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Determination of aqueous chlorothalonil with solid-phase microextraction and gas chromatography

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Abstract

Solid-phase microextraction coupled with GC–electron-capture detection was examined to analyze aqueous chlorothalonil residuals. The optimal conditions for chlorothalonil pre-concentration such as fiber polarity, temperature, salt addition, absorption time, as well as the interference were investigated in detail. In addition, the thermal desorption conditions in the injector were also systematically optimized. Experimental results indicated that an extraction with a 100-μm polydimethylsiloxane fiber for 40 min under conditions of 1250 rpm stirring rate, room temperature, and adding high concentration salt offered an optimal result. The thermal desorption of chlorothalonil at 240°C for 3 min (including fiber regeneration) offered the best sensitive detection. A standard addition method for calibration was recommended to reduce the deviation from matrix interference. The proposed method provided a simple and rapid analytical procedure for chlorothalonil in water bodies with detection limits of 2.86 μg/l for distilled water, 3.06 μg/l for ground water, 4.77 μg/l for tap water, and 9.23 μg/l for farm water. The relative standard deviations were all below 3.0% ($n=6$) besides the farm water being below 9.2%. The calibration graph in the range of 5 to 200 μg/l is linear with very good correlation coefficient ($r=0.999$), and $r=0.983$ for farm water. Application was illustrated by the analysis of water samples collected from tap water, ground water and farm water in the southern Taichung area.

Keywords: Water analysis; Environmental analysis; Chlorothalonil; Pesticides

1. Introduction

Chlorothalonil (tetrachloroisophthalonitrile) is an effective fungicide against a wide range of plant pathogens on many agronomic and vegetable crops. It is used extensively around the world and is the only organochlorine fungicide still not prohibited in Taiwan. Therefore, there has been an increasing contamination related to its residue and need for trace level determination in water matrices such as tap water, ground water and farm water. In general, most trace-level aqueous pesticides have to be extracted and enriched prior to their instrumental determination.

Several methods have been developed to extract aqueous pesticides. In the past, liquid–liquid extraction (LLE) [1–3] and solid-phase extraction (SPE) [4–8] were the dominant approaches for sample preparation. However, both methods are time-consuming, complicated, and LLE requires large amounts of organic solvents. In the past few years, the new extraction technique, solid-phase microextraction (SPME), offers an ideal sample preparation technique (simple, inexpensive, efficient and non-solvent) [9–22]. It has been widely applied to extract organic pollutants from aqueous samples,

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since it was introduced by Belardi and Pawliszyn [23]. For SPME–gas chromatography (GC), the analyte should be volatile and thermally stable at the injection temperature. However, the boiling point of chlorothalonil is 350°C and it may decompose at extremely high temperatures [24]. Thus, chlorothalonil in an aqueous sample was first analyzed successfully with SPME–high-performance liquid chromatography (HPLC) by Jinno et al. [25]. By comparing both desorption devices, SPME–GC is simpler than SPME–HPLC. Hence, in general, it is preferable to select the SPME–GC system if analytical deviation was acceptable under the analytical conditions. From the physical properties of chlorothalonil [24], it is worth investigating the appropriateness of the SPME–GC system to analyze aqueous chlorothalonil. Although Hu et al. [17] used SPME–GC–MS to determine chlorothalonil residue in strawberries, however, optimal conditions for extraction and desorption of chlorothalonil were not discussed in detail. Therefore, the SPME–GC system for trace amounts of chlorothalonil determination is worth examining.

In this paper, the applicability of SPME–GC–electron-capture detection (ECD) as a fast and simple method for the determination of aqueous chlorothalonil at trace level is evaluated. Conditions for optimizing the extraction efficiency and the thermal desorption as well as the interference were studied in detail.

2. Experimental

2.1. Apparatus

The SPME device consisting of a holder and fiber assembly for manual sampling was obtained from Supelco (Bellefonte, PA, USA) and used without modification. The fibers selected in the studies were of 1-cm length coated with polydimethylsiloxane (PDMS; 7 μm and 100 μm film thickness) and polyacrylate (PA; 85 μm film thickness).

The GC system used in this work was a Chrompack 9000 system with ECD, and a split/splitless injector (Middelburg, The Netherlands). Separations were conducted using a DB-5 column, 30 m×0.32 mm I.D., with a film thickness of 0.5 μm (J & W Scientific, Folsom, CA, USA). The temperature program used was as follows: 150°C hold for 3 min, 20°C/min to 300°C hold for 15 min. The injector was used in the splitless mode and held isothermally at 240°C for SPME desorption (3 min). The ECD system was maintained at 300°C. The carrier gas was nitrogen at a flow-rate of 3 ml/min, and the make-up gas was also nitrogen at a flow-rate of 17.5 ml/min. A Chem-Lab Data system (Chem-Lab., Taipei, Taiwan) was used to obtain the chromatogram and perform data calculations.

