

Comparison of Supercritical Fluid and Soxhlet Extraction Methods for the Determination of Chlorothalonil from Cranberry Bog Soils

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The development and validation of an analytical method to determine the concentration of chlorothalonil from cranberry bog soil using supercritical fluid extraction (SFE) are reported. A self-built supercritical fluid extractor using CO₂ as the supercritical fluid (SCF) was used. The recovery of chlorothalonil was optimized by varying extraction temperature, pressure, time (static and dynamic), organic modifiers, and SCF flow rate. This method was then compared to a Soxhlet extraction procedure. SFE had more consistent performance than the Soxhlet extraction method for the recovery of chlorothalonil from both fortified bog soils and field samples. SFE provided cleaner extracts, had shorter extraction times, and used less organic solvent than the Soxhlet extraction method. This result is consistent with other SFE methods for determining pesticides from various environmental matrices. Thus, SFE is a preferred method for the extraction of chlorothalonil from cranberry bog soil.

Keywords: *Supercritical fluid extraction; SFE; Soxhlet extraction; chlorothalonil*

INTRODUCTION

Chlorothalonil (tetrachloroisophthalonitrile, Figure 1), the active ingredient in Bravo and Daconil 2787 fungicides, is used on fruits, vegetables, and ornamental plants. Chlorothalonil was approved by the U.S. EPA for use on cranberries under controlled conditions in July 1985 (El-Nabarawy and Carey, 1988; Reduker et al., 1988).

Chlorothalonil is a white, crystalline solid. It is stable when stored at room temperature (Ballee et al., 1976). It is biodegraded in the soils of temperate regions at moderate levels of moisture to 4-hydroxy-2,5,6-trichloroisophthalonitrile (DAC3701) (Winnet et al., 1990; Davies, 1988; Ballee et al., 1976). The half-life in soil was determined to be 2.5–3 months (Davies, 1988). High moisture and temperature have been shown to accelerate the rate of chlorothalonil degradation in soils (Ballee et al., 1976).

In the past few years, supercritical fluid extraction (SFE) has gained more and more attention because of its advantages compared to solvent extraction. SFE has been shown to be easy to use and is less labor intensive with comparable recoveries of target analytes in shorter time periods than traditional extraction methods. In addition, SFE has been shown to use less organic solvent than Soxhlet extraction. SFE has been used in food, agricultural, pharmaceutical and environmental applications owing to its versatility.

As SFE offers several advantages over Soxhlet and other extraction procedures, it was used to develop and validate an analytical method to determine the concentration of chlorothalonil from soil. Since many factors can influence SFE efficiency, including extraction pressure, temperature, supercritical fluid (SCF) flow rate,

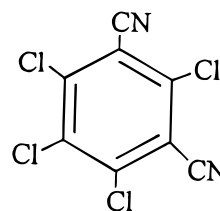


Figure 1. Chemical structure of chlorothalonil.

extraction time, and modifier, this investigation determined how these parameters affect the recovery of chlorothalonil from soil. The validated SFE method was then compared to the extraction efficiency of chlorothalonil from soil taken from cranberry bogs with a Soxhlet extraction procedure.

MATERIALS AND METHODS

Materials. The solvents used in this study were optima-grade methylene chloride, acetone, and *n*-hexane (Fisher Scientific, Springfield, NJ) and pesticide-grade methanol (J. T. Baker, Inc., Phillipsburg, NJ). Chlorothalonil (purity 99.4%) was obtained from Chem Service, Inc. (West Chester, PA).

Soils (Downers soil series; classified as coarse-loamy, siliceous, mesic family) were obtained from the Rutgers Blueberry and Cranberry Experimental Research Station, located near Chatsworth, NJ. To prepare the soil for the SFE validation studies, the following extraction procedure was used to eliminate the low-level chlorothalonil residues: Soxhlet extraction with methylene chloride/acetone (1:1 volume) for 24 h followed by hexane/acetone (1:1 volume) for 24 h. The soil was then dried in a laboratory fume hood and then placed in an isothermal oven at 105 °C for 5 h to remove moisture. The residue concentrations in soil following soil cleaning were determined to be 0.37 and 0.17 ppb, respectively, for SFE and Soxhlet extraction methods. These values were used for blank correction for their respective extraction methods.

