completed by some indications about the sensitivity of detection, which can be expected if GC-MS with the most intense ion and GC-ECD or GC-NPD are used. The names of the individual active substances are supplemented by the CAS number (Chemical Abstracts Service), which is useful for the search in data bases. It is usually taken from [2], but there can be several numbers in individual cases, e.g. for isomers and racemates.

The RRT data for columns HP-5MS and DB-35MS in Table 1 are relative retention times compared to parathion (RRT = 1,00). The units for numbers presented in columns Ion 1 to Ion 4 are Da (or m/z). Three crosses in the columns MSD, ECD or NPD indicate a better sensitivity compared to two or one crosses.

Table 1 — Parameters of 691 analytes

Pesticide name	CAS-Nr.	RRT HP5MS	RRT DB35MS	Ion1	Ion2	Ion3	Ion4	MSD	ECD	NPD
Acephate	30560-19-1	0,47	0,58	136	94	95	96	xx	x	xx
Aclonifen	74070-46-5	1,40	1,34	264	266	212	77	xxx	x	x
Acrinathrin, 1	101007-06-1	1,57	1,41	207	181	281	208	xx	xxx	xx
Acrinathrin, 2	101007-06-1	1,58	1,46	181	208	207	93	xxx	xxx	xx
Alachlor	15972-60-8	0,89	0,88	160	188	146	237	xxx	xxx	x
Aldicarb, -sulfone	1646-88-4	0,33	0,43	68	80	65	69	xx	x	x
Aldrin	309-00-2	0,97	0,93	263	66	265	261	xxx	xxx	
Allidochlor	93-71-0	0,40	0,47	56	138	132	70	xxx	xx	xx
Ametryn	834-12-8	0,89	0,93	227	212	170	185	xxx		xx
Amidithion	919-76-6	0,96	1,03	125	131	93	143	x	x	x
Aminocarb	2032-59-9	0,73	0,79	151	150	136	208	xx		xx
Amitraz	33089-61-1	1,56	1,46	121	162	132	293	xx		x
Amitraz hydrolysis product (Dimethylaniline, 2,4,-	95-68-1	0,35	0,41	121	120	106	77	xxx		x
Amitraz-metabolite (BTS 27271)	33089-74-6	0,55	0,61	162	132	120	106	x		xx
Ancymidol	12771-68-5	1,36	1,30	228	107	121	215	xx		xxx
Anilazine	101-05-3	1,09	1,11	239	241	178	143	x	xx	x
Anilofos	64249-01-0	1,53	1,46	226	125	184	334	xx	xx	xx
Aramite, 1	140-57-8	1,32	1,20	185	175	319	334	x	x	
Aramite, 2	140-57-8	1,35	1,22	185	175	319	334	x	x	
Aspon	3244-90-4	0,99	0,90	211	210	253	378	xxx	xx	xxx
Atraton	1610-17-9	0,69	0,74	196	211	169	154	xx		x
Atrazine	1912-24-9	0,71	0,76	200	215	202	173	xxx	x	xxx
Atrazine, -desethyl	6190-65-4	0,63	0,71	172	174	187	145	xx	x	x
Atrazine, -desethyl-desisopropyl	3397-62-4	0,56	0,66	145	110	68	147	x	x	xx
Atrazine, -desisopropyl	1007-28-9	0,61	0,72	173	158	145	68	x	x	x
Azaconazole	60207-31-0	1,32	1,30	217	219	173	175	xx	x	xx
Azamethiphos	35575-96-3	1,44	1,39	215	155	125	109	x	x	xx
Azinphos-ethyl	2642-71-9	1,55	1,59	132	160	77	105	x	xx	xxx
Azinphos-methyl	86-50-0	1,55	1,55	160	132	77	105	xx	xx	xxx
Azobenzene	103-33-3	0,60	0,66	77	182	105	51	x	x	xxx
Azoxystrobin	131860-33-8	1,82	2,28	344	388	345	372	xx	xx	x
Beflubutamid	113614-08-7	1,13	1,03	91	176	221	193	xx	x	x
Benalaxyl	71626-11-4	1,45	1,35	148	91	206	204	xxx		x
Benazolin-ethyl	25059-80-7	1,09	1,13	170	271	198	134	xxx	xxx	x
Benfluralin	1861-40-1	0,64	0,61	292	264	276	335	xx	xxx	xx
Benfuracarb	82560-54-1	1,58	1,50	190	163	164	102	xx	x	xx
Benfuresate	68505-69-1	0,84	0,90	163	256	121	164	xxx	x	x
Benodanil	15310-01-7	1,43	1,38	231	323	203	76	xxx	xx	x
Benoxacor	98730-04-2	0,82	0,87	120	259	261	176	xx	xxx	xx

