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Determination of trace amounts of chlorinated insecticides and fungicides in ginseng using capillary gas chromatography and ^{63}Ni electron capture detector

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Abstract— A method for the simultaneous determination of a series of chlorinated insecticides and fungicides as residues in ginseng is presented in this article. Pulverized samples are subjected to Soxhlet extraction with acetone-petroleum ether and the extract is partitioned between petroleum ether and aqueous sodium sulfate solution (2:98). The combined petroleum ether phase is cleaned up by sulfuric acid and analyzed by capillary gas chromatography using ^{63}Ni electron capture detector. Recoveries from the different concentrations for 11 kinds of chlorinated insecticides and fungicides are between 92.40 and 103.7% with coefficients of variations ranged 1.22 and 9.53% without samples, and between 89.00% and 104.10% with coefficients of variations between 1.16% and 9.16% with samples. The detection limits are 0.2— 7.0 ng/kg.

Keywords: chlorinated insecticides; fungicides; capillary GC; ginseng.

1 Introduction

The serious ecological consequences of the widespread use of chlorinated insecticides and fungicides have been well known, and numerous methods for the determination of the residues in samples of crop, soil, water and so on were reported (Ahmed, 1979; Baker, 1978; Klein, 1961; Smith, 1972). In recent years, extract cleaned up by sulfuric acid for the determination of BHC and DDT residues has successfully been used to analyze samples of plant, animal and soil in China (Yao, 1985 a; Yao, 1985 b; China Import and Export Commodity Inspection Technology Institute, 1986). However, a method for the multiresidue determination of a series of chlorinated hydrocarbon compounds in ginseng by capillary gas chromatography had not been presented. The aim of this paper is to present a sensitive and selective method for the simultaneous determination of a series of chlorinated insecticides and fungicides in ginseng. Problems and variables that must be considered when performing such

analyses are discussed.

2 Experimental

2.1 Materials

α-BHC of 99.3%, β-BHC of 99.1%, γ-BHC of 99.5%, δ-BHC of 99.0% and p, p′-DDE of 98.0%, o,p′-DDT of 96.2%, p,p′-DDD of 98.0%, p,p′-DDT of 96.4% purity were supplied by Department of Pesticide Sciences, Institute of Plant Protection, Chinese Academy of Agricultural Sciences. The standards were used without further purification. Quintozene was supplied by Shanxi Linfen Chemical Plant. Hexachlorobenzene and tecnazene were purchased from Beijing Chemical Company. The fungicide standards were used after further purification in our laboratory. All fungicide standards of at least 95.0% were used.

Acetone, petroleum ether (b.p 60－90 ℃) were purchased from Beijing 5295 Chemical Plant. The petroleum ehter was redistilled before use. Sodium sulfate anhydrous and sulfuric acid of 98% purity were purchased from Beijing Chemical Plant. All chemicals were of analytical-reagent grade and tested for blank.

2.2 Extraction and clean-up procedure

The ginseng was pulverized and an aliquot (10 g dry weight) was transferred into an extraction thimble (filter paper), and subjected to Soxhlet extraction for 8－10 hours with 150 ml of petroleum ether-acetone (2:1) on a water-bath at 75 ℃ . The extract was transferred into a 500 ml separating funnel and partitioned with 200 ml of sodium sulfate aqueous solution (2: 98). The petroleum ether was collected. The aqueous phase was partitioned with further 50 ml of petroleum ether. The combined petroleum ether extracts were transferred into a 250 ml separating funnel, and then 15ml of sulfuric acid was added (petroleum ether: sulfuric acid＝10: 1, v/v). The separating funnel was gently shaken for 1 min, and standing for separation. After separating sulfuric acid and sulfonated derivatives from petroleum ether extract, the layer containing sulfuric acid and sulfonated derivatives was discarded. The petroleum ether extract was cleaned up by additional 15 ml sulfuric acid 4 or 5 times. The petroleum ether extract thus cleaned up was transferred into a 500 ml separating funnel and partitioned with 2 further 200 ml sodium sulfate aqueous solution. The extract was collected and dried with sodium sulfate anhydrous and evaporated almost to dryness in a rotary evaporator (Rotavapor R110, BUCHL). The residue was dissolved in about 5 ml of petroleum ether and stored in the refrigerator at －20 ℃ for analysis.

