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Solid phase extraction of methomyl and thiodicarb from environmental water with an activated carbon cartridge and their determination by HPLC

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Abstract: A solid phase extraction procedure of methomyl and thiodicarb from environmental water was presented. This method utilizes a 40—60 mesh activated carbon cartridge and high performance liquid chromatography (HPLC). The 40—60 mesh activated carbon works faster and yield higher adsorption efficiency. Detection limits of methomyl and thiodicarb in environmental water are 0.1 $\mu\text{g/L}$ and 0.2 $\mu\text{g/L}$, respectively. Average recoveries of fortified methomyl and thiodicarb in water are in the range of 90.7%—98.8% and 88.9%—103.6%, respectively. The relative standard deviations are lower than 7%. This method is simple, rapid, accurate and precise.

Key words: HPLC; solid phase extraction; activated carbon; methomyl; thiodicarb

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Introduction

Both methomyl and thiodicarb are N-methylcarbamate pesticides. Methomyl is effective on a wide range of insects as an ovicide, larvicide, and adulticide. Thiodicarb is especially effective on scales. It has been reported that the total amount of N-methylcarbamate pesticides used on cottons, vegetables and fruits is increasing. As a consequence, the pesticides are present in all compartment of the natural environment (Glottfelty, 1987).

A traditional approach to the preparation of the water sample is to utilize liquid-liquid extraction (LLE). But this technique has been proved cumbersome, time consuming and using large volumes of organic solvent. All these shortcomings have led to the development of solid phase extraction technique (SPE). Among the sorbents available for SPE of pollutants from water, C18 bonded porous silica has become the most popular sorbent (Volmer, 1994). However, a comparative study performed by Bellar and Budde (Bellar, 1988) has shown that the extraction efficiency of a C18 cartridge for polar pesticides in water was lower than that of LLE technique. The SPE using graphitized carbon black and online cartridges for pesticides was introduced by Cappiello and Chiron (Cappiello, 1994; Chiron, 1994). The two cartridges were more adaptable than C18 for field use.

The activated carbon cartridge is available easier than graphitized carbon black and online cartridges because it is common and cheap. In this report, we describe the solid phase extraction of methomyl and thiodicarb from environmental water and determination of extracts by high performance liquid chromatography (HPLC). We also investigated the adsorption efficiency on activated carbon of different size and evaluated the ability of 40—60 mesh activated carbon rapidly and quantitatively extracting pesticides from the larger volume of water. The methods of the cartridge pre-washing and the solid phase extraction of methomyl and thiodicarb from water were optimized. This study demonstrated that the efficiency of the solid phase extraction of methomyl

and thiodicarb from water using 40—60 mesh activated carbon is higher than that of C18 bonded porous silica.

1 Experimental section

1.1 Reagents and chemicals

For chemicals used as standards, methomyl of >99% purity was supplied by Qingdao University (Qingdao, China), thiodicarb of >99% purity was supplied by Nankai University (Tianjin, China). Individual standard solutions at 1.0 g/L were prepared by dissolving 100 mg of each pesticide in 5.0 ml trichloromethane, then diluting to 100 ml with methanol. Acetonitrile and methanol were of HPLC grade. All other solvents were of analytical grade. Distilled water was further purified by passing it through an inorganic cartridge. Activated carbon (40—60 mesh size) was supplied by Jiexiang (Shandong, China).

1.2 Apparatus

500 mg of activated carbon (40—60 mesh size) was packed in a polypropylene tube (7.0 × 1.4 cm i. d.). Polyethylene frits, 20 μm pore size, were located above and below the sorbent bed to avoid crushing of cartridge particles. Before water samples were processed, the cartridge was washed with 5 ml of trichloromethane, followed with 2 ml of methanol and 10 ml of 10 g/L ascorbic acid in HCl acidified water (pH 2). The trap was fitted into a side arm filtering flask, and liquid was forced to pass through the cartridge by vacuum from a water pump.

1.3 Sample extraction

Aqueous samples were fortified with the known-volume of working standard solution. Water samples were agitated for 1 min, and then poured in a glass reservoir that was connected to the sorbent cartridge. Water was forced to pass through the cartridge at flowing rates of 15—20 ml/min by reducing the pressure in the vacuum apparatus to the minimum. Just after the samples were passed through the column, the pump was disconnected and the cartridge was filled with 5 ml of distilled water in order to remove sample water drops stuck on the plastic walls of the cartridge. The pump was again linked to the flask and the pressure suitably adjusted to allow water to pass through the cartridge at flow rates of 5—10 ml/min. After distilled water was passed through the trap, the major part of it was removed by pulling air through the cartridge for 3 min. Then the water pump was disconnected and a graduated tube was placed below the cartridge. The pesticides were eluted by passing through the trap drop by drop with 1.0 ml of methanol followed by 8.0 ml of trichloromethane. The last drops of this solvent were collected by decreasing the pressure in the flask. Trichloromethane was removed by evaporation in a water bath at 50°C under a gentle stream of nitrogen. Added 0.5 ml of methanol, then the evaporation procedure was performed again, so as to remove trichloromethane from extracts as clean as possible. The extracts were then concentrated to obtain final volumes of 0.5 ml.

