

Single SPE-step method for the simultaneous determination of GC- MS and LC-MS amenable pesticides in water

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Uruguay vs Greece:6/2

**Uruguayan have visited Greece in
the frame of APFA project**

Horacio Heinzen

Veronica Cesio

Lucia Pareja

Silvina Niell

Gabriel Gonzalez

Joaquin Gonzalez



Requite Visit

Marios Zortas

And now Zisis Vryzas

We feel we owe you more visits



6/6/2011

3rd Latin American Pesticide Residue
Workshop Food and Environment, Uruguay
8-11 May 2011

Universities

Orestiada



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Thessaloniki



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Equipment



1 Thermo TSQ Quantum Discovery MAX LC/MS/MS



3 GC-MSn (ion trap)



5 HPLC systems with various detectors



3 GC systems with various detectors

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This map illustrates the Thracian Peninsula and the surrounding Balkan region. Key geographical features include the Thracian Plain (Θράκη), the Chalkidiki Peninsula (Χαλκιδική), and the Macedonian region (Μακεδονία). Major rivers such as the Strymon (Στρυμώνα), Nestos (Νέστος), and Axios (Αχίος) are depicted. Significant lakes shown are Lake Vistonis (Α. Βιστωνίς), Lake Koronoi (Α. Κορώνειο), and Lake Petron (Α. Πετρών). The map also indicates the locations of various cities and towns, including Thessaloniki (Θεσσαλονίκη) and Kavala (Καβάλα). The map is framed by a red border.

Past Projects: INTERREG

Surface water quality of Macedonia-Thrace

Automated sampling and analysis of industrial wastes

Study of leaching mechanisms of herbicides in the major maize growing areas in Greece

Transboundary river contamination with pesticides

Target analysis of the past projects

Analytical Methods

- in-house method for 160 pesticides and metabolites
- 7 inorganic anions (Standard methods of American Public health association/American Water Works Association/ Water Environment)
- 19 metals
- pH, T, DO, TDS, Cond, Sal, Redox, BOD₅



New Project for monitoring pesticide residues in surface and groundwater of Northern Greece 2010-2013

**Single SPE-step method for the simultaneous
determination of GC-MSn (151 pesticides and
metabolites) and LC-MS/MS (124 pesticides and
metabolites) amenable pesticides in water.**

Target analysis for 275 pesticides and metabolites
Non target screening from NIST library in the GC-MS
system

Sampling of Surface water bodies

**Sampling sites: riparian drainage
canals, lakes, rivers, ponds,
surface water tank**



Groundwater sampling



Samples from field were brought to the Lab within 24 h and SPE was performed a day later



SPE

- LiChrolut EN 500 mg Cartridge
 - Conditioning
 - 5 ml MeOH
 - 5 ml H₂O
 - Sample application
 - Load 1 L water sample
 - Elution of absorbed pesticides
 - 5 ml Ethyl acetate/MeOH (90/10)
 - 6ml Hexane
 - Reduce to ~ 200 µL (in ethyl acetate)
 - 100 µL GC-MS analysis
 - 100 µL concentrate to dry, reconstitute to 1000 µL initial mobile phase : MeOH (90:10%), LC-MS/MS analysis
- Recovery studies
 - 5 and 2 stock solutions for GC and LC respectively (properties and retention time)
 - Each stock recoveries were studied separately



GC-MS method

GC - Ion Trap Mass Spectrometer operational conditions



OVEN PROGRAM

INITIAL TEMPERATURE	80	°C
RATE 1	4	°C/MIN
FINAL TEMPERATURE	200	°C
HOLD TIME	3	min
RATE 2	6	°C/MIN
FINAL TEMPERATURE	230	°C
HOLD TIME	10	min
RATE 3	20	°C/MIN
FINAL TEMPERATURE	270	°C
HOLD TIME	14	min

INJECTOR

BASE TEMPERATURE	220 °C
MODE	SPLITLESS WITH SURGE
SPLIT FLOW	70 ml/min
SPLITLESS TIME	2 min
SURGE PRESSURE	92 kPa
SURGE DURATION	0.5 min
STOP PURGE AT	2 min
SAMPLE VOLUME	2 µl

MS METHOD

ELECTRON IONISATION	EI
ION SOURCE TEMPERATURE	220 °C
TRANSFER LINE TEMPERATURE	280 °C
POLARITY	POSITIVE
MICRO SCANS	3
MAX ION TIME	25 ms
ELECTRON IMPACT	70 eV
EMISSION CURRENT	250 µA

CARRIER METHOD

MODE	CONSTANT FLOW
FLOW	1 ml/min
GAS SAVER	ON
GAS SAVER FLOW	10 ml/min
GAS SAVER TIME	10 min

GC CAPILLARY COLUMNS

VARIAN WCOT FUSED SILICA (30 m×0.25 mm I.D. with a 0.25-µm)
COATING CP-CIL 8 CB LOW BLEED /MS

GC detection mode (Full Scan and MS/MS)

No	COMPOUND	Quantitation	1st	2nd
1	ACLONIFEN	full scan 264	212	194
2	ACRINATHRIN	ms 181 181	152	
3	a-HCH	full scan 181	183	219
4	alachlor	ms 160 160	132	117
5	aldrin	full scan 263	293	257
6	alphamethrin	ms 181 181	152	
7	ametryne	full scan 227	212	170
8	ANTHRACENE	full scan 178	152	
9	atrazine	ms 200 200	122	164
10	azinphos ethyl	ms 160 132	104	105
11	azinphos methyl	ms 160 132	104	105
12	BENFLURALIN	ms 292 292	264	206
13	b-HCH	ms 181 145	146	181
14	bifenthrin	ms 181 166	165	181
15	bromacil	full scan 205	207	190
16	bromophos ethyl	full scan 359	303	357
17	bromopropylate	full scan 341	183	185
18	bupirimate	ms 193 193	165	
19	buprofezin	full scan 175	172	105
20	butachlor	ms 160 160	132	130
21	cadusaphos	ms 159 131	97	125
22	caffeine	ms 194 194	193	165
23	captafol	full scan 79	77	276
24	captan	ms 149 105	107	149
25	c-HCH (lindane)	ms 181 145	146	181
26	chinomethionate	ms 234 206	148	174
27	chlorfevinphos	full scan 267	269	323
28	chlorobenzilate	ms 251 251	139	179
29	chloropropylate	ms 251 251	139	
30	chlorothalonil	ms 266 266	231	
31	chlorpyrifos ethyl	ms 314 286	258	314
32	chlorpyrifos-Methyl	ms 286 286	271	241
33	CHLORTHAL			
33	DIMETHYL	ms 301 301	273	258
34	chlorthion	ms 297 280	250	267
35	cis- chlordan	full scan 375	373	266
36	COUMAPHOS	full scan 362	226	334
37	cyanazine	ms 225 225	189	172
38	cyanophos	ms 243 148	210	211
39	cycloate	full scan 154	55	83
40	cyfluthrin	ms 226 199	206	226
41	cypermetrin	ms 181 181	152,1	
42	DEA	ms 172 172	105	130
43	deltamethrin	ms 181 181	152	137
44	DEMETON O&S	full scan 88	60	126
45	desmetryn	full scan 213	198	171
46	d-HCH	full scan 181	183	219
47	dialifos	ms 208 208,1	181,1	167,1
48	diazinon	ms 179 179	137	164
49	dichlofluanid	full scan 167	123	224
50	dichlorvos	full scan 109	185	79

No	COMPOUND	Quantitation	1st	2nd
51	dieldrin	full scan 79	279	263
52	DIFLUBENZURON	ms 157 141	129	157
53	diphenylamine	ms 169 169	167	166
54	DISULFOTON SULFON	full scan 213	153	125
55	DISULFOTON SULFOXIDE	full scan 97	168	125
56	endosulfan I	full scan 195	207	160
57	endosulfan II	full scan 195	207	160
58	endosulfan sulfate	full scan 272	274	229
59	endrin	full scan 209	245	263
60	ETHALFLURALIN	ms 316 276	232	248
61	ethion	full scan 231	153	384
62	ETRIDIAZOLE	ms 211 183	140	211
63	fenamiphos	ms 303 195	180	260
64	FENAMIPHOS SULFON	full scan 320	292	214
65	FENAMIPHOS SULFOXIDE	full scan 304	160	196
66	fenarimol	ms 139 139	111	75
67	fenazaquin	ms 145 117	145	115
68	fenchlorphos	full scan 285	287	289
69	fenitrothion	ms 260 260	217	228
70	fenoxycarb	ms 255 186	255	157
71	fenpropimorph	ms 128 110	128	
72	fensulfothion	ms 293 293	265	237
73	fenthion	ms 278 278	245	169
74	FENTHION SULFONE	full scan 310	106	125
75	FENTHION SULFOXIDE	full scan 279	278	294
76	fenvalerate	ms 225 147	225	198
77	flutriafol	ms 219 123	219	
78	FLUVALINATE	ms 250 250	200	215
79	folpet	full scan 260	130	104
80	fonofos	full scan 137	109	246
81	furalaxyl	full scan 95	242	152
82	HCB	ms 284 284	249	214
83	heptachlor	full scan 272	274	337
84	heptachlor-exo- epoxide	full scan 353	355	351
85	ISODRINE	full scan 193	263	293
86	isophenphos	full scan 213	185	255
87	isopropalin	full scan 280	238	264
88	L-cyhalothrin	ms 181 181	152	
89	malaoxon	full scan 127	99	173
90	malathion	ms 173 127	99	145
91	mecarbam	full scan 160	131	296
92	methacrifos	full scan 208	180	125
93	methidathion	full scan 145	85	
94	methoxychlor	full scan 227	209	228
95	mevinphos cis/trans	ms 127 109	127	79
96	mirex	full scan 272	274	237
97	napropamide	full scan 72	128	271
98	nuarimol	full scan 139	107	235
99	o,p-DDD	full scan 235	237	165
100	o,p-DDE	full scan 246	248	318

