SLOVENSKI STANDARD
SIST-TP CEN/TR 15641:2007

01-november-2007

Analize živil - Določevanje ostankov pesticidov z LC-MS/MS - Parametri tandemske masne spektrometrije

Food analysis - Determination of pesticide residues by LC-MS/MS - Tandem mass spectrometric parameters

Lebensmitteluntersuchung - Bestimmung von Pestizidrückständen mit LC-MS/MS - Parameter für die Tandem-Massenspektrometrie

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Analyse des produits alimentaires - Détermination des résidus de pesticides par CL-SM/SM - Parametres de spectrométrie de masse en tandem

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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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2003-01.Slovenski inštitut za standardizacijo. Razmnoževanje celote ali delov tega standarda ni dovoljeno.

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TECHNICAL REPORT

RAPPORT TECHNIQUE

TECHNISCHER BERICHT

CEN/TR 15641

August 2007

ICS 67.050

English Version

Food analysis - Determination of pesticide residues by LC-MS/MS - Tandem mass spectrometric parameters

Analyse des produits alimentaires - Détermination des résidus de pesticides par CL-SM/SM - Paramètres de spectrométrie de masse en tandem

Lebensmitteluntersuchung - Bestimmung von Pestizidrückständen mit LC-MS/MS - Parameter für die Tandem-Massenspektrometrie

This Technical Report was approved by CEN on 25 July 2007. It has been drawn up by the Technical Committee CEN/TC 275.

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Foreword

This document (CEN/TR 15641:2007) 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 multi methods involving extraction of residues from foods and clean up of the extract to obtain as many pesticide residues as possible in the purified extracts. Afterwards the extracts can be analysed by different kinds of instruments.

The hyphenation of liquid chromatography (LC) and tandem mass spectrometry (MS/MS) has become one of the most universal, but selective and sensitive analysis techniques for identification and quantification of pesticide residues in extracts of foods.

For the ionization of the analytes (M) in LC-MS/MS, electro spray ionization (ESI) or atmospheric pressure chemical ionization (APCI) interfaces are most commonly used. Depending on the selected polarity of the ionization, protonated or deprotonated molecular ions like $[M+H]^+$ or $[M-H]^-$ are generated. Using ESI, relatively stable adducts (clusters) of the analytes (M) and components of the mobile phase like ions (e.g. ammonium, sodium or potassium ions) or solvent molecules (e.g. methanol) can be additionally formed. To obtain a high yield of quasi molecular ions and therefore to increase the sensitivity of the measurement these clusters have to be broken. When using ESI the formed adducts are accelerated by a potential (e.g. declustering potential or cone voltage) in the ion source at atmospheric pressure. Due to collision with neutral gas molecules the clusters (adducts) are broken in the ion source. Under certain conditions some adduct-ions formed are stable (e.g. with ammonium cation $[M+NH_4]^+$). It should be mentioned, however, that ammonium adducts are usually not generated in the APCI-mode and that their formation when using ESI strongly depends on the concentration of ammonium ions in the LC mobile phase. Adduct ions like $[M+NH_4]^+$ can also be used alternatively for quantification if they were shown to provide reproducible signals. Sodium adducts are usually not suitable for quantitative analysis as their formation and decomposition tends to be highly irreproducible.

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The selective determination of each target compound is performed by acquisition of characteristic product ions of the precursor ion (quasi molecular ion or adduct) in the 'selected reaction monitoring' (SRM). Decomposition of the precursor ions in the collision cell is induced by collision with molecules of the collision gas (nitrogen or argon). The collision energy (CE) necessary for fragmentation is a very substantial parameter of the MS/MS optimization for maximum sensitivity.

If LC-MS/MS measurement should be used not only for quantification but also for confirmation of positive findings, at least two SRM transitions have to be recorded.

