

Determination of Residual Chlorothalonil in Textiles

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Abstract

An effective method was established to determine the content of residual chlorothalonil in textiles by gas chromatography/mass spectrometry-selected ion monitoring coupled with ultrasonic extraction technique. Residual chlorothalonil in textiles was ultrasonically extracted using ethyl acetate as the extraction solvent. The extract was condensed and analyzed by gas chromatography/mass spectrometry in selected ion monitoring mode (GC/MS-SIM). The concentration of chlorothalonil was calibrated by the external standard method. Good linearity existed between the peak area and the mass concentration of chlorothalonil in the mass concentration range from 0.2 µg/mL to 42.8 µg/mL. The equation was $A = 95,399p - 50,848$, with a correlation coefficient of 0.9999. The limit of detection was 0.1 mg/kg for chlorothalonil. The blank samples were spiked at three concentration levels, and the spiked average recoveries changed from 81.9% to 95.4% while the relative standard deviation (RSD) changed from 1.8% to 5.2%. The proposed method was simple, rapid, sensitive and the limit of detection could meet the limit requirements of relevant regulations. Commercially available textiles were measured by this method, and chlorothalonil at different concentration levels was detected in some samples.

Keywords

Chlorothalonil, Textile, Ultrasonic Extraction, GC/MS-SIM

1. Introduction

Chlorothalonil is a broad-spectrum and high-efficiency agricultural fungicide. Chlorothalonil interacts with glyceraldehyde triphosphate dehydrogenase in fungal cells and binds to cysteine-containing proteins in the enzyme, thereby destroying the activity of the enzyme. Therefore, the metabolism of fungal cells is

destroyed and loses vitality [1]. Chlorothalonil has good bactericidal properties against fungi such as Ascomycetes, Basidiomycetes, and Deuteromycetes. Chlorothalonil is widely used in the United States, France, China, Brazil, and Japan. Chlorothalonil is widely used as a fruit preservative and insecticide in agriculture, and is used as an antifungal agent for leather, paint, paper and cloth in industry [2] [3]. However, chlorothalonil is a strong allergen that can cause delayed allergic dermatitis [4]. Chlorothalonil is listed in the list of Class 2B carcinogens by the World Health Organization's International Agency for Research on Cancer on October 27, 2019. The European Parliament issued Commission Implementing Regulation (EU) 2019/677 on April 29, 2019 to announce the non-renewal of the approval of the active substance chlorothalonil in accordance with Regulation (EC) No 1107/2009 [5]. The content of chlorothalonil in samples such as leather, food, environmental samples, paints and *et al.* can be determined by liquid chromatography, gas chromatography, gas chromatography-mass spectrometry, etc. [6]-[14], but no literature has been reported on the determination of residual chlorothalonil in textiles. In this paper, residual chlorothalonil in textiles was first ultrasonically extracted using ethyl acetate as the extraction solvents and the extract was then determined by GC/MS-SIM technique.

2 Experimental

Chlorothalonil standard (purity 99.0%) was purchased from Dr. Ehrenstorfer GmbH, Germany. Chromatographic pure methanol was purchased from Fisher Scientific, Pittsburgh, Pennsylvania, USA. Chlorothalonil was first dissolved in chromatographic pure methanol to prepare a standard stock solution with a mass concentration of 428 $\mu\text{g/ml}$, then diluted with methanol to prepare a series of standard working solutions whose mass concentration was 42.8, 21.4, 10.7, 5.4, 2.1, 1.1, 0.5, 0.2, 0.1 $\mu\text{g/ml}$, respectively.

Four positive samples were prepared through impregnation-baking technique. Chlorothalonil powder purchased from Sichuan Runer Technology Co., Ltd. was dissolved in water to obtain a high concentration aqueous solution of chlorothalonil. Polyester lining cloth, nylon lining cloth, cotton lining cloth and wool lining cloth were selected to be blank substrates. They were first dipped into the aqueous solution of chlorothalonil for two days. They were then washed completely by water and dried. Therefore, four positive samples (sample 1#: polyester, sample 2#: nylon, 3#: cotton, 4#: wool) with different concentration levels of chlorothalonil were prepared.

The samples were cut into 5 mm \times 5 mm pieces by QYB-3 automatic sample preparation machine purchased from Zhongshan Qiyuan Machinery Technology Co. Ltd., China Accurately weigh 1.0 g of the sample and placed in a 35 mL glass reaction flask containing 30 mL of ethyl acetate. The sample was ultrasonically extracted at 45°C for 35 min. The extract was then filtered to a chicken heart bottle and evaporated to near dryness in a Heidolph 4003 rotary evaporator purchased from Heidolph, Germany. The chicken heart bottle was trans-

ferred to an N-Evap 112 nitrogen blowing apparatus purchased from Organomation Associates USA and slowly dried with dry nitrogen. The residue was dissolved in 1 mL of methanol, and the resulting solution was filtered used 0.45 μm filtering membrane purchased from CNW Technologist Co. Germany.