Table 1 *(continued)*

Pesticide name	CAS-Nr.	RRT HP5MS	RRT DB35MS	Ion1	Ion2	Ion3	Ion4	MSD	ECD	NPD
Bentazone-methyl	61592-45-8	0,89	0,94	212	105	254	133	xxx	x	xx
Benzoylprop-ethyl	22212-55-1	1,50	1,39	105	77	292	294	xxx	xx	x
Bifenazate	149877-41-8	1,52	1,44	300	258	199	196	xx		x
Bifenazate-metabolite (5-Phenyl-o-anisidine)	39811-17-1	0,95	1,01	184	156	199		x	x	x
Bifenox	42576-02-3	1,53	1,46	341	343	310	173	xx	xxx	x
Bifenthrin	82657-04-3	1,52	1,36	181	165	166	182	xxx	xxx	
Binapacryl	485-31-4	1,37	1,22	83	55	84	53	x	x	x
Bioallethrin S-cyclopentyl (Esbiol)	28434-00-6	1,12	1,00	123	136	79	107	xx	xxx	
Bioallethrin, cis- (Allethrin)	584-79-2	1,11	1,00	123	136	79	91	x	xxx	
Bioallethrin, trans- (Allethrin)	584-79-2	1,12	1,00	123	136	79	91	xx	xxx	
Bioresmethrin	28434-01-7	1,49	1,35	123	171	143	128	xxx	x	
Biphenyl	92-52-4	0,45	0,51	154	153	152	155	xxx		
Bitertanol, 1	70585-36-3	1,60	1,55	170	168	171	112	xx	x	x
Bitertanol, 2	70585-38-5	1,61	1,57	170	168	171	112	xx	x	x
Boscalid	188425-85-6	1,67	1,78	140	342	142	344	xx	xxx	xx
Bromacil	314-40-9	0,96	1,05	205	207	206	188	x	xx	xx
Metobromuron-metabolite (4-Bromoaniline)	106-40-1	0,41	0,49	171	173	92	65	xxx	x	x
Bromfenvinfos, (E)-	58580-14-6	1,24	1,13	267	269	323	325	xx	xx	x
Bromfenvinfos, (Z)-	58580-13-5	1,20	1,19	267	269	323	325	x	xx	x
Bromocyclen	1715-40-8	0,81	0,80	357	359	361	355	xxx	xxx	
Bromophos	2104-96-3	1,04	1,03	331	329	125	333	xxx	xxx	xxx
Bromophos-ethyl	4824-78-6	1,17	1,09	359	303	357	97	xxx	xxx	xxx
Bromopropylate	18181-80-1	1,51	1,40	341	343	339	183	xxx	xxx	
Bromuconazole, cis-	116255-48-2	1,51	1,44	173	295	175	293	xxx	x	xx
Bromuconazole, trans-	116255-48-2	1,53	1,48	173	175	295	293	xxx	x	xx
Bupirimate	41483-43-6	1,34	1,24	273	208	316	166	xxx	xx	xx
Buprofezin	69327-76-0	1,31	1,20	105	172	106	175	xxx	x	x
Butachlor	23184-66-9	1,21	1,08	176	160	57	188	xxx	xxx	xc
Butafenacil	134605-64-4	1,63	1,58	331	333	180	332	xx	xx	x
Butamifos	36335-67-8	1,24	1,17	286	200	232	202	x	xxx	xxx
Butralin	33629-47-9	1,05	0,95	266	224	295	267	xx	xx	x
Butylate	2008-41-5	0,47	0,50	57	146	156	174	xx		xx
Cadusafos	95465-99-9	0,65	0,67	159	158	88	97	xxx	xxx	xxx
Cafenstrole	125306-83-4	1,64	1,68	100	188	72	119	xx	xx	x
Captafol	2425-06-1	1,48	1,43	79	80	77	183	xx	x	x
Captan	133-06-2	1,11	1,19	79	149	77	80	xx	xx	x
Captan-metabolite (Tetrahydrophthalimide)	1469-48-3	0,50	0,62	79	151	80	77	xxx	x	x
Carbaryl-GC-artifact (1-Naphthol)	90-15-3	0,52	0,53	144	115	116	145	xx		
Carbetamide	16118-49-3	1,03	1,04	119	120	91	64	x		
Carbofuran	1563-66-2	0,70	0,80	164	149	131	122	xx		x
Carbofuran, -phenol	1563-38-8	0,42	0,46	164	149	131	122	xx	x	
Carbophenothion	786-19-6	1,45	1,34	157	342	121	153	xxx	xx	xxx