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 of plant origin that use LC-MS/MS, such as the standards in preparation:

prEN 15637 "Foods of plant origin — Determination of pesticide residues using LC-MS/MS following methanol extraction and clean up using diatomaceous earth"

prEN 15662 "Foods of plant origin — Determination of pesticide residues using GC-MS and/or LC-MS/MS following acetonitrile extraction/partitioning by dispersive SPE — QuEChERS-method"

To facilitate the determination of active substances and/or metabolites using LC-MS/MS, Table 1 specifies the precursor ions and product ions suitable for quantification, which can be used independently of the type of triple quadrupole mass spectrometer. However, using an ion trap mass spectrometer other product ions can be generated or at least the relative intensities of the ions are different to triple quadrupole instruments. Furthermore, the additional parameters declustering potential (DP), collision energy (CE), relative retention times and an approximate classification of detection sensitivity are presented in Table 1. These were derived using the API 2000[1)] and should be applicable at least for other instruments of the API type (Applied Biosystems).

2 Analyte specific parameters for selective reaction monitoring of pesticides

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2.1 General

All values indicated in Table 2 were acquired using the above mentioned LC-MS/MS system 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 manufacturer or after adjustment also on devices of other manufacturers (see in 2.3)

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1) Instruments of the API type are products supplied by Applied Biosystems (Foster City, CA, USA). This information is given for the convenience of users of this Technical Report and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

2.2 LC Parameters

The following LC 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.

HPLC pump	HP1100®[2] Binary Pump (G1312A)
Autosampler	HP1100® (G1313A)
Injection volume	20 µl
Column	Phenomenex®[3] Aqua 5 µ C18 125 Å, 50 mm × 2 mm
Mobile phase A	Methanol/water 2+8 (*V/V*) with 5 mmol/l ammonium formate
Mobile phase B	Methanol/water 9+1 (*V/V*) with 5 mmol/l ammonium formate
Flow rate	0,2 ml/min
Column temperature	20 °C
Gradient	Linear:
	0 min 0 % B
	11 min 100 % B
	23 min 100 % B
	25 min 0 % B
	36 min 0 % B (equilibration time)

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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 Table 1 was Imazalil (RRT = 1,000).

It could be shown that the use of other mobile phase systems does not shift the order of elution substantially, except for those compounds which are sensitive to the pH of eluent. Often retention data can be transferred to HPLC columns of other manufacturers, if a typical reversed phase is used.

2.3 General MS/MS parameters

The following general MS/MS 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

MS/MS instrument	Applied Biosystems API 2000®
Ion source	Turbo Ion Spray® (ESI)

[2] Instruments of the HP type are products supplied by Agilent Technologies Inc. (Palo Alto, CA, USA). This information is given for the convenience of users of this Technical Report and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

[3] HPLC columns of the Aqua type are products supplied by Phenomenex (Torrance, CA, USA). This information is given for the convenience of users of this Technical Report and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Table 1 — Ion source and general parameters

Ion polarity	positive	Gas 2 temperature	400 °C
Curtain gas	nitrogen, 35 psi (241 kPa)	Resolution MS 1	unit
Collision gas	nitrogen, 2 arbitrary units	Resolution MS 2	unit
Ion spray voltage	5500 V	Dwell time	25 ms
Gas 1	nitrogen, 60 psi (414 kPa)	Focusing potential	360 V
Gas 2	nitrogen, 60 psi (414 kPa)		

2.4 Analyte specific MS/MS Parameters

The analyte specific parameters for selective reaction monitoring of pesticides are listed in Table 1 [1]. The names of the individual analytes are supplemented by the CAS number (Chemical Abstracts Service), which is useful for the search in databases. It is usually taken from [2], but there can be several numbers in individual cases, e.g. for isomers and racemates.

The values for the declustering potential (DP), indicated in Table 1 for the API 2000®, have to be increased by 20 V for tandem mass spectrometers of the type API 3000® or API 4000®. It is to be considered that DP breaks not only the clusters but can already induce fragmentation of the precursor ions (at too high values) in the ESI source before entering into the first MS.

NOTE It is not necessary to change the collision energy for API 3000® or API 4000® instruments as the differences for the CE are less than 5 V.