Supercritical Fluid Extractor. A self-built supercritical fluid extractor (Figure 2), built in our laboratory, was used

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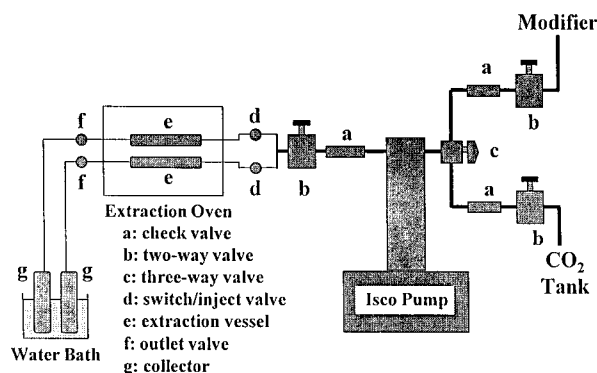


Figure 2. Design of self-combined supercritical fluid extractor.

for the extraction of chlorothalonil from soils taken from cranberry bogs. An ISCO (Lincoln, NE) 260D syringe pump with a controller was used to maintain the pressure and flow rate of SCF. The maximum pressure was 7500 psi (510 atm). Check valves (Scientific Systems, Inc.) with pressure limit of 10 000 psi were obtained from Fisher Scientific. Rheodyne model 7125 syringe loading sample injectors obtained from Supelco, Inc. (Bellefonte, PA) were chosen to be the switch/injection valves. Rheodyne model 7010 sample injection valves also obtained from Supelco were used as outlet valves. An LKB Bromma 2155 HPLC column oven was used for maintaining extraction temperatures. Extraction vessels with maximum pressure of 9000 psi [100 mm \times 4.6 mm (1.67 mL) and 200 mm \times 4.6 mm (3.35 mL)] were obtained from Keystone Scientific, Inc. (Bellefonte, PA). The outlet valves and tubings were heated by Thermolyne heating tape (Fisher) to \sim 64.5 $^{\circ}$ C to avoid possible clogging that might result from the depressurization of SCF. Twenty-five milliliters of hexane was heated to 58.5 $^{\circ}$ C and was used as the collecting medium in the collector for each extraction.

Gas Chromatography. A Hewlett-Packard 5890 series II gas chromatograph (GC) (Hewlett-Packard, Wilmington, DE) with dual ⁶³Ni electron capture detectors (ECD) and a Supelco SPB-5 (30 m \times 0.53 mm, 1.5 μ m film) fused silica column was used for the analysis of chlorothalonil. The injection port and the ECD temperatures were maintained at 260 and 350 $^{\circ}$ C, respectively. The temperature program was as follows: initial temperature of 150 $^{\circ}$ C for held for 4 min, elevated to 200 $^{\circ}$ C at 4 $^{\circ}$ C/min, and held for 11 min. The column was then heated to a final temperature of 250 $^{\circ}$ C at 15 $^{\circ}$ C/min and held for 5 min. The carrier gas was helium at 3 mL/min, and the makeup gas was 95% argon/5% methane at 32 mL/min. Both gases were obtained from Matheson (East Rutherford, NJ). Chlorothalonil standards for GC analysis, ranging from 1×10^{-12} to 1×10^{-10} g/ μ L, were used to make five-point linear calibration curves for quantification of chlorothalonil by plotting mass injected on column (nanograms) and peak area. A 1.2 μ L injection was used. The minimum r^2 value of the standard curves was 0.99.

Soil Fortification Procedures. One and a half grams of soil was weighed out and fortified with 0.5 mL of a chlorothalonil standard prepared in acetone (1.5×10^{-11} g/ μ L for 5 ppb soil samples, 3×10^{-11} g/ μ L for 10 ppb soil samples, 1.5×10^{-10} g/ μ L for 50 ppb soil samples, and 2.0×10^{-9} g/ μ L for 667 ppb soil samples). The acetone was uniformly spread over the soil surface and allowed to evaporate in a laboratory fume hood. The soil was then aged for 18 h prior to extraction and analysis.

Optimization of Supercritical Fluid Extraction Conditions. Presented in Figure 3 is the experimental scheme for developing and validating the SFE method. A series of fortified soil samples (667 ppb) were used to determine the effects of temperature, pressure, static and dynamic extraction, and modifiers on the extractability of chlorothalonil from soil. Matheson SFC grade carbon dioxide with helium pressurized to 1500 psi (Matheson) was used as the supercritical fluid.