1.4 HPLC

Liquid chromatography was carried out with a Waters HPLC, equipped with a 486 UV detector, a 510 pump and a U6K injector. The equipment was controlled by a Baseline 810 data system on a NEC 386 SX/16 computer. A 22 cm × 4.6 mm i. d. Spheri-5 reversed phase C18 HPLC column with a particle size of 5 μm was used. The initial mobile phase composition was 20% acetonitrile, 65% water, and 15% 0.03 mol/L ammonium acetate solution. This was programmed linearly to 70% acetonitrile, 15% water, and 15% 0.03 mol/L ammonium acetate solution in 20 min. The flow rate was 1.0 ml/min and the injection volume was 40 μl. Methomyl and thiodicarb

were detected with the UV detector set at 235 nm.

2 Results and discussion

2.1 Preparation of calibration curves

The stock solution was serially diluted. The working standard solutions contained 0.5, 1.0, 5.0, 10 and 20 $\mu\text{g}/\text{ml}$ of two pesticides. These working standard solution were analyzed three times at each concentration level. Peak areas were obtained from chromatograms of two pesticides. Linear calibration curves were generated with the linear correlation coefficients of 0.9993 for methomyl and 0.9991 for thiodicarb. The equations of the calibration curve were $C = -0.7012 + 3.19 \times 10^{-5} A$ and $C = -0.7208 + 4.48 \times 10^{-5} A$, respectively.

2.2 Recovery studies

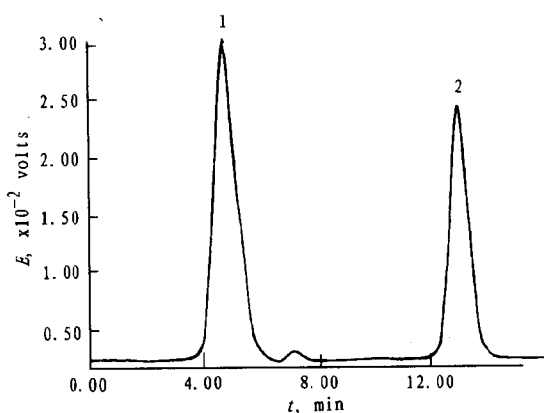


Fig. 1 Chromatogram of methomyl and thiodicarb spiked in water at 5.0 $\mu\text{g}/\text{L}$ before extraction
1. methomyl 2. thiodicarb

Recovery studies were performed at the 0.5, 2.5, 5.0 $\mu\text{g}/\text{L}$ fortification levels of each pesticide for four times in water. These samples were prepared by adding 0.02, 0.10, 0.20 ml of 50 mg/L working standard solution to 2L of water before solid phase extraction. The extracts were analyzed as previously described. Fig.1 shows the chromatogram of methomyl and thiodicarb is at 5.0 $\mu\text{g}/\text{L}$ fortification level in water. The recoveries of methomyl and thiodicarb at 0.5, 2.5, 5.0 $\mu\text{g}/\text{L}$ fortification levels in water are given in Table 1. Average recoveries were between 88.9% and 103.6%. Coefficients of variation were in range 3.12%–6.57%, with an average of

4.68%. The data in Table 1 show that the recoveries of using 40–60 mesh activated carbon are much higher than that of using C18 bonded porous silica.

Table 1 Recoveries of methomyl and thiodicarb in water

Pesticides	Fortification level, $\mu\text{g}/\text{L}$	40–60 mesh activated carbon		C18	
		Recoveries, %	CV, %	Recoveries, %	CV, %
Methomyl	0.5	90.7	5.82	52.1	7.91
	2.5	95.1	4.27	54.6	6.12
	5.0	98.8	3.62	57.4	7.69
Thiodicarb	0.5	88.9	6.59	61.9	8.22
	2.5	103.6	3.12	64.2	6.19
	5.0	92.5	4.66	66.3	7.87

2.3 Sensitivity determination

Appropriate amounts of the stock standard solution were added to 1 ml blank extracts of water. Assuming 100% extraction efficiency, these solutions were made to represent extracts of water spiked at approximately 0.05, 0.1, 0.2 $\mu\text{g}/\text{L}$ levels for each pesticide. These solutions were determined by HPLC ($N = 6$). Fig.2 shows the chromatogram of methomyl and thiodicarb is at

0.2 $\mu\text{g/L}$ fortification level. The detection limits of method were calculated with the minimum amount of injected into the HPLC apparatus when the peak height was just diploid electrical noise. The limits of detection of methomyl and thiodicarb in water were 0.1 and 0.2 $\mu\text{g/L}$, respectively. These may satisfy the detection requirements for environmental pollutants in polluted water.