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No	COMPOUND	Quantitation	1st	2nd
101	o,p-DDT	full scan 235	237	165
102	omethoate	ms 156 141	110	126
103	OXYFLUORFEN	full scan 252	317	300
104	p,p-DDD	full scan 235	237	165
105	p,p-DDE	full scan 246	318	248
106	p,p-DDT	full scan 235	237	165
107	paraaxon ethyl	ms 149 119	91	132
108	paraaxon methyl	ms 230 136	200	
109	parathion ethyl	ms 291 263	235	233
110	parathion methyl	ms 263 246	153	216
111	PCNB	ms 295 237	265	295
112	pebulate	ms 128 128	72	100
113	PENTACHLORO			
113	BENZENE	full scan 250	215	108
114	permethrin	ms 183 183	168	165
115	phenthoate	full scan 274	121	246
116	phorate	ms 260 231	260	203
117	phorate sulfone	ms 199 171	143	199
118	phorate sulfoxide	ms 199 171	143	199
119	phosalone	full scan 182	184	367
120	phosmet	ms 160 160	133	105
121	pirimiphos ethyl	full scan 168	318	333
122	pirimiphos methyl	full scan 290	276	180
123	procymidone	ms 283 255	254	283
124	profenofos	full scan 339	337	208
125	prometon	full scan 168	210	183
126	prometryne	ms 241 199	226	184
127	propachlor	full scan 120	176	93
128	propanil	ms 161 161	134	126
129	propazine	ms 214 172	214	
130	propham	full scan 93	137	179
131	PROQUINAZIDE	ms 288 245	288	217
132	prothoate	ms 115 73	97	115
133	pyrazophos	full scan 221	232	265
134	quinalphos	full scan 156	157	146
135	SILTHIOFAM	ms 252 252	197	210
136	simazine	ms 201 173	186	138
137	simetryne	full scan 213	170	155
138	TEFLUTHRIN	ms 177 177	127	137
139	terbacil	ms 161 144	161	133
140	terbufos	full scan 231	203	233
141	TERBUFOS			
141	SULFONE	full scan 199	153	125
142	terbumeton	full scan 169	210	154
143	terbutryn	full scan 185	226	170
144	tetrachlorvinphos	full scan 329	331	109
145	tetradifon	full scan 159	229	356
146	thiobencarb	full scan 100	72	125
147	tolyfluanid	full scan 137	181	238
148	TRALCOXYDIM	ms 283 227,1	265,2	226,1
149	triaozofos	ms 285 257	162	172
150	trifluralin	ms 264 264	206	160
151	vinclozolin	full scan 178	212	285

LC-MS/MS method



Column: Thermo HyPURITY C18
(150x2.1 mm, 5 μ m)

Injection Volume: 20 μ L Full loop injection
Column Temperature: 40 $^{\circ}$ C
Autosampler Tray Temperature : 20 $^{\circ}$ C

Mobile phase Gradient

Time (min)	%A
0	80
20	0
35	0
40	80
59	80

Mobile phase A: 90:10 water:acetonitrile
+ 5 mM ammonium acetate

Mobile phase B: 10:90 water:acetonitrile
+ 5 mM ammonium acetate

Flow rate: 0.2
mL/min

Optimization of MS/MS parameters for each analyte separately

Parent M/Z

Product M/Z

Collision energy

Probe Position

MS Parameters

Mode: Electro-Spray Ionization

Spray voltage: 4000 V

Seath gas pressure: 30

Aux gas pressure: 10

Capillary temperature: 325 $^{\circ}$ C

Collision pressure: 1.5 mTorr

LC-MS/MS optimization

A/A	COMPOUND	1st transition			2nd transition			polarity
		Q1	Q3	CE	Q1	Q3	CE	
1	acetamiprid	223	90,1	32	223	126	22	+
2	abamectin	890,6	305	24	890,6	567	15	+
3	acetochlor	270	148,1	20	270	224	10	+
4	acibenzolar-S-methyl	211,1	136	30	211,1	140	24	+
5	aminocarb	209,2	137,1	23	209,2	152,1	14	+
6	azoxystrobin	404	344	23	404	372	13	+
7	beflubutamid	373,1	91	19	373,1	162	32	+
8	benalaxyl	326,2	148,1	21	326,2	208,1	15	+
9	bitertanol	338,1	70,1	21	338,1	269,1	10	+
10	boscalid	343	139,8	18	343	306,9	19	+
11	carbendazim	192,2	132,1	31	192,2	160	18	+
12	carfentrazone-ethyl	412	345,8	21	412	365,8	18	+
13	chloridazone	221,9	92	28	221,9	104	20	+
14	chlorotoluron	213,1	72,1	16	213,1	140	24	+
15	cinidon-ethyl	411	106,9	39	411	347,9	21	+
16	clofentezine	303	101,9	33	303	137,9	15	+
17	clomazone	240,1	89	47	240,1	125	19	+
18	cyazofamid	325,2	108	12	325,2	261,2	10	+
19	cyhalofop-butyl	375,1	119,9	30	375,1	255,9	13	+
20	cyproconazole	292	70,1	25	292	125	32	+
21	cyromazine	167,1	108,1	20	167,1	125	18	+
22	diclofop-methyl	357,9	120,1	28	357,9	280,9	18	+
23	difenoconazole	406	251	29	406	337	14	+
24	diflufenican	395	245,9	41	395	265,9	21	+
25	dimethenamid	276	168	26	276	243,9	15	+
26	dimethoate	229,9	124,9	22	229,9	198,9	10	+
27	dimethomorph	388,2	165	33	388,2	301,1	18	+
28	dimoxystrobin	327,1	115,9	23	327,1	204,9	11	+
29	diuron	233,1	133	44	233,1	160	29	+
30	dodemorph	282,4	98,1	24	282,4	116,1	21	+
31	epoxyconazole	330	100,9	41	330	121	20	+
32	etofumasate	304	121	24	304	161	18	+
33	ethoprophos	243	97	29	243	130,9	19	+
34	etofenprox	394,2	107	36	394,2	177	14	+
35	etoxazole	360,2	112,9	52	360,2	140,9	34	+
36	famoxadone	392,1	238	18	392,1	331,1	10	+
37	fenamidone	312,1	92	26	312,1	235,9	15	+
38	fenbuconazole	337,1	70	19	337,1	124,9	33	+
39	fenhexamid	302	55	38	302	97	24	+
40	fenoxaprop-p-ethyl	362,1	121	31	362,1	287,9	17	+
41	fenpropimorph	304,2	117,1	59	304,2	147,1	28	+
42	fenpyroximate	422,2	134,9	33	422,2	366	15	+
43	flupyrifluorid	434,9	249,8	32	434,9	329,8	18	-
44	flonicamid	230	173,9	19	230	202,9	19	+
45	flufenacet	384,2	282	21	384,2	328,1	13	+
46	flufenoxuron	462,9	397,8	10	462,9	415,8	10	-
47	fludioxonil	247,1	126,1	33	247,1	169,1	37	-
48	flufenacet	364,1	151,9	17	364,1	194,2	10	+
49	flufenoxuron	489	140,8	47	489	157,8	21	+
50	flumioxazin	372,1	299	35	372,1	327	18	+
51	fluometuron	233	72,1	36	233	160	29	+
52	fluopicolide	382,9	144,8	52	382,9	172,8	32	+
53	fluoxastrobin	458,9	187,9	33	458,9	426,9	16	+
54	fluquinconazole	376	306,8	28	376	348,9	19	+
55	flurochloridone	311,9	145	46	311,9	292	21	+
56	flusilazole	316,2	165	31	316,2	247,1	18	+
57	flutolanil	324,1	241,9	24	324,1	261,9	18	+
58	fosthiazate	284	103,9	19	284	227,9	10	+
59	fuberidazole	185,1	65	43	185,1	157	21	+
60	hexythiazox	353,1	167,9	24	353,1	227,9	14	+
61	imazalil	297,1	158,9	32	297,1	200,9	17	+
62	imidachloprid	256	175	21	256	209	17	+
63	indoxacarb	528,1	149,8	24	528,1	202,8	41	+
64	iprovalicarb	321,1	119	19	321,1	203,1	10	+
65	isoproturon	207,3	72,1	16	207,3	165,1	12	+
66	isoxaflutol	377	219,7	51	377	250,9	22	+
67	kresoxym-methyl	314	116	33	314	206,1	10	+
68	lenacil	235	136	33	235	153	13	+
69	linuron	248,9	159,9	18	248,9	182	13	+
70	mepanipyrim	224,1	77	36	224,1	106	26	+
71	metaflumizone	505	284,9	52	505	301,9	20	-
72	metalaxyl	280,1	160,1	23	280,1	220,1	13	+
73	metamitron	203	104	29	203	175	16	+
74	metazachlor	278,1	134	23	278,1	209,9	11	+
75	metconazole	320,1	70	21	320,1	124,9	35	+
76	methiocarb	226,1	121,1	17	226,1	169,1	10	+
77	methomyl	163,1	88	10	163,1	106,1	10	+
78	methoxyfenozide	369,2	132,9	24	369,2	148,9	17	+
79	metrafenone	409,2	209,1	15	409,2	226,9	24	+
80	metribuzin	215	84,1	20	215	187,1	18	+
81	molinat	188,1	83,2	19	188,1	126,1	13	+
82	myclobutanil	289,1	70,1	20	289,1	124,9	32	+
83	oxadiazon	362	176,9	32	362	219,9	20	+
84	penconazole	284,1	70	15	284,1	158,9	32	+
85	penicuron	329,1	98,9	51	329,1	125	33	+
86	pendimethalin	282,1	193,9	12	282,1	212	11	+
87	pethoxamid	296,1	130,9	20	296,1	250	14	+
88	picolinafen	377,1	144,9	48	377,1	237,9	29	+
89	picoxystrobin	368,1	144,9	20	368,1	205,2	10	+
90	pirimicarb	239,1	72,1	22	239,1	182,1	16	+
91	prochloraz	375,9	265,9	10	375,9	308	10	+
92	promecarb	208,2	109,1	16	208,2	151,1	10	+
93	propaquizafop	444,1	99,9	16	444,1	298,9	25	+
94	propargite	368,1	231,2	10	368,1	175	15	+
95	propiconazole	342	69,2	12	342	159	33	+
96	propyzamide	256	172,9	23	256	190	15	+
97	prosulfocarb	252,1	91	21	252,1	128	12	+
98	pymetrozine	218	79,1	48	218	105,1	18	+
99	pyraclostrobin	388,1	162,9	23	388,1	194	12	+
100	pyraflufen-ethyl	413	252,8	31	413	338,8	20	+
101	pyridaben	365,1	147	25	365,1	308,9	13	+
102	pyridate	379,2	206,9	17	379,2	351,1	11	+
103	pyrimethanil	200,3	82,2	23	200,3	107,2	25	+
104	pyriproxyfen	322,1	95,9	15	322,1	128,9	34	+
105	quinoxifen	307,9	161,9	42	307,9	196,8	32	+
106	quizalofop-ethyl	373	271	24	373	298,9	17	+
107	S-metolachlor	284	176,1	22	284	252	15	+
108	spirodiclofen	411	212,8	32	411	312,8	10	+
109	spiromesifen	371,1	273	14	371,1	255	22	+
110	tebuconazole	308,2	70	20	308,2	124,9	35	+
111	tebufenozide	353,1	132,9	21	353,1	296,9	11	+
112	tebufenpyrad	334,1	116,9	39	334,1	144,9	28	+
113	teflubenzuron	379	338,9	13	379	358,8	11	-
114	tepraloxydim	342,1	166	24	342,1	250	11	+
115	terbuthylazine	230,1	104,2	38	230,1	174,1	17	+
116	tetraconazole	371,9	70,1	20	371,9	158,9	34	+
117	thiacloprid	253	126	23	253	186	15	+
118	thiamethoxam	291,9	181	16	291,9	211	13	+
119	thiofanox-sulfone	268,1	57,1	15	268,1	76	10	+
120	sulfoxide	252,2	57,1	36	252,2	104	12	+
121	triadimenol	296,1	70	10	296,1	227,2	10	+
122	trifloxystrobin	409,1	185,9	20	409,1	205,9	13	+
123	triticonazole	318,1	70,1	40	318,1	124,9	31	+
124	zoxamide	335,9	186,8	23	337,9	188,8	22	+