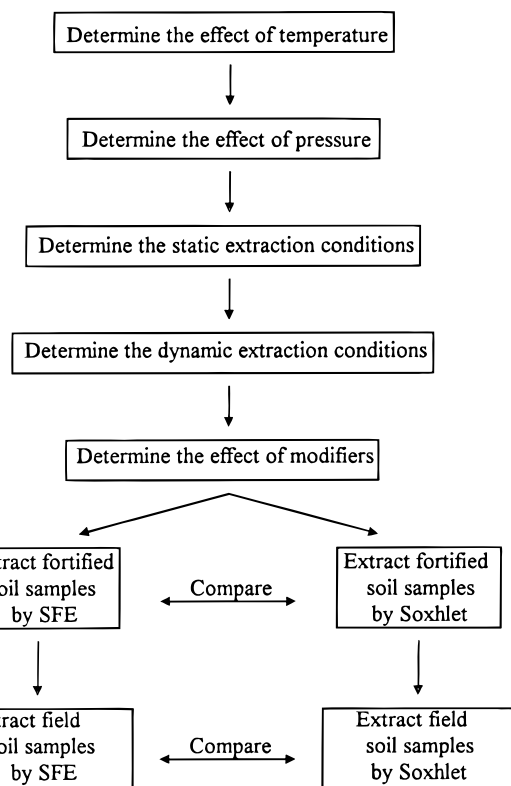


Figure 3. Experimental procedure scheme.

Summarized in Table 1 is the experimental design for studies indicated below:

To determine the effect of temperature, the following parameters were used: The static extractions were at 400 atm for 10 min. The dynamic extractions were at 400 atm and 0.7 mL/min for 15 min. The extraction temperatures for these three samples were 40, 60, and 80 $^{\circ}$ C.

To determine the effect of pressure, the following parameters were used: The static extractions were at 40 $^{\circ}$ C for 10 min. The dynamic extractions were at 40 $^{\circ}$ C and 0.7 mL/min for 15 min. The extraction pressures for these two samples were at 200 and 300 atm.

An experiment to determine the static extraction times was performed. Static extractions were tested at 0 (i.e. without static extraction stage), 5, and 10 min and were extracted with carbon dioxide modified with 15% methanol (molar fraction). The static extraction conditions were at 40 $^{\circ}$ C and 400 atm for 10 min. The dynamic extraction conditions were at 40 $^{\circ}$ C and 400 atm. The dynamic extraction times and flow rates were 10 min, 0.7 mL/min; 15 min, 0.7 mL/min; and 10 min, 1 mL/min, respectively.

To determine the effect of modifier, the following parameters were used: Carbon dioxide modified with 5%, 10%, and 15% methanol and 5%, 10%, and 15% acetone (in molar fraction) was used. The static extraction conditions were at 40 $^{\circ}$ C and 400 atm for 10 min. The dynamic extraction conditions were at 40 $^{\circ}$ C, 400 atm, and 0.7 mL/min for 10 min.

Method Validation Studies. After SFE optimum extraction conditions were determined, studies were conducted to validate the method. Triplicate extractions of 1.5 g of pre-cleaned soils fortified at 5, 10, and 50 ppb of chlorothalonil were made by SFE and Soxhlet extraction methods. The SFE extraction was as follows: carbon dioxide modified with 5% methanol. The static extractions were performed at 400 atm and 40 $^{\circ}$ C for 10 min. The dynamic extractions were at 400 atm, 40 $^{\circ}$ C, and 0.7 mL/min for 10 min.

The Soxhlet extraction method was as follows: Soil was placed into cellulose extraction thimbles and extracted with hexane/acetone 1:1 (v/v) for 24 h in a Soxhlet apparatus. The extractions were performed at \approx 5 min/cycle. The extracts were concentrated by a Kuderna-Danish (K-D) concentrator at 85

Table 1. Extraction Conditions for Determining the Effects of Various Parameters in SFE

temp (°C)	pressure (atm)	static extraction time (min)	dynamic time (min)/ flow rate (mL/min)	modifier (molar fraction)
40, 60, 80	400	10	15/0.7	pure CO ₂
40	200, 300, 400	10	15/0.7	pure CO ₂
40	400	0, 5, 10	10/0.7	15% MeOH
40	400	10	10/0.7, 15/0.7, 10/1	15% MeOH
40	400	10	10/0.7	5, 10, 15% MeOH 5, 10, 15% acetone

°C in a water bath with a three-chamber column reflux and a gentle stream of clean nitrogen gas to appropriate volumes.

