Multiresidue Screening of Agricultural Chemicals (I) and (II) in Food According to the Japan Positive List Using Agilent Cartridge-Based SPE and LC/MS/MS

Application Note

Food Testing and Agriculture

Authors

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Abstract

Japan implemented new regulations on May 29, 2006 for residues of agricultural chemicals in food. Japan's Ministry of Health, Labor, and Welfare (MHLW), equivalent to the US FDA, introduced the *Positive List* for detection of pesticides, feed additives, and veterinary drugs (collectively referred to as agricultural chemicals) remaining in foods [1]. The legislation was developed to prohibit the distribution of foods that contain agricultural chemicals above a certain level of maximum residue limits (MRLs). The regulations apply to all domestically produced and imported foodstuffs and lists almost 800 chemicals. The Western Pacific/Australasia region mostly tests according to this list, and, as Japan is the biggest importer in the region, all other countries tend to follow its guidelines. The regulation requires that analysts apply a set of testing protocols that use classic cartridge-based SPE and LC/MS or GC/MS techniques, and requires that no agricultural chemical exceed the MRL (0.01 ppm).

This application note describes two methods to screen multi-residues of agricultural chemicals in food extracts according to the analytical methods listed in the Japan Positive List. A mix of 67 neutral, basic, and acidic chemicals was analyzed by two different methods, both employing LC/MS/MS. Using high-resolution Agilent Pursuit XRs C18 columns and tandem MS/MS detection, good chromatographic and mass spectrometric separation was achieved for two pairs of isomers in one of the groups. The data generated offers a complete solutions package of Agilent Bond Elut Carbon/Amino (Dual phase), Bond Elut Silica SPE, and Pursuit HPLC products for screening challenging agricultural chemicals within the expected MRLs of the Japan Positive List in several food matrices.

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Introduction

The Japanese Positive List system

After the implementation date, foods containing residues exceeding the MRL levels on the Positive List are regarded as violations of the Food Sanitation Law and are prohibited from being sold or used as food in Japan [2,3]. The MHLW established a uniform limit of 0.01 ppm, which is the maximum allowable limit for combinations of chemicals and commodities that have no official or provisional MRLs. The MHLW also listed 15 chemicals for which no residues may be detected because of high human health risks and 65 substances used as agricultural chemicals for exemption from the regulation [4,5,6]. The MHLW established provisional MRLs on some processed foods besides raw commodities, mainly by adopting the Codex standards. For residues in processed foods without provisional MRLs, the MHLW is using the provisional MRLs of raw ingredients after converting them based on water content and taking into consideration concentration ratios. With these new regulations, the MHLW is not changing its monitoring plan for imported foods, except that each sample will be tested for more residues. The same number of samples, however, will be taken and there will be no new documentation or data requirements from the MHLW after the implementation.

Experimental

The MHLW has published several methods for the extraction and analysis of plant- and animal-based foods [7]. Depending upon the target compounds, the extracts are analyzed by LC/MS or GC/MS. Out of the 8 government recommended test methods, multi-residue screening of veterinary drugs in meat by Methods I and II and LC/MS has already been investigated [8]. In this particular study, multiresidue screening for agricultural chemicals in food following Methods I and II was looked at by LC/MS. Among the 799 compounds in the Japan Positive List, 67 compounds are analyzed by LC/MS methods, 42 analytes come under LC/MS Method I and 25 analytes fall under LC/MS Method II, as shown in Tables 1 and 2.

Table 1. MS/MS transition details for Method I.

Compound	Parent ion	Daughter ion 1	Daughter ion 2	ESI mode	Collision energy (V)
Abamectin Bla	891	305	567	(+)	25
Anilofos	368	199	125	(+)	12
Azinphos-methyl	318	160	77	(+)	10
Azamethiphos	325	183	112	(+)	15
Benzofenap	431	105	119	(+)	25
Butafenacil	492	331	180	(+)	20
Chloridazon	222	92	77	(+)	23
Chromafennozide	395	175	147	(+)	18
Clomeprop	324	120	105	(+)	15
Clonquintcet-mexyl	336	238	192	(+)	15
Clothianidin	250	169	132	(+)	11
Cyazofamid	413	295	241	(+)	12
Cyflufenamid	325	108	261	(+)	9.5
Dimethirimol	210	71	140	(+)	28
Fenoxycarb	302	116	88	(+)	10
Ferimzone (E)	255	132	91	(+)	20
Ferimzone (Z)	255	124	91	(+)	25
Furathiocarb	383	252	195	(+)	15
Imidacloprid	256	209	175	(+)	10
Indoxacarb	528	150	203	(+)	18.5
Iprovalicarb	321	119	203	(+)	20
Isoxaflutole	360	251	144	(+)	15
Lactofen	479	344	223	(+)	18
Methoxyfenozide	-367	-149	-105	(-)	18
Milbemectin A3	551	343.8	240	(+)	18
Milbemectin A4	565	337	240	(+)	27
Naproanilide	292	171	120	(+)	12
Oryzalin	-345	-281	-78	(-)	17.5
Oxycarboxin	268	175	147	(+)	12
Phenmedipham	301	168	136	(+)	7
Pyrazolynate	439	91	229	(+)	25
Pyriftalid	319	139	93	(+)	25
Quizalofop-ethyl	373	299	85	(+)	15
Simeconazole	294	70	73	(+)	15
Thiabendazole	202	175	131	(+)	21
Thiacloprid	253	126	90	(+)	18
Thiamethoxam	292	211	181	(+)	10.5
Tralkoxydim (isomer 1)	-328	-254	-66	(-)	22
Tralkoxydim (isomer 2)	-328	-254	-66	(-)	22
Tridemorph (isomer 1)	298	130	98	(+)	15
Tridemorph (isomer 2)	298	130	98	(+)	15
Triticonazole	318	70	125	(+)	12

Note: The negative sign before ions analyzed in negative mode is not a common way of differentiating positive and negative modes of ionization. However, they are represented in this manner in Tables 1 and 2 as per stipulations in the MHLW document [7].

Table 2. MS/MS transition details for Method II.

