Simultaneous determination of residual agricultural chemicals in food by GC–MS/MS - Sensitivity of standard solution 1ppb and linearity of calibration curve-

Product : Mass Spectrometer (MS)

As "food safety" is recognized as an increasingly important issue on a global scale, many nations have their own regulations on residual agricultural chemicals in food. In Japan, the positive list system, which was enforced at the end of May 2006, stipulates a uniform standard of 10 ppb as a quantity that is considered safe for human health. Under the positive list system, more agricultural chemicals need to be examined, and as a result, techniques capable of accurately and collectively analyzing residual agricultural chemicals in food are in increasing demand. While mass spectrometry (MS) is known for its high detection sensitivity, MS/MS is becoming the mainstream of pesticide analysis for its superior sensitivity and selectivity.

The JMS-TQ4000GC, JEOL's latest GC-MS/MS system, has a unique ion storage/ejection mechanism within the MS/MS collision cell and incorporates new firmware to support MS/MS analysis with up to 36,000 transitions. In this work, we report the verified results for pesticide residues sensitivity in food using the JMS-TQ4000GC.

[Sample and Method]

A pesticide standard solution from FUJIFILM Wako Pure Chemical Corporation (PL series) was used that consisted of equal amounts of PL 1, 2, 3, 4, 5, 6, 11, and 12. Afterwards, the solution was diluted to 1, 5, 10, 50 and 100 ppb. PEG 300 was used to protect the pesticides from thermal decomposition in the GC injection liner.

In this work, both the sensitivity and the linearity of the calibration curve were examined for 150 pesticides. Table 1 shows the measurement conditions used for the analysis.

GC-MS/MS, JMS-TQ4000GC

Table 1 Measurement Conditions

[GC-TQMS condition]

System	JMS-TQ4000GC (JEOL)
Ionization mode	EI+: 70eV, 50μA
GC column	VF-5ms(Agilent), 30m x 0.25mm, 0.25μm
Oven temp.	50˚C (1min)→25˚C /min→125˚C →10˚C /min→300˚C
Inlet temp.	250˚C
Inlet mode	Splitless, 2μL
He flow	1.0mL/min (Constant Flow)
MS/MS mode	Peak Dependent SRM

[Results and Discussion]

Figure 1 shows the calibration curves from 1-100ppb as well as the SRM chromatograms for 4 pesticides at 1ppb. The JMS-TQ4000GC showed excellent linearity and sensitivity for this range of concentrations. Fig 2 shows the retention times (R.T.), SRM information, and correlation coefficient for 150 pesticide calibration curves. Since the uniform criterion of the positive list system is 10 ppb, when the concentration ratio in the sample pretreatment is equal, the criteria concentration in the measurement sample for GC-MS/MS is also 10 ppb. A number of pesticides were detected with good sensitivity at 1 ppb which is 1/10 of criteria concentration. These results suggest that the JMS-TQ4000GC is the most effective tool for pesticide analysis.

