Application Note

810022S

Supercritical Fluid Extraction of Residual Pesticides in Wheat Flour

Introduction

In Japan on the 29th of May 2006 the Ministry of Health, Labor and Welfare (MHLW) promulgated the Positive List System for residual pesticides, food additives, and veterinary medicines remaining in foods, following the revision of the Food Hygiene Law. In this list approximately 800 kinds of those agricultural chemicals were registered. This system is to prohibit the distribution of foods that contain more than 0.01 ppm of each chemical.

The extraction of residual pesticides in foods has been performed by the solvent extraction method. This method, however, takes about 4-5 hours for each extraction, and requires a large volume of organic solvent. In recent years, supercritical fluid extraction (SFE) using supercritical carbon dioxide has attracted much attention as an alternative method to the solvent extraction method.

We have developed a fully automated residual pesticide extraction system, and applied this system to analysis of wheat flour sample. Extracted components were analyzed by GC-MS/MS.

Experimental

The newly developed fully automated residual pesticide extraction system was used throughout the experiment. The schematic diagram of this system is shown in Figure 1.

As an analytical sample, wheat flour was selected. Sixty-eight kinds of pesticides were added to the flour to be a concentration of 0.1 ppm for each pesticide except captan, 1 ppm and acetamiprid, 0.5 ppm. Four grams of the flour was loaded in each extraction vessel, the extracted components were adsorbed on a trap column, trapped components were eluted with acetonitrile, the acetonitrile solution was evaporated to dryness with nitrogen gas, and the residue was dissolved in 4 mL of acetone containing 0.05% of PEG200 and PEG400. A portion of this solution was injected onto the GC.

Results and Discussion

Chromatograms of the standard mixture (upper), the sample added with the standard (middle), and the blank (lower) are shown in Figure 2.

As shown in Table 1, among 68 components of the pesticides, 61 components exhibited more than 70% recovery, and 64 components more than 50% recovery. The recovery of acephate, acetamiprid, methamidophos, and pencycuron was as low as 10 - 50%. Acephate, acetamiprid, and methamidophos, due to their high hydrophilicity, indicated low solubility in supercritical carbon dioxide, resulting in a poor recovery in SFE. Low recovery of pencycuron seemed to be ascribed to the sample matrix.

References

1) Ministry of Health, Labor and Welfare Official Gazette No. 498
2) Ministry of Health, Labor and Welfare Official Gazette No. 497

