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Simultaneous Determination of Organochlorine, Organophosphorus, and Pyrethroid Pesticides in Bee Pollens by Solid-Phase Extraction Cleanup Followed by Gas Chromatography Using Electron-Capture Detector

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Abstract A method for routine determination of the residues of nine organochlorine pesticides (OCPs), ten organophosphorus pesticides (OPPs), and seven pyrethroid pesticides (PPs) in bee pollens was developed. Bee pollen samples were extracted by petroleum ether followed by solid-phase extraction cleaning and detected by gas chromatography–micro electron capture detection. Range of detection limits are 0.3–3.3 μg/kg for OCPs, 1.0–19.1 μg/kg for PPs and 1.1–19.7 μg/kg for OPPs. Recoveries of OCPs, OPPs, and PPs were in the range of 88.9–122.7 %, 86.8–123.1 %, and 90.8–118.7 %, respectively. The method was applied successfully to analyze real bee pollen samples. The results show a low level of contamination caused by pesticide residues indicating safe supply of bee pollen for consumers.

Keywords Residual pesticides · Organochlorine · Organophosphorus · Pyrethroid · Bee pollen · Gas chromatography · Solid phase extraction

Introduction

Bee products have been contributing to health protection of people for thousands of years. Bee pollens are collected from blossom and manufactured by bees, which is in turn made up of amino acids, vitamins, and trace elements. It is common practice to spray pesticides to avoid plant diseases and insect pests during the general large-scale cultivation, which causes contamination in surrounding environment in various intensities. Pesticides have been detected in different environmental matrices such as soil, water, and air (Smalling and Kuivila 2008; Wang et al. 2009; Schreck et al. 2008; Simon et al. 1998). Consequently, bee pollens are at the considerable risk of pesticide contamination. Such bee pollens products have been commonly used for many decades, which lead to dose accumulation and cause pesticide poisoning. Great attention has been paid to the safety of bee products in recent years; there are many strict requirements on all the contaminating toxins in bee products (Rial-Otero et al. 2007). Corresponding to these requirements, it is very necessary to monitor and control the pesticide multiresidues in bee pollens.

According to chemical compositions, more common and important synthetic pesticides are organochlorine, organophosphorus, pyrethroid, and carbamate. A number of methods had been developed for the determination of the pesticides, which include gas chromatography–electron capture detector (GC-ECD) for organochlorines (Yavuz et al. 2010; Wu et al. 2011; Rao et al. 2011), GC nitrogen phosphorus detector or GC flame photometric detector (FPD) for organophosphorus (Moinfar and Hosseini M 2009; Lu et al. 2007; Oh 2009), GC-ECD for pyrethroids (Li et al. 2009; Chang et al. 2010), high-performance liquid chromatography (HPLC) and gas chromatography–mass spectroscopy (GC-MS) (Przybylski and Bonnet 2009; Saraji and Esteki 2008) with chemical derivatization for carbamates (Santalad et al. 2009; Wu et al. 2009) were commonly used. However, these methods sometimes show inaccurate quantification caused by the limited detection range, occurrence of false positive, and interferences of unknown substances that are coeluting in the same retention time with

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analyzed pesticides (Ismail et al. 1993; Fenoll et al. 2007), although GC-MS and HPLC-MS can simultaneously determine two or more kinds of pesticides (Wang et al. 2010; Riederer et al. 2010; Chen et al. 2009a) with disadvantage of costly MS equipment itself and more expensive running cost than other detectors.

Commonly, the pretreatment of the nature product's samples before determination is required. Conventional methods for cleanup are liquid–liquid extraction (Blasco et al. 2004a), matrix solid-phase dispersion (Sánchez-Brunete et al. 2002), solid-phase extraction (SPE), solid-phase microextraction (Blasco et al. 2004b; Campillo et al. 2006), stir bar sorptive extraction (Blasco et al. 2004b), supercritical fluid extraction (Rissato et al. 2004), and so on. SPE is a common cleanup technique for the determination of samples in complex matrix having advantages of little requirement of organic reagent and time (Aguilar et al. 1997; Herrera et al. 2005; Chen et al. 2009b; Jin et al. 2006).

To the best of our knowledge, no publication has documented the simultaneous analysis method of three kinds of pesticide residues (organochlorine, organophosphorus, and pyrethroid pesticides) in bee pollen with GC-ECD. In this paper, the systematic studies including sample extraction, cleanup by SPE, and simultaneous determination with GC-ECD of the three kinds of pesticide residues in bee pollen were conducted. The proposed method is proved to be rapid, simple, and precise.

