Bull Environ Contam Toxicol (2010) 84:236–239
DOI 10.1007/s00128-009-9881-7

Determination of Oxadiargyl Residues in Environmental Samples and Rice Samples

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Received: 2 April 2009 / Accepted: 17 September 2009 / Published online: 27 September 2009

Abstract Oxadiargyl is a commonly used herbicide in China. We developed a simple, fast, and high-throughput method employing gas chromatography with electron capture detector to determine oxadiargyl residues in food samples (rice, straws) and environmental samples (soil, water). Samples were prepared by a modified QuEChERS procedure. In this method, acetonitrile was used as the extracting solvent. The purifying step was omitted when the chromatographic conditions were optimized. Recoveries ranged from 82.9 to 112.0% for oxadiargyl in all samples, with relative standard deviation values lower than 6.2% at 0.01 mg/kg fortified concentration level.

Keywords Oxadiargyl · Residue · QuEChERS · Gas chromatography

Oxadiargyl, 5-*tert*-butyl-3-(2,4-dichloro-5-propargyloxyphenyl)-1,3,4oxadiazol-2-(3H)-one (Fig. 1) is a selective herbicide that has been widely used for pre-emergence weed control in both transplanted and directly seeded rice. Oxadiargyl is effective again a broad-spectrum of broadleaf weeds, grass and annual sedges. So far many studies have examined the herbicidal activity of oxadiargyl against different crops (Dickmann et al. 1997; Tracchi et al. 1997; Frost et al. 2003; Gitsopoulos and Froud-Williams 2004). Only two published studies considered determination of oxadiargyl or its environmental behaviors (Chen et al. 1999; Shi et al. 2008). In Chen et al. (1999), a gas chromatography-electron capture detector (GC-ECD) method was established for straw and rice samples. The procedure consisted of immersion in dichloromethane, extraction in separatory funnel, purifying by column filled with Florisil and activated carbon. In Shi et al. (2008), a similar procedure was used for determination of oxadiargyl in water.

QuEChERS (QUick, Easy, CHeap, Effective, Rugged and Safe) is a sample preparation approach used prior to pesticide residue analysis (Anastassiades et al. 2003). The QuEChERS method has been widely used around the world because of its flexibility and unique facilities since the mid-1990's. With various modifications, the method can be applied to determining many types of pesticide residues in various samples. These methods are usually linked with gas and/or liquid chromatographic analyses with mass spectrometric (MS) detector (Korytar et al. 2002; Matisova and Domotorova 2003; Diez et al. 2005; Lehotay et al. 2005; Paya et al. 2007).

Most underdeveloped areas in China, as in some other regions, are not equipped with mass spectrometry detector to achieve high accuracy in monitoring of pesticide residues. Unfortunately, most newly developed analytical methods always use mass spectrometry detector for detection. Therefore, simple methods without the need for sophisticated equipment are always in great need.

In our study, a reliable and convenient GC approach with good sensitivity and accuracy was developed for the determination of oxadiargyl residue. In addition to that a modified QuEChERS method was established for the preparation of soil, water, rice and straw samples prior to analysis of oxadiargyl.

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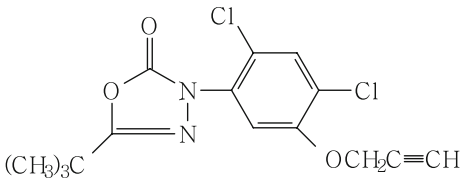

Fig. 1 Structure of oxadiargyl

Materials and Methods

Standard of oxadiargyl (99.0%) was purchased from Bayer CropScience (Beijing, China). Acetonitrile, ethyl acetate, sodium chloride (NaCl), bitter salt ($MgSO_4$), and anhydrous sodium sulfate (Na_2SO4) were of analytical grade and were purchased from Shuanglin (Hangzhou, China). Standard solutions were prepared in ethyl acetate, with concentrations covering the range of 0.001–10 mg/L.