Compound	Parent ion	Daughter ion 1	Daughter ion 2	ESI mode	Collision energy (V)
1-Naphthalenacetic acid	-185	-140.7		(-)	9.5
4-Chlorophenoxyacetic acid	-185	-126.7	-128.7 (-187)	(-)	13
Acifluorfen	-359.8	-315.8	-112.9	(-)	7
Bromoxynil	-276	-81	-79	(-)	22
Cloprop	-199.1	-127	-70.9	(-)	10.5
Cloransulam-methyl	430	398	370	(+)	16.5
Cyclanilide	-272	-159.9	-227.9	(-)	23
Dichlorprop	-233	161	-125	(-)	15
Diclosulam	406	378	160.9	(+)	9.5
Florasuram	360	129	360	(+)	15
Flumetsulam	326	129	109	(+)	15
Fluroxypyr	-252.7	-197.7	-233	(-)	12
Fomesafen	-437	-195	-285.9	(-)	38
Forchlorfenuron	248	129	93	(+)	15
Gibberellin	-345	-239	-143	(-)	18
Haloxyfop	362	-316	288	(+)	11
Imazaquin	312	267	199.1	(+)	21.5
Ioxynil	-370	-126.9	-214.9	(-)	36
MCPB	-227	-140.9	-227	(-)	10
Mecoprop (MCPP)	-213	-140.9	-70.9	(-)	13
Mecoprop (MCPP-P)	-213	-140.9	-70.8	(-)	13
Thidiazuron	-219	-99.8	-70.8	(-)	9.5
Thifensulfuron-methyl	388	167	205	(+)	16
Triclopyr	-255.7	-197.7	-218	(-)	11
Triflusulfuron-methyl	493	264	96	(+)	7.5

Materials and reagents

The matrixes investigated for screening agricultural chemicals involved vegetables and fruits (high moisture and low fat content). Tomato was selected as a high moisture content vegetable and lemon as a low fat content fruit.

Ammonium acetate (with minimum 98% purity) was purchased from Sigma. LC/MS grade water and methanol solvents were purchased from Fluka Analytical.

Standards

Pesticide standard mixtures for both methods were purchased from Wako Chemicals, Method I using Standard Pesticides Mixture PL-7-2 (p/n 169-23023), and Method II using Standard Pesticides Mixture PL-8-1 (p/n 166-23033), concentration of each pesticide in each mixture was 20 µg/mL in acetonitrile. However, Method I needed Clomeprop, Imidacloprid, Lactofen, Milbemectin A3, Milbemectin A4, Oxycarboxin, Phenmedipham, Quizalofop-ethyl, Tralkoxydim(isomer1), and Tralkoxydim(isomer2) to be purchased as individual solid standards from Wako and added to the mixture. Likewise, Method II mixture was short on Cyclanilide, Imazaquin, and Triflusulfuron-methyl which were purchased individually from Wako and added to the mixture (except Cyclanilide procured from Kanto Chemicals).

SPE cartridges	Method I: Agilent Bond Elut Carbon/NH_2, 500 mg/500 mg, 6 mL (p/n 12252202)
	Method II: Agilent Bond Elut Si, 500 mg, 10 mL (p/n 14113036)
Columns	Method I: Agilent Pursuit XRs C18, 2.0 × 150 mm, 3 µm (p/n A6001150X020)
	Method II: Agilent Pursuit C18, 2.0 × 150 mm, 3 µm (p/n A3001150X020)

Sample preparation

For each of the two methods, there is a 2-step protocol to process the samples before analysis: step 1 involves a liquid-liquid extraction with acetonitrile, followed by an SPE clean-up in step 2. The clean-up sorbents involved for both methods were, however, different. Bond Elut Carbon/NH_2 and Bond Elut Silica cartridges were used in Methods I and II respectively.

Step 1: Liquid-liquid extraction for Methods I and II

For fruits and vegetables, weigh out 20.0 g of the sample.

Add 50 mL of acetonitrile, and homogenize the sample. Filter by suction. Add 20 mL of acetonitrile to the residue on the filter paper, mix, and filter. Mix and vortex both filtrates. Add acetonitrile to the filtrate to make a 100 mL solution.

Method I

Take 20 mL of the extracted solution. Add 10 g of sodium chloride and 20 mL of 0.5 mol/L phosphate buffer (pH 7.0) and vigorously shake. Once the solution has separated into 2 layers, transfer the acetonitrile (top layer), dry over sodium sulfate (anhydrous), and filter.

Concentrate the filtrate to dryness at 40 °C. Dissolve the residue in 2 mL of acetonitrile/toluene (3:1).

Method II

Take 20 mL of the extracted solution. Add 10 g of sodium chloride and 20 mL of 0.01 mol/L hydrogen chloride and vigorously shake. Once the solution has separated into 2 layers, transfer the acetonitrile (top layer), dry over sodium sulfate (anhydrous), and filter.

Concentrate the filtrate to dryness at 40 °C. Dissolve the residue in 2 mL of acetone/triethylamine/n-hexane (20:0.5:80).

Step 2: SPE clean-up with Agilent Bond Elut Carbon/NH_2 (Method I) and Agilent Bond Elut Silica (Method II)

Method I

Condition an Agilent Bond Elut dual phase SPE cartridge containing graphite carbon black/aminopropyl (500 mg/500 mg) with 10 mL of acetonitrile/toluene (3:1). Load the solution obtained from the extraction step (method I) to the column, and allow the solution to pass through the column (do not collect). Elute the sample from the column with 20 mL of acetonitrile/toluene (3:1).

After collecting the effluent, concentrate the effluent to about 1 mL at 40 °C. Add 10 mL of acetone and concentrate to about 1 mL at 40 °C. Add 5 mL of acetone to the concentrated solution and concentrate to dryness.

Dissolve the residue in methanol to make a 4 mL solution, and analyze by LC/MS.

Method II

Condition an Agilent Bond Elut SPE silica cartridge (500 mg) with 5 mL of methanol, 5 mL of acetone, and then 10 mL of n-hexane. Load the solution obtained from the extraction step (method II), and allow the solution to pass through the column (do not collect).

Wash the column with 10 mL of acetone/triethylamine/n-hexane (20:0.5:80), and discard the effluent.

Elute the sample from the column with 20 mL of acetone/methanol (1:1), and collect.

Concentrate the effluent to dryness at 40 °C. Dissolve the residue in methanol to make a 4 mL solution, and analyze by LC/MS.

