



# Determination of Organophosphorus Pesticide Residues in Winter Bamboo Shoots by Homogenate Extraction Coupled with Gas Chromatography-Flame Photometric Detector

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## Authors' contributions

This work was carried out in collaboration of all authors. Author FQ designed the study and wrote the first draft of the manuscript. All authors contributed in practical work and managed the analysis of the study. All authors read and approved the final manuscript.

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## ABSTRACT

Excessive use of organophosphorus pesticides (OPPs) in fruits and vegetables may affect human health. In this paper, a simple, rapid and effective method for the determination of five OPPs in winter bamboo shoots by gas chromatography-flame photometric detector (GC-FPD) was developed. Three extractants and three extraction methods were examined respectively. The results showed that the recovery rate was higher when the samples were extracted by acetonitrile and treated with homogenate extraction method. Under the optimized conditions, recoveries ranged from 82.12% to 91.48% with the relative standard deviation (RSD) of 1.51-4.20% and the limit of detection (LOD) of 0.005-0.02 µg/mL. Results showed that using acetonitrile as extractants and homogenate extraction in sample preparation is an effective method in determination of pesticide residues in winter bamboo shoots.

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## 1. INTRODUCTION

Organophosphorus pesticides (OPPs) targeting on acetylcholinesterase have played an important role in the field of plant protection in the past decades. Most of the OPPs still in use have moderate to high toxicity, while people tend to increase the usage of organophosphorus pesticides due to the development of resistance [1]. OPPs are sprayed over fruits and vegetables, causing residues to be found in the surface, even in soil, groundwaters and drinking water [2]. The long-term consumption of food containing OPPs may be a great threat to human health. China and many other countries have prohibited the use of many high toxicity OPPs, and also stipulated the maximum residue limit for OPPs in different types of food [3,4].

Current analytical methods for the determination of OPPs are usually based on gas chromatography-mass spectrometry (GC-MS) [5,6], gas chromatography with flame photometric detection (GC-FPD) [7,8], gas chromatography-flame ionization detection (GC-FID) [9] and high performance liquid chromatography [10-12]. Since the majority of OPPs are volatile and thermally stable, GC is a classical analytical method for the determination of OPPs. In addition, GC-FPD is widely used because of its high separation efficiency, selectivity and sensitivity in OPPs analysis [13].

The main challenge in the analysis of pesticide residues is the sample preparation procedures. The pesticide residues extraction and enrichment are traditionally done by solid phase extraction [14], liquid-liquid extraction [15], solid phase microextraction [10] and liquid phase microextraction [9]. Most of these techniques require large sample volumes and special equipments as well as being time-consuming, which make them costly and difficult. In order to establish a rapid, sensitive and accurate method for the determination of OPPs in complex systems, three kinds of pretreatment methods coupling with GC-FPD were studied. The results showed that the improved sample pretreatment method was more suitable for the determination of multi-component residues of five OPPs (Fig. 1, ethoprophos, dimethoate, parathion-methyl, fenitrothion and triazophos) in winter bamboo shoots.

## 2. MATERIALS AND METHODS

### 2.1 Instrument

An Agilent 6890N gas chromatography with split/splitless injector coupled with flame photometric detector (FPD) was used. A DB-17 capillary column (50% polyphenylmethylsiloxane column, 30 m \*0.25 mm \*0.25  $\mu$ m, Agilent) was used to separate the pesticides using the following temperature program: Initial temperature of 80°C held for 1 min, ramped at 20°C/min to 260°C and held for 5 min. The injector temperature was maintained at 220°C and detector temperature was at 250°C. Nitrogen (purity > 99.999%) was used as carrier gas at 1 mL/min. Hydrogen (purity > 99.999%), 75 mL/min and air, 100 mL/min were used as combustion gases. A 1- $\mu$ L volume of the extract was injected in the splitless mode.