Water sample (10 mL) was transferred into a 50-mL centrifuge tube, followed by the addition of 4 g NaCl and 10 mL acetonitrile. After the sample tube was vigorously shaken for 1 min, the mixture was centrifuged at 2,000 rpm for 5 min. Five milliliters of the supernatant was transferred to a flask through a layer of anhydrous sodium sulfate. The extract in the flask was concentrated to near dryness by a Re2000 rotary vacuum evaporator (Rongsheng Co., Ltd., Shanghai, China). Blowed the residues to dry by nitrogen, then dissolved it in ethyl acetate for GC injection.

A 10 g sifted (through a 40-mesh sieve) soil sample was weighed into a 50-mL centrifuge tube, followed by the addition of 4 g $MgSO_4$, 1 g NaCl and 15 mL acetonitrile. After the sample mixture was vigorously shaken for 1 min, the mixture was centrifuged at 2,000 rpm for 5 min. A portion (5 mL) of the supernatant was transferred to a flask and concentrated to near dryness, then blowed to dry with nitrogen. The residues were re-dissolved in ethyl acetate for GC injection.

A 5-g aliquot of homogenized rice powder was weighed into a 50 mL centrifuge tube, which was followed by addition of 4 g $MgSO_4$, 1 g NaCl and 15 mL acetonitrile. After the sample mixture was vigorously shaked for 1 min, the mixture was centrifuged at 2,000 rpm for 5 min. A 10-mL portion of the supernatant was transferred to a flask, and was further concentration to near dryness. After blowed to dry, the residues were re-constituted in ethyl acetate for GC injection.

Straw samples were cut into pieces shorter than 0.5 cm prior to extraction. An aliquot (5 g of wet weight) of the chopped straw sample was weighed into a 50-mL centrifuge tube, and mixed with 4 g $MgSO_4$, 1 g NaCl and 25 mL acetonitrile. The mixture was similarly handled as for rice grains before analysis.

Table 1 Recoveries and relative standard deviations of oxadiargyl in different samples

Sample	Fortified concentration (mg/kg)	Mean recovery (%)	RSD (%)
Soil	0.01	112.0	2.8
	0.10	95.5	1.3
	1.00	96.3[a]	1.0
Straw	0.01	95.4	6.1
	0.10	97.6	6.1
	1.00	85.2[a]	3.8
Rice	0.01	82.9	2.7
	0.10	84.4	0.2
	1.00	84.8[a]	1.9
Water	0.01	103.8	6.2
	0.10	96.4[a]	1.5
	1.00	111.5[a]	3.7

[a] Ethyl acetate volume used for re-dissolution was 5 mL; the volume used for the other samples was 2 mL

To verify recoveries of oxadiargyl for the various samples, samples were fortified with the herbicide at three levels (0.01, 0.1, 1 mg/kg). These spiked samples were mixed thoroughly and settled for 30 min. The sample extraction procedures as above were applied to prepare sample extracts for GC analysis. Five replicates were analyzed for each fortified concentration.

Gas chromatographic analysis was performed using an Agilent 6890 GC equipped with an Agilent 7683 automatic injector. A capillary column (Zebron ZB-1 with 100% methylpolysiloxane, 30 m × 0.32 mm × 0.25 μm; Phenomenex, CA, USA) was used for separation. The carrier gas was nitrogen at 15 Psi pressure constantly. The makeup gas flow was at 50 mL/min. The oven temperature program was as follows: 60°C (held for 0.5 min) to 150°C at 30°C/min, then to 230°C (held for 2 min) at a rate of 10°C/min. The injector temperature was set 250°C. The injection mode was splitless, with 1 μL injected. The detector temperature was kept at 280°C.

Results and Discussion

The standard calibration curve of oxadiargyl during GC analysis was constructed by plotting the analyte concentration versus peak area, with five replicates used for each concentration step. The relative standard deviation (RSD) values varied from 3.1 to 5.4%. The regression equation of the standard calibration curve was $y = 115557x$ ($R^2 = 0.9999$). Therefore, the calibration curve showed excellent linearity in the concentration range 0.001–1 mg/L.