Instrument Conditions

Columns	Method I: Agilent Pursuit XRs C18, 2.0 × 150 mm, 3 µm Method II: Agilent Pursuit C18, 2.0 × 150 mm, 3 µm
Mobile phase	A: H_2O + 3 mM ammonium acetate B: CH_3OH + 3 mM ammonium acetate

Gradient

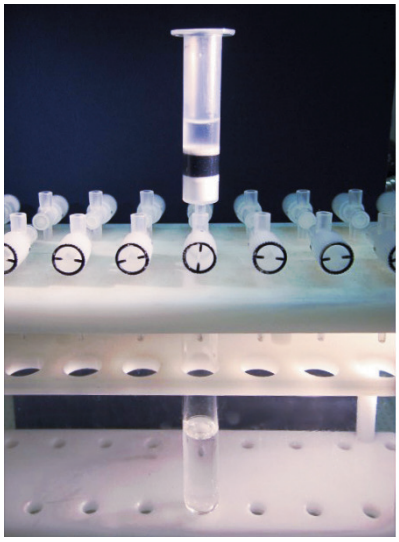
Time:	%A	%B
0:00	85.0	15.0
1:00	60.0	40.0
3.50	60.0	40.0
6:00	50.0	50.0
8:00	45.0	55.0
17:50	5.0	95.0
30:00	5.0	95.0
30:06	85.0	15.0
40:00	85.0	15.0

Flow rate	0.2 mL/min
Temperature	Ambient (Method I), 40 °C (Method II)
Source	ESI
Ionization mode	Positive/Negative
Collision gas	Argon
Instrument	Agilent 320 LC/MS/MS

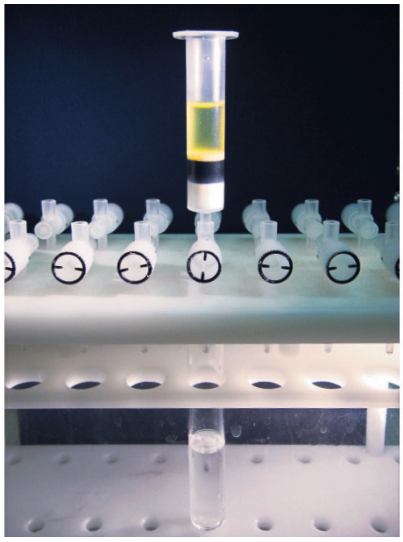
Results and Discussion

Clean-up with Bond Elut Carbon/NH_2: Ideal sorbent for pigment removal

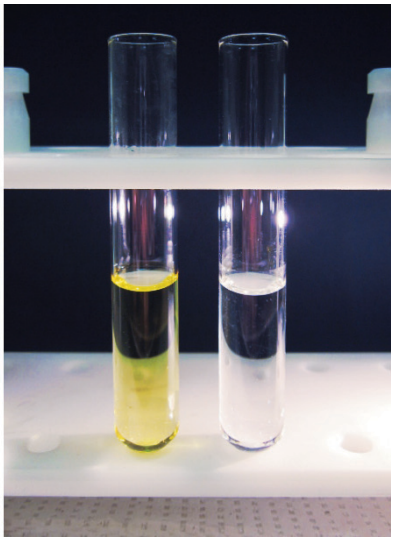
Agilent Bond Elut Carbon is an ultrapure graphitized carbon particle that has been optimized for the absorption of pigments in food, fruits, and vegetables, and small organic residues in waste water. This sorbent behaves both as a nonspecific sorbent for hydrophobic compounds and, to a certain extent, as an anion-exchanger. Bond Elut NH_2 is a weaker anion exchanger than sorbents such as SAX (quaternary amine sorbent), and is, therefore, a better choice for retention of very strong anions, removes polar organic acids, some sugars, and lipids. Thus, the amino function augments the anion exchange capabilities of carbon as well. This layered cartridge is an efficient means of withholding colored hydrophobic pigments such as lycopene in tomatoes and acidic species in different matrices. The dual layer SPE tube was specifically developed to offer superior cleanup when conducting multiresidue pesticide analysis from food.



Conditioning



Cleanup



Before and after cleanup

Figure 1. Pigment removal and clean-up offered by Agilent Bond Elut Carbon/NH_2 dual phase SPE cartridge.

Figure 2 shows LC/MS/MS multiresidue pesticide analysis using standard mixtures and Methods I and II. Figures 3 and 4 illustrate data generated in spiked matrices used in Methods I and II. Tomato and lemon were used for both Methods I and II, examples of spiked tomato and spiked lemon at 100 ppb concentrations are shown for Methods I and II respectively. There are 2 pairs of isomers in Method I - Tralkoxydim and Tridemorph. Both pairs are seen to separate with base-line resolution on Agilent Pursuit XRs C18 column (Figure 3). These columns are based on a 100Å high surface area silica, combined with a high ligand density, they offer superior resolution, excellent stability, easy scalability, and maximum loadability.

