

Use of Supercritical Fluid Extraction for Pirimicarb Determination in Soil

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The suitability of a variety of neat supercritical fluids (carbon dioxide, nitrous oxide, and chlorodifluoromethane) and modifiers (toluene, methanol, pyridine, triethylamine, and pyrrolidine) with different physical-chemical properties at two temperatures (50 and 100 °C) was evaluated for the extraction of incurred pirimicarb from topsoil. From the extraction efficiency obtained with the different modifiers and their chemical properties, the prevailing interactions between pesticide residue and the soil organic matter are proposed. The most effective extraction fluid was carbon dioxide modified with basic compounds (pyridine or triethylamine), which reflects the significance of acid-base interaction in the binding of pirimicarb to the matrix. Further, the developed SFE procedure using carbon dioxide (100 °C, 30 MPa, 20 mL) modified with triethylamine (5% cell volume) was compared with Soxhlet extraction (18 h) using methanol. Results indicate that the supercritical fluid extraction offers better precision, shorter analysis time, and a reduction in the solvent usage by a factor of 10.

Keywords: *SFE pesticides; modifiers of supercritical fluids; soil-matrix interactions; comparison of extraction techniques*

INTRODUCTION

Although extraction of agrochemicals from soil samples is currently carried out by Soxhlet methods (Clemen et al., 1993; Honing et al., 1993), analytical-scale supercritical fluid extraction (SFE) is gaining interest because of its inherent advantages over conventional extraction procedures. Very recently, analytical procedures based on SFE for the determination of polar agrochemicals from soils, such as phenylurea herbicides (McNally and Wheeler, 1988; Wheeler and McNally, 1989; Locke et al., 1993), triazine herbicides (Janda et al., 1989; Knipe et al., 1992), organophosphorus pesticides (Lopez-Avila et al., 1990; Wuchner et al., 1993), and phenoxyacid herbicides (Hawthorne et al., 1992a; Rochette et al., 1993; Lopez-Avila et al., 1993), have been reported. These polar substituted analytes usually required either the addition of polar modifiers (i.e. methanol, water) to carbon dioxide for their quantitative recovery from topsoil or the application of simultaneous derivatization and extraction. The strong interaction between soil and analyte is usually considered to be the limiting factor for the low recovery in carbon dioxide of nonderivatized compounds (Janda et al., 1993), despite the fact that they are extractable with carbon dioxide from glass wool, glass beads, or sand due to its solubility.

On the other hand, it has been recognized that the mechanisms of pesticide retention in soils is of primary importance for the assessment of their fate in the environment (Karickhoff, 1984; Gilchrist et al., 1993). The characterization of the interactions of polar pesticides with a variety of functionalities in different types of soils offers a great deal of complexity. The formation of bound residues for certain pesticides may be linked with phenolic -OH and -COOH groups of soil organic matter involving chemically stabilizing reactions between these functional groups and the pesticide. It has been suggested that humic materials consist of phenolic and benzenecarboxylic acids joined by hydrogen bonds to form a molecular sieve-type polymeric structure of considerable stability. One of the characteristics of this

proposed structure is that it would contain voids or holes of different molecular dimensions which could trap pesticides. However, the application of such a structural concept to the bound residues of pesticides in organic matter or humic material is still a matter of conjecture (Khan, 1991).

Cheng (1990) has suggested the use of solvent extraction to characterize the retention mechanisms, since extraction is essentially the breaking of bonds between a chemical and the soil surface. Differences in the effectiveness of specific solvents in extracting pesticides from soils can be used to determine the specific retention mechanism involved. Similarly, the use of supercritical fluids could be easily performed due to their change of solubility according to their density and composition. Nevertheless, until now most of the SFE of pesticides has been performed using carbon dioxide modified with methanol (Lopez-Avila et al., 1990) or acetone (Wuchner et al., 1993). However, very recently the great efficiency of basic modifiers of nitrous oxide for the extraction of aromatic amines from soils (Ostdyk et al., 1993; Ashraf-Khorassani et al., 1990) or dibenzo-*p*-dioxins from fly ash (Alexandrou and Pauliszyn, 1989) has been recognized. In addition, nitro-substituted and parent polycyclic aromatic hydrocarbons and polychlorinated biphenyls were successfully extracted with chlorodifluoromethane (Paschke et al., 1992; Hawthorne et al., 1992b).