The limit of detection (LOD) of oxadiargyl was defined as the minimum concentration of oxadiargyl that was

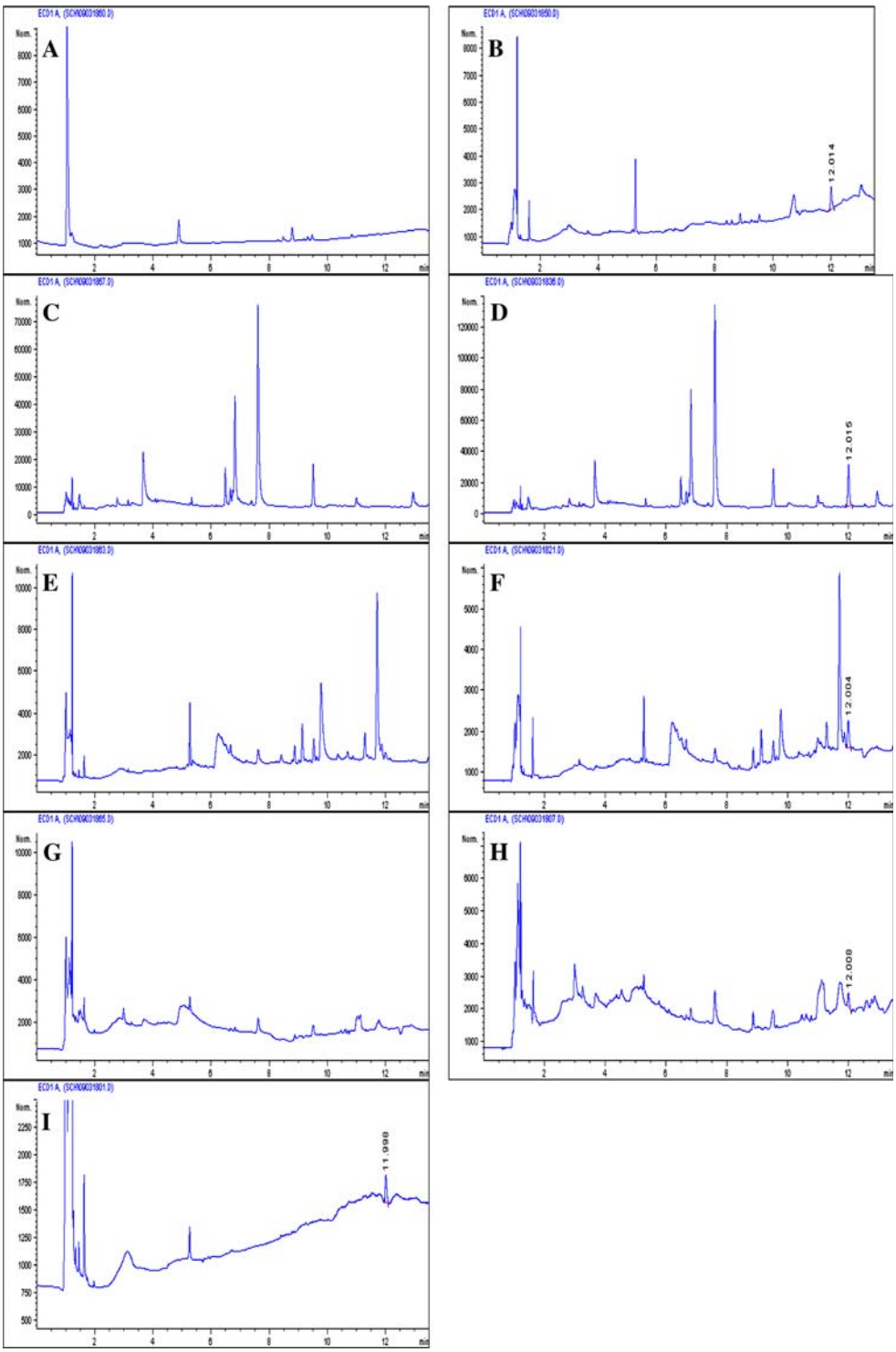

Fig. 2 GC chromatograms of **a** control water sample; **b** water sample fortified at 0.01 mg/L; **c** control straw sample; **d** straw sample fortified at 0.01 mg/L; **e** control soil sample; **f** soil sample fortified at 0.01 mg/L; **g** control rice sample; **h** rice sample fortified at 0.01 mg/L; **i** 0.01 mg/L oxadiargyl standard (retention time of oxadiargyl was approximately 12 min)

detected with acceptable certainty. The LOD was estimated to be 0.001 mg/kg for rice and water samples and 0.005 mg/kg for soil and straw samples. Each LOD value was calculated using three times the signal-to-noise ratio with five replicates. The limit of quantitation (LOQ) of this method was defined as the lowest concentration of oxadiargyl in samples that could be quantitatively measured with suitable precision and accuracy, with a signal-to-noise ratio of 10:1. The LOQ values were estimated to be 0.01 mg/kg for soil, water, rice and straw samples, corresponding to the lowest spiking level used.

Based on the original QuEChERS method, some parameters were slightly modified. To achieve thorough mixing of the sample with solvent and salt, 5 g straw or

rice powder was found to be adequate because of their light density. In our modified QuEChERS method, acetonitrile was the only solvent used for extraction. The amount of acetonitrile was increased in our method because a portion of extraction solution was withdrawn for concentration and final preparation in ethyl acetate for injection on GC.

The method developed in our study is simple and solvent-saving. For instance, only 5 g of rice or straw samples and less than 25 mL acetonitrile for the extraction of each sample. In the method established by Chen et al. (1999), 20 g of rice or straw samples was marinated for more than 12 h in 50 mL dichloromethane and then shaken for 30 min, while 50 mL water was extracted twice by using 50 mL dichloromethane each time in a 500-mL separatory funnel. In Chen et al. (1999), the recovery of oxadiargyl from rice samples was 88–96%, and RSD values varied from 5.6 to 13.3%. In comparison, for the method evaluated in our study, the recovery of oxadiargyl in rice samples was 82.9–84.8%, and RSD values were form 0.2 to 2.7% (Table 1).