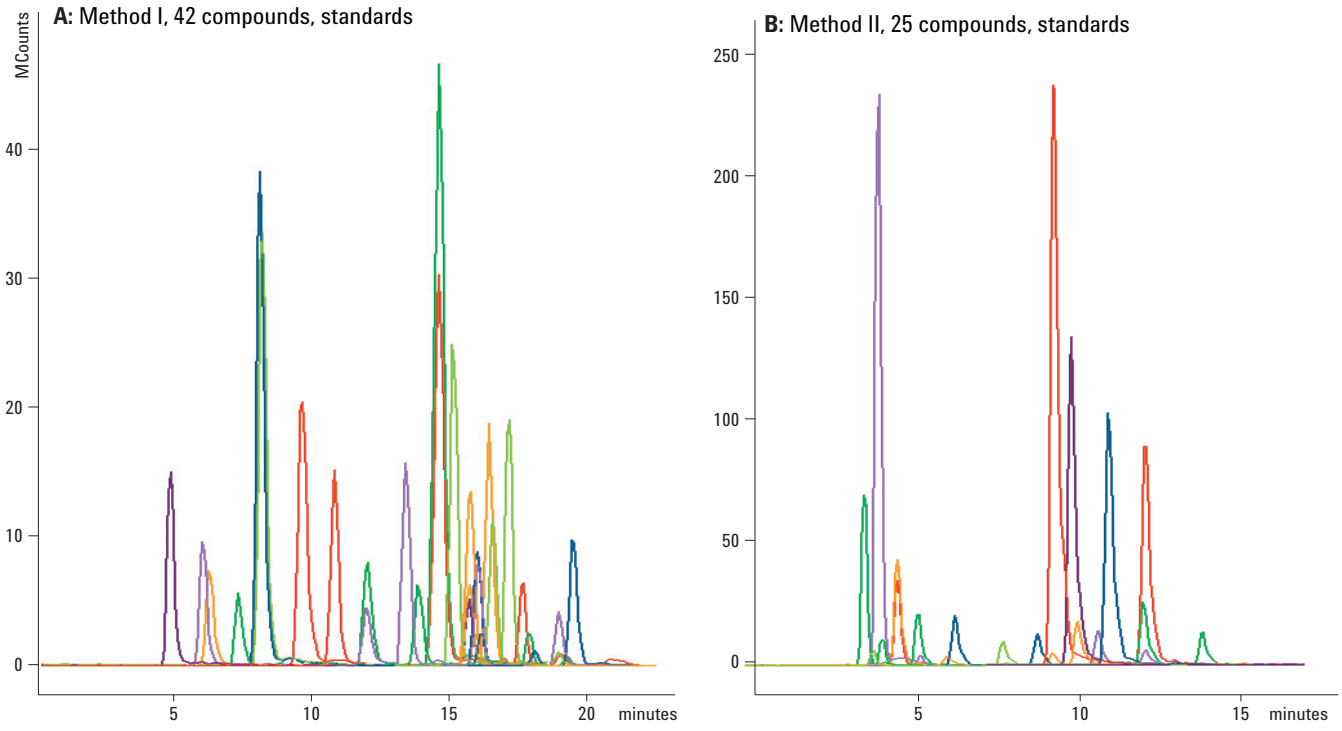


Figure 2. Analysis of multiresidue pesticide standards by Japanese Positive List Method I (A, 42 compounds) and Method II (B, 25 compounds). [See Table 1 for the pesticides identified in Chromatrogram A (from Method I) and Table 2 for the pesticides in Chromatogram B (from Method II)].

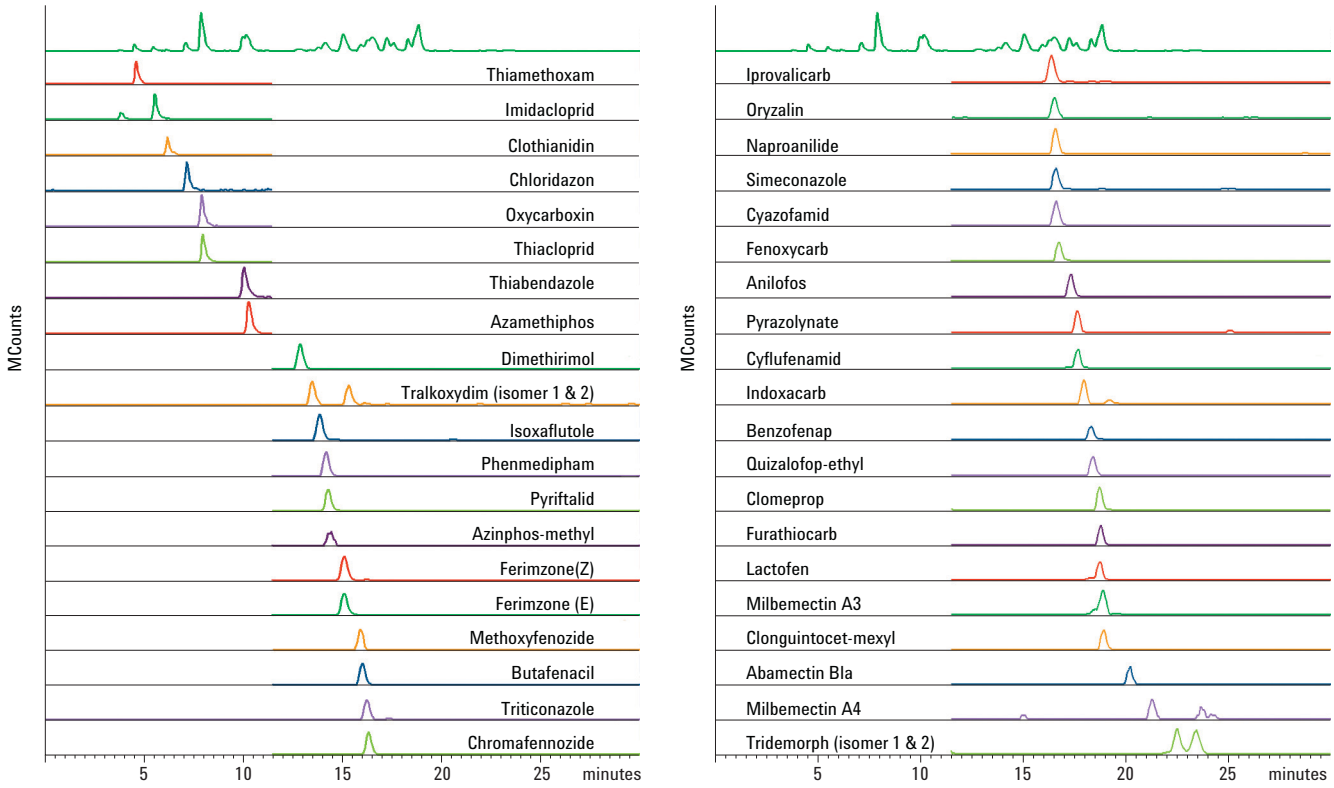


Figure 3. Analysis of multi-residue pesticides in spiked tomato by Japanese Positive List Method I - Total ion chromatogram and MRM chromatograms of 42 compounds in tomato at 100 ppb. [See Table 1 for the pesticides identified in Method I.]

