

Supercritical Fluid Extraction of the Pesticides Carbosulfan and Imidacloprid from Process Dust Waste

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Large amounts of contaminated process dust remain from the procedure of pesticide treatments applied to seed pellets. A pilot study in analytical-scale supercritical fluid extraction (SFE) was performed to determine the possibility of using supercritical carbon dioxide for the extraction of the nonpolar insecticide carbosulfan and the more polar insecticide imidacloprid present in contaminated dust waste, at concentrations of up to 20% (w/w). The effects of various experimental conditions, such as temperature, flow rate, and addition of modifier, on the recovery of the analytes were evaluated by extracting the pesticides both from spiked support material and from real dust samples. It was found that carbosulfan could easily be extracted from the dust waste within 30 min at 138 bar and 40 °C with a recovery of 98.9% (RSD = 2.3%, $n = 10$), compared to values obtained with a validated liquid extraction method. A sufficient removal of the more polar substance imidacloprid required the addition of a modifier, and the results showed a strong dependence of the extraction efficiency on the choice of modifier. Extractions at 276 bar and 80 °C with a solvent consisting of supercritical carbon dioxide modified with methanol (5%) gave a recovery of 97.0% (RSD = 3.6%, $n = 10$) using a 40 min extraction time. The results indicate that it seems to be possible to use process-scale SFE for the decontamination of pesticides from dust waste. The conditions outlined also permit analytical determinations of the two insecticides based on a combination of SFE and liquid chromatography.

Keywords: *Supercritical fluid extraction; SFE; insecticides; carbosulfan; imidacloprid; dust waste*

INTRODUCTION

Seeds have been pelleted in Europe since the 1960s to make irregularly shaped seeds more convenient to handle. Nowadays the procedure has been extended to incorporate pesticides in the filling material, to give each seed an appropriate amount of fungicides and insecticides (Dewar et al., 1987). Field studies by Winder (1990) and Drinkwater (1994) have pointed out the advantages of pesticide-pretreated seeds. However, these treatment procedures annually create tons of process dust waste contaminated with pesticides. In general, the dust is required to be nontoxic before disposal into a controlled landfill. This could be achieved by an extraction step with the intention to decrease the amounts of pesticides in the waste to a safe level. With supercritical carbon dioxide as extracting fluid, it would even be possible to collect the pesticides. Because the dust may contain up to 20% of the pesticide counted in weight by weight, the economical value of the extraction products is considerable.

Supercritical fluid extraction (SFE) as sample cleanup in analytical scale for extractions of different pollutants from solid samples has been well established. In the area of agrochemicals, SFE has been used for selective extractions of organophosphorus and organochlorine pesticides (Snyder et al., 1993; Ling et al., 1999; Hopper, 1999), carbamates (however, not including carbosulfan) (Howard et al., 1993; Izquierdo et al., 1996; Voorhees et al., 1998), and different herbicides (Howard and Taylor, 1993; Reighard and Olesik, 1997) from matrices

such as soils, sediments, plant tissues, and foods. In two papers by different groups (Koeber and Niessner, 1996; Valverde-Garcia et al., 1996) several pesticides including imidacloprid were extracted from soil and spiked vegetables with modified supercritical carbon dioxide. In both cases, the authors obtained poor recovery of imidacloprid, and to our knowledge, no further papers have appeared dealing with SFE of this substance.

Recently published papers concerning process-scale studies have shown the usefulness of SFE for the remediation of soil (Zaragosa et al., 1998), decontamination of fly ash (Gabarra et al., 1999), and removal of oil for recycling of steel (Fu et al., 1998). Thus, the development of a large-scale process for the extraction of pesticides from a solid matrix as dust waste seems to be possible.

In this paper we have used analytical-scale equipment to investigate conditions that allow different pesticides in dust waste to be efficiently extracted. We have also developed a methodology for the analytical determination of these pesticides. The two target substances, carbosulfan and imidacloprid, with a large difference in polarity, were chosen as model compounds to make it possible to extrapolate information to other pesticides.