### 2.2 Standards and Reagents

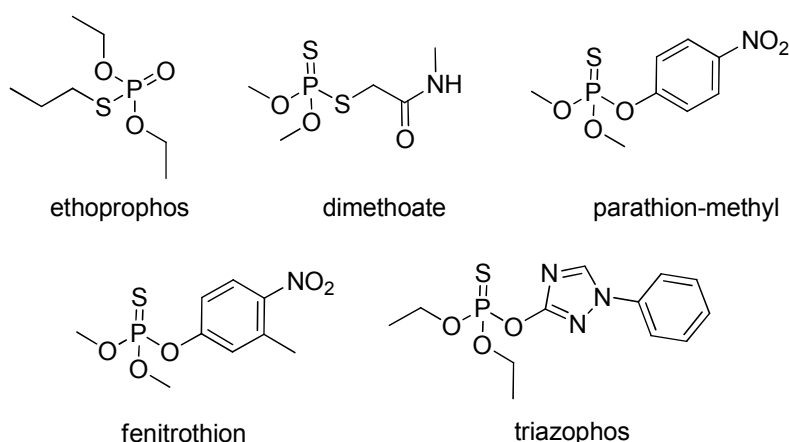
Standards of ethoprophos, dimethoate, parathion-methyl, fenitrothion and triazophos were obtained from ANPEL Laboratory Technologies (Shanghai) Inc. The stock solution containing 1000 mg/L of each pesticide in acetone were kept at -18°C. Other reagents were analytical pure and obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

### 2.3 Sample Preparation

Winter bamboo shoots, which were obtained from the main forest products producing areas in Zhejiang province, were finely chopped into small pieces, combined and smashed with a FW177 disintegrator (Tianjin Taisite Instrument Co., Ltd.). The crushed sample was treated by the following three methods.

Method A (Homogenate extraction): 25 g of the sample was accurately weighed into a homogenizer (T18 disperser, IKA-Werke GmbH & Co.KG, German), followed by the addition of 50 mL of extraction solvent (acetonitrile, dichloromethane or acetone). After 2 min of high-speed homogenization in the homogenizer, the extracts were filtered with filter paper.

Method B: A portion of 25 g of the crushed sample was accurately weighed and extracted with 50 mL of acetonitrile by swirling for 30 min at room temperature. The extracts were filtered with filter paper.



**Fig. 1. Chemical structures of the studied organophosphorus pesticides**

Method C: 25 g of the crushed sample was immersed in 50 mL of acetonitrile for 24 h at room temperature, and then the extracts were filtered with filter paper.

A portion of 50 mL of obtained filtrate was collected with a 100 mL stopper cylinder containing 5-7 g sodium chloride and shaken for 1 min. After standing for 30 minutes at room temperature, the supernatant of 10 mL was evaporated and then transferred to 5 mL volumetric flask with acetone. The obtained solution was used for subsequent GC analysis.

## 2.4 Preparation of Standard Solution

The mixed stock standard solution (10 µg/mL) was prepared by transferred 1.00 mL each of ethoprophos, dimethoate, parathion-methyl, fenitrothion and triazophos (all of them are 1000 mg/L standard solution) in a 100-mL volumetric flask and filled up to the mark with acetone. The standard solution was stored in a refrigerator at 4°C and was diluted into the standard solution of a series of concentration gradients (0.10 µg/mL, 0.20 µg/mL, 0.40 µg/mL, 0.60 µg/mL and 0.80 µg/mL) with acetone before use.

## 3. RESULTS AND DISCUSSION

### 3.1 Mixed Standard Solution Chromatography

The mixed standard solution of 0.80 µg/mL OPPs was used for chromatographic analysis under established chromatographic conditions. From the Fig. 2, it was showed that under these

conditions, five OPPs were completely separated in 23 min, and the peak shape was good, which indicated that the chromatographic conditions were suitable for the determination of the multi-component residues.

### 3.2 Optimization of Pretreatment Conditions

#### 3.2.1 Recoveries of different extractants

Seven portions of 25 g of the crushed samples were accurately weighed, and six samples were added with 1.00 mL of 10 µg/mL mixed standard solution of OPPs. The rest one was used as blank control. The homogenate extraction method (method A) was used, and then acetonitrile, dichloromethane and acetone were used as extractants respectively. The average recovery was calculated and shown in Table 1. It was indicated that acetonitrile was the relatively suitable solvent for extraction of the five pesticides, and the recoveries varied between 83.15% and 93.20%. The results obtained were found to be comparable to the previously reported by Lehotay [16].

#### 3.2.2 Recoveries of different extraction methods

The sample preparation procedure was similar with step 3.2.1, and acetonitrile was selected as extractant. The effect of different extraction methods (method A-C) on the recoveries was investigated (Table 2). Satisfactory recoveries (81.22%- 93.21%) for the studied pesticides were obtained by the homogenate extraction (method A), which was applied in pesticide multiresidue

screen method for determination of organophosphorus pesticides in many vegetables [17].