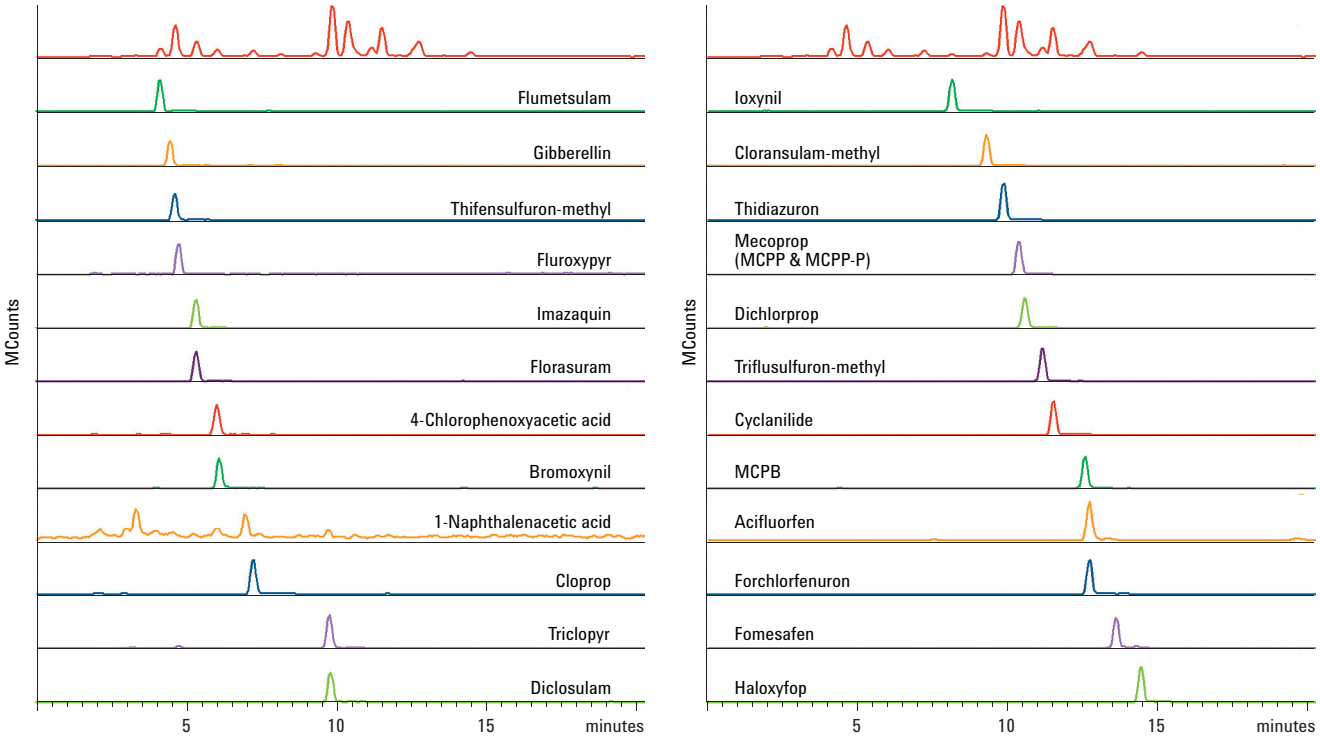


Figure 4. Analysis of multi-residue pesticides in spiked lemon by Japanese Positive List Method II - Total ion chromatogram and MRM chromatograms of 25 compounds in lemon at 100 ppb. [See Table 2 for the pesticides identified in Method II.]

For quantitation purposes, the matrices were spiked at 10 ppb as well. A 10 ppb amount was selected as per the MHLW regulations requiring that no agricultural chemical exceed the MRL (typically 10 ppb). Figures 5 and 6 show representative LC/MS/MS chromatogram comparisons of the pesticides in standard and spiked matrices (tomato and lemon) relative to the blank matrix at 10 and 100 ppb for both methods.

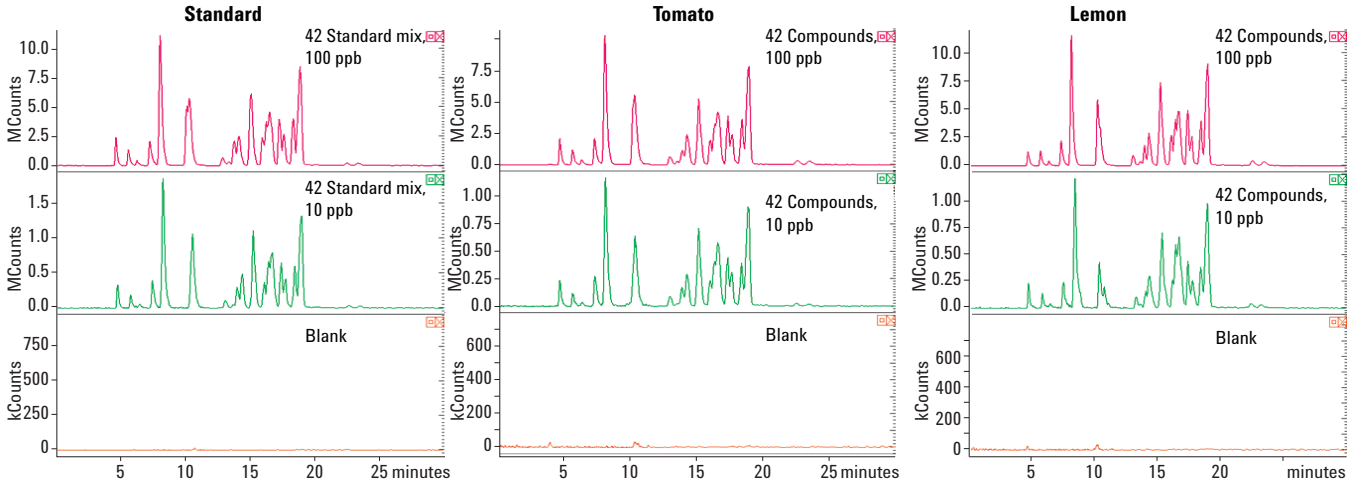


Figure 5. Method I: LC/MS/MS chromatogram comparisons of the compounds in standard and spiked matrices (tomato and lemon), relative to the blank matrix at 10 and 100 ppb.

