Intralab Validation of the EN 15662 Method for the Determination of Pesticide Residues Using a Fused-Core™ Ascentis® Express RP-Amide HPLC Column by LC-MS/MS and Clean-up by Dispersive SPE (QuEChERS)

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Abstract:
LC/MS/MS methods have become very popular for the analysis of pesticides in food. Several methods currently exist for their extraction from a variety of different food matrices. A new method, known as the "QuEChERS" (Quick, Easy, Cheap, Effective, Rugged, and Safe) method has recently been introduced and optimised. This employs dispersive solid phase extraction (SPE) and chromatography mass spectrometry (GC-MS and LC-MS-MS) techniques. Recently this method became the European Norm (EN 15662). Whilst this method typically uses C18 HPLC reverse phase columns, in this article we describe an intra-lab comparison and validation procedure using a new Ascentis Express RP-Amide column.

Experimental:

The European guideline SANCO/3131/2007 document (Method Validation and Quality Control Procedures for Pesticide Residues Analysis in Foods and Feeds) was followed for the following different representative fruit and plant origin matrices:

- Pear as sugar matrix
- Kiwi as acid matrix
- Lettuce as chlorophyll matrix
- Maize flour as cereal

Preparation of Standard Solution

Signal suppression in MS/MS detection can arise from the matrix and other interferences. To avoid this, the calibration standard solutions were prepared using acetonitrile blank matrix extracts.

As recommended in the EN 15662:2008 method, the results obtained for the analytes to be identified in the sample extract are compared with those obtained for the pesticides in the calibration solutions. Although the use of matrix-matched standards is preferred, for a first estimate of the residue level of pesticides in food, or to show their absence, standard solutions in pure solvent can be used. They can also be used for quantification if preliminary experiments indicate that any suppression or enhancement effects experienced do not significantly affect the results obtained. As soon as relevant residue concentrations are detected (e.g. suspected MRL violations), a more precise determination using matrix-matched standards, or using the standard addition method, should be used.

NOTE 1. Matrix effects influence the response of target analytes in sample extracts compared to the response of standard solutions in pure solvent.
NOTE 2. The calibration range should be appropriate to the residue concentrations to be quantified. Thus, it may be necessary to construct more than one calibration graph.

A group of 29 compounds (**Table 1**) was used as a representative group of different pesticides; these fall into the following categories: acaricides, insecticides, fungicides, and so forth.

Abamectina B1a	Acetamiprid	Aldicarb	Azoxystrobin
Buprofezin	Carbendazim	Carbofuran	Clothianidin
Cyazofamide	Cyprodinil	Difenconazol	Dimethoate
Ethoprofos	Ethofenprox	Fenhexamide	Fenpropimorph
Fenpyroximate	Flufenoxuron	Imidacloprid	Methiocarb
Methomyl	Pirimicarb	Rotenone	Setoxydim
Spinosad A e D	Spiroxamine	Tebufenozide	Thiabendazole
Thiametoxam			

Table 1 Representative group of pesticides for use in calibration

The calibration curve was prepared using six replicates of each of five concentrations over the ranges equivalent to the average concentrations expected:

- 0,006 mg/Kg (< LOQ)
- 0,01 mg/Kg (LOQ)
- 0,1 mg/Kg
- 0,2 mg/Kg
- 1 mg/Kg (MRL)

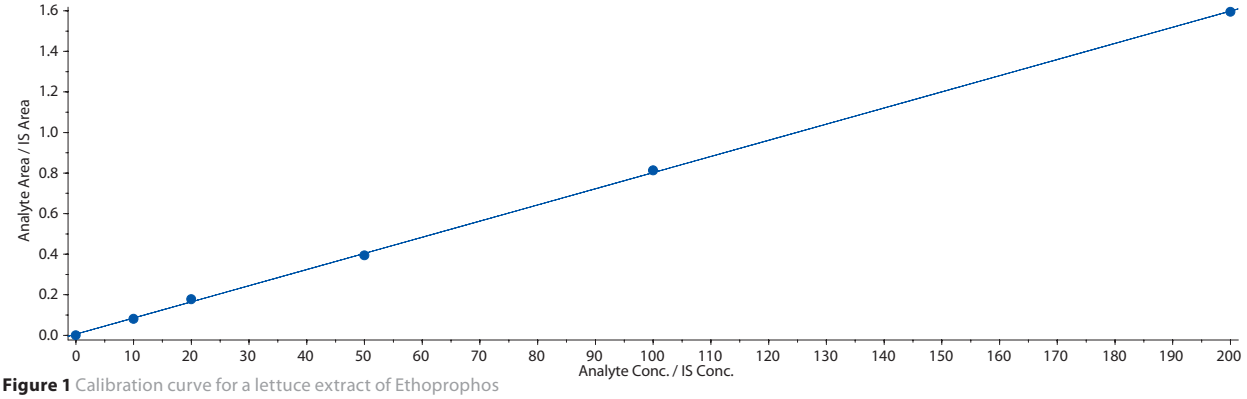

Figure 1 Calibration curve for a lettuce extract of Ethoprophos

(continued on page 4)

