ナッツ類中のシヘキサチン,2,4,5-Tを含む14農薬のGC/MS選択的イオンモニター(SIM)法の用いた測定

誌名	食品衛生学雑誌
ISSN	00156426
著者名	川崎,勝 福原,克治 勝村,利恵子 高坂,典子 内山,貞夫
発行元	[日本食品衛生学会]
巻/号	38巻3号
掲載ページ	p. 161-169
発行年月	1997年6月

Note

GC/MS (SIM) Determination of 14 Pesticides Including Cyhexatin and 2,4,5-T in Nuts

(Received September 30, 1996)

Masaru KAWASAKI, Katsuharu FUKUHARA, Rieko KATSUMURA, Noriko TAKASAKA and Sadao UCHIYAMA

(Hatano Research Institute Food & Drug Safety Center: 729–5, Ochiai, Hadano, Kanagawa 257, Japan)

GC/MS with selected ion monitoring ((GC/MS (SIM)) has been developed as a screening method for the determination of 14 pesticides residues including cyhexatin and 2,4,5-T in nuts. The pesticides were extracted with acetone from nuts, and then partitioned between *n*-hexane and acetonitrile. Clean-up was conducted by solid-phase extraction (SPE) with a Bond Elut Florisil column. Most of the pesticides were eluted in a mixture of *n*-hexane and acetone (17 : 3) from the column, and the eluate was examined by GC/MS (SIM). Cyhexatin and 2,4,5-T were analyzed after derivatization and SPE clean-up. Recoveries of 14 pesticides from 6 kinds of nuts were mostly over 80%. This method is effective for multi-residue analysis of pesticides in nuts.

Key words: gas chromatography–mass spectrometry (GC/MS); MS fragmentation; pesticide; solid-phase extraction (SPE); selected ion monitoring (SIM); cyhexatin; 2,4,5-T

Introduction

Much attention has been paid to pesticide residues in foods in Japan, particularly because of the increase in imported foods. The Ministry of Health and Welfare in Japan has specified the residue levels for 138 pesticides in the Law of Food Sanitation up to 1996[1)–6)]. Several GC/MS methods for newly specified pesticides have been reported recently[7)–10)]. The feasibility of multi-residue analyses of 53 of these 138 pesticides by a GC/MS (SIM) method was discussed in our previous paper[11)]. This paper deals with a study of multiresidue analysis with GC/MS (SIM) for 14 pesticides, including cyhexatin and 2,4,5-T, and with clean-up by the solid-phase extraction (SPE) from nuts, which contain oily components that are expected to disturb the analyses.

Materials and Methods

Solvents and reagents

Organic solvents such as acetone, *n*-hexane and acetonitrile were of pesticide residue analysis grade. Reagents were of the same grade or specific grade.

Pesticide standards

Standard reference materials of 14 pesticides, chlorfenvinphos (mixture of Z and E), cyfluthrin (mixture of isomers), cyhexatin, fenobucarb, fenvalerate, lenacil, methiocarb, myclobutanil, phoxim, pirimiphos-methyl, propiconazole, pyridaben, thiometon and 2,4,5-T, were purchased from Hayashi Pure Chemical Industries, Ltd. (Osaka, Japan) or Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

Pesticide standard solutions

Pesticide standard solutions (1000 μg/mL) were prepared by dissolving the pesticide in acetone.

Spiking solution

Spiking solution (each concentration: 2 μg/mL) was prepared by combining 14 pesticide

standard solutions and diluting the mixture with acetone.

Solid phase extraction (SPE) column

Bond Elut LRC (3 cc/500 MG) Florisil purchased from Varian Co. (U.S.A.) was used for solid phase extraction (SPE).

Samples

Macadamia nuts, hazel nuts, cashew nuts, pistachio nuts, peanuts and pine nuts were obtained from commercial sources in Japan.

Apparatus

Gas chromatograph-mass spectrometer: Shimadzu GC-17A gas chromatograph coupled with a Parvum QP 5000 mass spectrometer and a Shimadzu AOC-17 injector.

Data processing apparatus: Sanyo Co. AXAGEν computer, Shimadzu operating system software class 5000, and MS-Windows.