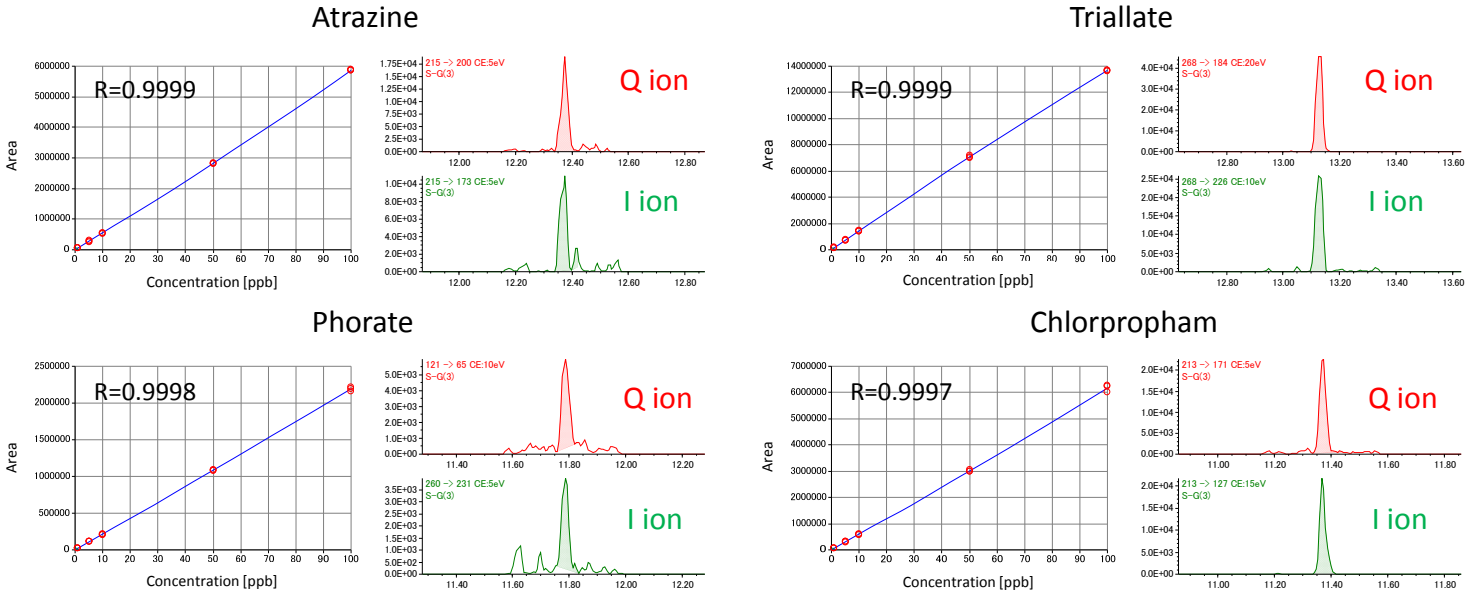

Fig.1 Calibration curves (1-100ppb) and SRM chromatograms for 1ppb data

Table 2 Calibration curve information for 150 pesticides using 1, 5, 10, 50 and 100 ppb standard solutions (n=3 each)