The calibration standard curve used the following five points of concentration: 0,01-0,02-0,05-0,1 and 0,2 µg/ml of each pesticide spiked into each of the above matrices. Triethylphosphate was used as internal standard as described in the EN 15662 method. A typical example of lettuce extract of Ethoprophos is shown on **Figure 1**.

Sample preparation:

As suggested in the SANCO document, frozen samples can be used to avoid the overheating that results from adding MgSO4. The samples were homogenised and then spiked with standard solutions.

The QuEChERS Multiresidue method (4) shown in **Figure 2** and described in EN 15662 was used to prepare the final samples to be injected into the LC/MS/MS system.

Figure 2 Summary of the QuEChERS Multiresidue method

The full-size chart can be downloaded from ***sigma-aldrich.com/quechers*** Technical Resources, QuEChERS Multiresidue Method (JWP)

Chromatography:

The HPLC method developed here utilises an Ascentis® Express RP-Amide (Supelco®, Bellefonte) as an alternative to the C18 column traditionally used in the EN 15662 method.

Ascentis Express RP-Amide HPLC columns are the most recent product additions to the Supelco HPLC product line. Combining an embedded polar group (EPG) stationary phase with the Fused-Core™ particles, Ascentis Express RP-Amide provides a host of useful benefits to the HPLC chromatographer. The benefits come from both the phase technology and the particle technology, and can be summarised as:

Fused-Core Benefits

- Twice the efficiency of traditional 3 µm HPLC columns
- Half the backpressure of sub-2 micron columns
- Capable of UHPLC performance on traditional HPLC systems

RP-Amide Benefits

- Alternative reversed-phase selectivity to C18
- Improved peak shape for bases
- 100 % aqueous compatible reversed-phase column

Alternative Selectivity

Ascentis Express RP-Amide provides increased selectivity for polar compounds, especially those that can act as a hydrogen-bond donor. The selectivity differences between the RP-Amide and the C18 can be a useful tool in method development. In many cases, when peaks co-elute on a C18 phase, the RP-Amide can be substituted to achieve separation without a change in mobile phase.

Operating conditions:

column: Ascentis Express RP Amide, 10 cm x 2.1 mm ID, 2.7 µm particle size
HPLC: Shimadzu Prominence UFLC XR
MS/MS Detector: Applied Biosystems API 3200
mobile phase A: ammonium formate solution in water (5 mmol/l, 0.1 % Formic Acid)
mobile phase B: ammonium formate solution in methanol (5 mmol/l, 0.1 % Formic Acid)
column temp.: 40 °C
injection volume: 2 µl
elution: gradient:

Time	Mobile Phase A %	Mobile Phase B %
0	95	5
0.5	90	10
12	5	95
15	85	95

Results:

The recovery data (**Table 2**) were compared with the data described in the EN 15662 method and were shown to have comparable results that demonstrate the validity of our method. In most cases, an improved RSD % was obtained.

The results (**Figure 3**) show that the Ascentis Express RP-Amide HPLC column is particularly suitable for the resolution of those components having a log K_{ow} < 0,5 that are weakly retained on a C18 column. The separation of a complex mix of 200 compounds on the Ascentis Express RP-Amide column under the same conditions is shown in **Figure 4**. The original method suggests that different columns and chromatographic conditions are needed for the analysis of this type of molecule, whereas our experimental conditions indicate that it is possible to resolve all molecules in one chromatogram with a good peak shape, speed and high resolution. This is particularly useful for routine analysis and for higher numbers of samples.

Conclusions

All of the analytical data that has been generated in this intra-lab validation complies with EN 15662:2008 method requirements and therefore we can assert that the Ascentis Express RP-Amide column is a valid alternative to C18. The selectivity differences between the RP-Amide and the C18 can be a useful tool in method development. In many cases, when peaks co-elute on a C18 phase, the Ascentis Express RP-Amide can be substituted to achieve separation without a change in mobile phase. Further, the QuEChERS extraction method provided good recovery and high reproducibility.