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Results

Pesticide Recoveries with GC-MSn

No	Compound	LOD	LOQ*	% RECOVERY	LOQ	%RSD
1	1aclonifen	0,01	0,025	98		9
2	2acrinathrin	0,01		51		12
3	3a-HCH	0,01	0,025	82		17
4	4alachlor	0,005	0,025	94		10
5	5aldrin	0,01		61		16
6	6alphamethrin	0,01	0,025	79		19
7	7ametryne	0,01	0,025	96		10
8	8anthracene	0,01	0,025	98		3
9	9atrazine	0,005	0,025	92		9
10	10azinphos ethyl	0,01	0,025	99		13
11	11azinphos methyl	0,025	0,1	120		15
12	12benfluralin	0,01	0,025	88		19
13	13b-HCH	0,01	0,025	100		11
14	14bifenthrin	0,001	0,025	82		21
15	15bromacil	0,01	0,025	91		16
16	16bromophos ethyl	0,005	0,025	88		18
17	17bromopropylate	0,01	0,025	102		9
18	18bupirimate	0,01	0,025	110		9
19	19buprofezin	0,01	0,025	104		7
20	20butachlor	0,01	0,025	99		7
21	21cadudaphos	0,005	0,025	109		11
22	22caffeine	0,01	0,025	97		6
23	23captafol	0,025	0,1	94		18
24	24captan	0,01	0,025	95		8
25	25c-HCH	0,005	0,025	87		10
26	26chinomethionate	0,001	0,01	110		11
27	27chlordan	0,01	0,025	95		13
28	28chlorfenvinphos	0,01	0,025	95		6
29	29chlorobenzilate	0,01	0,025	100		10
30	30chloropropylate	0,01	0,025	104		13
31	31chlorothalonil	0,01	0,025	92		14
32	32chlorpyrifos ethyl	0,001	0,01	85		20
33	33chlorpyrifos methyl	0,001	0,01	100		13
34	34chlorthal dimethyl	0,001	0,01	108		10
35	35chlorthion	0,025	0,1	114		5
36	36coumaphos	0,01	0,025	106		3
37	37cyanazine	0,01	0,025	94		8
38	38cyanophos	0,01	0,025	84		12
39	39cycloate	0,01	0,025	79		18
40	40cyfluthrin	0,01	0,025	82		12
41	41cypermethrin	0,01	0,025	87		15
42	42DEA	0,01	0,025	102		9
43	43deltamethrin	0,01	0,025	79		16
44	44demeton O & S	0,025		65		21
45	45desmetryne	0,01	0,025	96		12
46	46d-HCH	0,01	0,025	97		6
47	47dialifos	0,01	0,025	88		12
48	48diazinon	0,005	0,025	104		12
49	49dichlofluanid	0,01	0,025	99		12
50	50dichlorvos	0,025		49		14

No	Compound	LOD	LOQ*	% RECOVERY	LOQ	%RSD
51	51dielldrin	0,01	0,025	98		14
52	52diflubenzuron	0,025	0,1	102		6
53	53diphenylamine	0,005	0,025	99		16
54	54disulfoton sulfone	0,01	0,025	104		5
55	55disulfoton sulfoxide	0,01	0,025	104		5
56	56endosulfan I	0,01	0,025	91		19
57	57endosulfan II	0,01	0,025	93		9
58	58endosulfan sulfate	0,005	0,025	95		10
59	59endrin	0,01	0,025	90		11
60	60ethalfuralin	0,005	0,025	107		11
61	61ethion	0,01	0,025	100		10
62	62etridiazole	0,001	0,025	108		0
63	63fenamiphos	0,01	0,025	90		5
64	64fenamiphos sulfone	0,01	0,025	90		16
65	65fenamiphos sulfoxide	0,01	0,025	96		6
66	66fenarimol	0,001	0,01	96		17
67	67fenazaquin	0,01	0,025	95		8
68	68fenchlorphos	0,001	0,01	103		8
69	69fenitrothion	0,01	0,025	105		15
70	70fenoxycarb	0,01	0,025	93		12
71	71fenpropimorph	0,005	0,025	88		19
72	72fensulfathion	0,01	0,025	90		16
73	73fenthion	0,01	0,025	88		4
74	74fenthion sulfone	0,01	0,025	86		10
75	75fenthion sulfoxide	0,01	0,025	98		9
76	76fenvalerate	0,01		53		13
77	77flutriafol	0,001	0,025	85		15
78	78fluvalinate	0,01	0,025	81		12
79	79folpet	0,01	0,025	86		19
80	80fonofos	0,01	0,025	112		8
81	81furalaxyl	0,005	0,025	96		12
82	82HCB	0,001	0,025	81		15
83	83heptachlor	0,01	0,025	81		15
84	84heptachlor epoxide	0,001	0,025	94		11
85	85isodrin	0,01	0,025	92		12
86	86isophenphos	0,001	0,01	99		12
87	87isopropalin	0,01	0,025	84		7
88	88L-cyhalothrin	0,01		57		18
89	89malaoxon	0,025	0,1	103		13
90	90malathion	0,005	0,025	102		16
91	91mecarbam	0,01	0,025	97		9
92	92methacrifos	0,01	0,025	91		12
93	93methidathion	0,01	0,025	106		9
94	94methoxychlor	0,001	0,025	101		10
95	95mevinphos	0,01	0,025	98		14
96	96mirex	0,01		65		6
97	97napropamide	0,01	0,025	109		11
98	98nuarimol	0,01	0,025	102		10
99	99o,p DDD	0,001	0,01	94		16
100	100o,p DDE	0,001	0,01	94		18