2.3 Chromatographic analysis

A Varian model 3700 gas chromatography with ^{63}Ni electron capture detector (ECD) and a splitless injector was used. A 25m×0.22 mm I. D., 25 QCZ/BP 5–0.25, capillary column was used. The detector and injector temperatures were maintained at 300 ℃ and 250 ℃, respectively. The following temperature programme was used: 1 min at 110 ℃ increased at 5 ℃ /min to 230 ℃, the final temperature being held for 7 min. The carrier gas(hydrogen) was supplied at 1 ml/min for the capillary column and nitrogen(99.999% purity) at 30 ml/min as makeup to the detector. Injections of 1 μl were made manually. Typical elution times were 11.60 min for tecnazene, 13.70 min for αBHC, 13.90 min for hexachlorobenzene, 14.80 min for β-BHC, 15.0 0 min for γBHC, 15.20 min for quintozene, 16.10 min for δ-HBC, 23.50 min of p,p'DDE, 25.70 min for o,pDDT, 25.90 min for p,p'DDD and 28.10 min for p,p'DDT; total run time was 29 min per sample. All 11 compounds were completely separated within 29 min(Fig.1a).

3 Results and discussions

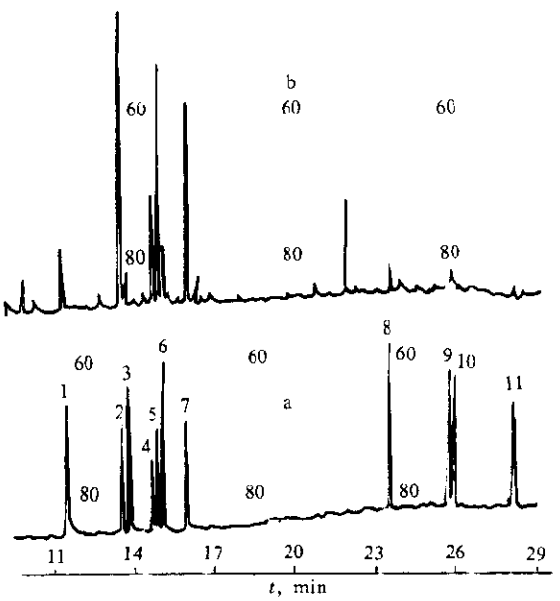

Fig.1 a: Chromatogram of 1. tecnazene; 2. α-HBC 3. hexachlorobenzene; 4. β-BHC; 5. γ-HBC 6. quintozene; 7. δ-BHC; 8. p,p'-DDE; 9. o,p'-DDT; 10. p,p'-DDD; 11. p,p'-DDT
b: Chromatogram of a ginseng sample

Experiments are carried out to determine the amounts recovered by extraction and clean-up procedure for each compound without and with samples of different concentrations ranging from 0.005 to 2.0 mg/kg. Recoveries from the different concentrations are between 92.40% and 103.70% with coefficients of variations between 1.22% and 9.53% without samples, and recoveries are between 89.00% and 104.10% with coefficients of variations between 1.16% and 9.16% with ginseng samples. Both results for recovery are illustrated in Table 1 and Table 2. The high recoveries show that the insecticides and fungicides tested are very stable to sulfuric acid, and even to heat. In other words, sulfuric acid can be used to clean up petroleum ether or n-hexane extract. The detection limits for all 11 compounds investigated are between 0.2 and 7 ng/kg

(Table 2). The levels could be determined with satisfactory accuracy and precision. It is also expected that this method would be quite effective when applied to environmental studies. It has successfully been used to analyze about 200 samples of ginseng in our laboratory (Table 3), and this method is readily adapted for analysis of other sorts of samples. Typical chromatogram of the ginseng sample was given in Fig.1b.