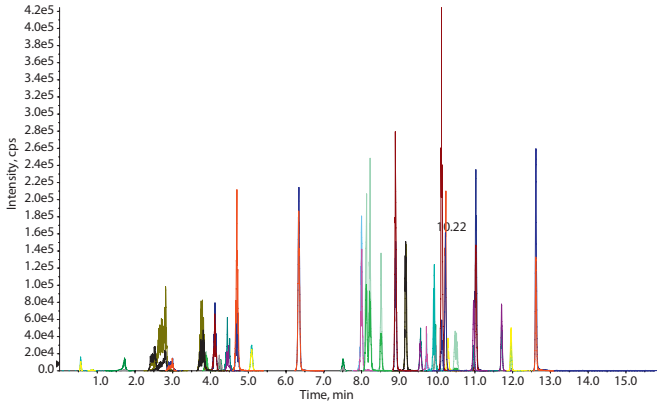

Figure 3 LC/MS/MS chromatogram of spiked group of 29 compounds used in this validation on Ascentis Express RP-Amide

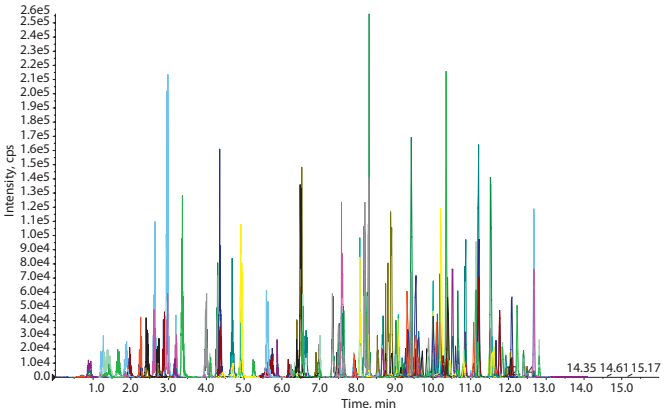

Figure 4 LC/MS/MS chromatogram of a mix of 200 compounds. The full list with this article can be downloaded from ***sigma-aldrich.com/quechers*** under Technical Resources

Under routine conditions with high numbers of samples, the Ascentis® Express RP-Amide column shows high robustness, reproducible peak shapes and excellent resolution. More than 1500 samples were injected before it was decided to replace the column.

References

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[5] S.J. Lehotay, Interlaboratory Validation of the QuEChERS Method to Analyze Pesticide Residues in Fruits and Vegetables, Proceedings AOAC Annual Meeting, St. Louis, MO USA (2004).
[6] S.J. Lehotay, K. Mastovska, A.R. Lightfield, Use of Buffering and Other Means to Improve Results of Problematic Pesticides in a Fast and Easy Method for Residue Analysis of Fruits and Vegetables, J. AOAC Int., Mar – Apr 2005; 88(2): 615 – 629.

Featured Products

Description	Cat. No.	Price £
HPLC Column		
Ascentis Express RP-Amide 10 cm x 2.1 mm	**53913-U**	**357.00**

Related Information

Additional information on QuEChERS methods and suitable products can be found under ***sigma-aldrich.com/quechers***

Compound (100 µg/Kg)	Rec %	EN 15662 Rec %	RSD %	EN 15662 RSD %
Abamectina b1a NH4	95.4		5.0	
Abamectina b1b NH4	92.5		17.6	
Acetamiprid	98.6	97.0	12.2	13
Aldicarb	107.7	85.0	5.9	23
Azoxystrobin	97.9	95.0	4.3	14
Buprofezin	97.3	95.0	2.6	6
Carbendazim	83.7	91.0	7.9	12
Carbofuran	100.7	99.0	3.3	11
Clotianidin	106.0		13.9	
Cyazofamide	101.3	90.0	9.3	17
Cyprodinil	101.5	93.0	13.1	14
Ciromazina	29.7		6.2	
Difenoconazol	97.6	97.0	5.9	12
Dimetoate	100.5	96.0	16.7	11
Ethoprophos	96.5	99.0	3.0	8
Etofenprox	82.9	94.0	6.1	12
Fenexamide	74.5	93.0	11.2	19
Fenpropimorph	107.3	100.0	4.7	11
Fenpyroximate	91.6	95.0	6.5	12
Flufenoxuron	91.7	96.0	5.4	17
Imidacloprid	105.3	102.0	5.4	18
Methiocarb	90.8		6.6	
Methomyl	98.5	99.0	5.1	18
Pirimicarb	103.8	95.0	5.7	11
Pimetrozine	36.8		5.1	
Rotenone	102.6		4.6	
Setoxydim	71.9		4.4	
Spinosad A	108.6		10.8	
Spinosad D	93.4		4.1	
Spiroxamine 1	89.5	90.0	4.2	17
Tebufenozide	88.1		9.9	
Tiabendazol	86.1	101.0	6.5	12
Thiametoxam	105.6	97.0	8.6	20