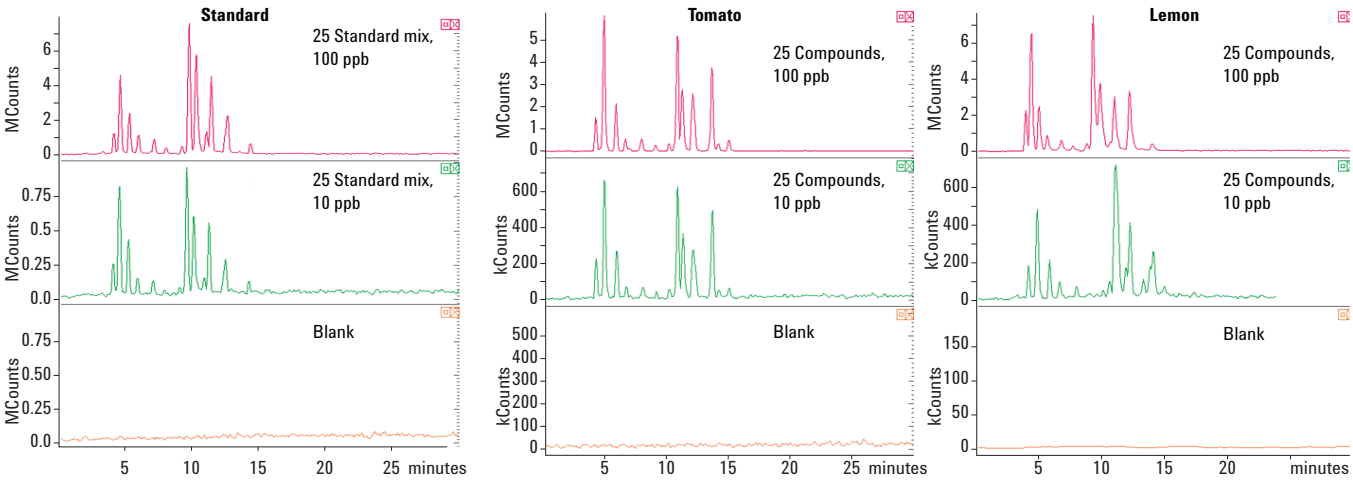


Figure 6. Method II: LC/MS/MS chromatogram comparisons of the compounds in standard and spiked matrices (tomato and lemon), relative to the blank matrix at 10 and 100 ppb.

Two fragment ions were monitored for each analyte for quantifier and qualifier transition channels. Figure 7 shows chromatograms of examples of an analyte extracted each from Methods I and II. At 10 ppb levels, fragment ions of Azinphos-methyl (Method I) show signal-to-noise ratios of 1947 and 558. The ion ratio of daughter ion 1 and ion 2 for this compound was 0.758 (comparing peak areas), which was used to identify this compound. In a similar manner, fragment ions of Imazaquin (Method II) at 10 ppb show signal-to-noise ratios of 6635 and 21380. The ion ratio of daughter ion 1 and ion 2 for this compound was 0.233, which was used for identification. All analytes were identified through the same evaluation procedure.

For both Methods I and II, not every analyte could be detected as a second daughter ion at 10 ppb levels. Thus modifications were made to the Positive List procedure to assess whether improvements could be made in terms of compound stability and resolution. The drying gas temperature for Method I was decreased from 400 °C to 220 °C as 3 compounds were not stable at higher temperatures. Figure 8 exemplifies this; there were no signs of any ions of Abamectin Bla, Azinphos-methyl, and Chromafennozide at 400 °C even when the y-axis was kept significantly lower than that obtained when the temperature was lowered to 220 °C. For the same reason, the drying gas temperature for Method II was also decreased, from 400 °C to 250 °C. The column temperature in Method I was switched from 40 °C to ambient for tridimorph isomers as resolution was better at ambient temperatures for these compounds.

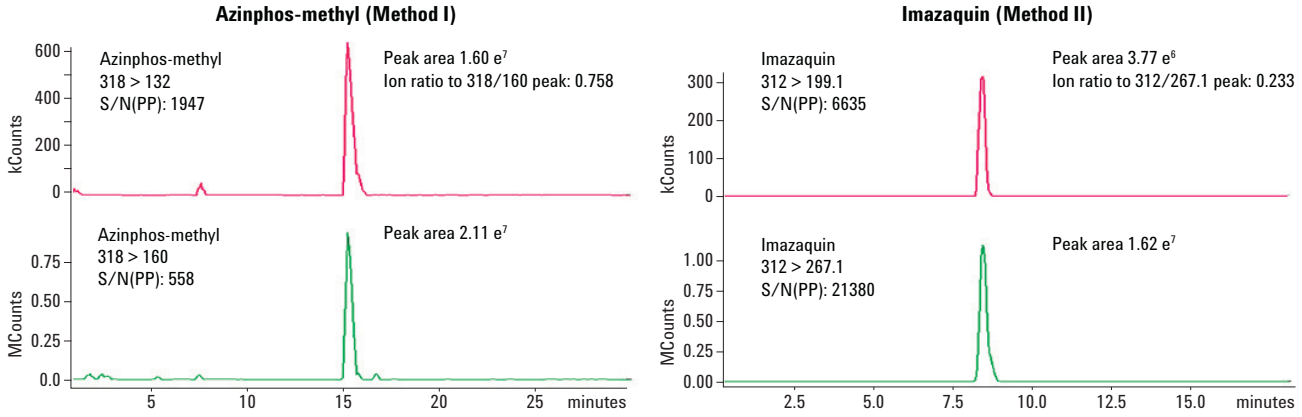


Figure 7. An example of the parameters used to identify the pesticides spiked within the matrix, namely, S/N ratio and ion ratio. Pesticides, Azinphos-methyl from Method I and Imazaquin from Method II, both at 10 ppb are selected for illustration.

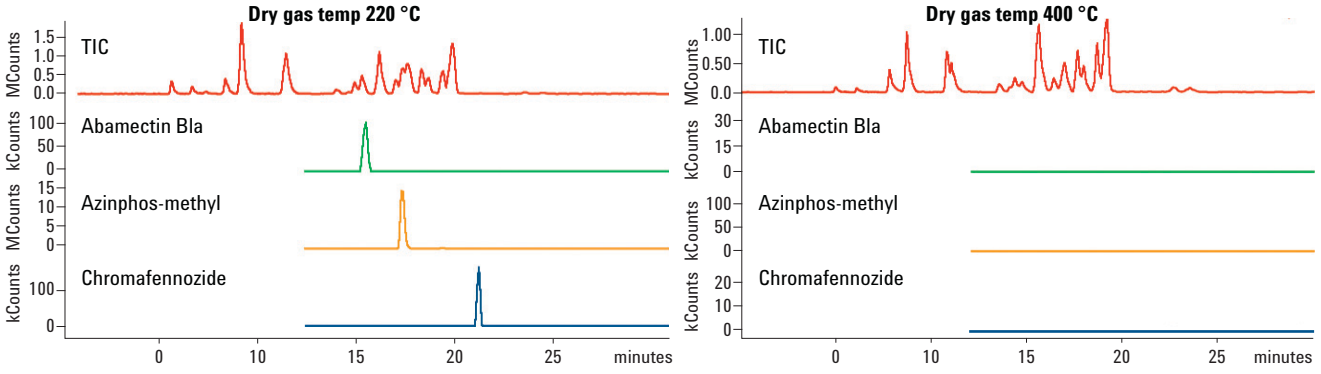


Figure 8. Modifications made to Method I to improve stability of thermally labile compounds.