2.2. Chemicals and reagents

Deionized water was produced using a Barnstead Nanopure water system (Thermolyne, Dubuque, IA, USA) for all aqueous solutions. All chemicals and solvents were of ACS reagent grade. A stock solution of 5000 mg/l chlorothalonil was prepared by dissolving 500 mg chlorothalonil (Chem-Service, Bellefonte, PA, USA) in 100 ml acetone. The solution was stored in a silanized brown glass bottle with PTFE-lined cap, and kept at 4°C. Fresh working solutions were prepared daily by appropriate dilution of the stock solution. Acetone, toluene and methanol were HPLC-grade obtained from Mallinckrodt (KY, USA). Sodium chloride and sodium hydroxide was obtained from Riedel-dehaen (Hannover, Germany). Hydrochloric acid (36.4%) was from J.T. Baker (Phillipsburg, USA). Humic acid with 20% ash was obtained from Fluka (Swiss, Freecall, Switzerland).

2.3. SPME

For SPME, a Supelco manual SPME fiber holder assembly was used equipped with a 100-μm PMDS coated fiber. Extraction occurred within a 50-ml sample vial with 25 ml sample solution, at room temperature, as the SPME septum piercing needle was inserted through the septa and the fiber was immersed in the liquid sample. Sorption time was 40 min during which the sample was stirred with a 1-cm stirring rod on the magnetic stir-plate set at 1250 rpm. Once sorption was complete, the fiber was retracted into the septum piercing needle and the apparatus was removed from the vial septum. The fiber was then directly inserted into the GC system for desorption and analysis.

3. Results and discussion

3.1. Selection fiber and extraction time

Fibers coated with PDMS phase (7 μm and 100 μm) and PA (85 μm) were employed to extract 10 μg/l aqueous chlorothalonil solution for 5 to 60 min to investigate the optimal absorption time. Fig. 1 describes the absorption isotherms of chlorothalonil on varied fibers. It is apparent from this figure that concentration equilibrium is achieved at about 40 min for both 100 μm PDMS and 85 μm PA phases, and about 30 min for 7 μm PDMS phase, under stirring of the solution. Although 7 μm PDMS has a shorter time, its extraction quantity is only 16% of the 100 μm PDMS absorption. The absorption of the 85 μm PA phase is about 50% of the 100 μm PDMS phase. Therefore, the fiber coated with 100 μm PDMS phase was used to extract chlorothalonil from aqueous solution during our studies.

3.2. Effect of salt addition

Salt-out effect often improves the recovery in conventional extraction processes. However, the addition of sodium chloride showed different behaviors on varied hydrophobic pesticides [14]. In this study, the addition of sodium chloride leads to enhanced extraction efficiency of chlorothalonil, doubling it at 30% addition. It also hints that the extraction efficiency might be affected by the ionic strength of the sample solution. Therefore, the addition of a salt is recommended to increase the extraction efficiency and decrease the effect of ionic strength in sample solution.

3.3. Extraction pH and temperature

The pH in sample solution is often adjusted to enhance the extraction efficiency in conventional extraction, SPE and SPME. In the study, the amounts extracted for chlorothalonil remained the same over a pH range of 2.0 to 8.0. In this pH range, chlorothalonil is in its neutral (molecular) form, thus, there is no significant variation of recovery for chlorothalonil. The absorption will be enhanced by the increase of temperature in the kinetic aspect, but it generally decreases due to the exothermal effect in the absorption process. Hence, the effect of solution temperature on the extraction efficiency was studied. Fig. 2 indicates that the extraction efficiency increases from 10°C to 30°C, and then decreases. Therefore, the SPME temperature for aqueous chlorothalonil extraction is recommended to be 30°C.

3.4. Interference from aqueous humic acid and metal ions

In this study, 10 μg/l of chlorothalonil was prepared in the aqueous solution with the concentration of humic acid varying between 0 and 150 μg/ml. After being extracted by PDMS for 40 min, and thermally desorped 3 min at 240°C for GC analysis, the result indicates that the humic acid does not significantly affect the extraction efficiency of chlorothalonil until 100 μg/ml in sample matrix. As to the interference by aqueous metal ions, there is a

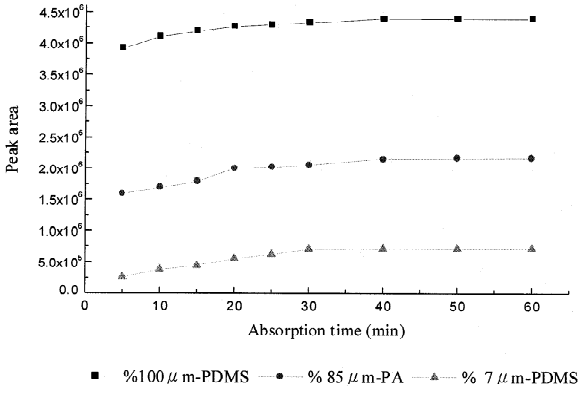

Fig. 1. Absorption isotherms of chlorothalonil on varied fibers.