Extraction and Analysis of Cranberry Bog Soil Samples. Soil samples (Downers soil series; classified as coarse-loamy, siliceous, mesic family) were collected from experimental cranberry bogs on the Rutgers Blueberry and Cranberry Experimental Research Station (bogs 12, 13, and 15) that had been treated with chlorothalonil. Triplicate bog samples from each site were analyzed for concentration of chlorothalonil. SFE extraction conditions were as follows: A sample size of 3.0 g was used for the extraction with supercritical CO₂ with 5% methanol (molar fraction). The static extractions were done at 400 atm and 40 °C for 10 min. The dynamic extractions were performed at 400 atm, 40 °C, and 0.7 mL/min for 20 min.

Soxhlet extraction conditions were as follows: Triplicate 4 g samples from each location were placed into cellulose extraction thimbles and extracted with hexane/acetone 1:1 (v/v) for 24 h in a Soxhlet apparatus. The extractions were performed at ≈5 min/cycle. The extracts were concentrated by a K-D concentrator at 85 °C in a water bath with a three-chamber column reflux and a gentle stream of clean nitrogen gas to appropriate volumes.

RESULTS AND DISCUSSION

Results from Supercritical Fluid Extraction Studies. At the constant pressure of 400 atm, when the extraction temperature was elevated from 40 to 80 °C, the chlorothalonil recovery dropped from 64.7% to 35.3%, indicating that higher extraction efficiency was achieved at lower extraction temperature. This result was not surprising since the solvent strength of a supercritical fluid usually increases with its density (Hawthorne et al., 1992; Riekkola et al., 1992; Lira, 1988; Marentis, 1988). Therefore, elevated temperatures would result in a decreased density of supercritical carbon dioxide. Thus, an extraction temperature of 40 °C was chosen for later experiments because of increased recovery of chlorothalonil from soil.

At the constant temperature of 40 °C, when the extraction pressure was increased from 200 to 400 atm, the recovery rate of chlorothalonil increased from 18.2% to 64.7%, indicating that higher extraction pressures resulted in higher the recovery of chlorothalonil. The results were expected because above the critical point, increasing the pressure at a constant temperature will increase the density of supercritical CO₂ and increase the solvating power of the SCF (Oostdyk et al., 1993; Snyder et al., 1993; Hawthorne et al., 1992; Velde et al., 1992; Lopez-Avila and Dodhiwala, 1990).

Liquid carbon dioxide is a nonpolar solvent. It is similar to hexane in many ways (Marentis, 1988). However, in addition to density, the dielectric constant of CO₂ increases with increasing pressure in the supercritical phase (Lira, 1988; Marentis, 1988). Thus, higher pressure would have more extracting capability. Because a better extraction recovery of chlorothalonil was achieved at the extraction pressure of 400 atm, it was chosen for later experiments.

Table 2 presents the results of the static extraction

Table 2. Extraction Conditions and Results of Static Extraction Research^a

static time (min)	dynamic time (min)	flow rate (mL/min)	av recov (%)	range (%)
0	10	0.7	90.9	±1.45
5	10	0.7	93.8	±5.76
10	10	0.7	95.3	±1.55

^a Extraction temperature = 40 °C; extraction pressure = 400 atm.

Table 3. Extraction Conditions and Results of Dynamic Extraction Research^a

static time (min)	dynamic time (min)	flow rate (mL/min)	total vol (mL)	av recov (%)	range (%)
10	10	0.7	7	95.3	±1.55
10	15	0.7	10.5	100	±3.84
10	10	1.0	10	89.3	±2.82

^a Extraction temperature = 40 °C; extraction pressure = 400 atm.

research. An increase in static extraction times has positive effect on the extraction of chlorothalonil from soil. Most of the swelling of the soil matrix would take place within the static extractions (Fahmy et al., 1993) and enhance the release of chlorothalonil into the supercritical fluid. Thus, 10 min of static extraction time was chosen for later research.