### 3.3 Validation of the Method

The analytical performance was investigated under the optimized conditions, and the results were list in Table 3. The results showed that good linear responses were observed over the range of 0.1-10  $\mu\text{g/mL}$  with the correlation

coefficients (R) among 0.9976 and 0.9991. The recoveries of 82.12-91.48% were obtained for the analysis of spiked samples with 10  $\mu\text{g/mL}$  of each target. The LODs (S/N =3) ranging from 0.005 to 0.02 were obtained. To evaluated the precision of the developed method, intraday repeatability (n= 6) was performed using the selected concentration level (0.4  $\mu\text{g/mL}$ ) of the studied pesticides. %RSD varied between 1.51% and 4.20%, which indicated that acceptable repeatabilities were obtained.

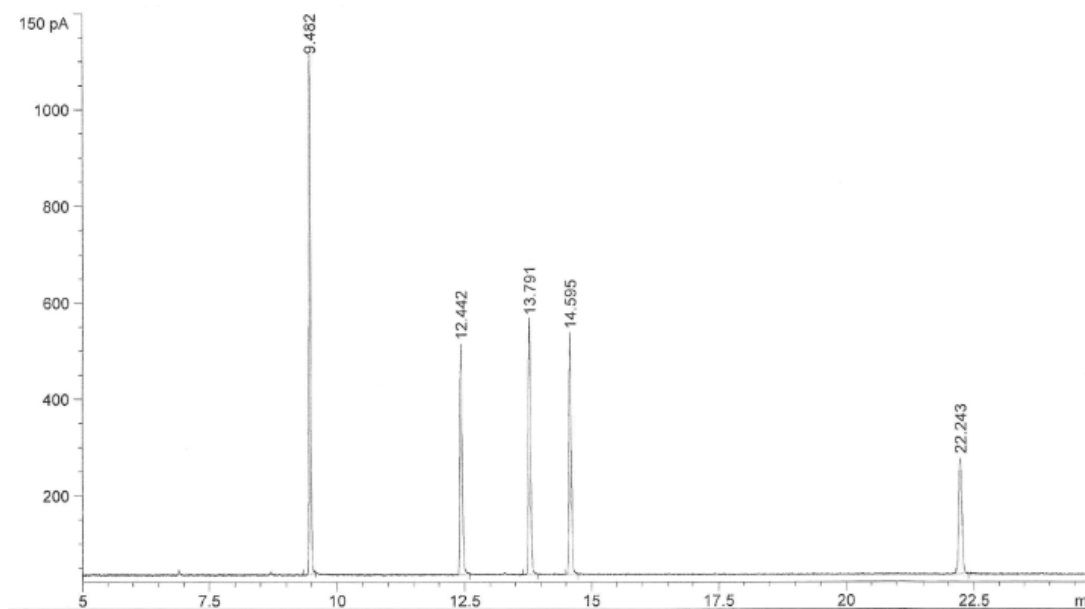


Fig. 2. Chromatogram of mixed standard solution

Table 1. Recoveries of the five pesticides with different extractants (% , n=6)

Pesticide	Acetonitrile	Dichloromethane	Acetone
Phosphor	85.14	74.07	65.30
Dimethoate	83.15	81.24	69.37
Methyl parathion	91.46	85.36	74.21
Phoxim	93.20	80.53	72.58
Triazophos	90.73	89.79	79.33

Table 2. Recoveries of different extraction methods (% , n=6)

Pesticide	Method A	Method B	Method C
Phosphor	81.22	75.51	65.39
Dimethoate	87.40	78.01	69.17
Methyl parathion	91.63	82.16	70.42
Phoxim	85.14	86.37	76.48
Triazophos	93.21	87.15	73.22

**Table 3. The retention time ( $t_R$ ), calibration curve and detectability of five organophosphorus in bamboo**

Pesticide	$t_R$ (min)	Recovery (%)	LOD ( $\mu\text{g/mL}$ )	RSD (%)	Equations of standard curve	R
Phosphor	9.482	82.12	0.005	1.51	$Y=2870.35838X+363.5858$	0.9991
Dimethoate	12.442	85.25	0.01	3.23	$Y=1525.7699X+177.64205$	0.9983
Methyl parathion	13.791	91.48	0.01	4.20	$Y=1977.62369X+195.28201$	0.9976
Phoxim	14.595	87.17	0.01	3.32	$Y=1622.04667X+287.39865$	0.9991
Triazophos	22.243	85.65	0.02	3.02	$Y=1483.76923X+172.18728$	0.9986

#### 4. CONCLUSION

A simple, easy to operate, time-saving, high accuracy and promised repeatability method for the determination of five OPPs in winter bamboo shoots was established. Using acetonitrile as extractant and homogenate extraction, good recovery rate and acceptable precision were obtained. It is presumed that this pretreatment method coupling with GC-FPD can also be applied to the rapid, sensitive and accurate detection of OPPs in complex systems of other agricultural products.

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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