Table 1 *(continued)*

Pesticide name	CAS-Nr.	RRT HP5MS	RRT DB35MS	Ion1	Ion2	Ion3	Ion4	MSD	ECD	NPD
Carbosulfan	55285-14-8	1,51	1,37	160	118	163	164	xx	x	xx
Carboxin	5234-68-4	1,30	1,30	143	235	87	236	xx	x	x
Carfentrazone-ethyl	128639-02-1	1,46	1,32	312	340	330	290	x	xx	xx
Carvone	99-49-0	0,39	0,44	82	108	93	54	xxx		
Chinomethionat	2439-01-2	1,15	1,20	206	234	116	148	x	xxx	xxx
Chlorbicyclen	2550-75-6	1,09	1,04	229	272	237	273	xx	xxx	
Chlordimeform-metabolite (Chloro-2-methyl-aniline)	95-69-2	0,41	0,48	141	106	140	143	xx	x	xx
Metoxuron-metabolite (3-Chlor-4-methoxyaniline)	5345-54-0	0,48	0,57	142	157	114	144	xx	x	xx
Chloroaniline, 3- (Carbamate-hydrolysis product)	108-42-9	0,36	0,44	127	129	65	92	xx	xx	x
Chloroaniline, 4- (Monuron-hydrolysis product)	106-47-8	0,37	0,44	127	129	65	92	xxx	xx	x
Chlorbenside	103-17-3	1,14	1,14	125	127	268	270	xx	xx	
Chlorbenside, -sulfone	7082-99-7	1,44	1,39	125	127	89	126	xx	xxx	
Chlorobenzilate	510-15-6	1,39	1,26	251	253	139	111	xx	xx	
Chlorbufam	1967-16-4	0,70	0,75	223	127	164	225	xx	x	x
Chlordane, cis-	5103-71-9	1,20	1,13	375	373	377	371	xxx	xxx	
Chlordane, oxy-	27304-13-8	1,09	1,02	115	185	387	187	xxx	xxx	
Chlordane, trans-	5103-74-2	1,15	1,11	373	375	377	371	xxx	xxx	
Chlordene, trans-	3734-48-3	0,77	0,77	66	237	101	232	xxx	xxx	
Chlordimeform	6164-98-3	0,63	0,68	196	181	117	152	xxx		xx
Chlorethoxyfos	54593-83-8	0,59	0,61	153	97	301	299	xxx	xxx	xx
Chlorfenapyr	122453-73-0	1,37	1,24	59	247	328	408	xx	xx	xx
Chlorfenethol (BCPE)	80-06-8	1,10	1,10	251	139	253	111	x	x	
Chlorfenprop-methyl	14437-17-3	0,57	0,63	125	165	196	197	xx	xxx	
Chlorfenson	80-33-1	1,23	1,24	175	111	302	177	xx	xxx	
Chlorfenvinphos, (E)-	18708-86-6	1,08	1,03	267	269	323	325	xxx	xx	x
Chlorfenvinphos, (Z)-	18708-87-7	1,12	1,09	267	323	269	325	xxx	xx	x
Chlorflurenol-methyl	2536-31-4	1,15	1,18	215	152	217	274	xxx	xxx	
Chloridazon (Pyrazon)	1698-60-8	1,46	1,45	221	77	220	223	x	x	x
Chlormephos	24934-91-6	0,48	0,54	121	97	234	154	xx	xx	xxx
Chlornitrofen	1836-77-7	1,44	1,34	317	319	287	289	x	xxx	x
Chloroneb	2675-77-6	0,52	0,58	191	193	206	208	xxx	xx	
Chlorpropham	101-21-3	0,62	0,66	127	213	171	154	xx	x	x
Chloropropylate	5836-10-2	1,38	1,24	251	253	139	111	xxx	xx	
Chlorpyrifos	2921-88-2	1,00	0,97	197	199	314	97	xxx	xxx	xxx
Chlorpyrifos-methyl	5598-13-0	0,87	0,89	286	288	125	290	xxx	xxx	xxx
Chlorthal-dimethyl	1861-32-1	1,02	0,97	301	299	303	332	xxx	xxx	
Chlorothalonil	1897-45-6	0,79	0,91	266	264	268	270	xx	xxx	x
Chlorthiamide	1918-13-4	0,85	1,00	170	172	205	171	x	x	x
Chlorthion	500-28-7	1,02	1,04	109	125	297	299	x	xxx	xxx
Chlorthiophos, 1	21923-23-9	1,38	1,26	222	224	257	97	x	xxx	xx
Chlorthiophos, 2	77503-29-8	1,40	1,28	269	325	271	97	xx	xxx	xx