GC conditions: GC column, J & W Scientific capillary column DB-5 ms (0.25 mm i.d.×30 m, film thickness 0.25 μm). Oven temp., 50℃ (1.5 min)→300℃ (10 min), increased at 10℃/min. Injection temp., 250℃; transfer line temp., 280℃; carrier gas, He at 20 mL/min; injection volume, 1 μL (splitless); sampling time, 1.00 min.

MS conditions: Electron impact ionization (EI); ion source voltage, 70 eV; detector gain, 1.75 kV; solvent elution time, 3.00 min; measurement time, 4.00–35.00 min; mass range, *m/z* 40.00–400.00.

Selected ion monitoring (SIM) method

SIM operating conditions were as follows. Detector gain, 1.75 or 2.5 kV; maximum ion set number, 20; solvent elution time, 3.00 min; sampling rate, 0.30 sec; micro scan width: 0.50. GC/MS operating software is class 5000 (Shimadzu), with the Windows 3.0 operating system.

Investigation of solid phase extraction (SPE) elution pattern

A Bond Elut Florisil column was conditioned with 2 mL of *n*-hexane, then 2 mL aliquots of standard solutions were applied to the column, and eluted with 5 mL of *n*-hexane (Fraction 1), 5 mL of *n*-hexane–acetone (17 : 3) (Fraction 2) and 5 mL of *n*-hexane–acetone (1 : 1) (Fraction 3). Each eluate was evaporated under N_2 gas, and the residue was dissolved in 2 mL of *n*-hexane. The solution was measured by GC/MS (SIM) to obtain the SPE elution pattern.

Preparation of the test solution

Pesticides except cyhexatin and 2,4,5-T were extracted twice from ground nuts (20 g) with 100 mL portions of acetone. After paper filtration, the combined extract was evaporated under reduced pressure to remove acetone. The residual aqueous solution was mixed with 100 mL of saturated NaCl solution and further extracted with two 100 mL portions of *n*-hexane. The *n*-hexane layers were combined and then dehydrated with anhydrous Na_2SO_4. The *n*-hexane solution was evaporated to a small volume and dried with N_2 gas. The residue was partitioned between two 30 mL portions of *n*-hexane–saturated MeCN and 30 mL of MeCN–saturated hexane. The MeCN layers were combined and evaporated to dryness with N_2 gas. The residue was dissolved in 20 mL of *n*-hexane. A 5 mL aliquot of the *n*-hexane solution was subjected to SPE clean-up as described above. Test solutions of cyhexatin and 2,4,5-T were prepared according to the Japanese standard methods[4] and then subjected to SPE as described above. Fraction 1 (5 mL) is for analysis of cyhexatin derivative and fraction 2 (5 mL) for analysis of other pesticides.

Recovery test

Fourteen pesticides were spiked in 6 kinds of nuts at the concentration of 0.2 ppm. Each recovery was obtained as the average of three trials ($n=3$).

Results and Discussion

In this experiment, three steps of extraction with organic solvent, clean-up by solid-phase extraction (SPE) and GC/MS (SIM) were adopted for a multiresidue analysis of pesticides in oily nuts.

1. Extraction and clean-up with SPE

Extraction of nuts with acetone, and partition between *n*-hexane and MeCN were useful for the purification of pesticides from oily nut samples. Further clean-up was conducted by the SPE

Table 1. List of Conditions of GC/MS (SIM) and SPE Elution Pattern of 14 Pesticides