Materials and Methods

Chemicals and Reagents

Pesticide Standards

Pesticide reference standards of organochlorine were purchased from the National Institute of Metrology of China, and those of pyrethroid and organophosphate were bought from Dr. Ehrenstorfer (Augsburg, Germany), with purity range of 96–100 %. All pesticides investigated are listed in Table 1.

Organic Solvents and Reagents

Petroleum ether, ethyl acetate, and acetonitrile, purchased from Merck (Darmstadt, Germany), were pesticide-free

Table 1 Basic information on pesticides studied in this work

Number	Pesticides	Class	CAS	Formula
1	α-1,2,3,4,5,6-Hexachlorocyclohexane (α-HCH)	Organochlorine	319-84-6	$C_6H_6Cl_6$
2	β-1,2,3,4,5,6-Hexachlorocyclohexane (β-HCH)	Organochlorine	319-85-7	$C_6H_6Cl_6$
3	Lindane (γ-HCH)	Organochlorine	58-89-9	$C_6H_6Cl_6$
4	Pentachloronitrobenzene (PCNB)	Organochlorine	82-68-8	$C_6Cl_5NO_2$
5	δ-1,2,3,4,5,6-Hexachlorocyclohexane (δ-HCH)	Organochlorine	319-86-8	$C_6H_6Cl_6$
6	1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene (pp′-DDE)	Organochlorine	72-55-9	$C_{14}H_8Cl_4$
7	1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (pp′-DDD)	Organochlorine	72-54-8	$C_{14}H_{10}Cl_4$
8	1,1,1-Tichloro-2-(2-chlorophenyl)-2-(4-chlorophenyl)ethane (op′-DDT)	Organochlorine	789-02-6	$C_{14}H_9Cl_5$
9	1,1,1-Trichloro-2,2-bis(4-chlorophenyl)ethane (pp′-DDT)	Organochlorine	50-29-3	$C_{14}H_9Cl_5$
10	Fenson	Pyrethroid	80-38-6	$C_{12}H_9ClO_3S$
11	Chlorfenson	Pyrethroid	80-33-1	$C_{12}H_8Cl_2O_3$
12	Tetramethrin	Pyrethroid	7696-12-0	$C_{19}H_{25}NO_4$
13	Fenpropathrin	Pyrethroid	39515-41-8	$C_{22}H_{23}NO_3$
14	Cypermethrin	Pyrethroid	52315-07-8	$C_{22}H_{19}Cl_2NO_3$
15	Fenvalerate	Pyrethroid	51630-58-1	$C_{25}H_{22}ClNO_3$
16	Deltamethrin	Pyrethroid	52918-63-5	$C_{22}H_{19}Br_2NO_3$
17	Dichlorvos	Organophosphate	62-73-7	$C_4H_7Cl_2O_4$
18	Fonofos	Organophosphate	944-22-9	$C_{10}H_{15}OPS_2$
19	Diazinon	Organophosphate	333-41-5	$C_4H_4N_2O$
20	Chlorpyrifos-methyl	Organophosphate	5598-13-0	$C_7H_7Cl_3NO_3$
21	Paraoxon-ethyl	Organophosphate	311-45-5	$C_{10}H_{14}NO_6P$
22	Fenitrothion	Organophosphate	122-14-5	$C_9H_{12}NO_5PS$
23	Malathion	Organophosphate	121-75-5	$C_{10}H_{19}O_6PS_2$
24	Chlorpyrifos	Organophosphate	2921-88-2	$C_9H_{11}Cl_3NO_3$
25	Quinalphos	Organophosphate	13593-03-8	$C_{12}H_{15}N_2O_3$
26	Methidathion	Organophosphate	950-37-8	$C_6H_{11}N_2O_4$

analytical grade. Bulk florisil (for pesticide residue) and activated carbon were used for homemade column. AccuBond SPE ODS-C18 cartridges (500 mg, 3 ml), AccuBond II SPE florisil cartridges (500 mg, 3 ml), and activated carbon cartridges (500 mg, 3 ml) were supplied by Agilent Technologies Co., Ltd of USA.