Table 2 Recovery data for the Ascentis Express RP-Amide method compared with the standard EN 15662 method

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Reference Table of Compounds and Ions

Ion 1: Quantifier
Ion 2: Qualifier

name	Rt time	Ion 1	Ion 2
Ciromazina 1	0,9	167,1	125,2
Ciromazina 2	0,9	167,1	108,2
Methamidophos 1	0,9	142	125
Methamidophos 2	0,9	142	94
Acephate 1	1,3	184,1	143
Acephate 2	1,3	184,1	125
Propamocarb 1	1,4	189,1	102,1
Propamocarb 2	1,4	189,1	144,1
Omethoate 1	1,7	214	125
Omethoate 2	1,7	214	109
pimetrozina 1	1,9	218,1	105,1
pimetrozina 2	1,9	218,1	78,1
Aldicarb sulfossido 1	2	207,1	132,1
Aldicarb sulfossido 2	2	207,1	89,1
Aldicarb solfone 1	2,3	223,1	148,1
Aldicarb solfone 2	2,3	223,1	166
Aldoxycarb 1	2,3	240,1	148,1
Aldoxycarb 2	2,3	240,1	86,1
Oxamyl 1	2,4	237	72
Oxamyl 2	2,4	237	90,1
Methomyl 1	2,7	163	88
Methomyl 2	2,7	163	106,1
Oxydemeton-methyl 1	2,7	247	109
Oxydemeton-methyl 2	2,7	247	169,1
Demeton-S-metil solfone 1	2,9	263	108,9
Demeton-S-metil solfone 2	2,9	263	169
Monocrotophos 1	3,2	224	126,9
Monocrotophos 2	3,2	224	98,1
Thiametoxam 1	3,2	292,1	211,2
Thiametoxam 2	3,2	292,1	181,1
Pirimicarb desmethil 1	3,3	225,2	168,2
Pirimicarb desmethil 2	3,3	225,2	72,1
Trichlorfon 1	3,9	273,9	109
Trichlorfon 2	3,9	273,9	220,9
Tiabendazolo 1	4	202,1	175,1
Tiabendazolo 2	4	202,1	131,1
Imidacloprid 1	4,1	256,1	175,2
Imidacloprid 2	4,1	256,1	209
Dimetoato 1	4,3	230	199
Dimetoato 2	4,3	230	125
Metiocarb Solfossido 1	4,3	242	185,1
Metiocarb Solfossido 2	4,3	242	170,1
3 Hidroxycarbofuran 1	4,4	238	181,1
3 Hidroxycarbofuran 2	4,4	238	163,2
Clotianidin 1	4,4	250,1	169
Clotianidin 2	4,4	250,1	132
Fenthion-oxon-sulfoxide 1	4,6	279,1	263,9
Fenthion-oxon-sulfoxide 2	4,6	279,1	104,1
Acetamiprid 1	4,7	223,2	126,1
Acetamiprid 2	4,7	223,2	90,1
Cymoxanil 1	4,7	199,1	128,1
Cymoxanil 2	4,7	199,1	111
Mevinfos 1	4,9	242,1	127
Mevinfos 2	4,9	242,1	193,1
Pirimicarb 1	4,9	239,2	72
Pirimicarb 2	4,9	239,2	182,2
Chlorotalonil 1	5	244,7	112
Chlorotalonil 2	5	244,7	174,8
Dicloran 1	5	204,8	175
Dicloran 2	5	204,8	168,5
Fenthion-oxon-sulfone 1	5	295,1	217,1
Fenthion-oxon-sulfone 2	5	295,1	104,1
Aldicarb 1	5,3	208,1	88,9
Aldicarb 2	5,3	208,1	116,1
Thiacloprid 1	5,6	253	126,1
Thiacloprid 2	5,6	253	186,1
Oxadixil 1	5,7	279,2	132,1
Oxadixil 2	5,7	279,2	219,2
Dicamba 1	5,8	219	144,5
Dicamba 2	5,8	219	174,8
Paraoxon-Methyl 1	5,8	248	202,1
Paraoxon-Methyl 2	5,8	248	109
Formothion 1	5,9	258	199,1
Formothion 2	5,9	258	125
Dichlorvos 1	6,2	221	108,9
Dichlorvos 2	6,2	221	127,1
Metribuzin 1	6,2	215,2	84,1
Metribuzin 2	6,2	215,2	187,2
Demeton-S-metil 1	6,3	231	89,1
Demeton-S-metil 2	6,3	231	61