To demonstrate linearity, 5 point calibration curves from 10 ppb to 400 ppb were constructed by spiking neat samples. Figure 9 displays calibration curves of two analytes each from Methods I and II. Linearity was excellent at R^2 = 0.9978 and above for all 4 analytes.

Analyte recoveries obtained in Method I are shown in Table 3, and those for Method II are shown in Table 4. Recoveries for most analytes in both methods were in the range of 60-140%, which are within EU and CDFA requirements [9].

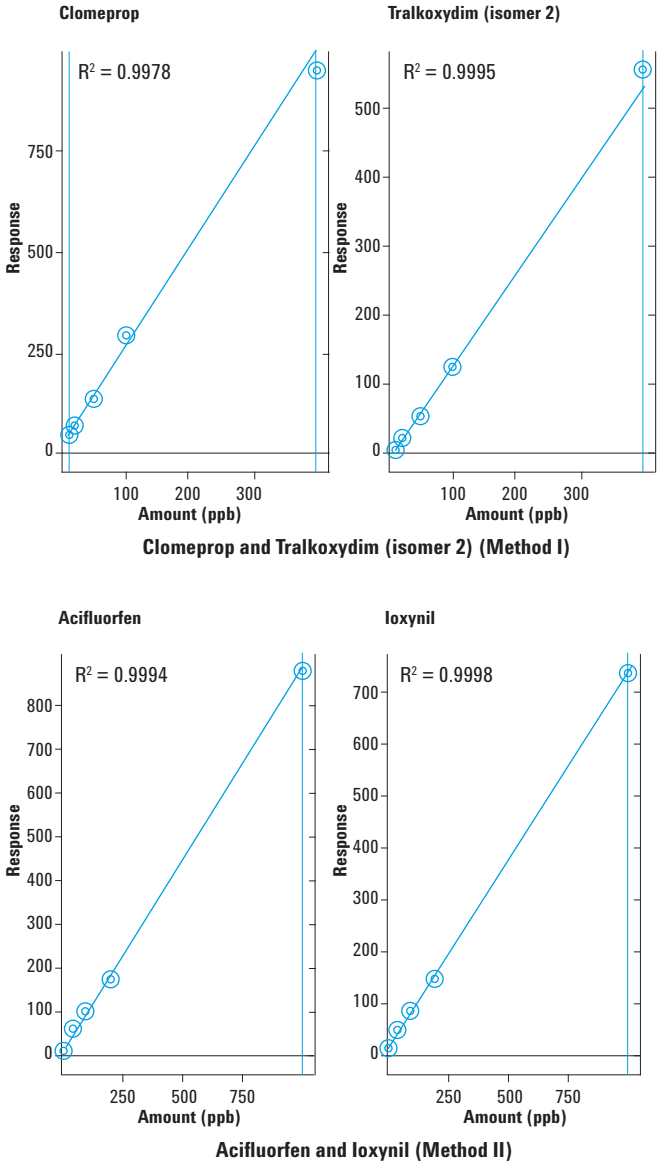


Figure 9. Calibration curves for some compounds from Methods I and II.

Table 3. Average recoveries from Method I for the 42 compounds in tomato spiked at 10 ppb and 100 ppb levels (n = 3).

	10 ppb			100 ppb		
Compound	**Amount**	**RSD%**	**Recovery%**	**Amount**	**RSD%**	**Recovery%**
Abamectin Bla	9.9	6.0	98.7	97.5	6.9	97.5
Anilofos	8.9	4.5	88.9	105.7	3.9	105.7
Azinphos	7.8	31.2	78.3	92.8	6.0	92.8
Azamethiphos-methyl	9.2	4.8	91.7	106.1	7.8	106.1
Benzofenap	9.7	10.1	96.5	97.8	8.3	97.8
Butafenacil	11.7	9.0	117.0	93.5	4.3	93.7
Chloridazon	9.4	9.1	94.4	96.3	4.4	96.3
Chromafennozide	10.2	5.5	102.3	112.3	4.1	112.3
Clomeprop	9.3	7.1	93.3	108.0	4.6	108.0
Clonguintocet-mexyl	9.4	2.1	93.5	105.6	4.5	105.6
Clothianidin	10.5	1.6	104.6	98.9	4.3	98.9
Cyazofamid	8.2	2.4	81.9	118.3	3.5	118.3
Cyflufenamid	9.7	15.8	97.0	84.3	4.8	84.3
Dimethirimol	9.6	2.8	95.8	109.3	3.5	109.3
Fenoxycarb	9.2	7.0	91.6	104.0	2.0	104.0
Ferimzone (E)	7.2	2.0	71.9	110.0	5.5	110.0
Ferimzone(Z)	9.4	6.7	94.0	106.3	5.8	106.3
Furathiocarb	10.2	7.2	101.7	108.3	5.5	108.3
Imidacloprid	8.3	6.0	83.3	88.3	5.7	88.3
Indoxacarb	9.3	4.7	92.7	89.8	9.3	89.8
Iprovalicarb	8.9	7.5	89.3	120.0	6.7	120.0
Isoxaflutole	10.0	2.0	100.3	66.5	3.9	66.5
Lactofen	12.1	5.8	121.0	67.5	5.5	67.5
Methoxyfenozide	6.4	26.8	63.5	121.0	5.9	121.0
MilbemectinA3	9.8	8.7	98.3	92.7	11.1	92.7
MilbemectinA4	7.3	7.7	73.2	95.6	5.1	95.6
Naproanilide	9.5	2.7	95.0	97.7	2.2	97.7
Oryzalin	6.9	5.2	68.7	105.3	3.7	105.3
Oxycarboxin	7.8	12.1	77.5	95.7	5.8	95.7
Phenmedipham	10.5	1.4	105.0	98.7	4.4	98.7
Pyrazolynate	9.8	8.7	98.3	89.8	9.3	89.8
Pyriftalid	9.1	1.4	91.2	108.1	4.4	108.1
Quizalofop-ethyl	9.9	4.7	99.1	93.3	4.8	93.3
Simeconazole	8.8	4.0	87.7	85.8	3.6	85.8
Thiabendazole	9.3	6.5	93.1	98.7	5.8	98.7
Thiacloprid	8.8	10.3	88.1	95.4	2.3	95.4
Thiamethoxam	7.8	8.2	77.5	60.0	3.3	60.0
Tralkoxydim (isomer 1)	7.6	3.5	75.7	118.6	4.4	118.6
Tralkoxydim (isomer 2)	9.0	9.2	90.0	105.0	4.0	105.0
Tridemorph (isomer 1)	9.4	7.8	93.6	95.9	5.8	95.9
Tridemorph (isomer 2)	9.3	6.7	93.1	100.5	7.3	100.5
Triticonazole	9.3	2.5	92.8	95.7	2.9	95.7

Table 4. Average recoveries from Method II for the 25 compounds in lemon spiked at 10 ppb and 100 ppb levels (n = 3).