Instruments

An ultrasonic cleaner (Branson, B8510E, USA) with the working frequency at 40 kHz was used to extract pesticides from bee pollen. Chromatographic analyses were performed on Agilent 7890N gas chromatographic instrument equipped with microelectron capture detector (μECD). An HP-5 column (30 m×0.25 mm i.d.×0.25 μm film) was used for chromatographic separation of target pesticides. Nitrogen with the purity of 99.999 % was used as the carrier gas and makeup gas.

The flow rate of column was held constantly at 1 ml/min and that of the makeup gas was 60 ml/min. The injector temperature was 250 °C, and the injection volume was 1 μl with splitless mode. The detector temperature was 300 °C. The column temperature was programmed as follows: initial temperature was 80 °C (hold 1 min), increased at 8 °C/min to 200 °C (hold 1 min), then increased at 2 °C/min to 250 °C (hold 1 min), followed by a third increase to 280 °C at 10 °C/min (hold 1 min), and a final increase to 290 °C at 1 °C/min. Figure 1 shows the chromatogram of 26 pesticides analyzed by GC-μECD.

Pollen Samples

Pollens of pine, water lily, rose, cole flower, *Papaver rhoeas*, *Schisandra chinensis* Baill., camellia, and fresh camellia were gathered in Anhui Province in China. Pollens of camellia were collected in March, 2009, while the pollens of pine, cole flower, and *Papaver rhoeas* were collected in April, 2009. Pollens of *Schisandra chinensis* Baill. and rose were picked successively in May, 2009. Similarly pollen of water lily and fresh camellia were collected in August, 2009 and March, 2010, respectively. All the pollens were stored in cool and dry place without processing. Collected pollens were grains of different colors with a little sweet taste.

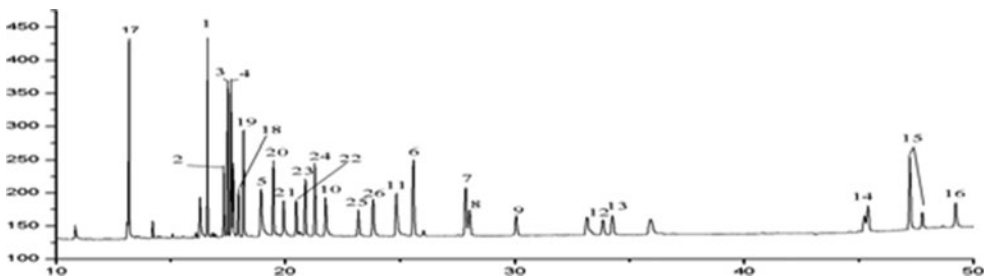

Fig. 1 GC Chromatograms of 26 pesticides analyzed under the proposed method. The *numbers* stand for 26 pesticides separately just as shown in Table 1

Extraction and Cleanup Procedure

Pollen samples (5 g) were ultrasonically extracted with 50 ml petroleum ether for 20 min. After filtration through filter paper, 25 ml filtrate was concentrated to nearly dryness using a rotary evaporator (Büch, German) in water bath at a temperature of 40 °C. Residue was dissolved by the addition of 2 ml fresh petroleum ether. The dissolved solution was cleaned by passing through activated carbon+C_{18} column preconditioned with 3 ml petroleum ether for further purification. Adsorbed pesticides were eluted with 10 ml petroleum ether–ethyl acetate (95:5, *v*/*v*). Collected extracts were concentrated under a gentle N_2 stream. The residues were transferred into a volumetric flask and made up to 2 ml. Finally, the solution is centrifuged for 5 min at a speed of 10,000 rpm, and the supernatant was taken as the test solution.

Recovery Study

Standard solutions of all the pesticides were prepared, as shown in Table 1. Bee pollens were separately spiked with 1, 3, and 5 ml of standard solution of pesticides and placed in a dark place for drying. After 12 h, the spiked samples were analyzed for recovery study. Figure 2 shows the chromatograms of control pollen sample and spiked pollen sample analyzed by GC-μECD.

Results and Discussions

The proposed method by SPE-GC-ECD is rapid, simple, and precise. SPE cleans the sample solution, which ultimately reduces the interference of impurities for detection and consumption of organic solvent. Limit of detection (LOD) shows that GC-ECD has good sensitivity for pesticides analysis. Recoveries indicate the precision and feasibility of method for pollen samples.