The dynamic extraction conditions and recoveries are listed in Table 3. At a 0.7 mL/min flow rate, a longer extraction time (15 min) increased the recovery rate. Some chlorothalonil was partitioned from the soil into the supercritical CO₂ during the static extraction stage. One possible explanation is that a larger supercritical fluid volume could sweep out the chlorothalonil that had been extracted from the soil more efficiently (Velde et al., 1992; Lopez-Avila and Dodhiwala, 1990). Furthermore, longer extraction time is beneficial because chlorothalonil dissolves continuously into the supercritical CO₂ from the soil matrix.

When the flow rate was elevated to 1.0 mL/min for 10 min, the total flow volume (10 mL) was almost the same as for 0.7 mL/min for 15 min (10.5 mL) and larger than 0.7 mL/min for 10 min (7 mL); nevertheless, the recovery rate was the lowest among these three extraction conditions. One possible reason is that a faster flow would decrease the contact time between the chlorothalonil in the soil and the molecules of supercritical CO₂ and would result in lower recovery even if the total flow volumes were identical. Higher flow rates might reduce the sample collecting efficiency as more bubbles were observed in the collecting tubes when CO₂ was vented from the system. A 10 min extraction time with a 0.7 mL/min flow rate was selected as dynamic extraction conditions. Excellent recovery was achieved (95.3%). Under the dynamic flow conditions, the extraction pressure required manual operator control within 400 ± 20 atm and a longer period was rejected for ease of operation.

Table 4. Extraction Efficiencies of Various Modifiers^a

modifier (molar fraction)	av recov (%)	range (%)
5% methanol	104	±4.86
10% methanol	95.6	±1.94
15% methanol	95.3	±1.55
5% acetone	84.7	±6.68
10% acetone	94.2	±0.07
15% acetone	96.6	±2.51

^a Extraction temperature = 40 °C; extraction pressure = 400 atm; static extraction time = 10 min; dynamic extraction time = 10 min; dynamic extraction flow rate = 0.7 mL/min.

The volume of extraction vessels used was 1.67 mL. Consequently, the total flow volumes in the dynamic extractions were between 4.2 and 6.3 times (7–10.5 mL) of extraction vessel volume. The experimental results indicate that 4.2 times the extraction vessel volume of supercritical fluid was large enough to sweep the analyte out of the extraction vessel. This result was consistent with those found by Oostdyk et al. (1993), Snyder et al. (1993), and Hawthorne et al. 1992.

The extraction recovery rates obtained using six different modifications of supercritical carbon dioxide are provided in Table 4. Using methanol or acetone as the modifier resulted in a satisfactory recovery rate (>80%) for chlorothalonil, even though the extraction temperature (40 °C) was lower than the critical temperatures of the solvent-modified CO₂. Chlorothalonil is a relatively polar compound (Gilvydis and Walters, 1988); therefore, the addition of a polar modifier would increase the solubility of chlorothalonil in the supercritical fluid. The polarity indices of methanol and acetone are 6.6 and 5.4, respectively (i.e. methanol is more polar than acetone; Waters, 1993).

The performance of methanol was superior to that of acetone perhaps because of the greater solubility of chlorothalonil in methanol than in acetone. Snyder et al. (1993) found that a methanol modifier could increase the recovery of organochlorine and organophosphate pesticides from soil, especially for polar pesticides. They proposed that the modifier may actually displace polar analytes from the adsorption surfaces of soils and make them become more soluble or easier to move into the supercritical fluid. In addition, the modifier may be able to swell the soil matrix and expose small internal cavities; therefore, the supercritical fluid can extract adsorbed analytes more easily. Fahmy et al. (1993) also concluded that matrix swelling is an important factor in modifier-enhanced SFE as well.

In short, the addition of either acetone or methanol into the supercritical carbon dioxide increased the extraction efficiency of chlorothalonil. Three mechanisms that can contribute to this increase on extraction efficiency are as follows: (1) acetone and methanol would increase the solubility of chlorothalonil in the supercritical CO₂ by increasing the polarity of supercritical CO₂; (2) displacement of chlorothalonil from the active sites of soil matrices because of their strong dipole moments (2.9 D for acetone and 1.7 D for methanol; Lira, 1988); and (3) by penetrating the soil matrix, thereby swelling its internal cavities so that the supercritical CO₂ is able to better extract the chlorothalonil. A 5% methanol modified supercritical carbon dioxide was selected for the further research of fortified and real-world samples.