name	Rt time	Ion 1	Ion 2
Propoxur 1	6,4	210,2	111
Propoxur 2	6,4	210,2	168,1
Carbofuran 1	6,5	222,2	123,1
Carbofuran 2	6,5	222,2	165,1
Malaoxon 1	6,5	315,1	126,9
Malaoxon 2	6,5	315,1	99
Bromacil 1	6,9	261	204,9
Bromacil 2	6,9	261	187,9
Fenitrothion 1	6,9	278,1	124,9
Fenitrothion 2	6,9	278,1	108,8
Fenthion sulfoxide 1	6,9	295	279,9
Fenthion sulfoxide 2	6,9	295	109,1
Imazalil 1	7	297,1	201,1
Imazalil 2	7	297,1	159
Disulfoton sulfoxid 1	7,3	291	185
Disulfoton sulfoxid 2	7,3	291	213,1
Carbaryl 1	7,4	202,1	145,1
Carbaryl 2	7,4	202,1	127,1
Metalaxyl 1	7,4	280,2	160,1
Metalaxyl 2	7,4	280,2	220,1
Metazachlor 1	7,5	278,1	134,1
Metazachlor 2	7,5	278,1	210,2
Disulfoton solfone 1	7,6	324,1	307,1
Disulfoton solfone 2	7,6	324,1	125
Ehtoxyquin 1	7,6	218,2	160,1
Ethoxyquin 2	7,6	218,2	174,1
Paraoxon 1	7,6	276,2	220
Paraoxon 2	7,6	276,2	94
Heptenophos 1	7,8	251,1	126,9
Heptenophos 2	7,8	251,1	109
Pyrimethanil 1	7,9	200,2	82,2
Pyrimethanil 2	7,9	200,2	107,1
Fenpropimorph 1	8	304,4	147,2
Fenpropimorph 2	8	304,4	117,1
2,4 D 1	8,1	218,8	160,9
2,4 D 2	8,1	218,8	124,9
Fenthion-oxon 1	8,1	263,1	231
Fenthion-oxon 2	8,1	263,1	216
Spiroxamine 1	8,1	298,3	144,2
Spiroxamine 2	8,1	298,3	100,1
Methidation 1	8,2	303	85
Methidation 2	8,2	303	145,1
Azinphos methyl 1	8,4	318,1	132,1
Azinphos methyl 2	8,4	318,1	160,1
Azoxystrobin 1	8,6	404,3	372,1
Azoxystrobin 2	8,6	404,3	344,1
Diethofencarb 1	8,6	268,3	226,1
Diethofencarb 2	8,6	268,3	180,1
Dimetomorf 1	8,6	388,2	301,01
Dimetomorf 2	8,6	388,2	165,11
Nuarimol 1	8,7	315,1	252,1
Nuarimol 2	8,7	315,1	81
Pyrifenox 1	8,7	295,1	93
Pyrifenox 2	8,7	295,1	262,9
Triforine 1	8,7	435	389,7
Triforine 2	8,7	435	215
Phosmet 1	8,8	317,9	133,1
Phosmet 2	8,8	317,9	160,1
Terbutilazina 1	8,8	230,1	174,1
Terbutilazina 2	8,8	230,1	104
Triforina 1	8,8	435	389,71
Triforina 2	8,8	435	215,01
Dimethomorph 1	8,9	388,2	301
Dimethomorph 2	8,9	388,2	165,1
Malathion 1	8,9	331,1	126,9
Malathion 2	8,9	331,1	99,1
Methiocarb 1	8,9	226,1	121,2
Methiocarb 2	8,9	226,1	169,1
Parathion-Methyl 1	8,9	264	125
Parathion-Methyl 2	8,9	264	232
Bromuconazole 1	9	378	159
Bromuconazole 2	9	378	70,2
Diclorprop 1	9	232,8	161
Diclorprop 2	9	232,8	124,9
Fluazifop 1	9	328,1	282,1
Fluazifop 2	9	328,1	254
Triadimefon 1	9	294,1	197,1
Triadimefon 2	9	294,1	225,1
Boscalid 1	9,1	343,1	307,1
Boscalid 2	9,1	343,1	140,1