Ion set	No.	Pesticide	Retention time (min)	Molecular weight	Target ion (*m/z*)	Proposed ion assignment	Determination limit (μg/mL)	Bond Elut Florisil Elution Pattern ($n=3$)[c]	
								(Fr. 1)[a]	(Fr. 2)[b]
#1[d]	1	Phoxim	6.18	298	103	$[C_7H_5N]^+$	0.01		86.5± 6.7
	2		9.21	298	103	$[C_7H_5N]^+$	0.01		104.6± 8.1
	3a	Fenobucarb	10.87	207	121	$[C_8H_8O+1]^+$	0.01		97.1± 6.4
	3b		10.87		150	$[C_{10}H_{13}O+1]^+$	0.01		96.4± 2.4
	4a	Methiocarb	14.74	225	153	$[C_8H_8OS+1]^+$	0.05		94.0± 1.9
	4b		14.74		168	$[C_9H_{11}OS+1]^+$	0.05		94.2± 0.6
	5a	Fenobucarb	15.47	207	121	$[C_8H_8O+1]^+$	0.01		98.3± 3.0
	5b		15.47		150	$[C_{10}H_{13}O+1]^+$	0.01		98.7± 3.6
	Measurement time (min): 4.00–16.50 Monitoring ion (*m/z*): 103, 121, 150, 153, 168								
#2[e]	6a	Thiometon	16.84	246	88	$[C_4H_8S]^+$	0.01		96.2± 6.8
	6b		16.84		125	$[C_2H_6O_2PS+1]^+$	0.01		95.0± 6.3
	7a	Pirimiphos-Me	19.31	305	290	$[M-15]^+$	0.01		104.8± 6.1
	7b		19.31		305	$[M]^+$	0.01		102.0± 7.0
	8a	Methiocarb	19.41	225	153	$[C_8H_8OS+1]^+$	0.005		100.7± 7.7
	8b		19.41		168	$[C_9H_{11}OS+1]^+$	0.005		110.4± 9.0
	9	2,4,5-T-Bu[h]	20.25	484	57	$[C_2H_2O_2-1]^+$	0.01		85.5± 3.8
	10a	Chlorfenvinphos	20.63	360	267	$[M-HCl-C_4H_8-1]$	0.01		83.6± 2.8
	10b		20.63		323	$[M-HCl-1]^+$	0.01		91.2± 9.4
	Measurement time (min): 16.50–21.00 Monitoring ion (*m/z*): 57, 88, 125, 153, 168, 267, 290, 305, 323								
#3[f]	1a	Myclobutanil	21.89	287	150	$[C_8H_4NCl+1]^+$	0.1		83.4± 4.5
	11b		21.89		179	$[C_{11}H_{12}Cl]^+$	0.1		92.7± 4.5

Table 1. continued

Ion set	No.	Pesticide	Retention time (min)	Molecular weight	Target ion (*m/z*)	Proposed ion assignment	Determination limit (μg/mL)	Bond Elut Florisil Elution Pattern ($n=3$)[c] (Fr. 1)[a]	(Fr. 2)[b]
	12a	Cyhexatin[i]	21.98	385	81	$[C_6H_9]^+$	0.02	100.4±5.8	
	12b		21.98		203	$[C_6H_{11}Sn+1]^+$	0.02	99.1±1.0	
	13a	Propiconazole	23.28	342	173	$[C_7H_3OCl_2]^+$	0.01		87.6± 2.9
	13b		23.28		259	$[M-C_3H_4N_3-1]^+$	0.01		89.4± 0.6
	14a	Propiconazole	23.41	342	173	$[C_7H_3OCl_2]^+$	0.01		88.4± 3.1
	14b		23.41		259	$[M-C_3H_4N_3-1]^+$	0.01		89.6± 6.2
	15	Lenacil	23.41	234	153	$[M-C_5H_7N]^+$	0.01		47.1±10.6
	Measurement time (min): 21.00–26.00 Monitoring ion (*m/z*): 81, 150, 153, 173, 179, 203, 259								
#4[g]	16	Pyridaben	26.48	364	147	$[C_{11}H_{15}]^+$	0.01		94.5± 5.5
	17	Cyfluthrin	26.86	434	163	$[C_7H_7Cl_2]^+$	0.1		94.7± 5.5
	18	Cyfluthrin	26.97	434	163	$[C_7H_7Cl_2]^+$	0.1		95.8± 3.7
	19	Cyfluthrin	27.04	434	163	$[C_7H_7Cl_2]^+$	0.1		103.4±18.2
	20	Cyfluthrin	27.09	434	163	$[C_7H_7Cl_2]^+$	0.1		106.3±12.0
	21	Fenvalerate	28.47	420	125	$[C_7H_5Cl+1]^+$	0.01		100.4± 4.0
	22	Fenvalerate	28.77	420	125	$[C_7H_5Cl+1]^+$	0.01		105.9± 8.2
	Measurement time (min): 26.00–31.00 Monitoring ion (*m/z*): 125, 147, 163								