Choice of Detector

Sensitivities of μECD, FPD, and MS have been compared in our study. Literatures showed that LOD of most pesticides of MS was higher than 0.01 mg/kg, such as aldrin (Nguyen et al. 2010), while that of μECD was <0.002 mg/kg (Chen et

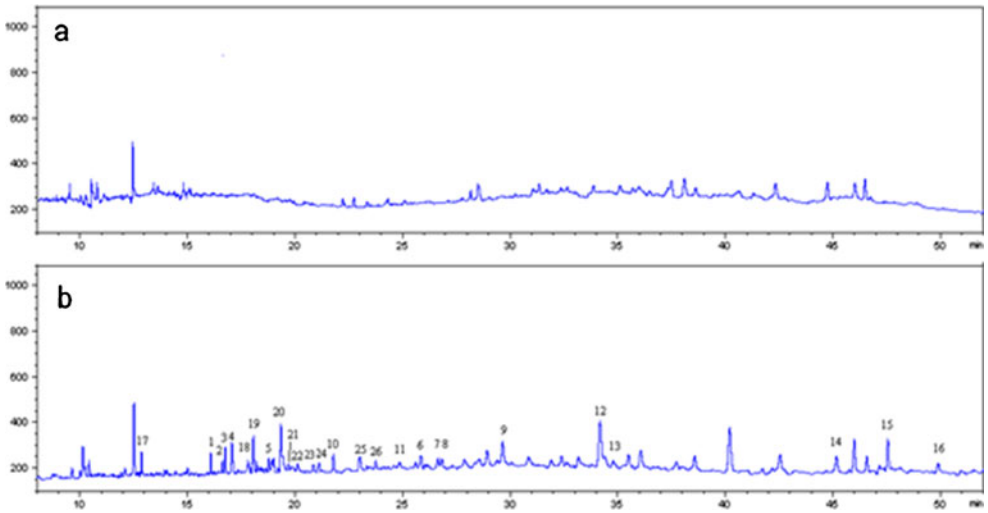

Fig. 2 GC chromatograms obtained for **a** control pollen sample and **b** spiked pollen sample

al. 2009b). Experiments indicated that the sensitivity of organophosphorus pesticides with μECD was higher than FPD having LOD more than 0.02 mg/kg. An appropriate purification method can exclude the interferences in estimation of pesticides with a reasonable and stable recovery, which give confidence to use a detector with high sensitivity like μECD. FPD is an optional detector for organophosphorus pesticides and cannot detect other compounds without phosphorus and sulfur. μECD is a commonly used detector for most pesticides. Due to simultaneous determination of

Table 2 Linearity, precision, limits of detection (LODs), and limits of quantification (LOQs) of the proposed method

Compound	Linear equation	Linearity range (ng/ml)	R^2	Precision RSD% (n=6)	LOD (μg/kg)	LOQ (μg/kg)
α-BHC	y=151.5589x−298.2389	1.00–100.00	0.9995	1.24	0.296	0.985
β-HCH	y=51.8266x−38.3112	1.00–100.00	0.9998	1.43	0.612	2.041
γ-BHC	y=123.7589x−221.8754	1.00–100.00	0.9995	2.08	0.368	1.227
PCNB	y=135.3171x−141.3856	1.00–100.00	0.9997	2.66	0.268	0.893
δ-HCH	y=101.4682x−181.2841	1.00–100.00	0.9990	2.65	0.500	1.667
pp′-DDE	y=119.7518x−156.6032	1.00–100.00	0.9997	0.51	0.341	1.136
pp′-DDD	y=73.5082x−16.7313	0.998–99.80	0.9997	0.69	0.620	2.066
op’-DDT	y=39.5579x−30.8482	1.002–100.20	0.9982	9.17	2.851	9.505
pp′-DDT	y=33.5680x−96.0198	1.00–100.00	0.9979	8.35	3.333	11.111
Fenson	y=81.1345x−36.9624	1.12–112.00	0.9996	1.17	0.959	3.195
Chlorfenson	y=90.4469x−73.6320	1.26–125.80	0.9998	1.12	1.009	3.364
Tetramethrin	y=8.1033x−4.3058	1.02–102.00	0.9994	1.05	19.125	63.750
Fenpropathrin	y=27.1363x+4.0716	1.00–100.00	0.9982	0.40	3.158	10.526
Cypermethrin	y=50.0941x−3.7839	1.07–107.00	0.9996	4.32	3.433	11.444
Fenvalerate	y=66.1436x−340.8418	4.17–417.20	0.9988	1.17	1.662	5.541
Deltamethrin	y=43.0725x−55.6226	1.08–107.80	0.9989	2.06	4.173	13.910
Dichlorvos	y=9.4751x−34.3950	1.31–262.40	0.9972	1.43	7.209	24.029
Fonofos	y=36.7430x+33.8394	1.11–211.76	0.9999	1.86	15.992	53.308
Diazinon	y=6.2717x+37.8076	1.10–219.04	0.9966	2.10	8.053	26.843
Chlorpyrifos-methyl	y=48.5760x+41.5810	1.06–212.48	0.9998	3.29	1.080	3.599
Paraoxon-ethyl	y=10.6329x−29.0033	1.04–208.00	0.9992	6.28	9.512	31.707
Fenitrothion	y=28.2916x−24.2012	1.12–223.60	0.9997	2.76	1.973	6.576
Malathion	y=10.3872x+28.7883	1.11–222.72	0.9998	2.60	5.740	19.134
Chlorpyrifos	y=51.0577x+100.5999	1.06–212.72	0.9997	0.90	1.139	3.796
Quinalphos	y=3.6507x−7.2100	0.96–191.68	0.9984	1.39	19.693	65.644
Methidathion	y=11.0417x−29.5502	1.04–207.52	0.9982	2.72	12.552	41.839