Therefore, a variety of extractant agents and modifiers with different physical-chemical properties were chosen in the present study to evaluate the extraction efficiency of pirimicarb from soil (Tables 1 and 2). While carbon dioxide is a nonpolar fluid but it is able to establish acid-base and quadrupolar interactions with analytes nitrous oxide and chlorodifluoromethane that have permanent dipolar moments. N₂O was chosen despite its explosion hazard (Sievers, 1991) because the matrix extracted contains low levels of organic matter (TOC = 3.3%), which minimizes the risk associated with its usage.

In addition, modifiers with a variety of polarity and

Table 1. Supercritical Fluids Used in This Study

compd	formula	T_c^a (°C)	P_c^b (MPa)	dipolar moment (D) ^c	solubility parameter (δ) ^d (cal/cm ³) ^{1/2}
carbon dioxide	CO ₂	31.1	7.38	0	10.8
nitrous oxide	N ₂ O	36.6	7.24	0.2	10.6
chlorodifluoro- methane	CHClF ₂	96.3	4.97	1.4	8.8

^a T_c , critical temperature. ^b P_c , critical pressure. ^c D, debyes. ^d Giddings et al. (1968).

Table 2. Physical Properties of Modifiers Used in This Study^a

compd	formula	acid/base pK _a	dipolar moment (D)	interaction ^b
methanol	CH ₃ OH	16	1.70–2.87	ID, HB
toluene	C ₇ H ₈		0.36–0.43	ID, DP, π - π
pyridine	C ₅ H ₅ N	5.2	2.19	ID, DP, π - π , A–B
triethylamine	C ₆ H ₁₅ N	11.01	0.66	ID, A–B
pyrrolidine	C ₄ H ₉ N	11.3	NA ^c	ID, A–B

^a Sources: Weast (1978); Page et al. (1992). ^b Potential solvent interactions of modifiers: ID, induced dipole; HB, hydrogen bonding; DP, dispersion; A–B, acid–base. ^c NA, not available.

Table 3. Characterization of the Soil Polluted with Pirimicarb

mineral composition (%)			TOC	CEC ^b	
clay	silt	sand	(%)	pH ^a	(mequiv/g)
31	57	12	3.3	6.8	7.1

^a Measured at 1:1 (w/v) of 0.01 M CaCl₂. ^b Cation exchange capacity.

Table 4. Physical–Chemical Properties of Pirimicarb

K_{ow}^a	$T_{0.5}^b$ (days)	GUS _{index} ^c (cm ³ /g)	K_{oc}^d
50	108	2.30	741.2

^a Octanol–water partition coefficient (*Agrochemicals Handbook*, 1992). ^b Half-life (Fielding et al., 1991). ^c GUS index: ground water ubiquity score (Fielding et al., 1991). ^d Soil water partition coefficient (Fielding et al., 1991).

basic properties were also chosen since pirimicarb is also a basic molecule with a moderate hydrophobicity. Aromatic, aliphatic amines and aromatic hydrocarbons were considered for investigation if π - π dispersive interactions (London) are synergistic to acid–base. In addition, the acid–base properties and miscibility with the primary fluid were also other criteria to select the modifiers used in this study (Francis, 1954; Page et al., 1992).

Therefore, the objectives of this work were (a) to evaluate the effect of temperature and fluid composition on the extraction efficiency of incurred pirimicarb from soil, (b) to intercompare Soxhlet and SFE in terms of precision, accuracy, and extraction time, and finally (c) to assess the class of prevalent interactions between soil and analyte from the physical–chemical properties of supercritical fluids efficiently used in SFE.