	10 ppb			100 ppb		
Compound	**Amount**	**RSD%**	**Recovery%**	**Amount**	**RSD%**	**Recovery%**
1-Naphthalenacetic acid	NA	NA	NA	80.1	15.3	80.1
4-Chlorophenoxyacetic acid	12.3	5.4	123.0	80.5	5.8	80.5
Acifluorfen	7.5	5.1	74.8	99.7	10.8	99.7
Bromoxynil	8.9	4.7	88.9	79.0	3.4	79.0
Cloprop	11.7	21.3	117.0	98.2	11.3	98.2
Cloransulam-methyl	9.5	19.7	94.6	95.4	2.1	95.4
Cyclanilide	9.4	5.6	94.2	85.6	2.8	85.6
Dichlorprop	8.6	19.3	86.0	100.5	6.3	100.5
Diclosulam	8.8	5.5	88.1	93.0	6.1	93.0
Florasuram	9.1	6.6	90.8	81.3	1.1	81.3
Flumetsulam	10.2	9.9	101.9	72.6	8.1	72.6
Fluroxypyr	8.6	17.3	86.1	75.9	4.1	75.9
Fomesafen	6.6	8.6	65.8	83.9	3.2	83.9
Forchlorfenuron	8.7	10.5	86.9	57.7	9.8	57.7
Gibberellin	12.5	19.1	124.5	89.1	2.5	89.1
Haloxyfop	8.7	2.8	86.6	91.3	0.5	91.3
Imazaquin	6.4	7.7	63.8	81.0	1.4	81.0
Ioxynil	11.8	17.1	118.3	75.9	7.1	75.8
MCPB	12.4	9.0	123.5	91.8	4.6	91.8
Mecoprop (MCPP)	8.7	6.9	86.7	77.1	9.9	77.1
Mecoprop (MCPP-P)	8.7	6.9	86.7	91.8	0.5	91.8
Thidiazuron	8.4	16.8	83.5	80.9	7.5	80.9
Thifensulfuron-methyl	10.6	8.7	105.5	98.9	5.3	98.9
Triclopyr	9.0	0.9	89.5	104.4	6.3	104.4
Triflusulfuron-methyl	11.9	19.3	119.3	79.7	6.7	79.7

Conclusions

A complete solutions package incorporating the use of the dual phase Agilent Bond Elut Carbon/NH_2 and Bond Elut Silica SPE coupled with robust Pursuit HPLC columns was developed for screening challenging agricultural chemicals in food within the expected MRLs (0.01 ppm) of the Japan Positive List. All 67 compounds included in multiresidue Methods I and II were analyzed in tomato and lemon matrices by using cartridge-based SPE and LC/MS/MS. Pursuit XRs column was able to separate 2 pairs of isomers with baseline resolution in Method I, illustrating the power of liquid chromatography when MS detection becomes a limitation. Good linearity from 10 ppb to 400 ppb was observed for most analytes with R^2 greater than 0.98. Recoveries for most analytes in both methods were in the range of 60-140%, which are within EU and CDFA requirements.

For both Methods I and II, not every analyte could be detected as a second daughter ion at 10 ppb levels. However, slight modifications made to the drying gas temperature and column temperature compared to the existing Positive List procedure resulted in stable daughter ions and isomers. Optimization of parameters associated with lower drying gas temperature in both Methods I and II lent qualifying ions for all pesticides that were not observed at the high drying gas temperature at 10 ppb for some of the pesticides.

References

1. "Positive List System for Agricultural Chemical Residues in Foods", http://www.ffcr.or.jp
2. "Introduction of the Positive List System for Agricultural Chemical Residues in Foods," Department of Food Safety, Ministry of Health, Labour and Welfare, June 2006 http://www.mhlw.go.jp/english/topics/foodsafety/positivelist060228/introduction.html
3. "Positive List System for Agricultural Chemical Residues in Foods," Ministry of Health, Labour and Welfare http://www.mhlw.go.jp/english/topics/foodsafety/positivelist060228/index.html
4. "Maximum Residue Limits (MRLs) List of Agricultural Chemicals in Foods," The Japan Food Chemical Research Foundation http://www.m5.ws001.squarestart.ne.jp/foundation/search.html
5. Table in item 6 (1), Section A General Compositional Standards for Food, Part I Food: The maximum residue limits of substances used as ingredients of agricultural chemicals in foods http://www.mhlw.go.jp/english/topics/foodsafety/positivelist060228/dl/index-1a.pdf
6. Table in item 7 (1), Section A General Compositional Standards for Food, Part I Food: The maximum residue limits of substances used as ingredients of agricultural chemicals in foods (Provisional MRLs List) http://www.mhlw.go.jp/english/topics/foodsafety/positivelist060228/dl/index-1b.pdf
7. "Analytical Methods for Residual Compositional Substances of Agricultural Chemicals, Feed Additives, and Veterinary Drugs in Food", Department of Food Safety, Ministry of Health, Labour and Welfare, http://www.ffcr.or.jp-zaidan-FFCRHOME.nsf
8. E. Chang, K. Yamashita, R. Arora, "Multi-residue Screening of Veterinary Drugs (I) and (II) in Meat According to the Japan Positive List using Cartridge-based SPE and LC/MS/MS", Agilent Application Note, Publication No.: 5990-8986EN.
9. "Quality Control Procedures for Pesticide Residues Analysis". SANCO/10232/2006, 24/March/2006. http://ec.europa.eu/food/plant/resources/qualcontrol_en.pdf.

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