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When using tandem mass spectrometers of other manufacturers the correct value for the collision energy should be determined in tuning experiments for analytes with particularly low and high collision energy since it has relevant influence on the intensity of the SRM transition. Based on these data, in a first approximation the values for the collision energy of further pesticides can be derived proportionally from the data in the table and the observed difference (difference of CE at instrument X to the API 2000®). The values of the declustering potential (other name “cone voltage”) for other instruments have to be determined individually. On the intensity of the SRM transitions this parameter has a smaller influence than the collision energy.

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Table 2 — MS/MS Parameters of 497 analytes

Pesticide (Metabolite)	CAS No.	Ionization	Quasi molecular ion	Q1 Mass (amu)	Declustering potential (V)	1st SRM Q3 Mass (amu)	1st SRM Collision energy (V)	2nd SRM Q3 Mass (amu)	2nd SRM Collision energy (V)	Relative retention on endcapped RP phase [a]	Sensitivity of detection [b]
2,4-D	94-75-7	ESI -	[M-H]-	219,0	-21	160,9	-14	124,9	-34	0,69	***
2,4-DB	94-82-6	ESI -	[M-H]-	247,0	-66	160,8	-12	124,9	-34	0,86	***
2-Naphthyloxyacetic acid	120-23-0	ESI +	[M+NH4]+	220,1	36	157,1	19	127,1	43	0,66	n.a.
2-Naphthyloxyacetic acid	120-23-0	ESI -	[M-H]-	201,1	-71	143,0	-18	114,9	-50	0,66	***
3,4,5-Trimethacarb	2686-99-9	ESI +	[M+H]+	194,1	61	137,1	15	122,0	35	0,86	****
4-CPA	122-88-3	ESI -	[M-H]-	185,0	-71	126,8	-18	140,7	-12	0,47	**
Acephate	30560-19-1	ESI +	[M+H]+	184,1	6	124,9	25	142,9	13	0,11	****
Acetamiprid	135410-20-7	ESI +	[M+H]+	223,0	36	126,0	27	90,1	45	0,58	****