Table 1 Recoveries for 11 kinds of chlorinated hydrocarbon compounds without samples

Compounds	Fortified level, mg/kg	Range of recoveries, %	Recovery ± *SD* ($n=3$), %	*C. V.*, %
Tecnazene	0.0050	89.30 – 101.70	95.60 ± 6.20	6.49
	0.0500	87.51 – 103.11	94.52 ± 7.83	8.40
	0.5000	93.72 – 96.20	94.51 ± 1.44	1.53
Hexachlo-	0.0050	92.29 – 101.11	98.70 ± 5.54	5.62
robenzene	0.0500	96.81 – 101.49	99.90 ± 2.71	2.72
	0.5000	90.91 – 97.49	94.11 ± 3.31	3.52
Quintozene	0.0050	90.51 – 104.69	95.89 ± 7.69	8.01
	0.0500	91.51 – 99.29	95.69 ± 3.93	4.11
	0.5000	93.71 – 100.00	95.81 ± 3.64	3.80
α-BHC	0.0050	97.71 – 105.00	101.41 ± 4.10	4.04
	0.0500	97.41 – 105.69	102.10 ± 4.25	4.16
	0.5000	90.72 – 98.88	94.41 ± 4.15	4.39
β-BHC	0.0125	86.41 – 99.89	92.40 ± 6.93	7.49
	0.1250	85.71 – 103.49	94.08 ± 8.96	9.53
	1.2500	90.71 – 95.69	93.80 ± 2.71	2.89
γ-BHC	0.0050	90.31 – 101.40	96.81 ± 5.81	6.00
	0.0500	90.41 – 101.89	96.30 ± 5.76	5.98
	0.5000	90.82 – 99.28	94.61 ± 4.32	4.57
δ-BHC	0.0050	90.51 – 104.80	95.81 ± 7.83	8.18
	0.0500	87.23 – 101.17	93.62 ± 7.09	7.57
	0.5000	90.24 – 95.76	92.89 ± 2.80	3.02
P.P'-DDE	0.0050	94.65 – 101.25	98.60 ± 3.55	3.60
	0.0500	87.06 – 103.64	95.50 ± 8.36	8.75
	0.5000	91.81 – 96.29	94.30 ± 2.29	2.43
O.P'-DDT	0.0100	88.73 – 104.77	96.20 ± 8.10	8.42
	0.1000	96.00 – 102.00	99.30 ± 3.06	3.08
	1.0000	96.05 – 100.95	99.00 ± 2.65	2.67
P.P'-DDD	0.0075	100.00 – 106.69	102.51 ± 3.68	3.59
	0.0750	90.04 – 97.06	93.52 ± 3.55	3.80
	0.7500	94.00 – 96.02	94.77 ± 1.15	1.22
P.P'-DDT	0.0200	100.08 – 106.12	103.70 ± 3.29	3.17
	0.2000	88.91 – 101.89	96.80 ± 6.92	7.15
	2.0000	94.44 – 98.86	96.70 ± 2.25	2.23

Table 2 Recoveries and detection limits for 11 kinds of chlorinated hydrocarbon compounds with ginseng