EXPERIMENTAL PROCEDURES

Surface soil sample was collected in the Ebro Delta (Tarragona, Spain) during July 1989 after 25 days of spraying at a dose of 1 kg of active ingredient/ha. Sample was frozen at –20 °C immediately after sampling, freeze-dried, crushed, and sieved through 120 μ m. Homogenization was carried out during 5 days using a kneader and a mixing machine. The soil characteristics and the physical–chemical properties of pirimicarb of environmental relevance are listed in Tables 3 and 4, respectively. The K_{ow} and K_{oc} partition coefficients of pirimicarb are low, falling within the transition leacher (TL)

category according to its GUS index (Fielding et al., 1991). However, because of the relatively high TOC value and the low cation-exchange capacity of soil, the interaction of pirimicarb might be through the organic matter, which is consistent with the almost neutral pH value of soil.

Pirimicarb and atrazine were purchased from Dr. Ehrenshofer (Augsburg, Germany) and Riedel de Haën (Seelze-Hannover, Germany), respectively. Pesticide grade diethyl acetate, toluene, and methanol were obtained from Merck (Darmstadt, Germany). Pyridine (**Caution:** Pyridine may cause central nervous system depression and irritation of skin and respiratory tract.), triethylamine, and pyrrolidine were purchased from Aldrich Chemical Co. (Milwaukee, WI). *N,O*-Bis(trimethylsilyl)trifluoroacetamide (BSTFA) was provided by Fluka (Buchs, Switzerland). SFC grade carbon dioxide was obtained from Air Products and Chemicals Inc. (Allentown, PA), and 99.997% nitrous oxide (**Caution:** Nitrous oxide is an oxidizer; therefore, the extraction of matrices with high organic content at elevated temperatures should be avoided.) and 99.8% chlorodifluoromethane (R_{22}) were from Carburios Metalicos (Barcelona, Spain). Extraction cells of 5 mL were obtained from Suprex (Pittsburgh, PA). Flow rate through the extraction cell was adjusted by means of a fused silica linear restrictor (50 μ m i.d. \times 20–30 cm length) (MicroQuartz, Munchen, Germany) in the range of 2 mL/min as fluid, which was measured from the pump reading.

Soxhlet extraction was performed with methanol for 18 h. The recovered extracts were carefully concentrated in a rotary evaporator (30 °C) to small volume and then evaporated to dryness under a gentle stream of nitrogen. Recovered extracts were derivatized with BSTFA at 70 °C under nitrogen atmosphere to allow the cGC-NPD determination without further cleanup. Extracts were reconstituted with ethyl acetate prior to cGC analysis. Supercritical fluid extraction (SFE) was performed in the Fisons SFE-30 apparatus (Milano, Italy). Liquefied carbon dioxide was delivered by a high-pressure syringe pump of 150 mL. Extraction cell was allocated into an air-heated oven where two high-pressure eight-port Valco valves (Untertamberg, Switzerland) allowed the extraction cell loading without pump depressurization and the selection from dynamic and static extraction modes. The flow restrictor was heated at 150 °C, and extracts were collected at room temperature under 10 mL of ethyl acetate. Modifiers were added directly into the extraction cell, and their percentage is referred to the extraction cell volume. Extraction was performed in the static (5 min) followed by the dynamic (20 mL) mode. Atrazine was used as internal standard, spiking with 210 ng onto the sample right after the extraction cell loading. Extraction time was calculated at each pressure according to the flow rate reading of the pump to be ca. 4–5 extraction cell bed volumes. Recovered extracts were concentrated to small volume using a gentle stream of nitrogen and derivatized with BSTFA as described above. Figure 1 shows a characteristic cGC-NPD chromatogram obtained from a SFE extract.