No	Compound	LOD	LOQ*	% RECOVERY	LOQ	%RSD
101	101o,p DDT	0,01	0,025	74		11
102	102omethoate	0,025	0,1	108		17
103	103oxyfluorfen	0,01	0,025	102		8
104	104p,p DDD	0,001	0,01	90		16
105	105p,p DDE	0,01	0,025	82		12
106	106p,p DDT	0,01	0,025	86		9
107	107paraaxon methyl	0,025	0,1	88		17
108	108paraaxon ethyl	0,01	0,025	99		16
109	109parathion ethyl	0,01		67		13
110	110parathion methyl	0,01	0,025	107		9
111	111PCNB	0,001	0,025	86		10
112	112pebulate	0,01	0,025	99		17
113	113pentachlorobenzene	0,01		52		22
114	114permethrin	0,01	0,025	92		18
115	115phenthoate	0,005	0,025	106		6
116	116phorate	0,025		59		8
117	117phorate sulfone	0,01	0,025	103		15
118	118phorate sulfoxide	0,01	0,025	99		8
119	119phosalone	0,01	0,025	103		9
120	120phasmet	0,001	0,025	98		20
121	121pirimiphos ethyl	0,001	0,01	96		19
122	122pirimiphos methyl	0,001	0,01	107		14
123	123procymidone	0,005	0,025	97		11
124	124profenofos	0,001	0,01	105		11
125	125prometone	0,01	0,025	92		7
126	126prometryne	0,005	0,025	94		14
127	127propachlor	0,01	0,025	104		16
128	128propanil	0,01	0,025	94		7
129	129propazine	0,005	0,025	90		9
130	130propham	0,01	0,025	96		12
131	131proquinazide	0,001	0,01	93		14
132	132prothoate	0,001	0,01	100		12
133	133pyrazophos	0,01	0,025	103		7
134	134quinalphos	0,01	0,025	96		12
135	135silthiofam	0,001	0,025	0.001/103		4
136	136simazine	0,01	0,1	106		9
137	137simetryne	0,01	0,025	98		3
138	138tefluthrin	0,01	0,025	78		10
139	139terbacil	0,025	0,1	100		14
140	140terbufos	0,005	0,025	86		18
141	141terbufos sulfone	0,01	0,025	104		5
142	142terbumeton	0,01	0,025	98		9
143	143terbutryn	0,01	0,025	101		10
144	144tetrachlorvinphos	0,01	0,025	101		8
145	145tetradifon	0,01	0,025	99		6
146	146thiobencarb	0,01	0,025	106		11
147	147tolylfluandide	0,01	0,025	99		14
148	148tralcoxydim	0,01	0,025	94		8
149	149triazophos	0,01	0,025	92		13
150	150trifluralin	0,005	0,025	77		14
151	151vinclozolin	0,01	0,025	97		13

*n=8

Recovery: 70-120% Quantitative?
Recovery: < 70 or >120 or RSD >20 Screening

Pesticide Recoveries with LC-MS/MS

No	Compound	LOQ (µg/L)	% RECOVERY	LOQ	%RSD
1	acetamidrid	0.01	102	2	
2	abamectin	0.025	59	2	
3	acetochlor	0.01	83	3	
4	acibenzolar-S-methyl	0.025	63	6	
5	aminocarb	0.025	71	13	
6	azoxystrobin	0.025	85	7	
7	beflubutamid	0.025	95	2	
8	benalaxyl	0.025	94	4	
9	bitertanol	0.025	86	13	
10	boscalid	0.025	102	1	
11	carbendazim	0.025	53	8	
	carfentrazone				
12	ethyl	0.025	92	7	
13	chloridazone	0.025	94	2	
14	chlorotoluron	0.025	106	5	
15	cinidon-ethyl	0.025	67	5	
16	clofentezine	0.025	86	10	
17	clomazone	0.025	73	7	
18	cyazofamid	0.025	91	12	
19	cyhalofop-butyl	0.025	73	7	
20	cyproconazole	0.025	95	13	
21	cyromazine	0.025	59	9	
22	diclofop-methyl	0.025	92	7	
23	difenoconazole	0.01	102	2	
24	diflufenican	0.025	101	6	
25	dimethenamid	0.025	80	3	
26	dimethoate	0.01	93	1	
27	dimethomorph	0.025	94	5	
28	dimoxystrobin	0.025	92	9	
29	diuron	0.025	94	1	
30	dodemorph	0.025	97	6	
31	epoxyconazole	0.025	85	14	
32	ethofumasate	0.025	89	3	
33	ethoprophos	0.025	61	12	
34	etofenprox	0.025	109	5	
35	etoxazole	0.025	89	2	
36	famoxadone	0.025	91	4	
37	fenamidone	0.025	90	7	
38	fenbuconazole	0.025	84	16	
39	fenhexamid	0.025	80	1	
	fenoxaprop-p-ethyl	0.025	98	3	
40	ethyl	0.025	98	3	
41	fenpropimorph	0.01	99	2	

No	Compound	LOQ (µg/L)	% RECOVERY	LOQ	%RSD
42	fenpyroximate	0.025	81	11	
43	fipronil	0.01	81	8	
44	flonicamid	0.025	100	4	
	fluazifop-P-butyl				
45	butyl	0.025	97	5	
46	fluazinam	0.01	89	5	
47	fludioxonil	0.025	101	16	
48	flufenacet	0.01	89	7	
49	flufenoxuron	0.025	70	11	
50	flumioxazin	0.025	69	9	
51	fluometuron	0.01	108	8	
52	fluopicolid	0.025	87	4	
53	fluoxastrobil	0.025	87	9	
54	fluquinconazole	0.025	92	9	
55	flurochloridone	0.025	102	16	
56	flusilazole	0.025	94	9	
57	flutolanil	0.025	95	1	
58	fosthiazate	0.025	48	16	
59	fuberidazole	0.025	85	2	
60	hexythiazox	0.025	92	2	
61	imazalil	0.025	77	3	
62	imidachloprid	0.01	92	8	
63	indoxacarb	0.025	69	15	
64	iprovalicarb	0.025	98	6	
65	isoproturon	0.025	98	7	
66	isoxaflutol	0.025	65	16	
	kresoxym-methyl				
67	methyl	0.025	86	7	
68	lenacil	0.01	91	1	
69	linuron	0.01	103	1	
70	mepanipyrim	0.025	92	11	
71	metaflumizone	0.025	82	5	
72	metalaxyl	0.025	78	15	
73	metamitron	0.025	43	23	
74	metazachlor	0.025	96	4	
75	metconazole	0.025	89	10	
76	methiocarb	0.025	53	15	
77	methomyl	0.025	61	12	
	methoxyfenozide				
78	de	0.025	89	11	
79	metrafenone	0.025	93	8	
80	metribuzin	0.025	47	10	
81	molinate	0.025	44	23	
82	myclobutanil	0.01	96	8	

No	Compound	LOQ (µg/L)	% RECOVERY	LOQ	%RSD
83	oxadiazon	0.025	85	5	
84	penconazole	0.01	91	3	
85	pencycuron	0.025	94	3	
86	pendimethalin	0.025	76	3	
87	pethoxamid	0.025	98	5	
88	picolinafen	0.025	83	8	
89	picoxystrobin	0.025	99	3	
90	pirimicarb	0.025	83	4	
91	prochloraz	0.025	78	5	
92	promecarb	0.025	52	11	
93	propaquizafop	0.025	76	18	
94	propargite	0.025	90	2	
95	propiconazole	0.025	96	4	
96	propyzamide	0.025	71	8	
97	prosulfocarb	0.025	74	11	
98	pymetrozine	0.025	68	6	
99	pyraclostrobin	0.025	85	3	
100	pyraflufen ethyl	0.025	109	19	
101	pyridaben	0.025	89	2	
102	pyridate	0.025	108	8	
103	pyrimethanil	0.025	94	2	
104	pyriproxyfen	0.025	35	16	
105	quinoxyfen	0.025	82	4	
106	quizalofop-ethyl	0.025	90	2	
107	S-metolachlor	0.025	87	4	
108	spirodiclofen	0.025	89	3	
109	spiromesifen	0.025	100	5	
110	tebuconazole	0.025	99	4	
111	tebufenozide	0.025	85	8	
112	tebufenpyrad	0.01	92	5	
113	teflubenzuron	0.025	84	14	
114	tepraloxymdim	0.025	97	17	
115	terbuthylazine	0.025	80	2	
116	tetraconazole	0.01	100	3	
117	thiacloprid	0.01	98	1	
118	thiamethoxam	0.01	90	9	
119	thiofanox sulfone	0.025	66	13	
120	thiofanox sulfoxide	0.025	56	12	
121	triadimenol	0.025	97	9	
122	trifloxystrobin	0.01	92	2	
123	triticonazole	0.01	90	4	
124	zoxamide	0.025	84	6	