LOD (S/N=3); *LOQ* (S/N=10)

Table 3 Average recoveries and relative standard deviations (RSD%) of pesticides (n=9) spiked at low, medium, and high levels per gram of sample

Compound name	Added pesticides (ng)			Recoveries (%)			Mean (%)	RSD (%)
	Low level	Medium level	High level	Low level	Medium level	High level		
α-BHC	30	90	150	88.53	94.12	93.79	92.15	3.40
β-BHC	30	90	150	102.74	105.1	106.95	104.93	2.01
γ-BHC	30	90	150	96.39	100.83	102	99.74	2.97
PCNB	30	90	150	78.92	87.92	88.24	85.03	6.22
δ-BHC	30	90	150	113.92	111.54	115.36	113.61	1.70
pp′-DDE	30	90	150	79.74	83.06	83.71	82.17	2.59
pp′-DDD	30	90	150	82.42	89.67	90.15	87.41	4.95
op′-DDT	30	90	150	93.59	97.38	105.08	98.68	5.93
pp′-DDT	30	90	150	99	103.79	105.59	102.79	3.31
Fenson	31	93	155	90.84	99.03	97.22	95.70	4.50
Chlorfenson	35	105	175	86.33	95.52	96.6	92.82	6.08
Tetramethrin	122	366	610	98.71	103.47	103.58	101.92	2.73
Fenpropathrin	50	150	250	103.01	105.96	108.75	105.91	2.71
Cypermethrin	64	192	320	77.54	85.32	89.12	83.99	7.03
Fenvalerate	83	249	415	95.69	98.46	97.3	97.15	1.43
Deltamethrin	65	195	325	79.69	84.8	85.07	83.19	3.64
Dichlorvos	262	786	1310	84.15	90.18	92.04	88.79	4.65
Fonofos	55	165	275	80.35	86.35	89.2	85.30	5.30
Diazinon	219	657	1095	83.07	86.85	90.96	86.96	4.54
Chlorpyrifos-methyl	53	159	265	99.98	104.06	107.11	103.72	3.45
Paraoxon-ethyl	208	624	1040	86.77	90.3	95.23	90.77	4.68
Fenitrothion	56	168	280	91.25	96.22	95.49	94.32	2.85
Malathion	223	669	1115	101	106.67	108.14	105.27	3.58
Chlorpyrifos	53	159	265	87.29	92.51	93.7	91.17	3.74
Quinalphos	383	1149	1915	106.8	110.44	113.02	110.09	2.84
Methidathion	208	624	1040	98.39	101.97	100.54	100.30	1.80

different kinds of pesticides, μECD is superior to FPD. Moreover, to use MS is expensive as compared to μECD, which again make this detector convenient.