Extracts were analyzed in a Fisons Instruments 5300 Mega Series cGC equipped with split–splitless injector and the NPD-40 detector. Injector and detector temperatures were held at 220 and 280 °C, respectively. A fused silica capillary column of 30 m \times 0.25 mm i.d., coated with 0.25 μ m of DB-1701, was used. Column temperature was programmed from 80 to 220 °C at 15 °C/min after an isothermal period of 2 min. Final temperature was held for 5 min. Hydrogen was used as carrier gas at 50 cm/s. Data were acquired by a Nelson-PE intelligent interphase with a sampling frequency of 100 Hz and handled with a PS computer using the PE 2600 software. Samples were injected dissolved in ethyl acetate. Calibration plots were obtained for each compound and were linear ($r = 0.99994$) at least in 2 orders of magnitude. Blanks were obtained for every extractant agent using the same volume as the real sample. SFE extraction efficiency was calculated from the data obtained from Soxhlet extraction using atrazine as internal standard.

False positive confirmation was carried out by cGC–MS in the EI ionization (70 eV) using a Fisons Instruments MD 800. Ion source and transfer line temperatures were held at 200 and 300 °C, respectively. Scans were acquired every second.

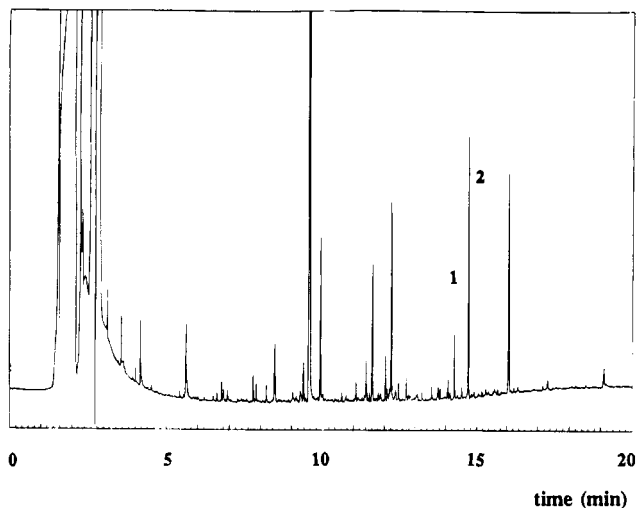


Figure 1. Characteristic cGC-NPD chromatogram obtained from a SFE extract. Compound identification is as follows: 1, atrazine (I.S.); 2, pirimicarb.

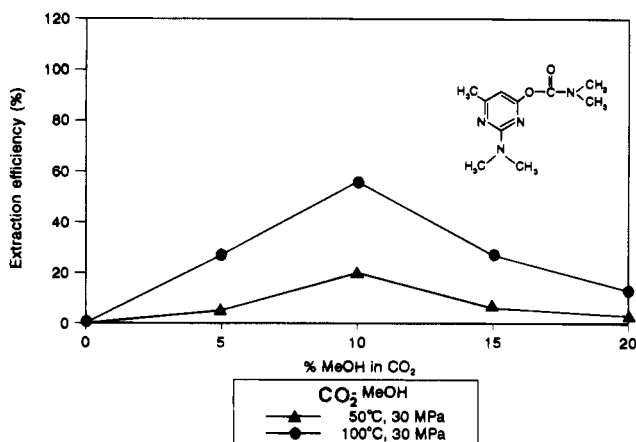


Figure 2. Extraction efficiency of pirimicarb from topsoil according to the percentage (v/v) of methanol (MeOH) as static modifier of CO₂ at 50 and 100 °C and 30 MPa. All data points correspond to the mean of two replicates.

Helium was used as carrier gas at 30 cm/s. Other chromatographic conditions were similar to those reported above.

RESULTS AND DISCUSSION

Effect of Extractant Agent Composition. Initially, several fluids commonly used in SFE were evaluated (Figures 2–4). It is remarkable that only chlorodifluoromethane was able to extract pirimicarb from soil but at low recovery ranging from 10 to 15%. The highest dipolar moment of this fluid, among the others evaluated, could be responsible for the partial pirimicarb extraction. In a previous comparison of the extraction efficiency for the recovery of nonionic and ionic compounds from a variety of matrices using CO₂, N₂O, and CHClF₂, the same trend was found (Hawthorne et al., 1992). In the case of environmental solids, the former authors concluded that the ability of the supercritical extraction fluid to interact with the sorptive sites on sample matrices may ultimately control the SFE rates and recoveries.