2.4 Adsorption efficiency of different size activated carbon

The experiments of adsorption efficiency of different size activated carbons were performed by using < 10 mesh, 40–60 mesh and activated carbon powder respectively. The cartridges were packed and washed. The samples were prepared by adding 0.4, 1.0, 2.0 and 4.0 ml of 50 mg/L working standard solution to 10 ml water. These water samples were passed through each cartridge separately. The concentrations of pesticides in the water effluent were determined. The adsorption efficiency of different size activated carbon is shown in Table 2. The data show that the adsorption efficiency of 40–60 mesh and activated carbon powder are much higher than that of < 10 mesh activated carbon. Averages are 98.8%, 98.6% for methomyl and 96.5%, 97.3% for thiodicarb respectively. Because particle sizes of activated carbon powder are too small, it is very difficult to pass 2L of water through it. The time of using activated carbon powder for analysis is taken much longer than that of using 40–60 mesh activated carbon. Therefore, the 40–60 mesh activated carbon was selected as the sorbent for solid phase extraction of methomyl and thiodicarb from water.

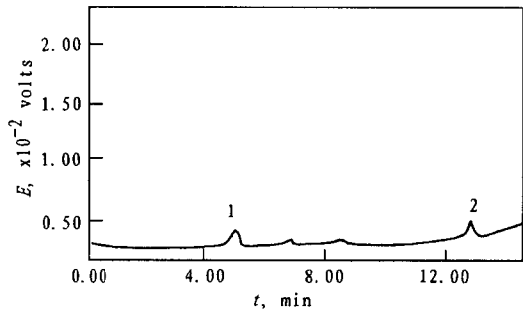


Fig. 2 Chromatogram of methomyl and thiodicarb spiked in water at 0.2 $\mu\text{g/L}$ before extraction
1. methomyl 2. thiodicarb

Table 2 Adsorption efficiency on activated carbon of different size, %

Pesticides	Concentration, $\mu\text{g/L}$	< 10 mesh	40–60 mesh	Powder
Methomyl	2.00	35.2	99.1	98.7
	5.00	39.6	97.9	99.5
	10.0	40.1	99.6	97.2
	20.0	38.7	98.4	98.9
Thiodicarb	2.00	37.2	98.3	99.1
	5.00	32.8	95.7	96.3
	10.0	39.6	96.8	97.2
	20.0	35.1	95.2	96.7

2.5 Studies of pre-washing method

When using unwashed activated carbon of 40–60 mesh for extracting pesticides spiked in distilled water at the 5.0 $\mu\text{g/L}$ level, the losses of methomyl and thiodicarb were observed. The trace amount of methomyl and thiodicarb was found in water effluent. Recoveries of methomyl and thiodicarb were not complete after eluting with methanol and trichloromethane. When using pre-washed activated carbon of 40–60 mesh by trichloromethane and methanol, no methomyl and thiodicarb was found in water effluent, but recoveries were not complete after eluting with methanol and trichloromethane. This may result from occurring the irreversible chemisorption for particular adsorbates of the oxidative materials presented on the surface of the activated carbon.

When using prewashed activated carbon of 40—60 mesh by trichloromethane, methanol and 10 g/L ascorbic acid (pH 2), no methomyl and thiodicarb was found in water effluent and recoveries were complete after eluting with methanol and trichloromethane. It is because trichloromethane can active the surface of the activated carbon and methanol can take the place of trichloromethane from the surface of the activated carbon, while ascorbic acid reduces the oxidative materials on the surface of activated carbon to avoid the irreversible adsorption. Therefore, in this study, we used 5.0 ml trichloromethane, 2 ml methanol and 10 ml of 10 g/L ascorbic acid to pre-wash the activated carbon, successively.

2.6 Selection of eluants

Methanol, trichloromethane, dichloromethane, $\text{CHCl}_3/\text{MeOH}$ (80:20), $\text{CHCl}_3/\text{MeOH}$ (60:40) were used as eluants. The results show that the efficiency of elution was the highest when using 1.0 ml of methanol followed by 8.0 ml of trichloromethane.

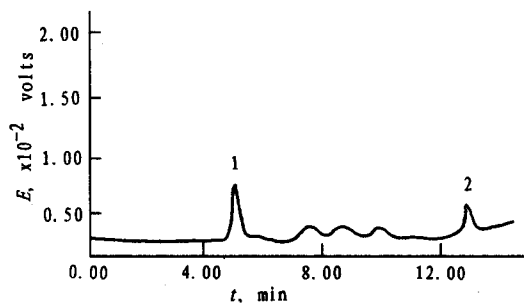


Fig. 3 Chromatogram of methomyl and thiodicarb extracted from 2L of the polluted river water
1. methomyl 2. thiodicarb

3 Analysis of environmental water sample

Water samples were collected from a small river near the field, and pesticide contents were determined. The chromatogram is shown in Fig. 3. The samples were collected after applying methomyl and thiodicarb in field. The average contents of methomyl and thiodicarb in polluted water were $0.63 \mu\text{g/L}$ and $0.71 \mu\text{g/L}$, respectively ($N=6$).

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