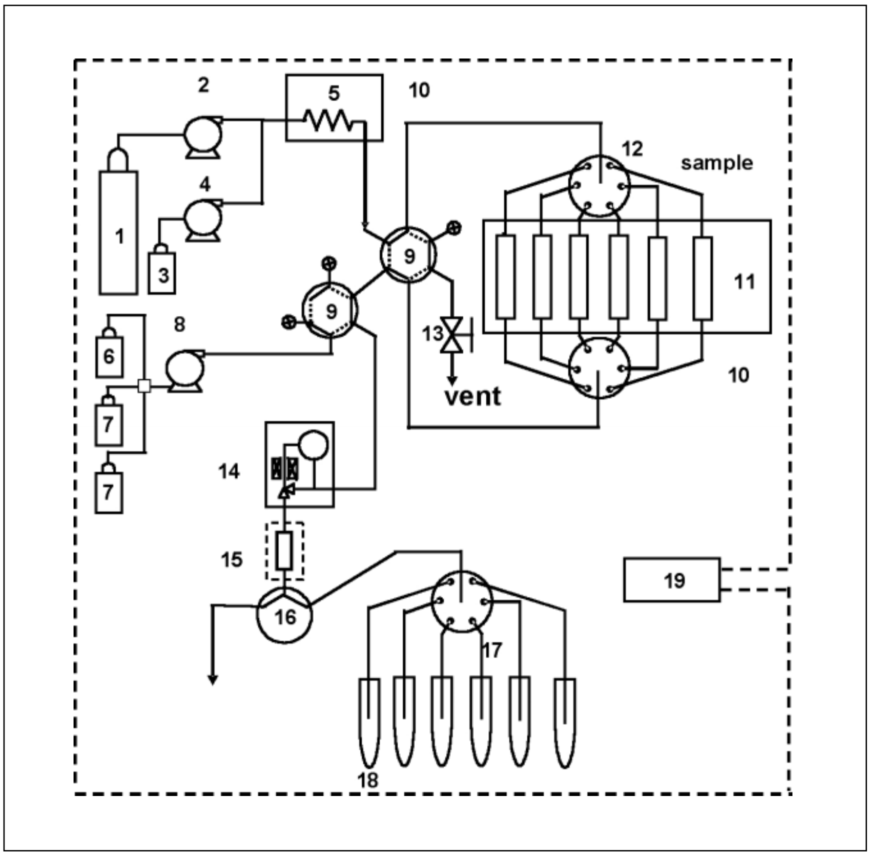

Figure 1 Schematic Diagram of fully automated system for supercritical fluid extraction of residual pesticides
System configuration: 1 = carbon dioxide cylinder, 2 = liquefied carbon dioxide delivery pump, 3 = modifier, 4 = modifier delivery pump, 5 = preheating coil, 6 = solvent for trap elution, 7 = rinse solution for trap column, 8 = solvent delivery pump, 9 = switching valve for flow line, 10 = oven, 11 = extraction vessels, 12 = 6-vessel changer, 13 = release valve, 14 = automatic back pressure regulator, 15 = trap column, 16 = 3-way valve, 17 = 6-way flow line switching valve, 18 = collection tubes, 19 = system controller
Supercritical fluid extraction conditions: extraction tube = 10 mL(10 mm x 127 mm), supercritical fluid = CO_2, back pressure = 15 MPa, extraction time = 30 min, flow rate = 2 mL/min, trap column = ODS(4.6 mm x 50mm, 30 μm), solvent for trap elution = acetonitrile 2 mL(flow rate = 2 mL/min).
Supercritical CO_2 delivered by pump 2 passes through one of the vessels 11 in which the sample is loaded and then pesticides are extracted. The extracted pesticides are concentrated by the trap column and is eluted by acetonitrile (2 mL) delivered by pump 8, and is collected in one of collection tubes 18. This system is automatically controlled by 19, system controller.

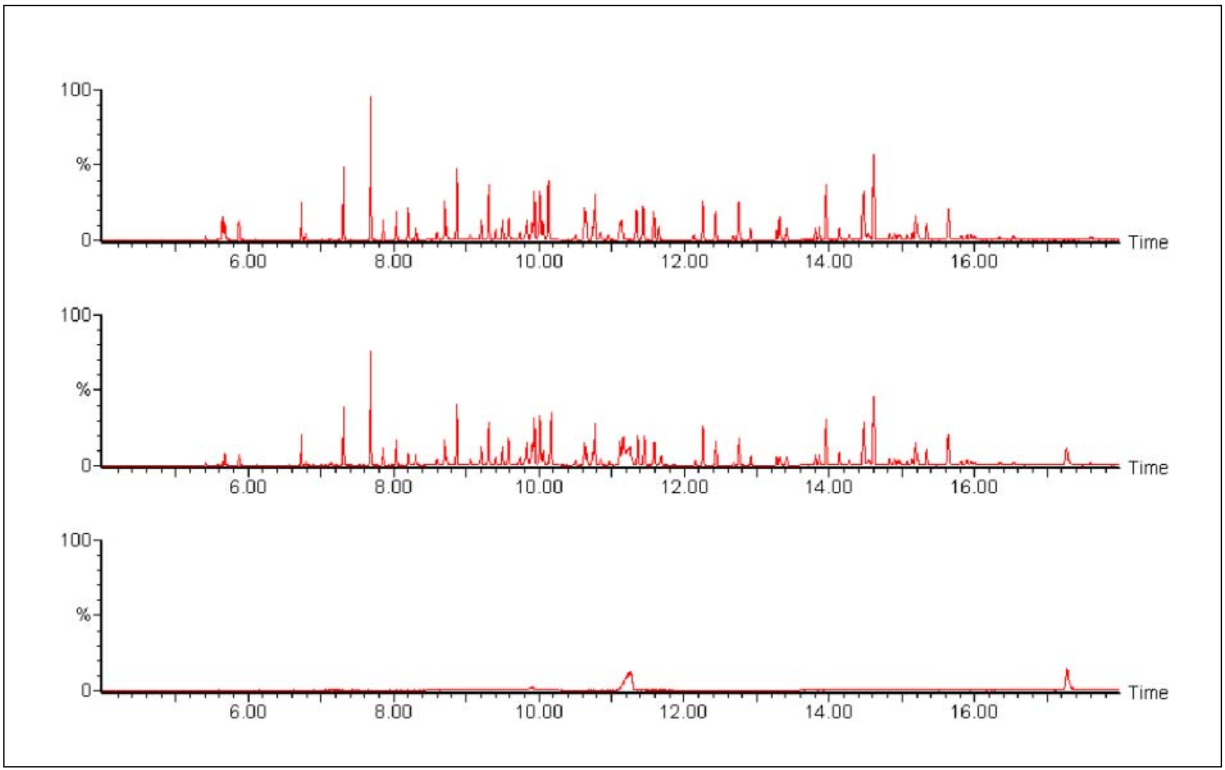

Figure 2 GC chromatograms of wheat flour sample. Upper：standard mixture (68 components), Middle： sample added with standard mixture, and Lower：Blank.
Measurement conditions：Instrument=Quattro micro GC (Waters micromass), Ionization method = EI, Measurement mode=MRM, SIM, Ionization source temperature=280 ºC, Interface temperature=280 ºC, GC=6890N(Agilent), Injection method=Splitless, Injection volume=1μL, Inlet temperature=250 ºC, Column＝DB-5MS(30 m x 0.25 mm), Column temperature=50 ºC (0 min) — 50ºC (1 min) — 200 ºC (7 min) — 250 ºC (9 min) — 300 ºC (11 min).