Analysis was carried out with an Agilent 6890A-7000B triple quadrupole gas chromatography/mass spectrometry supplied by Agilent USA. Chromatographic separation was performed on a DB-5MS column (30 m \times 0.25 mm \times 0.25 μm) supplied by Agilent USA with an initial temperature of 90°C. The temperature raised to 290°C at the rate of 40°C/min after maintained for 1 min at the initial temperature and then maintained for 2 min at 290°C. The carrier gas was high purity helium (purity > 99.999%) and the carrier gas flow rate was 1 mL/min. The sample was injected in splitless mode and the injection volume was 1 μL . The inlet temperature, the transmission line temperature and the ion source temperature was 270°C, 280°C and 290°C, respectively. The ionization mode was EI and the ionization energy was 70 eV. The qualitative analysis was carried out in full scan mode and the qualitative ion was m/z 264, m/z 268, and m/z 109. The quantitative analysis was carried out in selected ion monitoring mode and the quantitative ion was m/z 266.

3 Results and Discussion

3.1. Optimization of Analysis Conditions

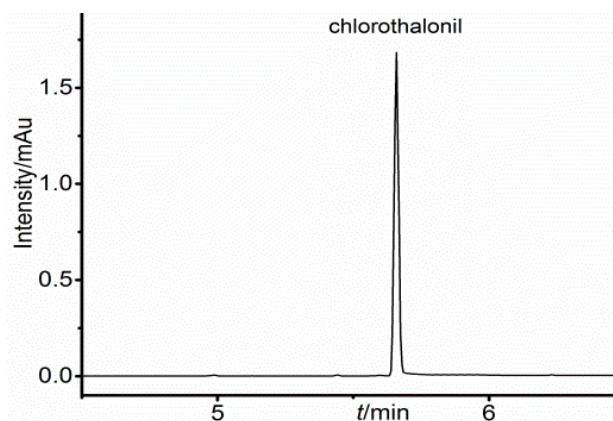
The intensity of the mass spectrometry signal in splitless injection mode was affected by the inlet temperature (factor A), ion source temperature (factor B), and carrier gas flow rate (factor C). The effects of these three factors on the intensity of the mass spectrometry signal were first investigated separately. The results showed that the peak area of chlorothalonil reached the maximum when the inlet temperature was 260°C or the ion source temperature was 280°C or the carrier gas flow rate was 1.2 ml, respectively. Therefore, the orthogonal experiment was carried out according to the conditions in **Table 1**. The peak area under the nine experimental conditions was determined, and the k value and the maximum difference of each factor were calculated, thus the optimal scheme was given out, as shown in **Table 1**. It could be seen from the data in **Table 1** that the factor A had the largest maximum difference and the factor B had the smallest maximum difference. Therefore, the factor that had the greatest impact on the peak area was the inlet temperature (factor A), followed by the carrier gas flow rate (factor C) and the ion source temperature (factor B). Through the orthogonal experiment, it was determined that the optimal scheme is $A_3B_3C_2$, that is to say, the 9th condition in **Table 1**. The standard solution was analyzed under this conditions and the obtained GC/MS-SIM chromatogram was shown in **Figure 1**. A sharp peak corresponding to chlorothalonil appeared at about 5.659 min in **Figure 1**.

3.2. Optimization of Ultrasonic Extraction Conditions

The ultrasonic extraction efficiency depended on four factors such as the type of

Table 1. The orthogonal experiment of analysis conditions.

No.	Factor A/°C	Factor B/°C	Factor C/ml	Area
1#	260	280	1.2	1,417,084
2#	260	270	1.0	1,539,826
3#	260	290	1.1	1,347,606
4#	250	280	1.0	921,204
5#	250	270	1.1	878,664
6#	250	290	1.2	1,069,374
7#	270	280	1.1	1,425,087
8#	270	270	1.2	1,584,478
9#	270	290	1.0	1,670,361
k1	1,434,839	1,254,458	1,356,979	
k2	956,414	1,334,323	1,377,130	
k3	1,559,975	1,362,447	1,217,119	
Maximum difference	603,561	107,989	160,011	
Optimal scheme	A ₃ B ₃ C ₂			