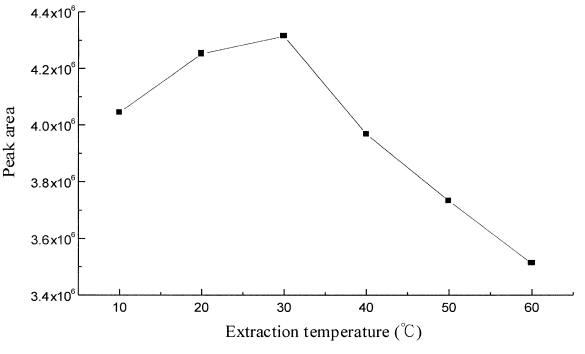

Fig. 2. Effect of solution temperature on the extraction efficiency.

10% depression of extraction efficiency for Ca^{2+}, Mg^{2+}, and Cu^{2+}, until 150, 100 and 10 μg/ml, respectively, a 5% depression by 100 μg/ml Fe^{3+} due to gelatinous precipitation, and no significant interference by Al^{3+} and Co^{2+} up to 150 μg/ml.

3.5. Thermal desorption temperature and desorption time

For better separation efficiency and resolution, thermal desorption requires a time as short as possible. However, chlorothalonil is unstable at high temperatures, hence, an optimal desorption temperature and desorption time in the hot GC injector were investigated to obtain an acceptable result. Fig. 3a shows the influence of desorption temperature on the detection signal (peak area). As can be seen, the peak area increases up to 240°C, and then decreases. From the chromatogram of high-temperature desorption, a peak appeared at 6.80 min ahead of the chlorothalonil peak at 7.02 min. This peak was identified by GC–MS as pentachlorobenzonitrile, which is the thermal degradation product of chlorothalonil. Fig. 3b depicts the effect of thermal desorption time on the detection peak area. It indicates that 1 min is enough for 240°C thermal desorption. To prevent and remove possible memory effect, the fiber was kept in the liner for an additional 2 min after thermal desorption. After this period no significant blank values were observed. Thus, no further regeneration mode for the fiber was necessary, and a total of 3 min is required for each thermal desorption run.

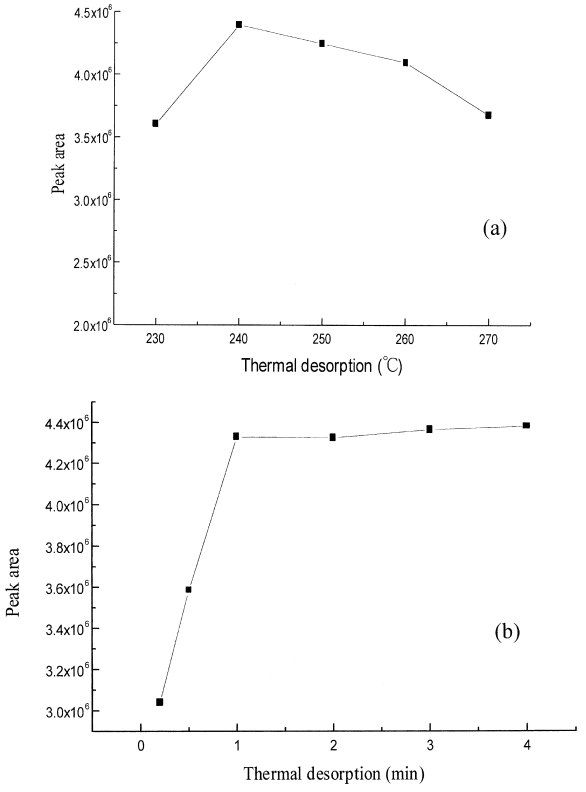

Fig. 3. (a) Effect of desorption temperature on detection area. (b) Effect of desorption time on detection area.