[a]: Fr. 1 eluted with 5 mL of hexane.
[b]: Fr. 2 eluted with 5 mL of hexane–acetone (17 : 3).
[c]: Recovery of pesticides from Varian Bond Elut LRC, 3 CC/500 MG, (%, mean±SD)
[d]: #1 is grouped under measurement time 4.00–16.50 and monitoring ions *m/z* 103, 121, 150, 153, 168.
[e]: #2 is grouped under measurement time 16.50–21.00 and monitoring ions *m/z* 57, 88, 125, 153, 168, 267, 290, 305, 323.
[f]: #3 is grouped under measurement time 21.00–26.00 and monitoring ions *m/z* 81, 150, 153, 173, 179, 203, 259.
[g]: #4 is grouped under measurement time 26.00–31.00 and monitoring ions *m/z* 125, 147, 163.
[h]: Butylated 2,4,5-T
[i]: Hydrogenated cyhexatin

method. The SPE with a Bond Elut-Florisil column gave good separation and recoveries of pesticides[11]. In the present experiment, we adopted the same column and eluant system. As described in experimental, the pesticides were eluted in three fractions. Cyhexatin and 2,4,5-T were subjected to SPE after derivatization. Most of the pesticides were eluted in Fr. 2 (*n*-hexane–acetone (17 : 3)), and the cyhexatin derivative was eluted in Fr. 1 (*n*-hexane). No pesticides were observed in Fr. 3.

Recoveries of most of these pesticides through the SPE column were over 80%, but that of lenacil was low (47.1%). Lenacil is well known to be adsorbed on a Florisil column[12] and to show poor recovery from the column. 2,4,5-T and cyhexatin derivatives gave good recoveries by SPE. Thus, SPE appears to be useful for the clean-up of pesticides except lenacil.

2. Target ions in GC/MS

GC/MS of pesticides were examined to select the optimum fragment ions for identification of pesticides. GC/MS of cyhexatin and 2,4,5-T were taken after derivatization. The structures of major fragment ions were determined by well established methods[11] of MS analysis, and target ions for characterizing each pesticide were selected as shown in Table 1.

3. GC/MS (SIM) method

Most of the pesticides were measured by the GC/MS (SIM) method using the target ions in Table 1, which gives the retention time, target ions (*m/z*) and proposed ion assignments. Most of the pesticides afforded two suitable target ions.

Fourteen pesticides were grouped into 4 ion sets (#1–#4) for effective SIM measurement on the basis of retention time. Most of the 14 pesticides were detectable by the GC/MS (SIM) at levels of 1/5 to 1/10 of the maximum residue limits permitted by the Japanese Law of Food Sanitation.

Under the experimental conditions, the retention time of propiconazole was very close to that of lenacil, and they could not be separated on the total ion chromatogram (TIC). However, when two target ions of *m/z* 173 and 259 for propiconazole and one ion of *m/z* 153 for lenacil were chosen, as shown in Fig. 1 (#3), they could be measured separately. A single base peak was observed in the MS of lenacil, so one target ion (*m/z* 153) was selected.

Thus, 14 pesticides including cyhexatin and 2,4,5-T could be analyzed at the same time with high sensitivity by this method.

Standard solutions in hexane were prepared at three different concentrations ranging from 0.01 to 0.2 μg/mL. Linear least-squares regression analysis was used and every pesticide showed good linearities. Determination limits of pesticides were in the range of 0.005 to 0.1 μg/mL as described in Table 1. The total ion chromatograms for the standard solution and macadamia nuts extract are shown in Fig. 2. No interfering peaks were observed in any sample solution.

Although cyfulthrin, cyhexatin, phoxim and methiocarb have been analyzed by GC-ECD, GC-FPD or HPLC as Japanese official methods, GC/MS (SIM) is also available for the analyses of these pesticides. We are currently attempting to combine the SIM approach for the 53 pesticides reported in the previous paper[11] with that for the 14 pesticides in this paper.