Standard mixture solution contains 68 components as below.: 1: Acephate, 2: Acetamiprid, 3: Bendiocarb, 4: Bitertanol, 5: Butylate, 6: Captan, 7: Carbaryl 8: Chinomethionat, 9: Chlorfenvinphos, 10: Chlorpyriphos, 11: Cyfluthrin, 12: Cypermethrin, 13: Deltamethrin, 14: Diazinon, 15: Dichlofluanid, 16: Dichlorvos, 17: Diethofencarb, 18: Dimethylvinphos, 19: EPN, 20: Esprocarb, 21: Ethiofencarb, 22: Ethoprophos, 23: Fenarimol, 24: Fenitrothin, 25: Fenobucarb, 26: Fensulfothion, 27: Fenvalerate, 28: Flucythrinate, 29: Flusilazole, 30: Flutolanil, 31: Fluvalinate, 32: Flutoranil, 32: Imibenconazole, 33: Iprodione, 34: Isofenphos , 35: Isofenphos P=O, 36: Isoprocarb, 37: Lenacil, 38: Malathion, 39: Mefenacet, 40: Mepronil, 41: Methamidophos, 42: Metolachior, 43: p,p'-DDE, 44: Paclobutrazol, 45: Pencycuron, 46: Pendimethalin, 47: Permethalin, 48: Phenthoate, 49: Phosalone, 50: Pirimifos-methyl, 51: p,p'-DDD, 52: Pretilachior, 52: Pretilachlor, 53: Propiconazole, 54: Pyraclofos, 55: Pyridaben, 56: Pyridaphenthion, 57: Pyrimidifen, 58: Quinalphos, 59: Tefluthrin, 60: Terbucarb, 62: Thenylchlor,

63: Tolclofos-methyl, 64: Triadimenol, 65: α-BHC, 66: β-BHC, 67: γ-BHC, 68: δ-BHC .

Table 1 The recovery of each pesticide

No	Pesticide	Recovery (%)	No	Pesticide	Recovery (%)	No	Pesticide	Recovery (%)
1	Acephate	57.1	24	Fenitrothion	110.8	47	Permethrin	97.8
2	Acetamiprid	39.4	25	Fenobucarb	94.8	48	Phenthoate	102.6
3	Bendiocarb	98.7	26	Fensulfothion	95.8	49	Phosalone	101.0
4	Bitertanol	91.4	27	Fenvalerate	103.7	50	Pirimifos-methyl	97.0
5	Butylate	94.0	28	Flucythrinate	103.9	51	p,p'-DDD	101.6
6	Captan	90.2	29	Flusilazole	101.6	52	Pretilachlor	97.5
7	Carbaryl	98.6	30	Flutolanil	96.4	53	Propiconazole	103.0
8	Chinomethionat	103.7	31	Fluvalinate	114.4	54	Pyraclofos	112.5
9	Chlorfenvinphos	108.5	32	Imibenconazole	101.0	55	Pyridaben	91.9
10	Chlorpyriphone	102.7	33	Iprodione	109.3	56	Pyridaphenthion	92.1
11	Cyfluthrin	105.1	34	isofenphos	99.5	57	Pyrimidifen	113.2
12	Cypermethrin	99.0	35	Isofenphos P=O	90.7	58	Quinalphos	97.0
13	Deltamethrin	85.3	36	Isoprocarb	96.7	59	Tefluthrin	103.7
14	Diazinon	92.5	37	Lenacil	80.9	60	Terbucarb	97.6
15	Dichlofluanid	85.6	38	Malathion	94.7	61	Terbufos	99.6
16	Dichlorvos	87.2	39	Mefenacet	93.3	62	Thenylchlor	91.0
17	Diethofencarb	99.0	40	Mepronil	97.3	63	Tolclofos-methyl	103.9
18	Dimethylvinphos	96.8	41	Methamidophos	15.6	64	Triadimenol	86.5
19	EPN	89.9	42	Metolachlor	94.4	65	α-BHC	99.3
20	Esprocarb	102.0	43	p,p'-DDE	100.0	66	β-BHC	96.9
21	Ethiofencarb	93.4	44	Paclobutrazol	87.5	67	γ-BHC	101.5
22	Ethoprophos	100.9	45	Pencycuron	88.5	68	δ-BHC	94.6
23	Fenarimol	117.9	46	Pendimethalin	110.8			

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