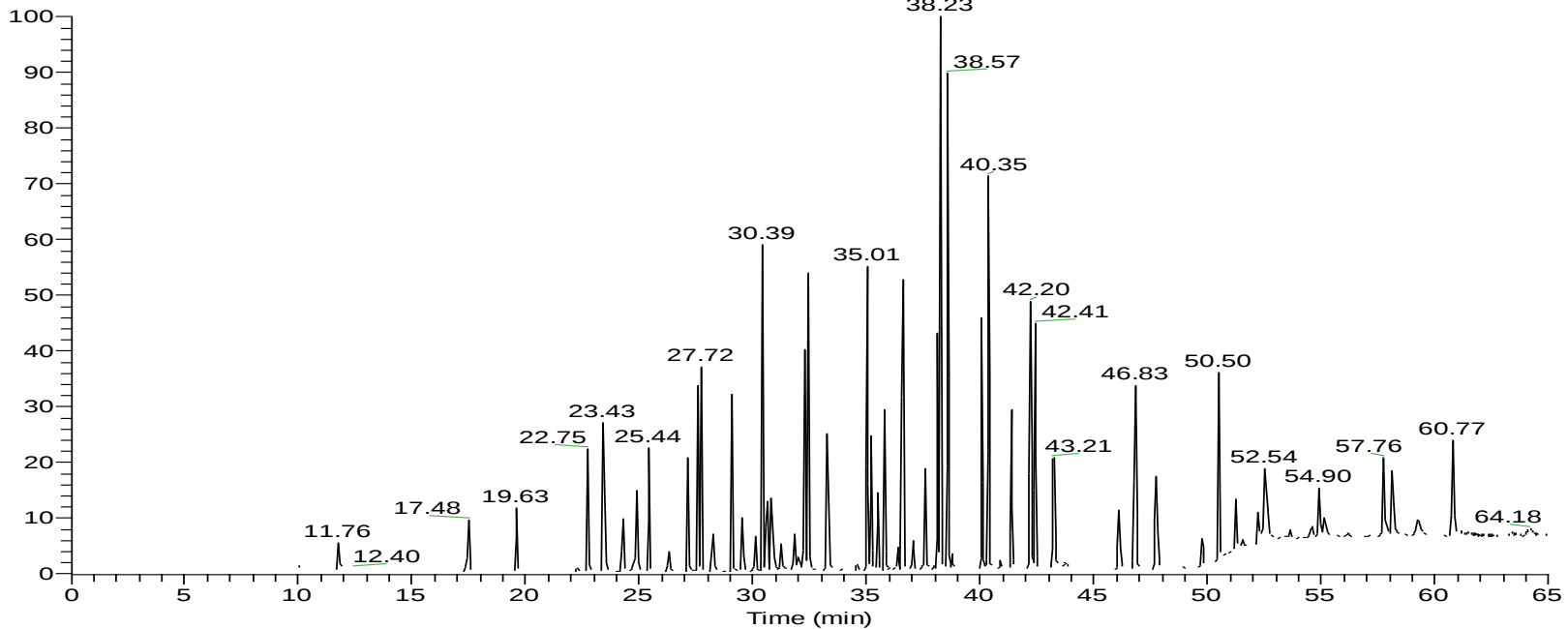
*n=5

Recovery: 70-120% Quantitative ?

Recovery: < 70 or >120 or RSD >20 Screening ?

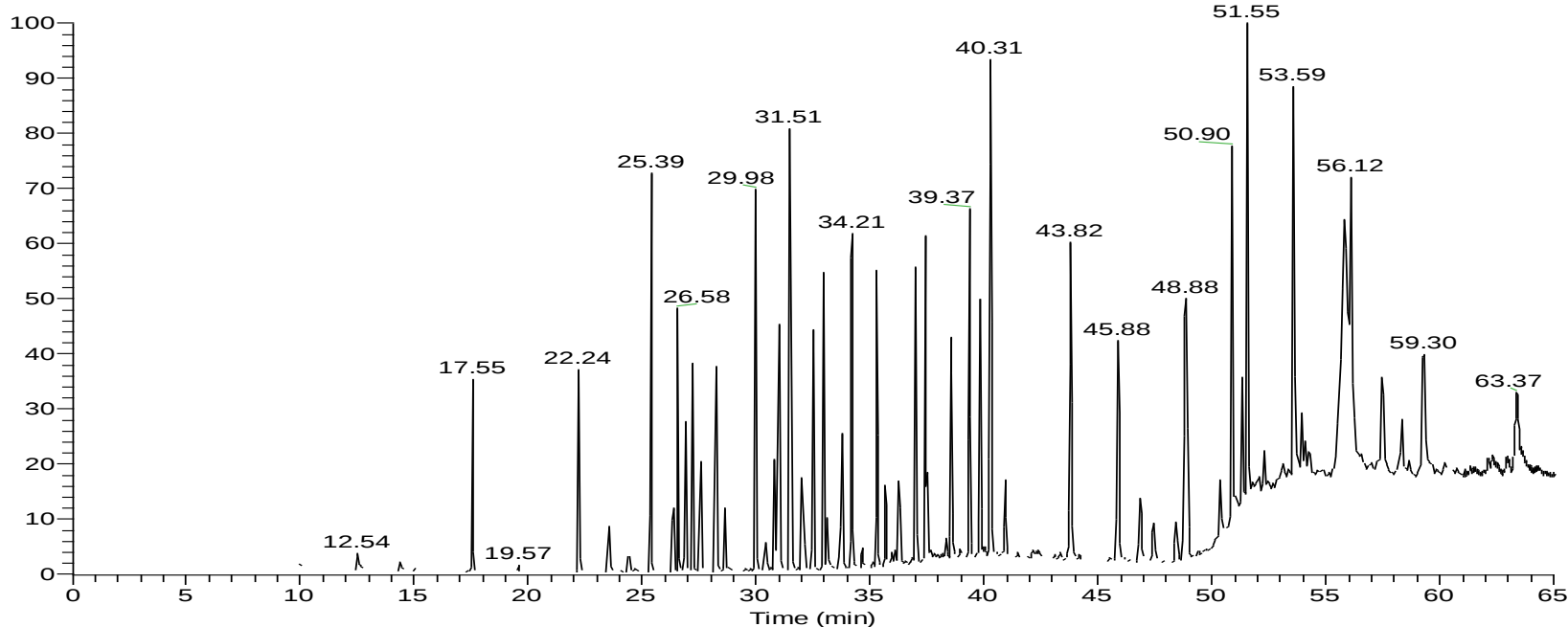
GC-MSn Chromatographic profile of Stock A (49 compounds) full scan TIC