4. Recoveries

Pesticides equivalent to 0.2 ppm were spiked in 20 g of homogenized samples. The recoveries from nuts are shown in Table 2. Most of the pesticides except thiometon in pistachio nuts gave good recoveries (80–105%). The recovery of thiometon for pistachio nuts was low (26.8, 30.6%). Although the reason for this is unclear, it may be related to the abundance of chlorophyll in pistachio nuts. On the other hand, lenacil dissolved in *n*-hexane showed a low recovery from the SPE column, but, as shown in Table 2 it gave high recovery from nuts (87.8–100.8%). Lenacil may be well eluted from the column in the presence of certain components in nuts. Further study is necessary on the recovery of pesticides from various foods, especially on the effects of food components on the affinity of the Florisil SPE column for pesticides.

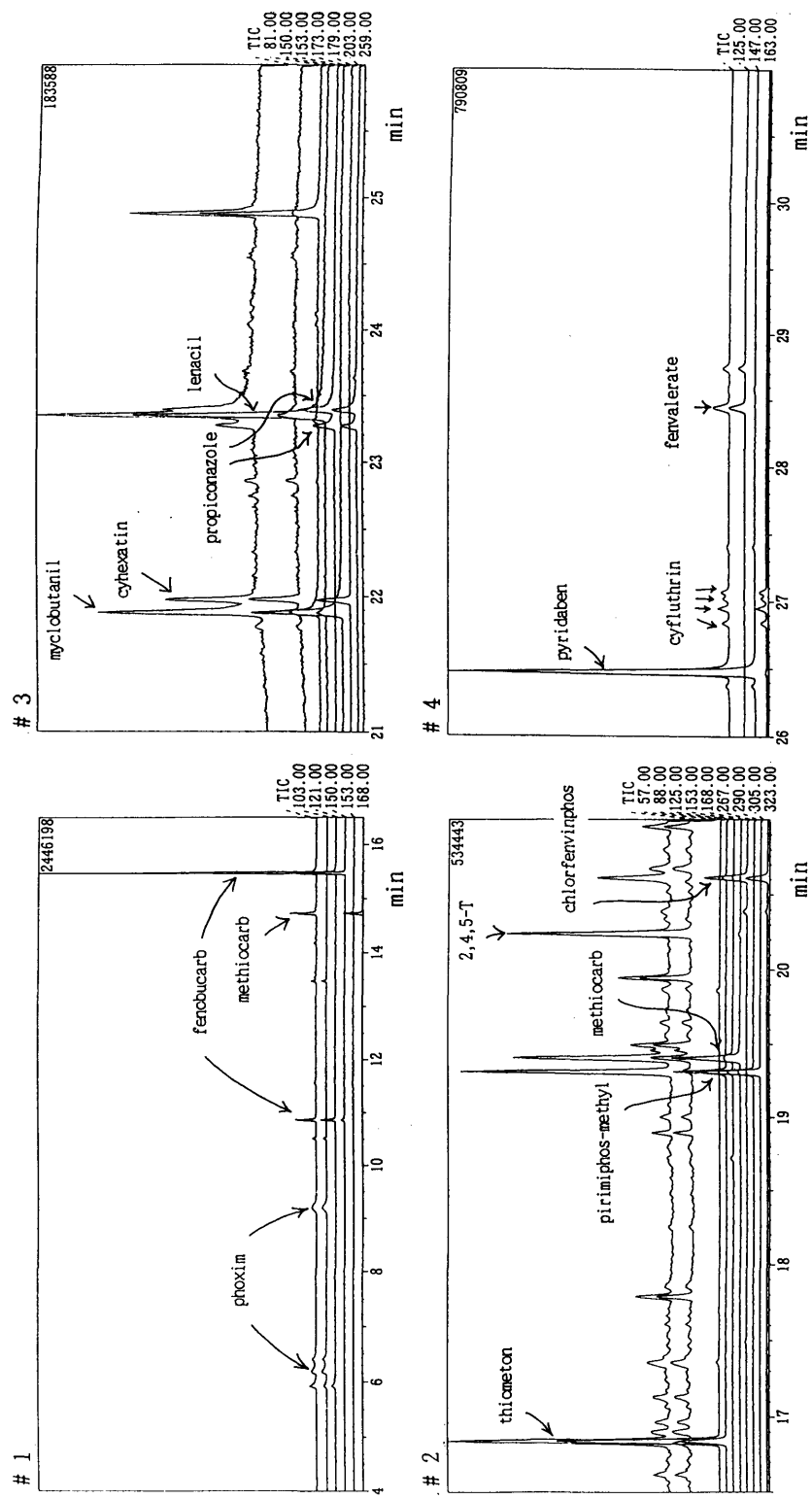

Fig. 1. GC/MS (SIM) chromatograms of 14 pesticides
Aliquots of 1 μL of pesticide solutions corresponding to 0.2 μg/mL were injected.