name	Rt time	Ion 1	Ion 2
Cyproconazolo 1	9,1	292,2	70
Cyproconazolo 2	9,1	292,2	125
Myclobutanil 1	9,1	289,1	70,1
Myclobutanil 2	9,1	289,1	125
Pyridaphenthion 1	9,1	341,1	189,1
Pyridaphenthion 2	9,1	341,1	205,1
Triadimenol 1	9,1	296,2	69,9
Triadimenol 2	9,1	296,2	227
2,4,5 T 2	9,2	254,8	160,8
2,4,5,T 1	9,2	254,8	196,8
Ethoprophos 1	9,2	242,9	97
Ethoprophos 2	9,2	242,9	130,9
Bupirimate 1	9,3	317,2	108
Bupirimate 2	9,3	317,2	166,2
Ciproconazolo 1	9,3	292,2	70,01
Ciproconazolo 2	9,3	292,2	125,01
Iprovalicarb 1	9,3	321,2	119,2
Iprovalicarb 2	9,3	321,2	203,2
Triazophos 1	9,3	314,2	162,2
Triazophos 2	9,3	314,2	119,2
Ditalimfos 1	9,4	300,1	130,1
Ditalimfos 2	9,4	300,1	148,1
Epoxiconazolo 1	9,4	330,2	121,2
Epoxiconazolo 2	9,4	330,2	101,1
Fluquinconazolo 1	9,4	376	306,9
Fluquinconazolo 2	9,4	376	349
Ioxinyl 1	9,4	369,8	126,8
Ioxinyl 2	9,4	369,8	242,8
Iprodione 1	9,4	330	101
Iprodione 2	9,4	330	143
Mecarbam 1	9,4	330,1	97
Mecarbam 2	9,4	330,1	227,1
Mepanipyrim 1	9,4	224,2	106,1
Mepanipyrim 2	9,4	224,2	76,9
Mepronil 1	9,4	270,2	119,2
Mepronil 2	9,4	270,2	228,1
Dichlofluanid NH4 1	9,5	350,1	224
Dichlofluanid NH4 2	9,5	350,1	123
Methoxyfenozide 1	9,5	369,3	149,1
Methoxyfenozide 2	9,5	369,3	133,2
Propyzamide 1	9,5	256	173
Propyzamide 2	9,5	256	190
Chlorpropham 1	9,6	231,1	154,1
Chlorpropham 2	9,6	231,1	172
Cyprodinil 1	9,6	226,2	93
Cyprodinil 2	9,6	226,2	77
Fenarimol 1	9,6	331,1	81
Fenarimol 2	9,6	331,1	268
Tetraconazolo 1	9,6	372,1	158,9
Tetraconazolo 2	9,6	372,1	69,9
2,4 DB 1	9,7	246,9	160,9
2,4 DB 2	9,7	246,9	124,9
Bromuconazolo 1	9,7	378	159,01
Bromuconazolo 2	9,7	378	70,21
Fenbuconazolo 1	9,7	337	125
Fenbuconazolo 2	9,7	337	70
Flusilazole 1	9,7	316,2	165,2
Flusilazole 2	9,7	316,2	247
Rotenone 1	9,7	395,3	213,1
Rotenone 2	9,7	395,3	192,1
Benalaxyl 1	9,8	326,2	148,1
Benalaxyl 2	9,8	326,2	208,1
Difenilammina 1	9,8	170,1	93,1
Difenilammina 2	9,8	170,1	153,1
Fludioxonyl 1	9,8	246,9	126
Fludioxonyl 2	9,8	246,9	169
Kresoxym-methyl 1	9,8	314,2	116,1
Kresoxym-methyl 2	9,8	314,2	206,1
Fenexamide 1	9,9	302,1	97,1
Fenexamide 2	9,9	302,1	55,1
Fenoxicarb 1	9,9	302,3	88,1
Fenoxicarb 2	9,9	302,3	116,1
Penconazole 1	9,9	284,1	159
Penconazole 2	9,9	284,1	70
Phenthoat 1	9,9	321,1	163,1
Phenthoat 2	9,9	321,1	79,1
Propiconazole 1	9,9	342,1	158,9
Propiconazole 2	9,9	342,1	68,9
Quinalphos 1	9,9	299,1	163,1
Quinalphos 2	9,9	299,1	147