RT: 0.00 - 65.00

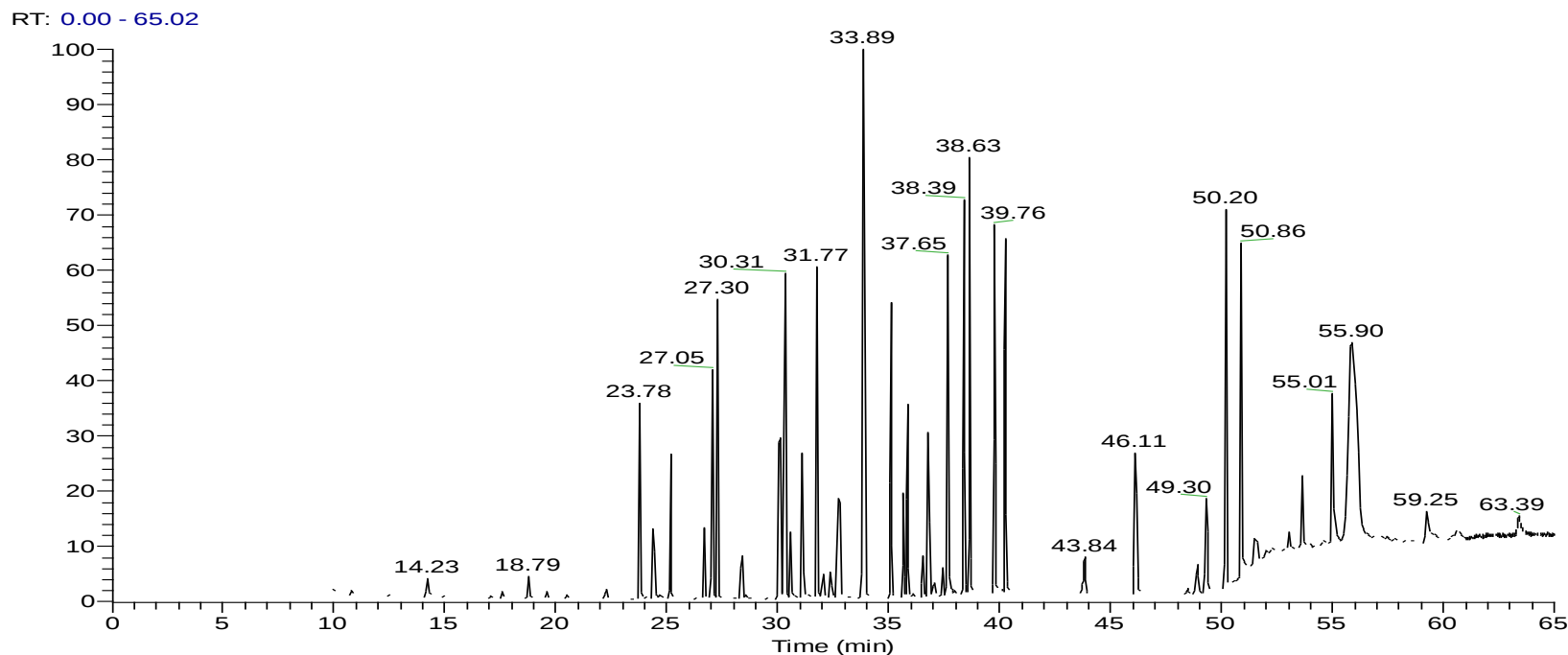


GC-MSn Chromatographic profile of Stock B (36 compounds)full scan TIC

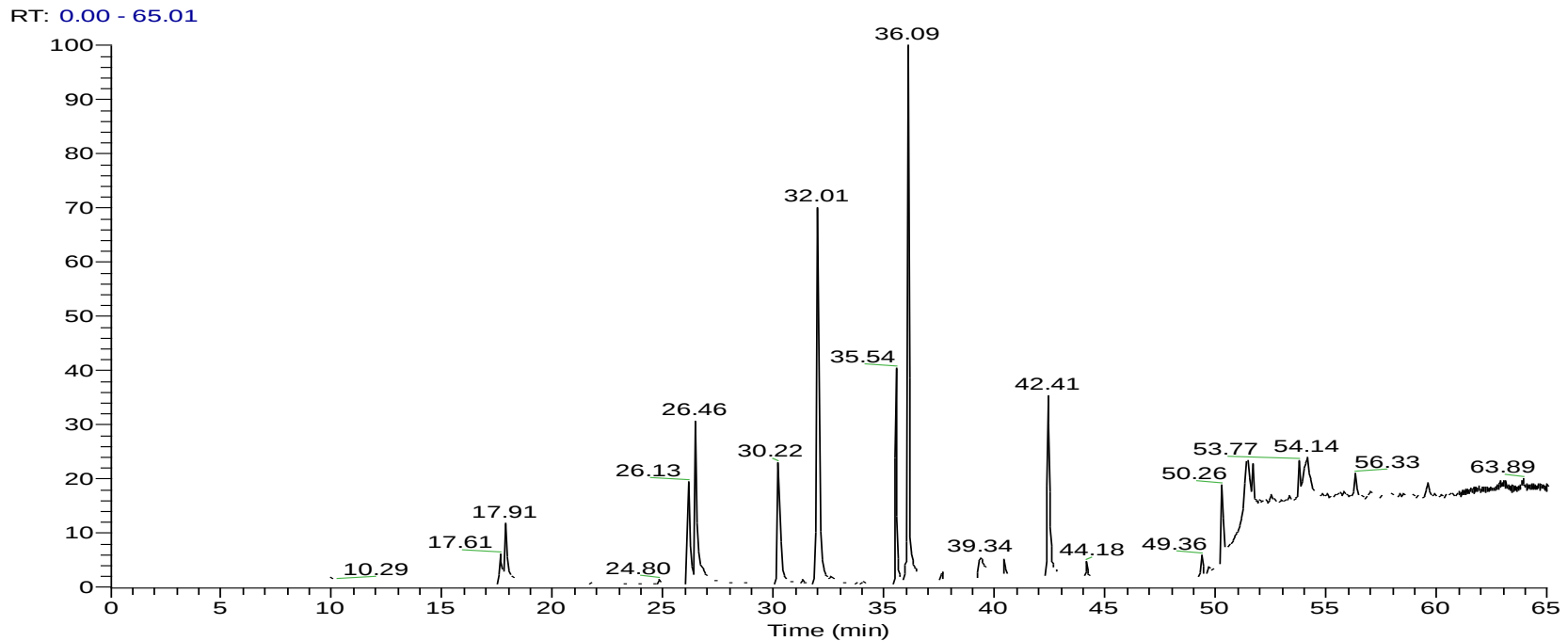
RT: 0.00 - 65.03



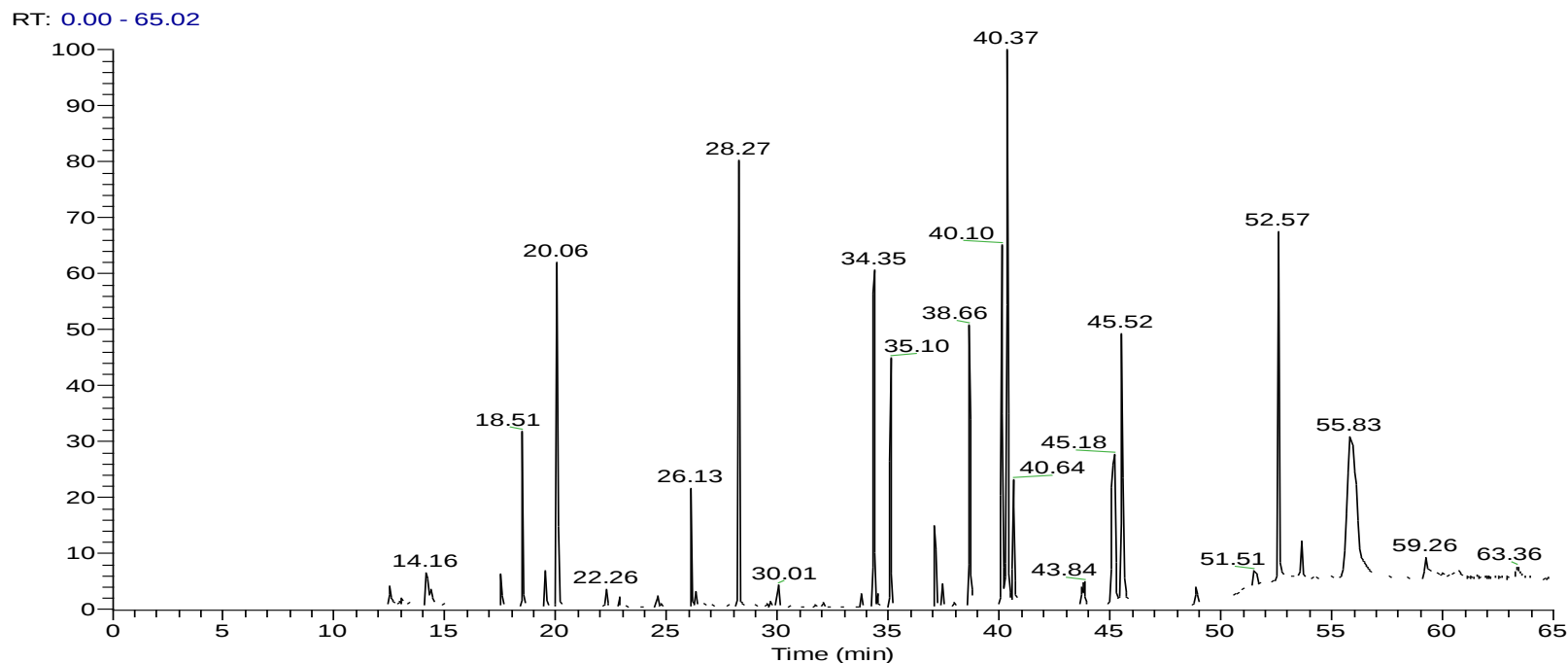
GC-MSn Chromatographic profile of Stock C (33 compounds)full scan TIC