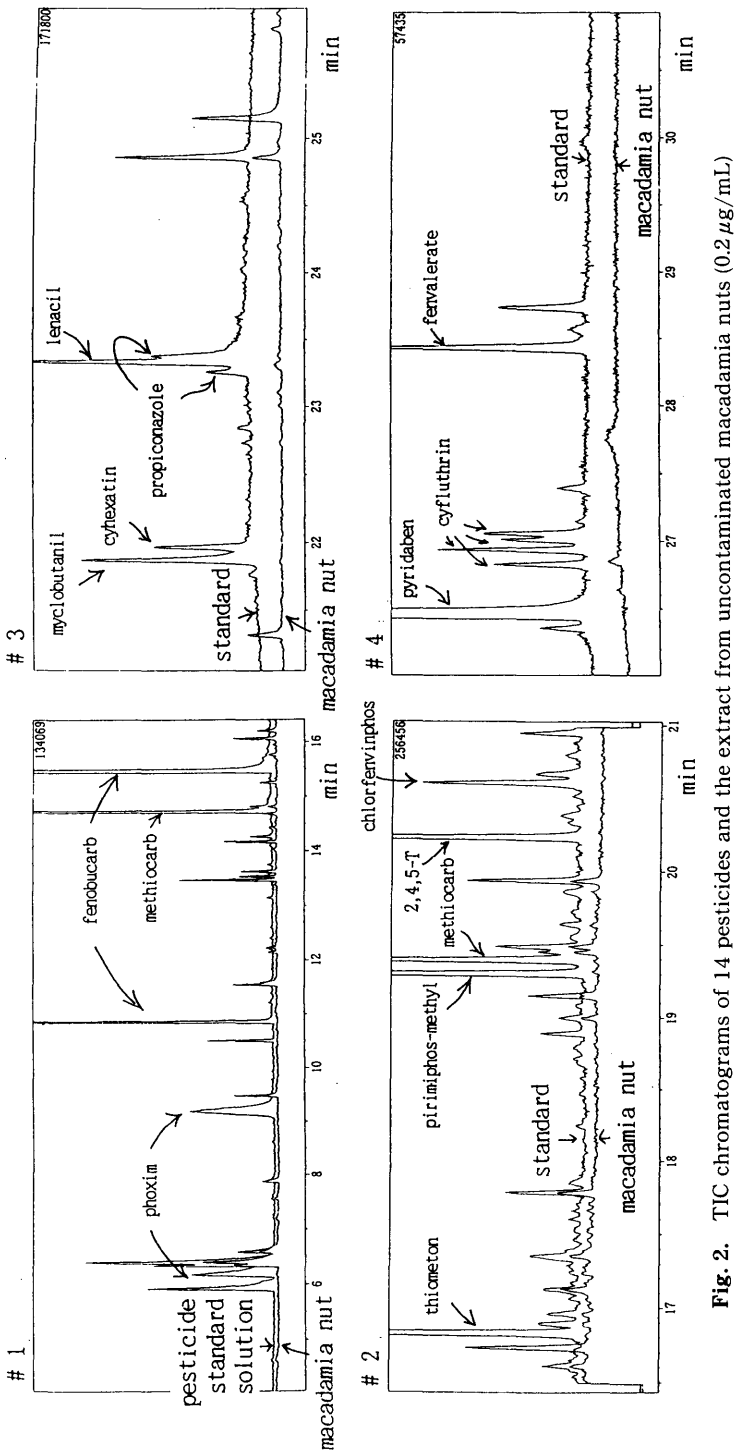

Fig. 2. TIC chromatograms of 14 pesticides and the extract from uncontaminated macadamia nuts (0.2 μg/mL)

Table 2. Recovery of 14 Pesticides from 6 Nut Samples and Conditions of GC/MS (SIM)[a)]