**Figure 1.** GC/MS-SIM chromatogram of chlorothalonil standard solution.

extraction solvent, extraction temperature (factor A), extraction time (factor B), and extraction solvent volume (factor C). In order to investigate the effect of Factor A, Factor B and Factor C on the extraction amount, four self-made positive samples were ultrasonically extracted with acetone as the extraction solvent. In each experiment, only one factor changed while the other two factors remained the same. The results showed that the extraction amount reached the maximum when the extraction time was 30 min for sample 1# and sample 2# while the extraction amount reached the maximum when the extraction time was 35 min for sample 3# and sample 4#. The extraction amount reached the maximum when the extraction temperature was 35°C for sample 2# and 40°C for sample 1#, sample 3# and sample 4#. The extraction amount reached the maximum when the volume of the extraction solvent was 20 ml, 30 ml, 20 ml

and 25 ml for sample 1#, sample 2#, sample 3# and sample 4#, respectively. In order to investigate the combined effects of these three factors on the extraction amount, an orthogonal experiment was designed according to **Table 2**. Four self-made positive samples were tested under each condition using acetone as the extraction solvent, and the extraction amounts were listed in **Table 2**. The *k* value and the maximum difference of each factor were calculated according to data in **Table 2** to give out the optimal scheme as shown in **Table 3**. The results showed that the optimal schemes of sample 1#, sample 2#, sample 3# and sample 4# were $A_3B_3C_3$, $A_3B_2C_3$, $A_3B_3C_3$, and $A_3B_3C_1$, respectively. Taking all factors into consideration, the final optimal scheme was $A_3B_3C_3$, that is to say, the extraction temperature, extraction time and extraction solvent volume were 45 °C, 35 min, and 30 ml, respectively. Under the ultrasonic extraction conditions mentioned above, four self-made positive samples were ultrasonically extracted using common solvents such as ethyl acetate, acetone, n-hexane, methanol, ethanol, acetonitrile, dichloromethane, petroleum ether, t-butyl methyl ether, ethyl acetate/dichloromethane (1:1, V/V) and n-hexane/acetone (1:1, V/V) as the extraction solvents. The extraction results were shown in **Table 4**. Samples of different materials had different optimal extraction solvents. The optimal extraction solvent was ethyl acetate for sample 1# and sample 3# whose substrate was polyester and

Table 2. The orthogonal experiment of ultrasonic extraction.

No.	Factor A/°C	Factor B/min	Factor C/ml	Sample 1# /mg/kg	Sample 2# /mg/kg	Sample 3# /mg/kg	Sample 4# /mg/kg
1#	40	30	25	1420	1462	1764	925
2#	40	25	20	1572	1475	1994	928
3#	40	35	30	2159	1576	1952	885
4#	35	30	20	1178	1492	2007	984
5#	35	25	30	2293	1811	2113	886
6#	35	35	25	2058	1086	2377	1003
7#	45	30	30	2012	1599	2299	968
8#	45	25	25	1762	1524	2012	1046
9#	45	35	20	2075	1651	2280	991

Table 3. Analysis of data of the orthogonal experiment of ultrasonic extraction (mg/kg).

	Sample 1#			Sample 2#			Sample 3#			Sample 4#		
	A	B	rC	A	B	C	A	B	C	A	B	C
k1	1717	1537	1747	1504	1518	1357	1903	2023	2051	913	959	991
k2	1843	1876	1608	1463	1603	1539	2166	2040	2094	958	953	968
k3	1950	2097	2155	1591	1438	1662	2197	2203	2121	1002	960	913
Maximum difference	233	560	547	128	165	305	294	180	70	89	7	78
Optimal scheme	$A_3B_3C_3$			$A_3B_2C_3$			$A_3B_3C_3$			$A_3B_3C_1$		

Table 4. Extraction effects of various solvents/mg/kg.

Solvent	Sample 1#	Sample 2#	Sample 3#	Sample 4#	Sum
Ethyl acetate	2430.9	1829.4	2826.3	1090.4	8177.0
Acetone	2094.8	1861.4	2278.6	1074.2	7309.1
n-Hexane	1755.7	1773.0	2168.7	1098.7	6796.2
Mathanol	1619.0	2191.5	2373.3	1088.7	7272.4
Ethanol	2011.8	1959.2	2763.0	1104.7	7838.6
Acetonitrile	2322.2	1921.1	2670.3	1099.9	8013.4
Dichloromethane	2294.3	2268.8	2434.5	981.0	7978.6
Petroleum ether	2034.5	1855.0	1922.5	978.4	6790.4
t-Butyl methyl ether	1221.4	1703.8	1944.9	780.4	5650.4
Ethyl acetate/dichloromethane(1:1,V/V)	2088.4	1982.3	2451.9	1070.3	7592.8
n-Hexane/acetone(1:1,V/V)	1693.7	1771.0	1949.8	823.3	6237.8

cotton, respectively. The optimal extraction solvent was dichloromethane and ethanol for sample 2# and sample 4#, respectively whose substrate was nylon and wool, respectively. In order to ensure that the final optimal extraction solvent had a good extraction effect on all samples, the solvent with the largest total extraction amount was selected as the final optimal extraction solvent. According to the data in **Table 4**, the total extraction amount reached the largest when ethyl acetate was used as the extraction solvent. Therefore, the ultrasonic extraction conditions were finally optimized as follows: 30 ml of ethyl acetate was used as the extraction solvent, the extraction temperature was 45°C, and the extraction time was 35 min.

