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Note

Small-scale method for the determination of organophosphorus insecticides in tea using sulphuric acid as clean-up reagent

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Some organophosphorus pesticides, such as malathion, fenitrothion and quinalphos, are regarded as suitable pesticides for tea plantation use because of their relatively low mammalian toxicity, low persistence on tea plants and high loss rate during the tea manufacturing process[1]. Many methods for determining residues of organophosphorus pesticides on crops have been reported[2,3]. Generally a volume of several hundred millilitres solvent is needed for the analysis of one sample in these methods, which makes them expensive. Sulphuric acid has been used successfully in the determination of some organochlorine pesticides and pyrethroids on tea[4,5]. This paper reports a simple and inexpensive method for the determination of organophosphorus pesticides in tea in which sulphuric acid as a clean-up reagent.

EXPERIMENTAL

Materials

Toluene, methanol and sulphuric acid (98%) were all of analytical-reagent grade and were used as received. Florisil (60–100 mesh) was heated at 600°C for 6 h and then deactivated by mixing with 5% (w/w) of distilled water.

The chromatographic mini-column (12 × 0.5 cm I.D.) used, with a solvent reservoir (5 ml) was of a similar size to of a Pasteur pipette.

A Hewlett-Packard HP-5790A gas chromatograph equiped with a nitrogen–phosphorus detector and a glass column (1.2 m × 2 mm I.D.) packed with 6% OV-101 on Chromosorb W (80–100 mesh) was used for residue analysis.

Method

Tea (10 g) was blended for 4 min with 100 ml of toluene–methanol (3:1, v/v) and the slurry obtained was filtered by suction through filter-paper on a Buchner funnel. The filtrate was shaken vigorously and an aliquot (10 ml) was transferred immediately into a 20-ml test-tube. After distilled water (1 ml) and sulphuric acid (1 ml) had been added, the test-tube was stoppered and shaken vigorously ten times and then allowed

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to stand for 10 min to effect phase separation. The upper (toluene) phase was transferred to the chromatographic mini-column or a Pasteur pipette packed with Florisil (1 g), using a Pasteur pipette. The test-tube was washed with toluene (1 ml) and the washings were added to the column. The column was then eluted with toluene–acetone (98:2, v/v; *ca.* 3 ml) until 10 ml of the eluate had been collected. The eluate was analysed by gas chromatography under following conditions: column temperature, 200°C; injector temperature, 230°C; detector temperature, 250°C; carrier gas (nitrogen) flow-rate, 50 ml/min; air flow-rate, 80 ml/min; and hydrogen flow-rate, 1.5 ml/min.

The retention times of dimethoate, fenitrothion, malathion and quinalphos were 1.9, 3.6, 3.9 and 5.7 min, respectively. The detection limit was 0.01 mg/kg for quinalphos and 0.02 mg/kg for malathion and fenitrothion.

Recovery test

Dimethoate, malathion, fenitrothion and quinalphos dissolved in benzene (1 μg/ml) were added to tea (10 g) at the level of 0.1–0.3 mg/kg. The fortified samples were extracted and analysed immediately after the fortification, following the above procedure.

Field test and sample analysis

Fenitrothion (50% emulsifiable concentrate) was sprayed on tea plants at 900 g active ingredient per ha. Tea shoots were collected at random over the test plot (300 m^2) at various intervals, and processed to green tea by the commonly used methods.

The green tea samples were analysed by the above method. To investigate the extraction efficiency, the residue from the blending extracted samples was Soxhlet extracted with 100 ml of chloroform–methanol (9:1, v/v) for 6 h with about six solvent exchanges per hour. The extract was concentrated to *ca.* 1 ml at 50°C, and then dissolved in 10 ml of toluene–methanol (3:1, v/v). The solution was transferred into a 20-ml test tube and analysed following the procedure described above.

RESULTS AND DISCUSSION

Recoveries of pesticides

The recoveries of dimethoate, malathion, fenitrothion and quinalphos are given in Table I.

TABLE I

RECOVERIES OF PESTICIDES

Means of four replicate determinations.

Pesticide	*Recovery ± S.D. (%)*	*Fortified level (mg/kg)*
Dimethoate	21.9 ± 9.2	0.3
Fenitrothion	97.2 ± 0.8	0.1
Malathion	94.4 ± 7.1	0.3
Quinalphos	96.1 ± 8.1	0.3

Fenitrothion, malathion and quinalphos all showed recoveries above 90%, but dimethoate was nearly totally lost, suggesting that fenitrothion, malathion and quinalphos were satisfactorily stable to the sulphuric acid treatment but dimethoate was not.

Extraction efficiency

The tea samples collected during the field test were first analysed by the blending method, and then Soxhlet extracted. The results are given in Table II.

TABLE II

FENITROTHION RESIDUES ON TEA SAMPLES COLLECTED DURING THE FIELD TEST

Means of two replicate determinations: (A) by blending method; (B) by Soxhlet extraction.

Days after spraying	*Residues (mg/kg)*		*Ratio B/A*
	A	*B*	
0	9.46		
2	1.27	0.017	0.013
5	0.20	0.002	0.010
8	0.09	0.012	0.13
15	0.02	0.007	0.35

The ratio of the residues extracted by Soxhlet extraction to that given by the blending method was proportional to the period of time the sample had weathered in the field. It has been reported that the recoveries of organophosphorus pesticides were best when Soxhlet extraction with chloroform–methanol (9:1, v/v) was used[6]. The present results suggest that most of the fenitrothion residues in tea were removed by the blending method.

Clean-up effect

The coextractives were mainly caffeine and polyphenols. Caffeine has a very similar polarity to those of many non-polar organophosphorus pesticides. Its retention behaviour and detection limit are also very close to those of malathion and fenitrothion, making the gas chromatographic determination of these two pesticides very difficult by commonly used residue methods.

The present method was able to remove caffeine completely from the extract, while still giving good recoveries of non-polar organophosphorus pesticides. The chromatograms showed no impurity peaks which would affect the analysis. After over 50 injections the response and the baseline of the gas chromatograph were still steady, which indicates that the clean-up of the samples was adequate.

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