No.	Compound	RT (min)	Q ion		Correlation coefficient, R (1-100ppb)
			Precursor ion	Product ion	
1	Atrazine	12.37	215	200	0.9999
2	Benthiocarb	14.68	100	72	0.9997
3	cis-Permethrin	20.68	183	153	0.9999
4	Diflufenican	18.31	266	218	0.9999
5	Fenamiphos	16.24	303	195	0.9998
6	Fenarimol	20.20	139	111	0.9999
7	Fenpropimorph	14.74	128	110	0.9998
8	Norflurazon	17.94	303	145	0.9997
9	Oxadiazon	16.50	175	112	0.9996
10	Penconazole	15.45	248	192	0.9999
11	Pendimethalin	15.29	252	162	0.9990
12	Procymidone	15.70	283	255	0.9980
13	Spiroxamine 1	13.78	100	72	0.9997
14	Spiroxamine 2	14.31	100	72	0.9995
15	Tefluthrine	12.92	177	127	0.9999
16	Terbufos	12.63	231	175	0.9998
17	Terbutryn	14.31	241	170	0.9999
18	trans-Permethrin	20.68	183	153	0.9999
19	Alachlor	13.84	188	160	0.9994
20	Buprofezin	16.68	172	115	0.9993
21	cis-Chlorfenvinphos	15.49	323	267	0.9998
22	Cyproconazole 1	17.03	139	111	0.9998
23	Cyproconazole 2	17.03	139	111	0.9998
24	Difenoconazole 1	23.10	323	265	0.9998
25	Difenoconazole 2	23.18	323	265	0.9999
26	Ethion	17.34	231	175	0.9998
27	Fenitrothion	14.33	277	260	0.9989
28	Fenthion	14.73	278	245	0.9997
29	Fluridone	22.18	328	259	0.9997
30	Hexazinone	18.24	171	71	0.9997
31	Isofenphos oxon	14.79	229	201	0.9999
32	Isophenphos	15.43	255	185	0.9998
33	Isoprothiolane	16.44	189	145	0.9997
34	Propargite 1	18.31	135	107	0.9996
35	Propargite 2	18.31	135	107	0.9996
36	Propiconazole 1	17.93	173	145	0.9998
37	Propiconazole 2	18.07	173	145	0.9996
38	Propyzamide	12.73	175	147	0.9998
39	Pyriproxyfen	19.72	136	96	0.9999
40	trans-Chlorfenvinphos	15.25	323	267	0.9993
41	Triadimenol 1	15.70	168	70	0.9997
42	Triadimenol 2	15.84	168	70	0.9994
43	Triallate	13.13	268	184	0.9999
44	Vinclozoline	13.76	212	172	0.9997
45	Acetamiprid	18.92	152	116	0.9997
46	Allethrin 1	15.43	123	81	0.9994
47	Allethrin 2	15.51	123	81	0.9991
48	Bitertanol 1	20.66	170	141	0.9999
49	Bitertanol 2	20.76	170	141	0.9997
50	Bromopropylate	19.00	183	155	0.9998
51	Chlorobenzilate	17.19	251	139	0.9998
52	Chlorpyrifos	14.63	197	169	0.9997
53	Oxyfluorfen	16.59	252	196	0.9955
54	Parathion	14.80	291	109	0.9979
55	Pirimiphos methyl	14.24	290	233	0.9998
56	Propanil	13.67	217	161	0.9999
57	Pyridaben	20.87	147	119	0.9999
58	Quinoxyfen	18.00	237	208	0.9998
59	Simazine	12.29	201	173	0.9999
60	Tebuconazole	18.38	250	125	0.9998
61	Triadimefon	14.87	208	181	0.9993
62	Triazophos	17.65	161	134	0.9998
63	Ametryn	14.00	227	170	0.9999
64	Azaconazole	16.83	217	173	0.9998
65	Bupirimate	16.66	273	193	0.9998
66	Butachlor	16.01	176	147	0.9994
67	Chlorthal dimethyl	14.73	299	221	0.9999
68	Dicloran	12.19	206	176	0.9993
69	Diethofencarb	14.63	267	225	0.9999
70	Dimepiperate	15.74	119	91	0.9997
71	Dimethenamid	13.61	230	154	0.9999
72	Etoxazole	19.03	204	176	0.9998
73	Fluacrypyrim	17.38	204	189	0.9999
74	Lenacil	18.14	153	136	0.9998
75	Pyriminobac methyl 1	17.96	302	256	0.9996
76	Pyriminobac methyl 2	17.13	302	256	0.9997
77	Pyroquilon	12.88	173	130	0.9996
78	Tetradifon	19.53	159	131	0.9999
79	Tolclofos-methyl	13.87	265	250	0.9998
80	Uniconazole P	16.61	234	165	0.9996
81	Acetochlor	13.66	146	131	0.9997
82	Benalaxyl	17.83	204	176	0.9996
83	Benfuresate	13.57	256	163	0.9998
84	Cadusafos	11.71	159	131	0.9997
85	Chlorpropham	11.37	213	171	0.9997
86	Diclocymet 1	15.61	277	221	0.9995
87	Diclocymet 2	15.91	277	221	0.9999
88	Dimethametryn	15.40	212	122	0.9997
89	Esprocarb	14.49	222	91	0.9998
90	Etofenprox	21.83	163	135	0.9998
91	Fenothiocarb	16.08	160	72	0.9996
92	Iprobenfos	13.27	204	91	0.9998
93	Isoxathion	16.92	177	130	0.9997
94	Mepronil	17.61	119	91	0.9998
95	Prometryn	14.04	241	184	0.9999
96	Propachlor	10.85	120	92	0.9996
97	Prothiofos	16.41	267	239	0.9990
98	Pyrifenox 1	15.99	262	200	0.9998
99	Pyrimethanil	12.89	198	183	0.9998
100	Simetryn	13.94	213	170	0.9999
101	Terbacil	13.06	161	144	0.9999
102	Tetraconazole	14.82	336	218	0.9998
103	Thenylchlor	18.31	127	99	0.9994
104	Tribufos	16.58	202	147	0.9995
105	Tricyclazole	16.66	189	161	0.9996
106	Zoxamide (decomposed)	15.72	187	159	0.9992
107	Benoxacor	13.40	259	120	0.9995
108	Bromacil	14.44	205	188	0.9996
109	Bromobutide	13.70	119	91	0.9998
110	Butamifos	16.17	286	202	0.9997
111	Dichlofenthion	13.56	279	223	0.9998
112	Diphenamid	15.12	167	152	0.9999
113	Hexaconazole	16.42	214	172	0.9996
114	Mefenoxam	14.00	206	132	0.9998
115	Napropamide	16.33	128	72	0.9997
116	Oxadixyl	17.40	163	132	0.9998
117	Paclobutrazol	16.07	236	125	0.9998
118	Phenothrin 1	19.31	183	153	0.9998
119	Phenothrin 2	19.42	183	153	0.9999
120	Piperophos	18.98	320	122	0.9998
121	Prohydrojasmon 1	12.94	153	97	0.9998
122	Prohydrojasmon 2	13.23	153	97	0.9996
123	Propazine	12.42	214	172	0.9997
124	Pyributicarb	18.63	165	108	0.9998
125	Pyrifenox 2	15.51	262	200	0.9995
126	Quinalphos	15.63	146	118	0.9999
127	Tebufenpyrad	19.16	333	171	0.9998
128	Tolfenpyrad	24.05	197	154	0.9999
129	Aldrin	14.78	263	193	0.9988
130	cis-Chlordane	16.26	375	266	0.9998
131	Dicofol	14.97	139	111	0.9998
132	Dieldrin	16.78	277	206	0.9988
133	Endrin	17.19	263	193	0.9996
134	Heptachlor	14.07	272	237	0.9997
135	trans-Chlordane	16.02	373	266	0.9998
136	1-Naphthylacetamide	14.40	141	115	0.9999
137	Bromophos ethyl	15.87	357	301	0.9998
138	Carboxin	16.80	235	143	0.9999
139	Chlorbenside	15.98	268	125	0.9995
140	Chlorofenson	16.42	175	111	0.9995
141	clomazone	12.47	125	89	0.9998
142	Disulfoton	12.98	88	60	0.9997
143	Epoxiconazole	18.61	192	138	0.9999
144	Ethofumesate	14.37	207	161	0.9997
145	Fenamidone	19.17	268	180	0.9998
146	Flutriafol	16.28	219	123	0.9999
147	Isazophos	12.96	161	119	0.9998
148	Phorate	11.79	121	65	0.9998
149	Picolinafen	18.97	376	238	0.9995
150	Propaphos	15.89	220	140	0.9998

JEOL Ltd.

3-1-2 Musashino Akishima Tokyo 196-8558 Japan Sales Division Tel. +81-3-6262-3560 Fax. +81-3-6262-3577

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