Although nitrous oxide has shown remarkable solubility for aliphatic and aromatic amines from soil (Ashraf-Khorassani et al., 1990) or dibenzo-*p*-dioxins and dibenzofurans (Alexandrou and Pawliszyn, 1989; Alexandrou et al., 1992), this fluid was completely inefficient for the extraction of incurred pirimicarb from

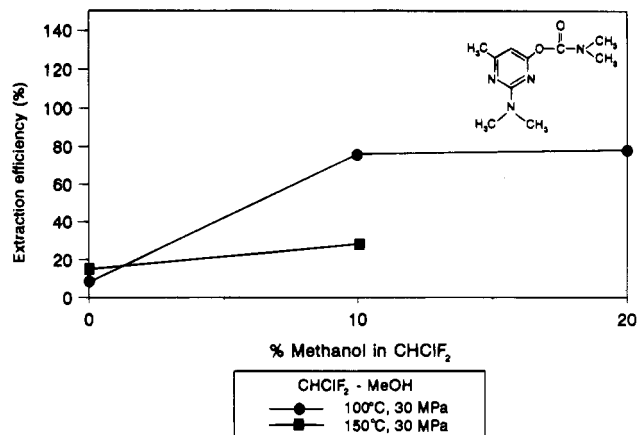


Figure 3. Extraction efficiency of pirimicarb from topsoil according to the percentage (v/v) of methanol (MeOH) as static modifier of supercritical CHClF₂ at 100 and 150 °C and 30 MPa. All data points correspond to the mean of two replicates.

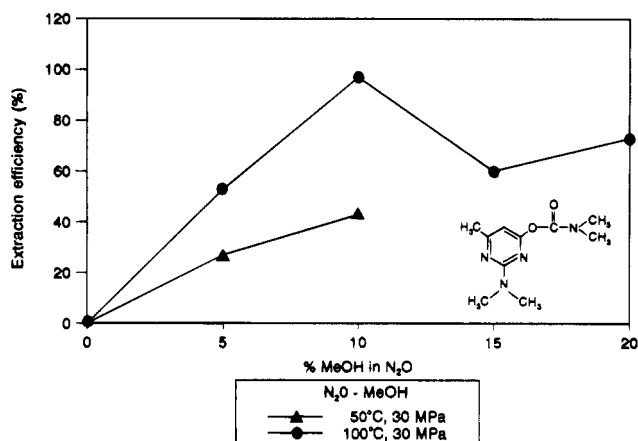


Figure 4. Extraction efficiency of pirimicarb from topsoil according to the percentage (v/v) of methanol (MeOH) as static modifier of N₂O at 50 and 100 °C and 30 MPa. All data points correspond to the mean of two replicates.

soil (Figure 4), probably because of the stronger binding behavior of this pesticide to the soil.

Considering the poor recoveries of pirimicarb from soil found with all of the neat fluids used in the present study and its moderate solubility with all of the neat extractant agents used (Ashraf et al., 1992), it is plausible that matrix analyte interaction is the limiting factor in the extraction process. Therefore, we assume that whenever extractant agent is able to compete with a higher affinity for the same active points of the matrix, the analyte should be released and, thereby, the extraction efficiency maximized (Dooley et al., 1987). In this way, according to the extraction efficiency of pirimicarb obtained with the different fluids and their physical-chemical properties, we would be able to characterize its mechanism of interaction with the matrix.

Accordingly, a variety of primary fluid modifiers were examined (Table 2) to improve the extraction efficiency of pirimicarb. The addition of from 0 to 20% methanol in CO₂ led only to a moderate increase in the extraction efficiency (20–60%) at 5% MeOH in CO₂, decreasing at higher concentration of the fluid-modifier added (Figure 2). These results could be explained by a mismatch between the solubility parameter of modifier fluid versus analyte, which leads to a decrease in solubility (King and France, 1992). A similar trend was found in the case of N₂O-methanol, but quantitative extractions were achieved using 10% methanol in N₂O at 100 °C.