name	Rt time	Ion 1	Ion 2
spinosad A1	9,9	732,6	142
2 Fenil fenolo 1	10	171,1	72
2 Fenil fenolo 2	10	171,1	89
Chlorfenvinphos 1	10	359	155,1
Chlorfenvinphos 2	10	359	99,1
Diazinon 1	10	305,2	97,1
Diazinon 2	10	305,2	169,2
Etrimfos 1	10	293,1	125
Etrimfos 2	10	293,1	265
Prochloraz 1	10	376,1	308
Prochloraz 2	10	376,1	265,9
Tebuconazolo 1	10	308,2	70,1
Tebuconazolo 2	10	308,2	125
Teflutrin 1	10	436,1	177,1
Teflutrin 2	10	436,1	127
Diflubenzuron 1	10,1	309	155,9
Diflubenzuron 2	10,1	309	289
Parathion 1	10,1	292,1	236
Parathion 2	10,1	292,1	94,1
Tebufenozide 1	10,1	353,3	133,1
Tebufenozide 2	10,1	353,3	297,2
Tholilfluanid 1	10,1	364,1	137
Tholilfluanid 2	10,1	364,1	237,7
Bitertanol 1	10,2	338,2	70,1
Bitertanol 2	10,2	338,2	269,1
Dichlofenthion 1	10,2	315,1	258,81
Dichlofenthion 2	10,2	315,1	286,91
Fenthion 1	10,2	279,2	169,1
Fenthion 2	10,2	279,2	247
Fipronil 1	10,2	434,8	329,8
Fipronil 2	10,2	434,8	249,9
Hexaconazole 1	10,2	314,1	70,1
Hexaconazole 2	10,2	314,1	158,9
spinosad D 1	10,2	746,6	142
TFF 1	10,2	327	152,1
TFF 1	10,2	327	152,1
TFF 2	10,2	327	77,1
TFF 2	10,2	327	77,1
Pirimiphos-methyl 1	10,3	306,2	108
Pirimiphos-methyl 2	10,3	306,2	164,1
Pyrazophos 1	10,3	374	222,1
Pyrazophos 2	10,3	374	194,1
Difenoconazolo 1	10,4	406,1	251,1
Difenoconazolo 2	10,4	406,1	337
Famoxadone 1	10,4	392,2	330,9
Famoxadone 2	10,4	392,2	238
Pyraclostrobin 1	10,4	388,2	194,1
Pyraclostrobin 2	10,4	388,2	163,1
Disulfoton 1	10,5	275,1	89,1
Disulfoton 2	10,5	275,1	61
Phosalone 1	10,5	367,9	182,1
Phosalone 2	10,5	367,9	111
Tolclofos metile 1	10,5	301	268,8
Tolclofos metile 2	10,5	301	175,1
Bromophos metile 1	10,6	366,9	334,7
Bromophos metile 2	10,6	366,9	125
Diniconazolo 1	10,6	326,2	70
Diniconazolo 2	10,6	326,2	159
Chlorpyrifos-metile 1	10,7	322	124,9
Chlorpyrifos-metile 2	10,7	322	289,8
Clofentezin 1	10,7	303,1	138,1
Clofentezin 2	10,7	303,1	102,1
Indoxacarb 1	10,7	528,2	203,1
Indoxacarb 2	10,7	528,2	218,1
Trifloxystrobin 1	10,7	409,1	186
Trifloxystrobin 2	10,7	409,1	206,1
Triflumizole 1	10,7	346	278
Triflumizole 2	10,7	346	73
Iprodione 1	10,8	328	140,6
Profenofos 1	10,9	372,9	302,8
Profenofos 2	10,9	372,9	97,1
Buprofezin 1	11	306,2	201,2
Buprofezin 2	11	306,2	116,1
Piperonil butossido 1	11,1	356,3	177,1
Piperonil butossido 2	11,1	356,3	119,2
Pirimiphos-ethyl 1	11,1	334,2	198,2
Pirimiphos-ethyl 2	11,1	334,2	182,2
Tebufenpyrad 1	11,1	334,2	145,1
Tebufenpyrad 2	11,1	334,2	117,1
Amitraz 1	11,2	294,3	163,2
Amitraz 2	11,2	294,3	122,2