Pesticide (Metabolite)	CAS No.	Ionization	Quasi molecular ion	Q1 Mass (amu)	Declustering potential (V)	1st SRM Q3 Mass (amu)	1st SRM Collision energy (V)	2nd SRM Q3 Mass (amu)	2nd SRM Collision energy (V)	Relative retention on endcapped RP phase [a]	Sensitivity of detection [b]
Acibenzolar-S-methyl	135158-54-2	ESI	+ [M+H]+	210,9	26	136,1	39	140,0	31	0,92	**
Aclonifen	74070-46-5	ESI	+ [M+H]+	265,0	56	182,1	39	218,0	33	0,99	**
Acrinathrin	101007-06-1	ESI	+ [M+NH4]+	559,1	26	208,1	23	181,1	43	1,20	*
Alachlor	15972-60-8	ESI	+ [M+H]+	270,1	31	238,1	15	162,2	25	0,97	****
Aldicarb	116-06-3	ESI	+ [M+NH4]+	208,1	1	89,1	21	116,0	13	0,66	****
Aldicarb-sulfoxide	1646-87-3	ESI	+ [M+H]+	207,1	36	89,1	17	131,9	11	0,15	****
Aldoxycarb	1646-88-4	ESI	+ [M+NH4]+	240,1	11	148,0	19	86,1	27	0,19	****
Alloxydim	55634-91-8	ESI	+ [M+H]+	324,2	11	178,3	27	234,2	19	0,77	****
Ametryn	834-12-8	ESI	+ [M+H]+	228,1	36	186,2	25	96,1	35	0,90	****
Amidosulfuron	120923-37-7	ESI	+ [M+H]+	370,0	21	217,9	31	260,9	19	0,46	****
Aminocarb	2032-59-9	ESI	+ [M+H]+	209,1	16	152,1	19	137,2	31	0,74	****
Amitraz	33089-61-1	ESI	+ [M+H]+	294,2	16	163,1	21	122,1	41	1,19	****
Amitrole	61-82-5	ESI	+ [M+H]+	85,0	51	58,2	29	57,0	23	0,07	**
Aramit	140-57-8	ESI	+ [M+NH4]+	352,1	41	191,2	19	105,0	57	1,09	****
Atrazine	1912-24-9	ESI	+ [M+H]+	216,1	21	174,0	25	103,9	27	0,83	****
Atrazine, 2-hydroxy-	2163-68-0	ESI	+ [M+H]+	198,1	66	69,0	47	156,2	25	0,65	****
Atrazine, desethyl-	6190-65-4	ESI	+ [M+H]+	188,1	56	104,0	33	146,0	25	0,59	***
Atrazine, desethyl-2-hydroxy-	6190-65-4	ESI	+ [M+H]+	170,1	66	128,1	23	86,0	31	0,14	****
Atrazine, desisopropyl-	1007-28-9	ESI	+ [M+H]+	174,1	56	104,2	31	96,0	27	0,39	***
Avermectin B1a	65195-55-3	ESI	+ [M+NH4]+	890,5	41	305,1	35	145,2	43	1,33	***
Avermectin B1b	65195-56-4	ESI	+ [M+NH4]+	876,5	41	291,1	35	145,2	43	1,26	***
Azaconazole	60207-31-0	ESI	+ [M+H]+	300,0	56	231,0	23	159,0	37	0,86	****
Azamethiphos	35575-96-3	ESI	+ [M+H]+	325,0	16	183,0	21	139,2	33	0,74	****
Azimsulfuron	120162-55-2	ESI	+ [M+H]+	425,1	31	182,1	23	156,1	43	0,55	***
Azinphos-ethyl	2642-71-9	ESI	+ [M+H]+	346,0	26	132,2	21	160,2	15	0,96	****
Azinphos-methyl	86-50-0	ESI	+ [M+H]+	318,0	16	132,2	21	160,2	13	0,89	****
Azocyclotin	41083-11-8	ESI	+ [M-OH]+	369,2	76	204,8	23	287,0	17	n.a.	n.a.
Azoxystrobin	131860-33-8	ESI	+ [M+H]+	404,1	36	371,9	19	343,9	29	0,90	****
Beflubutamid	113614-08-7	ESI	+ [M+NH4]+	373,1	26	91,2	47	162,1	39	1,00	***
Benalaxyl	71626-11-4	ESI	+ [M+H]+	326,2	26	148,2	27	208,2	21	1,01	****
Bendiocarb	22781-23-3	ESI	+ [M+H]+	224,1	6	167,2	13	108,9	21	0,76	****
Benfuracarb	82560-54-1	ESI	+ [M+H]+	411,2	1	195,1	31	252,0	19	1,05	****
Benomyl	17804-35-2	ESI	+ [M+H]+	291,1	16	160,1	35	192,2	17	1,03	**
Bensulfuron-methyl	83055-99-6	ESI	+ [M+H]+	411,1	51	148,9	27	119,0	51	0,85	***