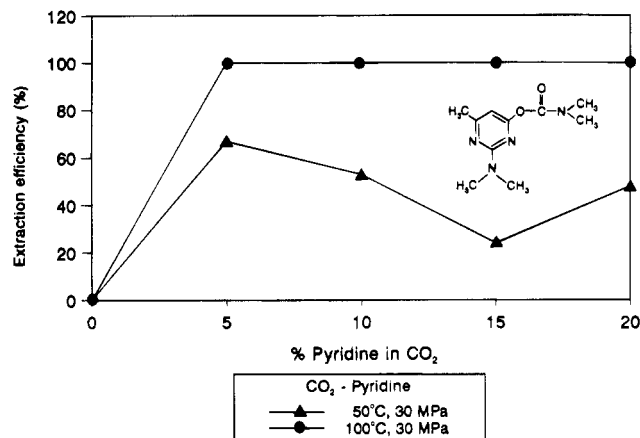


Figure 5. Extraction efficiency of pirimicarb from topsoil according to the percentage (v/v) of pyridine as static modifier of CO₂ at 50 and 100 °C and 30 MPa. All data points correspond to the mean of two replicates.

At lower temperatures the recovery was poorer. The basic properties of the primary fluid (N₂O) combined with the strong dipole moment of methanol could be responsible for this behavior. The use of modified N₂O with methanol has been evaluated previously for the extraction of spiked aromatic amines from soil, and it has been found that the presence of a secondary modifier greatly improved their extraction efficiency (Oostdyk et al., 1993).

On the other hand, modified chlorodifluoromethane with methanol was attempted to further increase the primary fluid polarity (**Caution:** Spark formation was encountered during the decompression of chlorodifluoromethane–methanol.) Indeed, only a moderate improvement of extraction efficiency was found (Figure 3), which could be attributable to the fact that increasing further the extractant agent polarity and the hydrogen bonding ability did not improve either the desorption or the elution rates of analyte (Pawliszyn, 1993).

To confirm the significance of acid–base interactions in the pirimicarb extraction found previously with nitrous oxide–methanol, carbon dioxide modified with pyridine was used (Figure 5). A significant increase in extraction efficiency was obtained even at low concentrations of static modifier added (5%) when higher temperature was used (100 °C). These results clearly point out the relevance of pirimicarb binding onto acidic points of the matrix. Oostdyk et al. (1993) have also found a significant improvement on the extraction of aliphatic and aromatic amines when 1,6-hexanediamine in methanol was used as modifiers of nitrous oxide.

Further experiments were carried out to ascertain the binding mechanism of pirimicarb to soil since the high extraction efficiency found when pyridine was used as modifier could be attributable to several kinds of interactions (dispersive and dipolar, see Table 2) in addition to acid–base. Accordingly, modifiers without acid–base interactions were used (Figure 6). Toluene was chosen to determine the extent of dispersive and π – π interactions, methanol as dipolar and pyrrolidine and triethylamine as acid–base. Triethylamine exhibited a high extraction efficiency at 100 °C, likewise pyridine; both of them matched the Soxhlet results. Conversely, pyrrolidine and toluene were completely ineffective. While the former compound could react with carbon dioxide since the reactivity of secondary amines in supercritical conditions is well-known (Ashraf-Khorassani et al., 1990), the second modifier confirms the

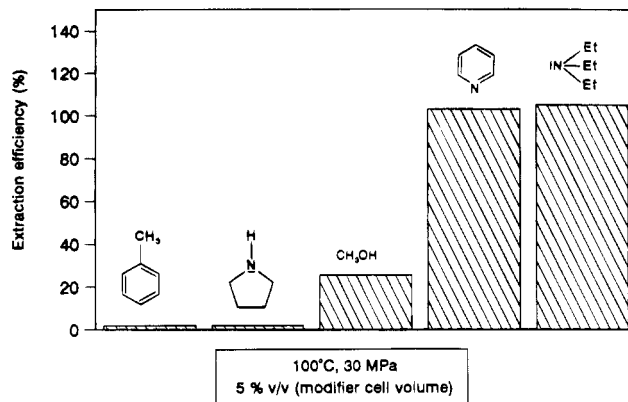


Figure 6. Intercomparison of the extraction efficiency of pirimicarb from topsoil according to the static modifier of CO₂ (5% v/v/cell volume) at 100 °C and 30 MPa.