name	Rt time	Ion 1	Ion 2
Hexaflumuron 1	11,3	459	438,7
Hexaflumuron 2	11,3	459	275,9
Dichlofenthion 1	11,4	315	258,9
Dichlofenthion 2	11,4	315	286,9
Ethion 1	11,4	384,9	199
Ethion 2	11,4	384,9	171
Pyriproxifen 1	11,4	322,2	96,1
Pyriproxifen 2	11,4	322,2	185,1
Quinoxyfen 1	11,4	308	197,2
Quinoxyfen 2	11,4	308	162,1
Chlorpyrifos 1	11,5	350	97
Chlorpyrifos 2	11,5	350	198
Hexytiazox 1	11,5	353,3	228,1
Hexytiazox 2	11,5	353,3	168,1
Procymidone 1	11,5	301,1	256,3
Procymidone 2	11,5	301,1	67,1
Spiromesifen 1	11,5	371,2	273
Spiromesifen 2	11,5	371,2	255,3
Bromopropylate 1	11,6	446,2	209,2
Bromopropylate 2	11,6	446,2	410,9
Fluazinam 1	11,6	462,9	415,6
Fluazinam 2	11,6	462,9	397,5
Pendimethalin 1	11,6	282,2	212,2
Pendimethalin 2	11,6	282,2	194,1
Propargite 1	11,6	368,2	231,2
Propargite 2	11,6	368,2	175,1
Fenpyroximate 1	11,7	422,2	366,1
Fenpyroximate 2	11,7	422,2	135,1
Flucitrinate 1	11,7	469,3	199,2
Flucitrinate 2	11,7	469,3	181,1
Teflubenzuron 1	11,7	379	338,9
Teflubenzuron 2	11,7	379	358,6
abamectina b1b NH4 1	11,8	876,5	291,1
abamectina b1b NH4 2	11,8	876,5	145,2
Fenpropathrin 1	11,8	350,2	125,1
Fenpropathrin 2	11,8	350,2	97,2
Lufenuron 1	11,8	510,9	158,2
Lufenuron 2	11,8	510,9	141,2
Profluralin 1	11,8	348,2	55,2
Profluralin 2	11,8	348,2	275,9
Spirodiclofen 1	11,8	411,2	313,1
Spirodiclofen 2	11,8	411,2	294,9
Fenazaquin 1	11,9	307,1	161,3
Fenazaquin 2	11,9	307,1	147,2
Flufenoxuron 1	11,9	489	158,1
Flufenoxuron 2	11,9	489	141,1
abamectina b1a NH4 1	12	890,5	305,1
abamectina b1a NH4 2	12	890,5	145,1
Cyflutrin 1	12	451,2	191,1
Cyflutrin 2	12	451,2	127
Lambda-cyhalothrin 1	12	467,1	225
Lambda-cyhalothrin 2	12	467,1	141,1
Cypermetrin 1	12,1	433,1	190,9
Cypermetrin 2	12,1	433,1	127,2
Deltametrina 1	12,1	523,1	280,6
Deltametrina 2	12,1	523,1	181,3
Pyridaben 1	12,1	365,2	147,2
Pyridaben 2	12,1	365,2	309,1
Bromophos etile 1	12,2	394,9	338,8
Bromophos etile 2	12,2	394,9	366,6
Esfenvalerate 1	12,2	437,3	125,01
Esfenvalerate 2	12,2	437,3	167,01
Fenvalerate 1	12,2	437,3	125
Fenvalerate 2	12,2	437,3	167
Acrinathrin 1	12,3	559,2	208
Acrinathrin 2	12,3	559,2	181,1
Carbosulfan 1	12,3	381,3	118,2
Carbosulfan 2	12,3	381,3	160,1
Prothiofos 1	12,3	344,9	240,9
Prothiofos 2	12,3	344,9	132,9
Permethrin 1	12,4	408,2	183,1
Permethrin 2	12,4	408,2	153,2
Permethrina 1	12,4	408,2	183,11
Permethrina 2	12,4	408,2	153,21
tau-Fluvalinate 1	12,4	520,2	181,1
tau-Fluvalinate 2	12,4	520,2	208
Etofenprox 1	12,6	394,3	177,2
Etofenprox 2	12,6	394,3	107,1
Bifenthrin 1	12,7	440,1	181,2
Bifenthrin 2	12,7	440,1	166,2
Chlofenapyr 1	13,6	426	409,1
Chlofenapyr 2	13,6	426	59,1