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Pesticide (Metabolite)	CAS No.	Ionization	Quasi molecular ion	Q1 Mass (amu)	Declustering potential (V)	1st SRM Q3 Mass (amu)	1st SRM Collision energy (V)	2nd SRM Q3 Mass (amu)	2nd SRM Collision energy (V)	Relative retention on endcapped RP phase [a]	Sensitivity of detection [b]
Bentazone	25057-89-0	ESI -	[M-H]-	239,1	-51	132,0	-32	197,0	-24	0,33	***
Benzoximate	29104-30-1	ESI +	[M+H]+	364,1	1	199,1	17	105,1	35	1,02	****
Bifenox	42576-02-3	ESI +	[M+NH4]+	358,9	6	309,9	17	189,1	35	1,04	**
Bifenthrin	82657-04-3	ESI +	[M+NH4]+	440,1	36	181,2	21	166,2	55	1,33	****
Binapacryl	485-31-4	ESI +	[M+NH4]+	340,1	26	83,2	21	54,9	63	1,23	*
Bioresmethrin	28434-01-7	ESI +	[M+NH4]+	356,2	21	171,2	21	128,1	53	1,23	n.a.
Bitertanol	55179-31-2	ESI +	[M+H]+	338,2	1	70,0	25	269,2	15	1,02	***
Boscalid	188425-85-6	ESI +	[M+H]+	343,0	71	307,0	27	139,9	27	0,92	****
Bromacil	314-40-9	ESI +	[M+H]+	261,0	21	205,0	19	187,9	37	0,75	***
Bromophos-ethyl	4824-78-6	ESI +	[M+H]+	394,9	51	338,7	23	366,9	17	1,20	**
Bromoxynil	1689-84-5	ESI -	[M-H]-	273,9	-46	79,0	-36	80,9	-40	0,56	***
Bromuconazole	116255-48-2	ESI +	[M+H]+	378,0	46	159,0	37	69,9	35	0,95	***
Bupirimate	41483-43-6	ESI +	[M+H]+	317,1	31	166,1	33	108,1	35	0,98	****
Buprofezin	69327-76-0	ESI +	[M+H]+	306,2	6	201,2	17	116,2	21	1,09	****
Butafenacil	134605-64-4	ESI +	[M+NH4]+	492,1	36	180,1	59	331,0	29	0,95	**
Butocarboxim	34681-10-2	ESI +	[M+NH4]+	208,1	1	116,1	11	75,0	15	0,66	****
Butocarboxim-sulfoxide	34681-24-8	ESI +	[M+H]+	207,1	6	131,9	11	75,0	19	0,13	****
Butoxycarboxim	34681-23-7	ESI +	[M+NH4]+	240,1	6	106,0	19	166,0	13	0,18	**
Buturon	3766-60-7	ESI +	[M+H]+	237,1	41	84,1	21	126,1	37	0,85	n.a.
Butylate	2008-41-5	ESI +	[M+H]+	218,2	66	57,1	29	156,2	17	1,07	***
Cadusafos	95465-99-9	ESI +	[M+H]+	271,1	66	159,0	19	97,0	47	1,05	***
Carbaryl	63-25-2	ESI +	[M+H]+	202,1	11	144,9	15	127,0	35	0,79	****
Carbendazim	10605-21-7	ESI +	[M+H]+	192,1	41	160,0	25	132,0	41	0,64	****
Carbetamide	16118-49-3	ESI +	[M+H]+	237,1	21	118,1	19	192,0	13	0,72	****
Carbofuran	1563-66-2	ESI +	[M+H]+	222,1	16	165,1	17	123,0	29	0,75	****
Carbofuran, 3-hydroxy-	16655-82-6	ESI +	[M+H]+	238,1	21	181,1	15	163,1	19	0,56	***
Carbosulfan	55285-14-8	ESI +	[M+H]+	381,2	36	118,1	25	160,2	21	1,31	***
Carboxin	5234-68-4	ESI +	[M+H]+	236,1	26	142,9	21	86,9	33	0,78	****
Carfentrazone-ethyl	128639-02-1	ESI +	[M+H]+	412,0	66	365,9	25	345,9	31	0,99	***
Cartap hydrochloride	15263-52-2	ESI +	[M+H]+	238,1	26	73,0	37	150,1	19	0,14	**
Chinomethionat	2439-01-2	ESI +	[M+H]+	234,9	41	207,1	21	163,0	39	0,72	*
Chlorbromuron	13360-45-7	ESI +	[M+H]+	292,9	51	182,1	23	204,0	21	0,92	***
Chlorbufam	1967-16-4	ESI +	[M+NH4]+	241,0	6	172,1	17	154,1	27	0,91	***
Chlorfenvinphos	470-90-6	ESI +	[M+H]+	358,9	36	155,0	19	99,2	43	1,00	****

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