Comparison of Supercritical Fluid and Soxhlet Extractions for Fortified Soil Samples. After the optimum extraction conditions of the SFE method were

Table 5. Recovery of Fortified Samples with SFE and Soxhlet Extraction

spike level (ppb)	method ^a	trials (n)	av recov ^b (%)	SD ^c	RSD ^d (%)
5	SFE	3	106	4.2	3.9
	Sox	3	119	12.9	10.8
10	SFE	3	97.3	13.2	13.6
	Sox	3	111	26.7	24.1
50	SFE	3	92.9	7.1	7.6
	Sox	3	114	5.9	5.1

^a SFE, supercritical fluid extraction; Sox, Soxhlet extraction. ^b Av recov, average recovery rate. ^c SD, standard deviation. ^d RSD, relative standard deviation.

Table 6. Quantification of Chlorothalonil in Field Samples

sample sites	method ^a	trials (n)	av concn ^b (ppb)	SD ^c	RSD ^d (%)
12	SFE	3	269.0	62.1	23.1
	Sox	5	351.7	75.8	21.5
13	SFE	3	7.9	0.7	8.7
	Sox	3	7.3	0.8	10.8
15	SFE	4	11.4	0.8	7.0
	Sox	3	14.0	0.9	6.4

^a SFE, supercritical fluid extraction; Sox, Soxhlet extraction. ^b Av concn, average concentration of chlorothalonil in soil. ^c SD, standard deviation. ^d RSD, relative standard deviation.

determined, this procedure was compared with the Soxhlet extraction method, a conventional method, for validation. The results are shown in Table 5. The mean recoveries of the SFE method and the Soxhlet method were evaluated statistically at each fortification level using the Student *t* test at the 95% confidence level (Zar, 1974). There were no significant differences between these two methods in mean recovery rate at 5 and 10 ppb fortified levels. However, the SFE method had slightly better precision at 5 and 10 ppb, even though this was not significantly different. There was a significant difference at 50 ppb fortified level between these two methods in mean recovery rate (92.9% vs 114% recovery, respectively, for SFE and Soxhlet methods). Thus, the SFE method can offer comparative extraction efficiency with Soxhlet extraction. The variances of these two methods evaluated at each fortification level using the *F* test at the 95% confidence level (Zar, 1974) indicated that there were no significant differences between these two methods. Thus, the precision of the SFE method was not different from the Soxhlet method for these soil samples.

The SFE method showed excellent accuracy (overall average recovery 98.8%) and precision (overall RSD 9.1%). In addition, the SFE method offered statistically equivalent recovery efficiency and precision in comparison with the Soxhlet extraction method.

Comparison of Supercritical Fluid Extraction and Soxhlet Extraction of Chlorothalonil in Cranberry Bog Soil. The concentration of chlorothalonil in soil was determined by both SFE and Soxhlet extraction methods, and the results are listed in Table 6. The mean amounts recovered by the two methods were compared statistically using the Student *t* test at 95% confidence level (Zar, 1974). There were no significant differences in residue levels in site 12 and 13 samples determined by the SFE and Soxhlet methods. There were significant differences in residue concentrations in site 15 samples between these two respective methods at 5% level of significance. The variances of these two methods were evaluated by using the *F* test

at the 95% confidence level (Zar, 1974). There were no significant differences between these two methods at the three sampling locations.

However, the %RSD values of site 12 soil samples of two methods were both much larger than those of site 13 and 15 soil samples. Since all samples of three cranberry sites were well mixed by the same technique before extraction and small %RSD values were obtained for site 13 and 15 samples, one possible explanation is that the higher %RSD of site 12 is dependent on the concentration of chlorothalonil.

For both fortified and real-world soil samples, the SFE method obtained satisfactory method accuracy (>90%) and precision in comparison to Soxhlet extraction. In addition, the SFE provided cleaner extracts, had shorter extraction times, and used much less organic solvent than the Soxhlet extraction method. This result is consistent with other SFE methods for determining pesticides from various environmental matrices. Thus, SFE is a preferred method for the extraction of chlorothalonil from cranberry bog soil.

SAFETY

Chlorothalonil is toxic and should be handled only in a fume hood. This chemical can cause skin irritation, and protective laboratory gear, such as latex gloves, lab coat, and eye protection should be worn when this compound is handled to minimize exposure. Carbon dioxide can cause suffocation. Acetone and methanol should be stored in tight containers or used in a fume hood. These chemicals should be disposed of in a legal and environmentally safe manner.

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