GC-MSn Chromatographic profile of Stock D (18 compounds)full scan TIC

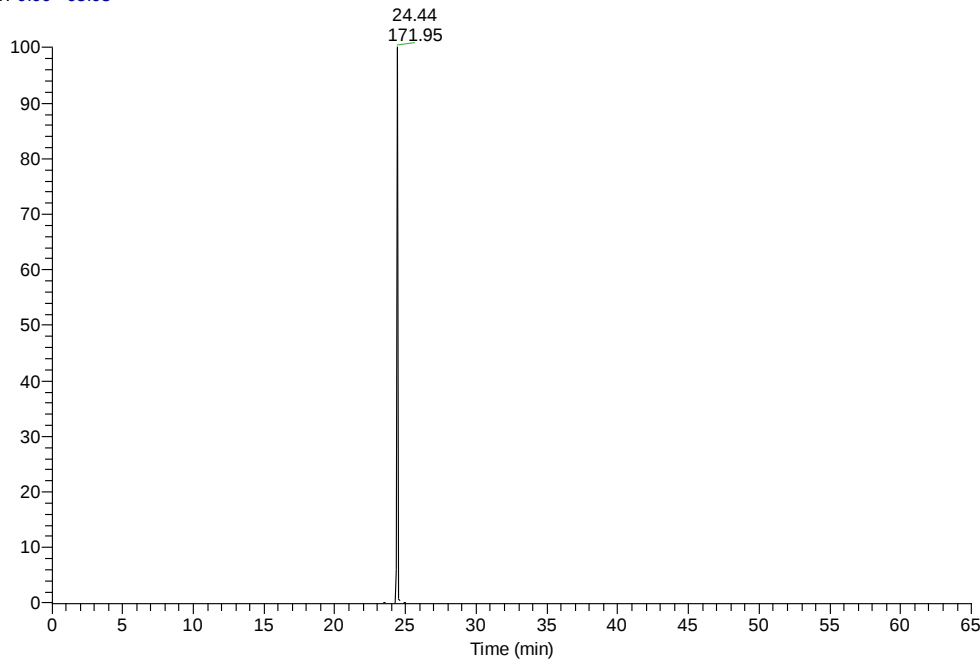


GC-MSn Chromatographic profile of Stock E (15 compounds)full scan TIC



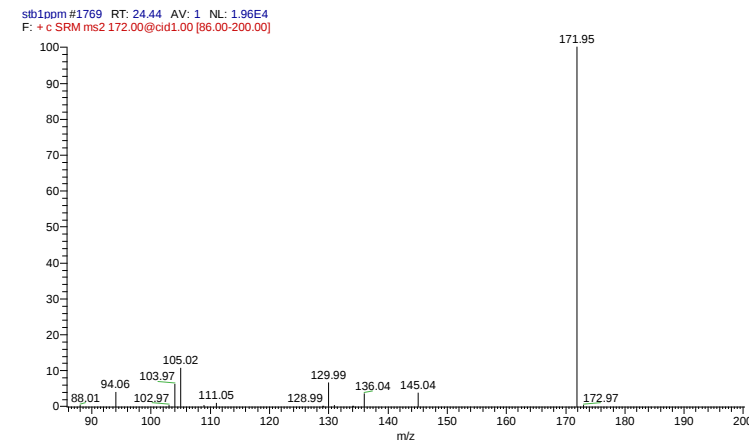
GC-MSn (SRM 172)

RT: 0.00 - 65.03

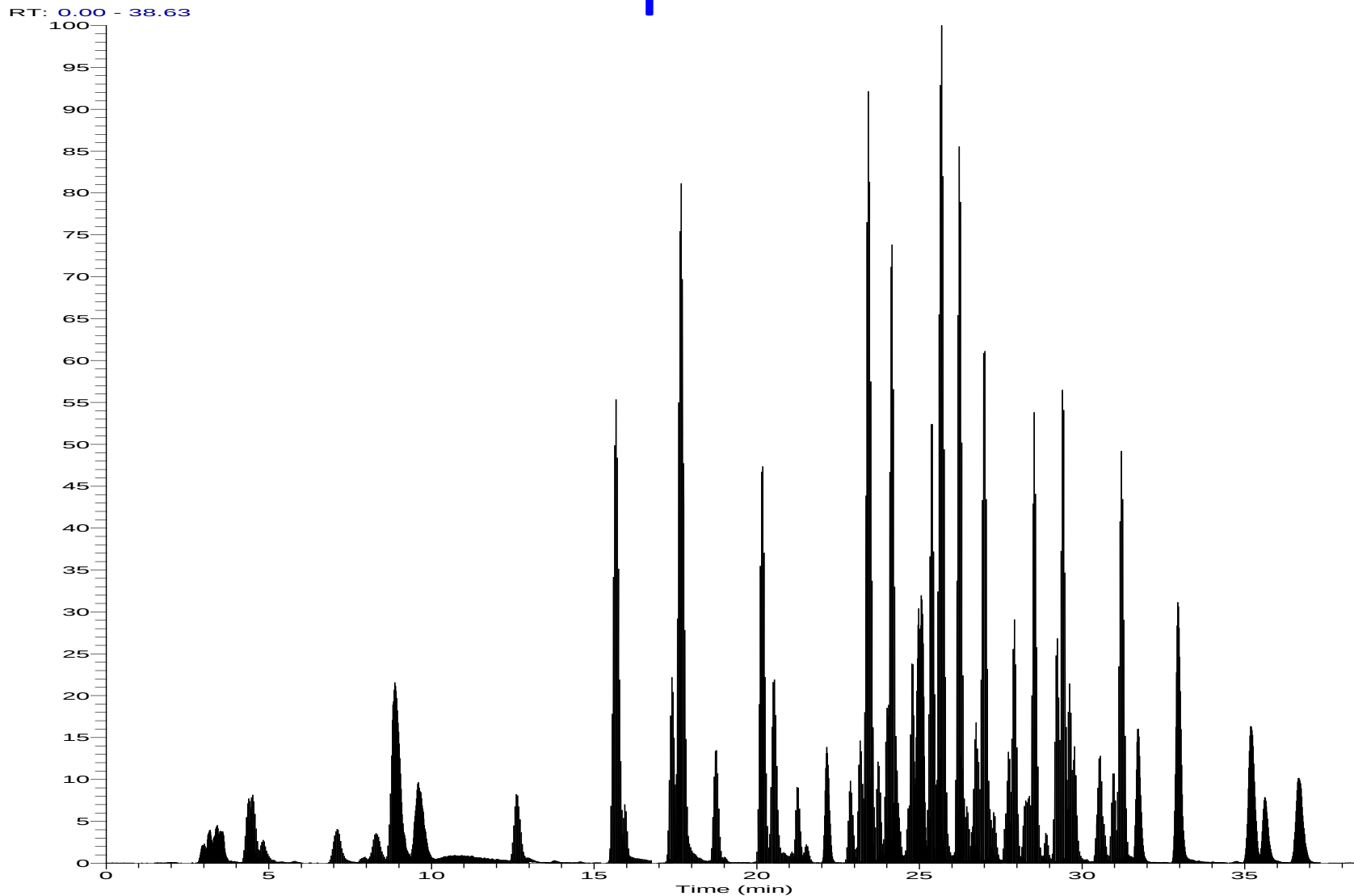


DEA

Selected reaction monitoring of the 172
m/z characteristic for (DEA)
DEA was used as an indicator for GC
system maintenance



LC-MS/MS Chromatographic profile



LC-MS/MS chromatogram

S-metolachlor-positive

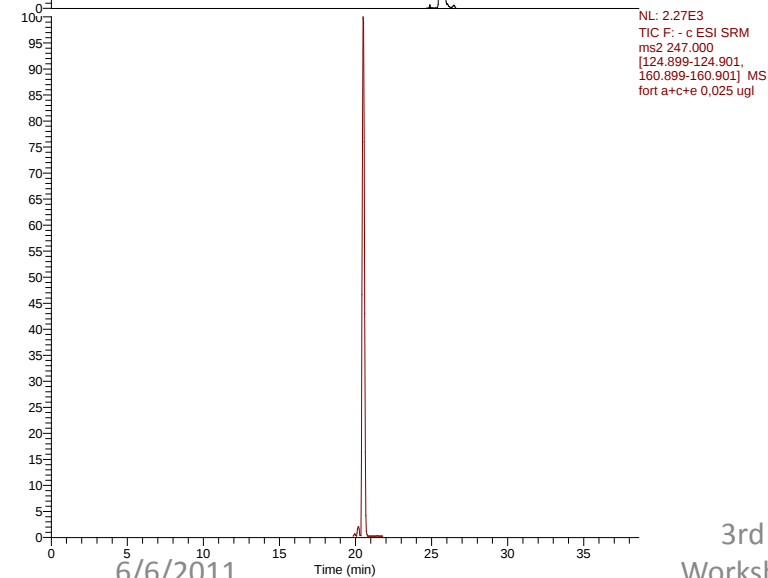


Selected reaction monitoring of the 284
m/z characteristic for S-metolachlor

and

of 247 m/z characteristic for fludioxonil

fludioxonil-negative



Analysis of surface and ground water samples

- Up to now
 - More than 1000 samples were analyzed (plan for 10.000 in 3 years period)
 - rivers
 - lakes
 - ground water
- Also the GC-MS and LC-MS instrumental analytical methods were used for the determination of pesticide residues in sediment of the above mentioned surface water bodies

LC-MS/MS positive detection (real sample)

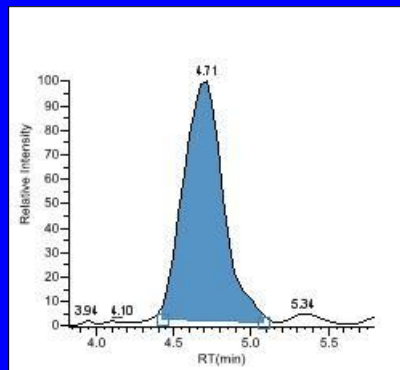
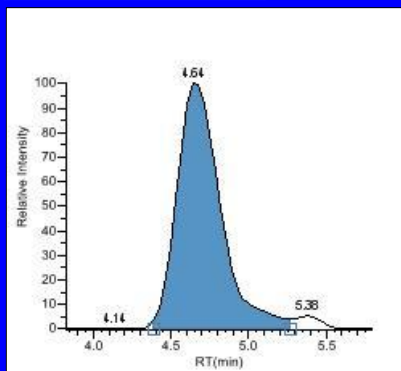
thiamethoxam