3.6. Exposed loss prior to thermal desorption

In order to observe the exposed loss due to the delay injection, in this study, after sorption being complete and removed from the vial septum, the fiber was exposed to air from 0 to 60 min prior to insertion into the GC injector. Fig. 4 demonstrates the decrease of the detection peak area with the exposed time intervals. It is apparent that the chlorothalonil absorbed on the fiber has been lost during the delay interval before injection. In the exposed period, the absorbed chlorothalonil evaporates into air gradually to reach a new equilibrium between the fiber and air. Thus, once sorption was complete and

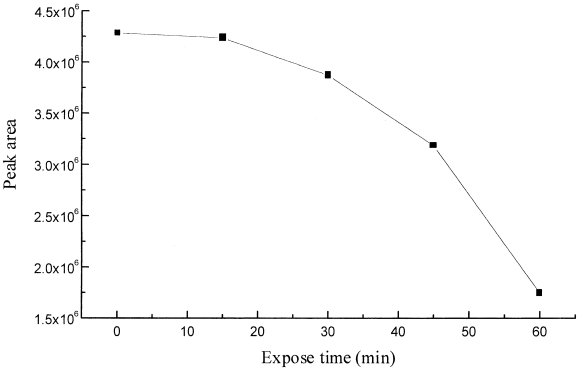

Fig. 4. Effect of the exposed time on detection peak area.

the fiber removed from the vial septum, the fiber should be directly inserted into the GC injector as soon as possible.

3.7. Calibration plot, detection limit and repeatability

In order to test the applicability of the SPME–GC–ECD method for quantitative determination of chlorothalonil, a calibration plot was built-up over the concentration range 5 to 200 μg/l. The linear relationship between the peak area and the injected quantity was very good with the correlation coefficient being 0.9999. The repeatability was examined with six replicated injections of the six concentrations in the calibration plot. The relative standard deviations (RSDs) of their peak areas were all within 2.0%. The detection limit was calculated from three times the average background noise divided by the detection sensitivity (slope of calibration plot), which was 2.86 μg/l. By spiking 10 μg/l chlorothalonil (from 100 mg/l Certified Reference Method (C.R.M.) sample) in water, after extraction–thermal desorption–GC determination by the proposed optimal condition, the relative error is 4.1%. The accuracy is acceptable even at such a low concentration level.

3.8. Matrix effect and analysis of chlorothalonil in environmental samples

In order to investigate the matrix effect in real environmental samples, standard solutions of chlorothalonil were spiked into chlorothalonil-free tap water, ground water and farm water from 5 to 200 μg/l. The characteristics of these waters related to prospective interference are listed in Table 1. After SPME and GC determination, calibration plots for the standard additions were built up. Table 2 lists the calibration data and detection limits in various water matrices. The detection limits and the precision were evaluated as described previously. The RSDs were all below 3.0% ($n=6$) besides the farm water being below 9.2%. It can be seen that the linear correlation coefficient of chlorothalonil in farm water being 0.983 is less than the others. It depicts that some levels of matrix effect existed in farm water, and there is no significant matrix effect in tap water and ground water. Referring to the characteristics of the water samples listed in Table 1, only the humic acid in farm water is close to the significant concentration of interference. So, the lower linear correlation coefficient of chlorothalonil in farm water is due to the existence of humic acid. From the slope of calibration plot with farm water and its detection limit, it also indicates the matrix effect existing in farm water. Therefore, for determination of chlorothalonil in matrix-effect water, the standard addition method with linear regression and extrapolation evaluation was used. The chlorothalonil contents in both tap water and ground water (collected from our university) were below the detection limits (i.e., below 4.77 μg/l and 3.06 μg/l, respectively), and in farm water (collected from southern Taichung city) was 43.81 μg/l. Compared to the result (45.12 μg/l) from LLE prior to GC–ECD determination for farm water, they were very comparable.

Table 1
The characteristics of water samples related to prospective interference

Water sample	Tap water	Ground water	Farm water
pH	6.85	7.12	7.18
Hardness (as $CaCO_3$)	110 μg/l	99 μg/l	235 μg/l
Al^{3+}	34 μg/l	Trace	82 μg/l
Fe^{3+}	78 μg/l	58 μg/l	252 μg/l
Cu^{2+}	21 μg/l	10 μg/l	23 μg/l
Co^{2+}	–	–	–
Humic acid	–	–	75 μg/l

4. Conclusion

In this paper, determination of aqueous chlorothalonil by SPME–GC with conventional ECD has been studied. The optimal conditions have been obtained and an analytical protocol has been built up. From the results, it has proved the applicability of the SPME method to analyze chlorothalonil in environmental water samples.

Table 2
Calibration data and detection limits in various water matrices

Water solution	Concentration range (μg/l)	Calibration plot	Correlation coefficient (r)	Detection limit (μg/l)	Relative standard deviation (%)
Pure water	5–200	$y=4.10\cdot10^6+20\,028x$	0.9999	2.86	1.1–2.0
Tap water	10–200	$y=4.03\cdot10^6+19\,835x$	0.9999	4.77	1.7–3.0
Ground water	10–200	$y=4.03\cdot10^6+19\,920x$	0.9999	3.06	1.1–2.8
Farm water	10–200	$y=4.00\cdot10^6+16\,473x$	0.9983	9.23	2.8–9.2

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