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A quick analytical method using direct solid sample introduction and GC-ECD for pesticide residues analysis in crops

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ABSTRACT

In this work, an analytical method for GC using direct solid sample introduction was developed to tackle the problem regarding quick detection of pesticide residue in crops and large-scale screening of samples. 10 mg of the crop solid sample without sample pre-treatment was directly introduced into a modified split/splitless injector for GC analysis. A split/splitless injector was modified to quickly remove oxygen and low boiling-point matrices of the sample. The whole sampling procedure was simple and it required less than 5 min. The experimental parameters including injector-port temperature, removal of oxygen and low boiling point matrices, size and the amount of the solid sample, oven temperature program were studied. Satisfactory recoveries of 6 pesticides (methyl parathion, fenitrothion, aldrin, dieldrin, endosulfan, o,p′-DDT) were obtained in maize and rice sample. Relative standard deviation was less than 15%. Experimental results showed that the proposed method was quick and reliable for pesticide residues analysis in crops.

1. Introduction

Pesticides are being used to increase production and quality in crops over the past few decades. Excessive usage of pesticides contaminates the crop itself and the environment, eventually causing disease to human beings. China is one of the biggest crop product exporters in the world. Over 52% of the crop products are exported to countries like Japan, US and Europe. Food safety becomes a hot issue because it is not only concerning about consumers but also an international trade mark. Therefore the monitor for pesticide residue in crops is a must to the Chinese government.

A lot of analytical methods are reported in order to effectively detect the pesticide residues in crops [1,2]. Traditional pesticide residues analysis requires a large amount of organic solvent for sample extraction and a series of steps for clean-up and pre-concentration, which is complicated, tedious and expensive. The most commonly used sample preparation methods at present include accelerated solvent extraction (ASE) [3], solid-phase extraction (SPE) [4], supercritical fluid extraction (SFE) [5], solid-phase micro-extraction (SPME) [6], liquid-phase micro-extraction (LPME) [7], microwave-assisted extraction (MAE), etc. In addition, QuEChERS (Quick Easy Cheap Effective Rugged Safe) is another very popular analytical method in pesticide residue analysis [8,9]. These kinds of solvent-extraction methods have shortened the whole analytical time and enhanced the extraction efficiency. However, these methods are not simple and quick enough with regard to the problem that more and more crop-products needed to be detected.

In 2003, Shim et al. examined a Keele solid injector in GC analysis to determine vinclozolin and procymidone residues in lettuces and ginseng, respectively [10,11]. A small amount of solid sample was sealed in a glass tube and then directly introduced into the Keele solid injector for detection. Volatile flavor components in dang-gui ciltivars were also successfully determined by using a similar method [12]. Direct sample introduction (DSI), or named dirty sample injection, was also being studied for pesticide residues analysis in food [13–15]. Solid or liquid samples were directly transferred to a micro-vial and then introduced into a DSI injector for GC analysis. Detection by using Keele solid injector or DSI injector was quick and simple since there is no need for any sample preparation and clean-up procedure. However, they require a special injector installed on the GC system, which is not convenient and also costs extra expense for the analysis.

In the previous work, Zhang et al. have developed a new method for pesticide residue analysis in vegetables [16]. Sample without any pre-treatment was directly introduced into the split/splitless injector for GC–MS determination. This method was proven to be quick, convenient and accurate. It also worked well for rapid detection of pesticide residues in food and large-scale screening of samples in field detection. In this paper, a direct solid sample introduction for pesticide residues analysis in crops was developed based on Zhang's previous work. Little related research work was reported by using the similar technique for pesticide residue anal-

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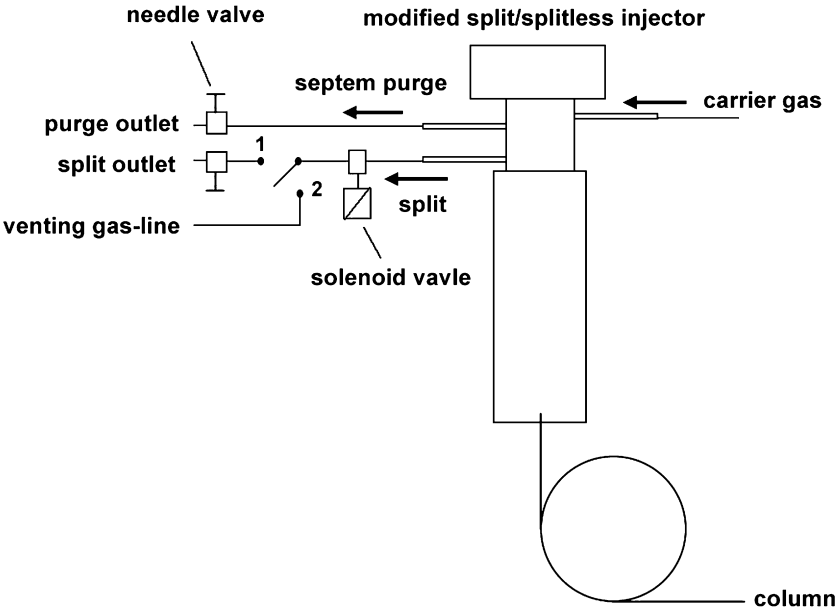