3.3. Linearity and Limit of Detection

The sensitivity was tested by analyzing a series of standard working solution. Linear calibration curve was studied by plotting the peak areas against the mass concentrations of chlorothalonil. Excellent linearity was found over the range of 0.2 µg/ml to 42.8 µg/ml for chlorothalonil and the correlation coefficient was 0.9999. The limit of detection (LOD) was taken when the ratio of signal to noise (S/N) was three and the limit of detection (LOD) was 0.1 mg/kg for chlorothalonil.

3.4. Recoveries and Precision Studies

Three levels (1.1 µg, 5.4 µg and 21.4 µg) of chlorothalonil were added to polyester lining cloth, nylon lining cloth, cotton lining cloth and wool lining cloth, which originally contained no chlorothalonil. The spiked average recoveries and the relative standard deviations (RSDs) of nine replicate measurements were determined as shown in **Table 5**. The spiked average recoveries ranged from 81.9% to 95.4% while the relative standard deviations (RSDs) varied from 1.8% to 5.2%.

The inner-day and inter-day RSDs were used to examine the repeatability of the proposed method. Inner-day precision was evaluated using nine injection

containing chlorothalonil at 5.4 µg/ml in 1 day while inter-day precision was assessed using nine determinations containing chlorothalonil at 5.4 µg/ml on different days. The inner-day and inter-day precision ($n = 9$) for chlorothalonil was 2.5% and 3.9%, respectively, which could be considered acceptable. This result demonstrated that no significant influence of the chlorothalonil stability on the experimental results was found during sample preparation and GC/MS-SIM determination.

3.5. Analysis of Commercial Textile Samples

To evaluate the applicability of the proposed method, the contents of residual chlorothalonil in 157 commercial textile samples were determined using the previous described procedure. Quantification was based on the external standard method using calibration curves fitted by linear regression analysis. Chlorothalonil was detected in a striped knitted cotton women's trousers sample and the content of chlorothalonil was 456.3 mg/kg. GC/MS-SIM chromatogram of this positive sample was shown in **Figure 2**. A sharp peak corresponding to chlorothalonil appeared at about 5.655 min in **Figure 2**.

4. Conclusion

An effective method was established to determine the content of residual chlorothalonil in textiles using gas chromatography/mass spectrometry in selected ion monitoring mode, coupled with ultrasonic extraction technique. A good

Table 5. The recovery experiments.

Sample	Added /µg/mL	Average recovery/%	RSD /%	Added /µg/mL	Average recovery/%	RSD /%	Added /µg/mL	Average recovery/%	RSD /%
Cotton	1.1	83.2	4.5	5.4	89.6	3.2	21.4	95.4	1.8
Polyester	1.1	81.9	4.9	5.4	87.9	4.1	21.4	94.7	2.8
Wool	1.1	82.3	5.2	5.4	88.5	3.6	21.4	91.5	2.4
Nylon	1.1	82.6	4.7	5.4	91.3	2.9	21.4	93.6	2.2

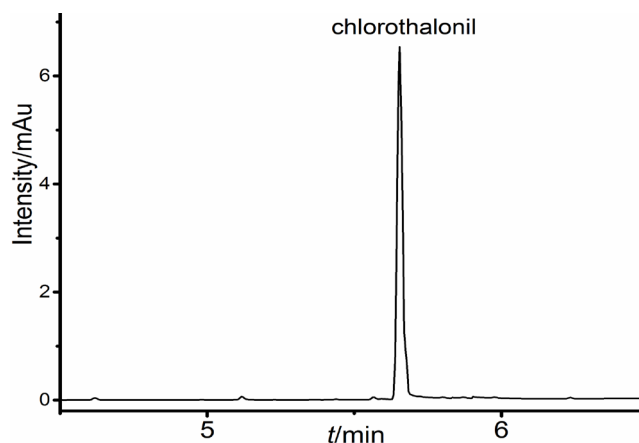


Figure 2. GC/MS-SIM chromatogram of a positive sample.

linearity existed between the peak area and the mass concentration of chlorothalonil in the mass concentration from 0.2 µg/ml to 42.8 µg/ml. The proposed method was simple, rapid and sensitive. The limit of detection was as low as 0.1 mg/kg, far lower than the requirements of relevant regulations. The proposed method was applied in the routine analysis of chlorothalonil in commercially available textiles and chlorothalonil was detected in some of the samples.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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