Ion set	No.	Pesticide	Retention time (min)	Mass no. (m/z)	Macadamia nuts	Hazel nuts	Cashew nuts	Pistachio nuts	Peanuts	Pine nuts
#1	1	Phoxim	6.18	103	90.3± 7.7	93.3± 9.1	89.1± 6.4	82.4 ± 6.2	89.8± 9.0	84.3± 0.5
	2		9.21	103	91.7± 2.9	93.0± 9.7	99.2± 6.8	96.4 ± 8.8	96.1± 5.7	94.8± 7.7
	3a	Fenobucarb	10.87	121	86.1±12.5	84.5± 8.5	87.9± 4.3	86.2 ± 9.3	96.7± 5.9	88.4±11.0
	3b		10.87	150	88.9± 6.5	101.9± 4.7	92.0±10.4	103.9 ± 9.2	84.0± 8.6	92.7± 8.1
	4a	Methiocarb	14.74	153	100.0± 3.8	84.6± 4.8	96.3± 6.7	87.5 ± 9.5	93.3± 2.8	102.2± 1.8
	4b		14.74	168	88.9± 8.1	86.6±11.8	89.9± 6.2	84.14±14.8	92.3± 5.9	92.5±12.1
	5a	Fenobucarb	15.47	121	90.1±11.7	96.9± 3.1	93.6± 6.6	93.13± 2.7	92.7± 7.2	94.6± 9.1
	5b		15.47	150	84.6±10.9	88.3± 6.5	87.7±10.5	86.5 ±10.9	92.0± 7.8	95.6± 7.3
#2	6a	Thiometon	16.84	88	84.1±14.5	91.0± 4.3	91.1± 7.9	26.8 ± 8.2	83.0±11.4	98.3± 2.3
	6b		16.84	125	89.5± 8.6	96.2± 3.3	95.4± 7.6	30.6 ± 6.8	92.2± 8.0	86.4± 3.2
	7a	Pirimiphos-Me	19.31	290	84.7±18.0	86.2± 7.4	88.6±10.4	84.7 ±12.1	99.2± 5.0	90.7± 4.1
	7b		19.31	305	89.8±14.0	91.4± 1.0	88.7± 3.6	93.9 ±10.6	90.1±10.8	85.3± 8.2
	8a	Methiocarb	19.41	153	97.1± 3.5	99.4± 3.5	104.4± 4.3	100.3 ± 4.8	101.8± 1.5	100.1± 2.6
	8b		19.41	168	96.3± 4.3	96.2± 7.4	97.3± 2.6	92.1 ± 3.9	90.9± 5.0	99.6± 5.3
	9	2,4,5-T-Bu	20.25	57	95.5± 3.8	82.8± 3.2	93.2± 3.8	87.7 ± 5.0	95.3± 4.9	86.8± 4.7
	10a	Chlorfenvinphos	20.63	267	81.5± 9.8	90.7±10.7	84.3±11.4	83.8 ±13.5	81.7±15.3	80.1±13.3
	10b		20.63	323	79.8±11.1	91.5± 9.2	93.6±11.7	88.6 ±11.8	97.4± 8.6	93.5± 3.5
#3	11a	Myclobutanil	21.89	150	97.5± 1.9	97.7± 4.7	96.2± 2.1	90.3 ± 2.2	95.1± 7.8	96.7± 2.4
	11b		21.89	179	94.0± 6.2	96.6± 1.4	97.1± 3.6	97.4 ± 4.5	92.2± 2.1	97.3± 3.5
	12a	Cyhexatin	21.98	81	96.8± 6.8	97.3± 3.6	73.8± 1.0	99.9 ± 3.5	92.9± 5.7	103.5± 2.7
	12b		21.98	203	97.1± 2.4	95.8± 1.0	89.4± 0.9	97.7 ± 3.1	99.0± 2.3	99.1± 2.6
	13a	Propiconazole	23.28	173	91.8± 7.7	95.2± 7.9	91.0±12.8	91.3 ± 5.5	96.7± 3.2	85.2±12.4
	13b		23.28	259	92.4± 2.2	97.6± 5.0	90.6±12.1	100.4 ± 4.9	100.3± 6.8	85.6±10.5
	14a	Propiconazole	23.41	173	86.9± 4.6	97.2± 1.6	87.3± 9.2	93.1 ±13.5	96.2± 7.6	83.7±11.5
	14b		23.41	259	92.2± 8.0	99.3± 1.6	97.6± 8.1	96.4 ± 4.5	96.5± 3.6	99.1± 6.0
	15	Lenacil	23.41	153	87.8± 3.8	99.2± 7.1	91.1± 7.5	100.8 ± 2.0	89.6± 7.0	88.3± 5.3
#4	16	Pyridaben	26.48	147	89.3± 5.4	97.0± 4.5	96.1± 5.4	99.3 ± 6.3	90.9± 7.4	88.3± 9.7
	17	Cyfluthrin	26.86	163	92.2± 5.8	86.6± 3.5	90.6± 3.9	100.1 ±11.3	80.9± 3.3	91.6±11.4
	18	Cyfluthrin	26.97	163	84.6± 7.4	104.4± 4.7	88.3± 4.1	84.8 ±10.7	91.5± 7.1	89.2±11.3
	19	Cyfluthrin	27.04	163	95.9± 5.8	88.5± 1.6	86.1± 5.5	85.3 ± 7.5	90.9± 3.5	97.9±10.6
	20	Cyfluthrin	27.09	163	92.3± 5.3	97.0± 0.7	87.3±12.8	95.0 ± 9.2	93.9±11.2	89.7± 4.9
	21	Fenvalerate	28.47	125	100.3± 1.1	98.2± 3.6	97.6± 1.9	104.5 ± 5.2	90.0± 2.6	91.8± 0.8
	22	Fenvalerate	28.77	125	97.1± 0.4	95.2± 4.9	93.9± 5.4	91.5 ± 7.3	94.9± 4.7	91.1± 8.1