Study of Extraction Process

According to the appendix Q of Chinese Pharmacopoeia, petroleum ether was used for the extraction of organochlorine and pyrethroid pesticides, whereas ethyl acetate was used for organophosphorus pesticides. In the preliminary examination, the bee pollen samples were separately extracted by petroleum ether and ethyl acetate, then concentrated and analyzed by GC. The sample in which pesticides were not detected was used as a control sample. The control sample added with pesticides standard solution was extracted by petroleum ether, ethyl acetate, acetonitrile, petroleum ether–ethyl acetate (1:1), respectively. The extractive rates were compared and optimized. Results indicates that too many impurities existed in the samples after extraction by ethyl acetate and acetonitrile, and the baseline in chromatogram was too fluctuant for most pesticides to be integrated reasonably. Extractive rates of petroleum ether–ethyl acetate (1:1) were beyond 150 % due to the matrix effects. Extractive rates of petroleum ether were between 101.5 and 119.7 %. Peaks of impurities were relatively fewer, and the baseline was smooth in chromatogram. As a conclusion, petroleum ether was selected as extraction solvent.

Study of Purification Method

Purification step was optimized by comparison of different solid-phase extraction adsorbents such as C_{18}, florisil, activated carbon, activated carbon combined with C_{18}, and activated carbon combined with florisil. Solid-phase extraction adsorbents involved in commercial and self-made models. The self-made florisil column contains 5 g florisil and 0.5 g sodium sulfate anhydrous, which requires 100 ml

eluant. Recovery rates of pesticides in bee pollen purified by homemade florisil column were all favorable, but too much organic solvent was used for elution. In case of commercial columns, the effect of activated carbon combined with C_{18} showed the best performance. The peaks of impurities in the test with activated carbon combined with C_{18} column were less than that with C_{18} column only. In addition, the recovery rates in the test with activated carbon combined with C_{18} column were higher than those with florisil column. Furthermore, less amount of organic solvent was used for elution in the test by activated carbon combined with C_{18} solid-phase extraction adsorbents.

In this study, the estimated pesticides were medium- and nonpolar compounds. Different organic solvents or the mixtures with different polarities were tested, such as petroleum ether–ethyl acetate (1:1) and (95:5). The results indicate that petroleum ether–ethyl acetate (95:5) can elute most of the pesticides.

Method Validation

Results of the validation of this method are presented in Table 2. The stock standard solutions of each pesticide were diluted into the solutions of seven concentrations with ethyl acetate. Correlation coefficients ranged from 0.9966 to 0.9999, which showed good linear correlation at the chromatographic condition. The standard mixture, containing about 10 ng/ml pesticides, was injected six times with the relative standard deviation between 0.5 and 9.2 %. The LODs and limits of quantification (LOQs) were defined as three times of signal/noise ratio (S/N=3) and ten times signal/noise ratio (S/N=10), respectively.

Recovery Results and Fittingness of Methods

The recovery study was conducted with spiked with three concentrations standard solutions in pine pollen. The average recovery values are listed in Table 3. The formula of recovery was shown as: recovery(%)=(concentration of spiked sample/concentration of standard spiked in sample)×100 %. Recoveries of target pesticides ranged from 78.7 to 101.5 %, 81.3 to 113.7 % and 85.7 to 97.3 % at the low, medium, and high concentrations, respectively. Relative standard deviation (RSD%) was <7.0 %, indicating a good precision and accuracy of the established method.

Experiments were carried out to verify the method for pollens of water lily, rose, *Papaver rhoeas*, cole, *Schisandra fructus*, camellia, and fresh camellia. Recovery rates of all above pollens except cole were between 70~120 % which show that the methods can be applied for the determination of pesticides in most real bee pollen samples. GC chromatogram of cole pollen showed impure peaks, which were high enough to interfere with separation of target peaks of pesticides. This might be attributed to the fact that cole pollen had more oil, which could not be effectively removed by pretreatment of the proposed methods. This problem requires further research work on this type of pollens.

Application of the Method to the Real Samples

A low level of α- and γ-HCH were detected in water lily and rose. The water or sediments in which the water lily resided might be polluted slightly by α- and γ-HCH, which degraded slowly. Any residual pesticides were not detected in other pollens. Therefore, the pollens on sale could be eaten safely as a whole.

Conclusions

In this study, a multiresidue determination method was proposed for determining three kinds of pesticide residues in bee pollens. Method involves the dissolution of bee pollens in petroleum ether, using a SPE column (activated carbon+C_{18}) for cleanup, then determination by GC-μECD. Beauty of this method is that a number of OCPs (9), OPPs (10), and pyrethroids (7) can be determined simultaneously. Additionally, this method is very simple, rapid, consuming small amount of organic solvent, and consequently produces little hazardous waste. Due to high accuracy and precision, the method may be easily implemented in routine determinations of pesticide residues in bee pollens.

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