Table 5. Comparison between Extraction Techniques

extraction technique	concn (ng/g)	SD (%)	RSD	N
Soxhlet	120.2	10.89	9.05	4
SFE ^a	123.7	2.59	2.01	9

^a Extraction was performed at 100 °C, 30 MPa, 5% (v/v) pyridine cell volume.

lack of significance of dispersive and π – π interactions in the SFE of pirimicarb.

Very recently, Langenfeld et al. (1994) have evaluated a variety of CO₂ organic modifiers for the extraction of PCB and PAH in a variety of matrices, and they concluded that modifiers should be selected according to matrix and analyte characteristics.

Effect of temperature was investigated for the three neat fluids and in the presence of methanol (Figures 2–4) and pyridine (Figure 5) as modifiers. Usually, the higher the temperature, the higher the recovery. Only chlorodifluoromethane exhibited an opposite trend, probably associated with the higher temperatures evaluated (100–150 °C), taking into account its higher critical temperature compared to the other fluids used (Table 1), which could lead to a limited thermal stability of the analyte during the SFE. Langenfeld et al. (1993) found a remarkable increase in the extraction efficiency of PAHs and PCBs with neat fluids by raising the extraction temperature, and it was suggested as an alternative method to the use of modifiers. In the present study, the presumably reduced thermal stability of analyte (*Agrochemicals Handbook*, 1993) did not enable evaluation of the extraction efficiency at higher temperatures as suggested for PCB and PAH (200 °C), but when the temperature was raised from 50 to 100 °C, the extraction efficiency increase was only significant in the case of modified fluids. Another possible explanation of this effect could be attributable to the lack of miscibility between the primary fluid and modifier at lower temperatures, which could result in different types of flow patterns (Coulson and Richardson, 1977). Further research is necessary to understand the phase behavior of binary systems other than CO₂.

Comparison between Soxhlet and SFE. Quantitative results of the pirimicarb determination in the soil sample are shown in Table 5. There is remarkable agreement between the extraction techniques when 5% of either pyridine or triethylamine was used as carbon dioxide modifier. Nevertheless, SFE provided a significantly higher precision compared to Soxhlet extraction, although the number of replicates was higher (Table 5). The lower extraction selectivity in the Soxhlet procedure

could be due to more interferences in the cGC-NPD determination in comparison with SFE. Furthermore, extraction time is remarkably reduced from 18 h in the Soxhlet procedure to 30 min in SFE. The solvent usage is also reduced by a factor of 10 from Soxhlet to SFE.

Conclusions. Despite the solubility of pirimicarb into the neat fluids investigated (CO_2 , N_2O , and CHClF_2), its SFE extraction from incurred topsoil sample was ineffective in the range from 50 to 100 °C at 30 MPa. The addition of polar modifiers to carbon dioxide led only to a moderate increase in the extraction efficiency, but the use of a primary fluid with basic properties such as nitrous oxide modified with 10% MeOH or the use of carbon dioxide modified with basic compounds (triethylamine or pyridine) led to comparable quantitative results to those obtained with Soxhlet extraction with methanol. Extraction time and solvent usage were considerably reduced in the SFE in comparison with the Soxhlet extraction procedure. Moreover, the precision of whole analytical procedure was improved by a factor of 4.

The high extraction efficiency of pirimicarb obtained only with the basic modifiers of carbon dioxide used at high temperature suggests that a specific competition mechanism between analyte and modifier for the same active points of the matrix is the prevailing factor for its quantitative extraction by SFE. Therefore, the binding mechanism of pirimicarb to the soil sample could be attributable to the interactions with the acidic active points of the soil sample. Further research is needed to fully assess the use of SFE as a tool for the characterization of the binding mechanisms of pesticides in soils.

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