[a)]: Recovery tests were conducted by spiking pesticides corresponding to 0.2 ppm and the data represent the average of three trials ($n=3$). Retention times and mass numbers in the table are those adopted in the recovery test.

Conclusions

1. Multi-residue analysis of 14 pesticides was studied by a combination of GC/MS (SIM) and SPE.

2. Most of the 14 pesticides had high recoveries (over 80%) from 6 kinds of nuts except thiometon from pistachio nuts.

3. Clean-up with SPE is available for cyhexatin and 2,4,5-T derivatives.

4. Cyfulthrin, cyhexatin, phoxim and methiocarb were analyzed more specifically by the GC/MS (SIM) method than by the Japanese official methods.

References

1) Ministry of Health and Welfare of Japan: Bulletin 239, Oct. 27 (1992).
2) Ministry of Health and Welfare of Japan: Bulletin 68, Mar. 4 (1993).
3) Ministry of Health and Welfare of Japan: Bulletin 200, Sep. 14 (1993).
4) Ministry of Health and Welfare of Japan: Bulletin 199, Jun. 9 (1994).
5) Ministry of Health and Welfare of Japan: Bulletin 153, Aug. 14 (1995).
6) Ministry of Health and Welfare of Japan: Bulletin 198, Sep. 2 (1996).
7) Nemoto, S., Shimizu, R., Kikawa, H., Sasaki, K., Saito, Y.: J. Food Hyg. Soc. Japan **36**, 233–243 (1995).
8) Akiyama, Y., Takeda, N., Adachi, K.: *ibid.* **36**, 42–49 (1995).
9) Miyata, M., Hirahara, Y., Narita, M., Kimura, M., Watanabe, Y., Ito, S., Takeda, H., Kobayashi, A., Tonogai, Y., Nakamura, Y., Tsumura, Y., Shibata, T.: *ibid.* **37**, 158–164 (1995).
10) Fillion, J., Hindle, R., Lacroix, M., Selwyn, J.: J. AOAC Int. **78**, 1,252–1,266 (1995).
11) Kawasaki, M., Fukuhara, K., Uchiyama, S.: J. Food Hyg. Soc. Japan **35**, 479–496 (1994).
12) Goto, S., Kato, S.: "Analytical Methods of Pesticides Residues Addendum" p. 319–320 (1988) Soft Scientific Co., Tokyo.