Compounds	Fortified level, mg/kg	Rang of recoveries, %	Recovery ± *SD.*, ($n=5$) %	*C.V.*, %	Detection limit, ng/kg
Tecnazene	0.0050	98.31 – 105.19	101.71 ± 3.45	3.39	0.3
	0.0500	86.24 – 93.06	89.00 ± 3.63	4.08	
	0.5000	90.06 – 96.14	93.10 ± 3.10	3.33	
Hexachlo-	0.0050	96.40 – 108.99	100.62 ± 7.33	7.29	0.2
robenzene	0.0500	96.41 – 101.79	100.00 ± 3.12	3.12	
	0.5000	94.81 – 99.49	97.43 ± 2.39	2.45	
Quintozene	0.0050	97.45 – 102.05	100.00 ± 2.40	2.40	0.3
	0.0500	87.74 – 103.36	93.61 ± 8.57	9.16	
	0.5000	92.50 – 98.70	95.60 ± 3.10	3.24	
α-BHC	0.0050	94.30 – 105.70	101.40 ± 6.22	6.13	0.3
	0.0500	94.15 – 105.85	99.00 ± 6.13	6.19	
	0.5000	90.57 – 98.33	93.31 ± 4.42	4.74	
β-BHC	0.0125	98.00 – 100.00	99.30 ± 1.15	1.16	0.7
	0.1250	90.91 – 98.19	94.51 ± 3.65	3.86	
	1.2500	90.74 – 101.16	95.40 ± 5.35	5.61	
γ-BHC	0.0050	94.73 – 103.17	98.31 ± 4.38	4.46	0.3
	0.0500	97.50 – 102.00	98.40 ± 1.56	1.58	
	0.5000	91.21 – 97.59	93.90 ± 3.33	3.55	
δ-BHC	0.0050	100.00 – 109.40	103.70 ± 5.03	4.85	0.3
	0.0500	103.10 – 106.19	104.10 ± 1.79	1.72	
	0.5000	90.21 – 97.89	92.81 ± 4.45	4.79	
P,P′-DDE	0.0050	92.33 – 97.67	95.85 ± 3.12	3.25	0.2
	0.0500	101.10 – 106.20	102.80 ± 2.94	2.86	
	0.5000	89.27 – 94.03	91.51 ± 2.47	2.70	
O,P′-DDT	0.0100	92.00 – 96.00	94.70 ± 2.31	2.44	2.0
	0.1000	93.81 – 95.79	95.81 ± 2.05	2.14	
	1.0000	90.90 – 3.15	92.00 ± 2.00	2.17	
P,P′-DDD	0.0075	94.74 – 105.26	98.20 ± 6.12	6.23	4.0
	0.0750	87.88 – 90.82	89.91 ± 1.79	1.99	
	0.7500	89.24 – 97.06	92.60 ± 4.08	4.44	
P,P′-DDT	0.0200	90.60 – 93.70	92.70 ± 1.78	1.93	7.0
	0.2000	92.81 – 103.49	97.61 ± 5.44	5.58	
	2.0000	95.50 – 98.70	97.20 ± 1.47	1.52	

In conclusion, the complete clean-up step, the sensitivity and time used for one run, and the selective response of the electron capture detector provide us with an effective procedure for the simultaneous quentitative analysis of many chlorinated hydrocarbon compounds.

Table 3 Concentrations of chlorinated insecticides and fungicides in the ginseng (dry weight, average value, ppm)

Growth period, years	Sample number	Tecnazene	HCB[1]	Quintozene	α-BHC	β-BHC	γ-BHC	δ-BHC	p,p'-DDE	o,p'-DDT	p,p-DDD	p,p'-DDT
2	14	0.0390	0.0102	0.1631	0.0087	0.0037	0.0072	0.0042	0.0017	0.0023	0.0010	0.0090
3	35	0.0224	0.0057	0.0712	0.0090	0.0040	0.0063	0.0053	0.0016	0.0033	0.0004	0.0068
4	36	0.0249	0.0085	0.0995	0.0103	0.0042	0.0081	0.0047	0.0016	0.0021	0.0006	0.0113
5	45	0.0392	0.0098	0.1445	0.0089	0.0041	0.0082	0.0041	0.0013	0.0020	0.0010	0.0101
6	52	0.0411	0.0117	0.1833	0.0111	0.0045	0.0079	0.0044	0.0014	0.0021	0.0012	0.0085

1. hexachlorobenzene

A notable problem in the clean-up step is that the emulsification of sulfuric acid with petroleum ether extract may occur in the separating funnel if it is shaken very strongly. In fact, this kind of problem frequently crops up, especially in samples that are rich in fat. Satisfactory results of recovery could hardly be achieved if the emulsification was not effectively overcame during the extraction, as emulsification would make considerable amounts of substances of interest remained in the aqueous phase. However, the emulsion will disappear as soon as a few drops of distilled water or sodium sulfate aqueous solution (2:98) is added.

It should be noted that the separating funnel may be detonated due to gas and heat produced in the reactions of sulfuric acid with foreign substances and/or water. Therefore, it is necessary that the gas should be blown off in the process of shaking. We maintain that gentle shaking of the separating funnel is of critical importance at the first addition of sulfuric acid, and then shaking vigorously.

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