Fig. 1. Pneumatic system of the modified GC split/splitless injector. Spliting mode (1. Split outlet was connected): carrier gas goes through the split outlet with split ratio of 30:1. Venting mode (2. Venting gas-line was connected): all of the carrier gas only goes through the venting gas-line, column head pressure becomes zero.

ysis in crops. In addition, the GC split/splitless injector was simply modified to quickly remove oxygen and low boiling point matrices of the sample by adding a venting gas-line on the original pneumatic system. No sample pre-treatment was needed and the sampling procedure required less than 5 min. The injector's modification can be conducted on portable GC. Hence this method is potential for field analysis of pesticide residues in crops and large-scale screening of samples.

2. Experimental

2.1. Chemicals and materials

Pesticide standards (methyl parathion, fenitrothion, aldrin, dieldrin, endosulfan, o,p′-DDT) were purchased from Shanghai Pesticide Research Institute (Shanghai, China) with the purities from 95.4% to 99.0%. N-hexane (analytical grade) was purchased from Shanghai Ling Feng Chemical Reagent Co. Ltd. (Shanghai, China). Individual stock solution (200 μg/ml) of each pesticide standards was prepared by dissolving 2 mg of ingredient in 10 ml n-hexane. The mixed working solution of pesticide standards at different concentrations of interest was prepared by diluting the stock solution with n-hexane. All solutions were stored at 4 °C. Crop samples (maize, rice and wheat flour) were organic products from local market and were guaranteed from contamination of pesticides.

2.2. Modified GC split/splitless injector

The modified GC split/splitless injector was capable of changing the spit ratio from 30:1 to the largest within a second. An extra venting gas-line was added on the original pneumatic system of the GC (Tempcom GC7890II, Shanghai, China) as shown in Fig. 1. The system was in splitting mode when the split outlet was connected. The carrier gas would go through the spilt outlet with the split ratio of 30:1. Since the venting gas-line was connected, the system was changed into venting mode and then all of the carrier gas would go through the venting gas-line. The column head pressure became zero at the same time.

2.3. Direct solid sample introduction

5 g of the solid samples were crushed into small solid particles by using a mortar. The crushed solid samples were transferred to a 1.5 mm mesh sieve. 10 mg of the solid samples remained on the upper side of the sieve (diameter of solid sample >1.5 mm) were carefully weighted and then transferred to a glass sample vial ready for detection. The straight glass liner (78 mm long × 6.2 mm o.d. × 4.0 mm i.d.) was taken out from the injector for solid sample introduction. The pre-weighted solid sample was put in the middle of the glass liner and supported by a little bit glass wool as shown in Fig. 2(a). Finally the glass liner was installed back to the injector for GC analysis. The solid sample was disposable after each test. Next sample could be transferred into the liner for another experiment immediately. The whole sampling procedure is shown in Fig. 2(b).

2.4. GC analysis

This proposed method was performed on a GC 7890II (Tempcom, Shanghai, China) coupled with electron capture detector (ECD). A PCB-Octyl capillary column (Supelco Inc., USA) of 8 m × 0.25 mm i.d. and 0.25 μm film thickness was used. Carrier gas was N_2 (purity >99.999%) and the flow rate was 1.5 ml/min. The injector-port temperature was set at 60 °C and the injector was in splitting mode with the split ratio of 30:1 at the beginning. After the sample introduction finished, the venting gas-line was connected for 30 s to vent oxygen and low-boiling point matrices of the solid sample. The split outlet was re-connected and the injector-port temperature was immediately increased from 60 °C to 180 °C, held for 2 min, and then cooled down to 60 °C. The oven temperature program ran simultaneously from 40 °C (held for 0.5 min) to 180 °C at a rate of 8 °C/min, from 180 °C to 240 °C at a rate of 20 °C/min (held for 2 min). The detector temperature was 300 °C.

2.5. Calibration curve

A revised external calibration was used for the quantification in this method. Pesticide standards were firstly injected into the injector at an initial injector-port temperature of 60 °C. The venting