Sample Conc: 0.012 µg/L

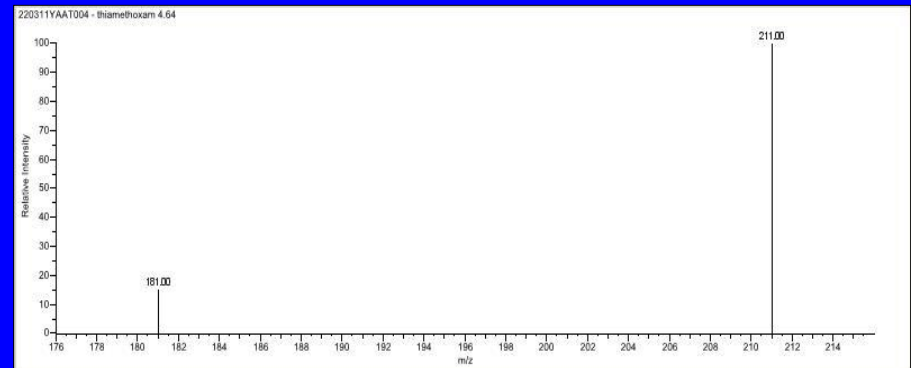
Quant Ion: 211.00

Qual Ion 1: 181.00

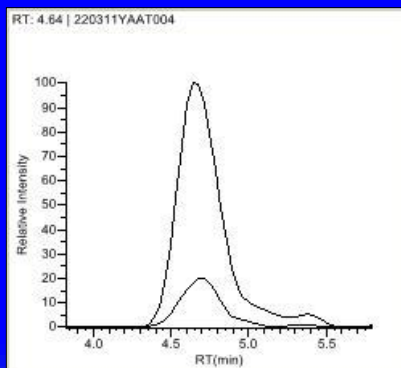
Ratio: 18.24% Range:0.00 - 47.02%



MS-Data



Overlay



The parent ion is 291.9 and the quantitation ion is from the second transition the 211. While the ion 181 is used for confirmation.

LC-MS/MS positive detection (real sample)

imidacloprid

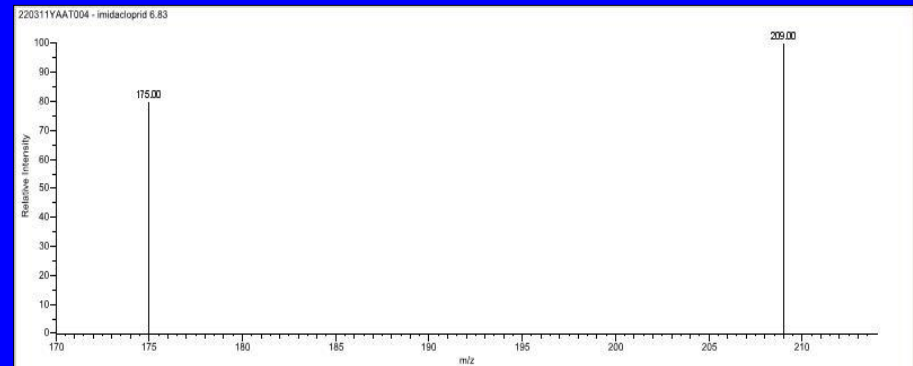
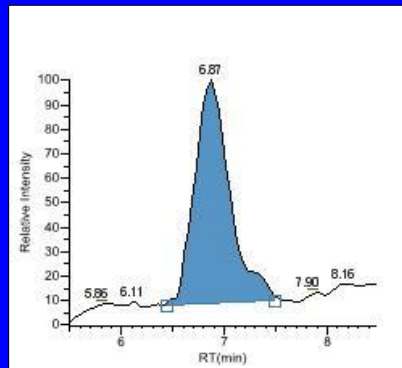
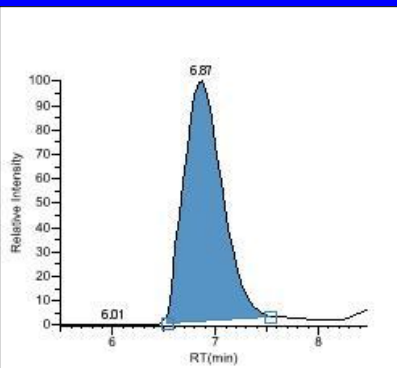
Sample Conc: 0.017 µg/L

Quan Ion: 209.00

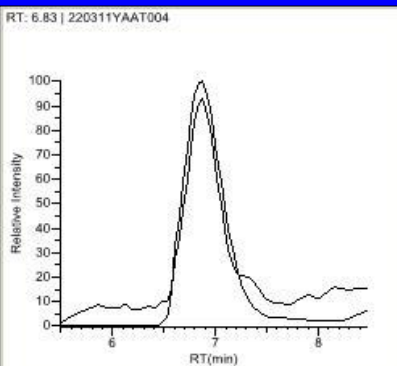
Qual Ion 1: 175.00

Ratio: 78.21% Range: 55.34 - 95.34%

MS-Data



Overlay



The parent ion is 256 and the quantitation ion is from the second transition the 209. The ion 175 is used for confirmation.

LC-MS/MS positive detection (real sample)

fluometuron

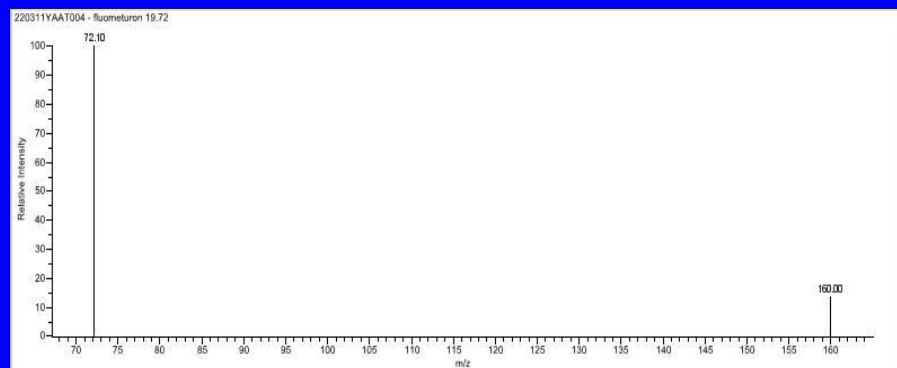
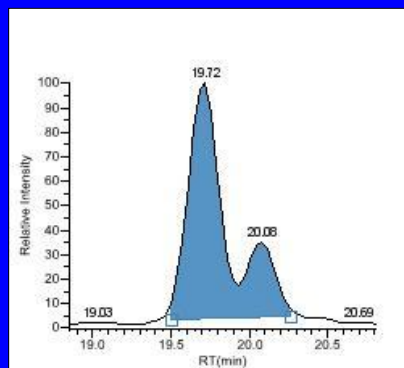
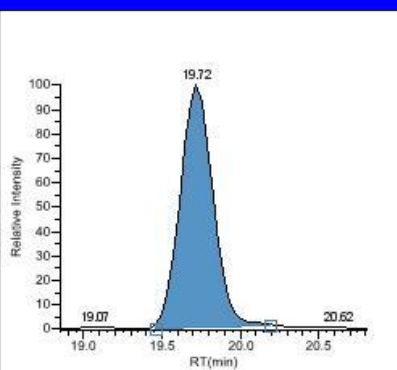
Sample Conc: 0.068 µg/L

Quan Ion: 72.10

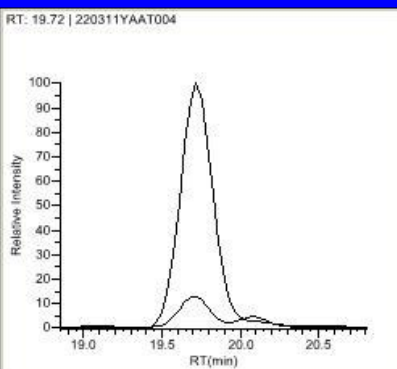
Qual Ion 1: 160.00

Ratio: 15.54% Range: 0.00 - 42.50%

MS-Data



Overlay



parent ion 233

Preliminary Results

- Most frequently detected pesticides

Chlorpyriphos ethyl	Molinate	Trifluralin	boscalid
Prometryne	Malathion	Caduzaphos	Bubirimate
Alachlor	Phorate sulfone /sulfoxide	Pirimiphos methyl	Fensulfothion
Diphenylamine	HCB	Metribuzin	λ-Cyhalothrin
Caffeine	PCNB	Profenofos	Deltamethrin
S-metolachlor	Diazinon	Tralcoxydim	Ethion
Fluometuron	Propazine	Phosmet	Thiamethoxam
Etridiazole	Flutriafol	Fenthion	DEA
Chlorthal Dimethyl	Permethrin	Fenoxycarb	Thiacloprid
Imidacloprid	Bifenthrin	Terbutryn	Therbuthylazine
Atrazine	Fenpropimorph	Prometon	Fenamiphos
Simazine	Captan	Napropimide	C-HCH

Greece Famous for ...

- History-Mythology
- Ancient culture
- Hospitality
- Islands
- Mediterranean diet
- Sun and Sea
- Deptocracy ?

Parthenon



Ancient Athens
coins 450-
400 BC



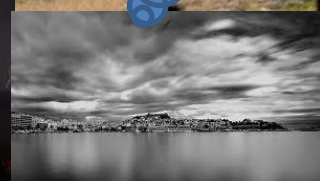
Ancient
Epidauros
theater



Thunderbolts
around
Greece:
IMF



"Greece is
going to be
sold at a
bargain
price"



Future:
Ninemia
Lull



Thank you very much
for your attention