Solid phase extraction (SPE) columns are commonly used to purify samples for prior to GC/MS or LC/MS/MS analysis. In this study, it was found that the interference of matrix was insignificant after modification of GC parameters (Fig. 2). Accordingly, a purification step was found to be unnecessary for this method.

For soil samples, there was a small matrix peak at approximately 12 min in the sample chromatograms (Fig. 2e, f). This matrix peak was found to overlap with the peak of oxadiargyl standard. Therefore, the area caused by the soil matrix was subtracted in the calculation of recoveries for soil samples. This problem, however, did not exist in the analysis of water, and rice grain and straw samples.

The typical acceptable recovery values at the level of 10 μg/L for pesticide analysis are 70–125% (AOAC 2006). In our study, the recoveries of oxadiargyl from the four different sample matrices were 82.9–112.0%. Each recovery value was the mean of five replicated measurements, and the RSD values varied from 0.2 to 6.2%, suggesting adequate performance of this method. The specific values are listed in Table 1. Some typical GC chromatograms for oxadiargyl standard, control samples, and fortified samples are shown in Fig. 2.

In conclusion, a rapid, simple, and sensitive method based on the QuEChERS procedure with GC-ECD for detection was developed and found adequate for the detection of oxadiargyl residues in water, soil, and rice grain and straw samples. Recoveries and variations from fortified samples suggested good method sensitivity and accuracy. Therefore, the derived method met our goal by serving as a time-, cost-, and labor-saving method that may be used in underdeveloped areas without access to expensive facilities for the analysis of oxadiargyl in a range of environmental and biological samples.

Acknowledgment This study was supported by the Chinese Ministry of Agriculture and Bayer Cropscience Co. Ltd (China).

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