EXPERIMENTAL PROCEDURES

Equipment. The SFE system used was a Hewlett-Packard (HP) 7680T extraction unit (Wilmington, DE) equipped with a Hewlett-Packard 1090 LC pump for addition of modifier. This is a computer-driven system with total software control. The SFE system is divided into two steps, one extraction and trapping step and one step to rinse the extracted analytes from the trap out into vials. HP standard 7 mL extraction vessels

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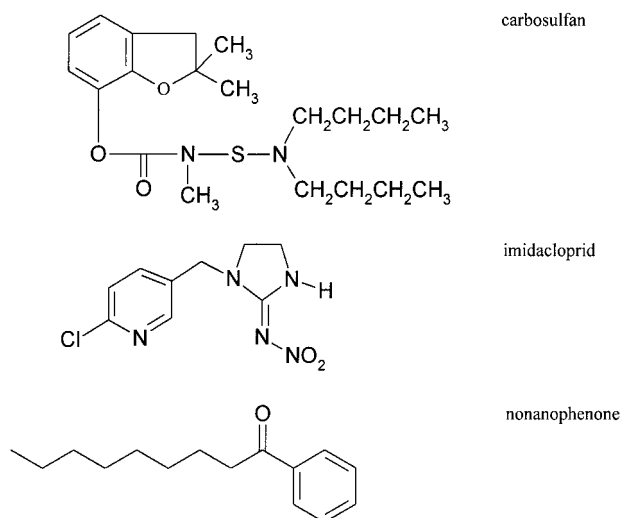


Figure 1. Chemical structures of carbosulfan [2,3-dihydro-2,2-dimethyl-7-benzofuran-7-yl(dibutylsminothio)methylcarbamate], imidacloprid [1-(6-chloro-3-pyridinylmethyl)-*N*-nitroimidazolidin-2-ylideneamine], and nonanophenone (internal standard).

and standard traps were used with octadecyl silica (ODS) as trapping material.

All extracts were analyzed by a liquid chromatography (LC) system consisting of an LKB 2150 high-pressure pump (LKB, Bromma, Sweden) run at 1 mL/min, a Kontron HPLC autosampler 460 (Kontron Instruments SpA, Milan, Italy), and a UV detector LDC/Milton Roy Spectromonitor (Milton Roy Co., Riviera Beach, FL) with the wavelength set to 220 nm for the analysis of carbosulfan and to 270 nm for the analysis of imidacloprid. A reversed phase C₁₈ column (5 μ m, 3.9 \times 250 mm, Hichrom, Reading, U.K.) was used for the separation. The mobile phases for LC used for the analysis of carbosulfan and imidacloprid were acetonitrile/water (85:15, v/v) or acetonitrile/water (80:20, v/v) at pH 2.5, respectively. The acidic water was prepared by adding 1.2 mL of phosphoric acid to 1 L of water. Chromatographic data were collected with Borwin (JMBS Developments, Le Fontanil, France) chromatographic data system software (version 1.21).

Samples. Dust samples were gathered and collected from filter wastes in the seed pellet production areas. The dust consisted of a solid polymer matrix, contaminated with either carbosulfan or imidacloprid. Because the pesticides in the dust could have a large difference in concentration (2–20% w/w), sample sizes of the dust ranged from 20 to 100 mg throughout the SFE experiments. Using these sample sizes it was found that no breakthrough of analytes occurred in the trapping procedure. All samples were stored in sealed beakers at 8 °C before they were extracted.

Chemicals. Carbon dioxide (4.8 grade, AGA gas AB, Sundbyberg, Sweden) was used as the extraction medium throughout. Methanol, acetonitrile, and acetone were all of HPLC grade and purchased from Merck (Darmstadt, Germany). All water used was of analytical quality. Orthophosphoric acid, triethylamine, and ethanolamine, all of analytical reagent quality, were obtained from Merck. Carbosulfan and imidacloprid were from Larodan Fine Chemicals AB (Malmö, Sweden), and nonanophenone (internal standard, I.S.) was from Lancaster (Morecambe, England). The chemical structures of carbosulfan, imidacloprid, and nonanophenone are presented in Figure 1.

Stock standard solutions of carbosulfan (20 mg/mL), imidacloprid (5.0 mg/mL), and nonanophenone (30 mg/mL) were all prepared in acetonitrile. All solutions were stored in darkness at 8 °C.

Procedures. *Supercritical Fluid Extraction.* Initially experiments were performed by extracting spiked insecticides from support materials to check their extractability in supercritical carbon dioxide and in methanol-modified carbon

Table 1. Recovery of Carbosulfan and Imidacloprid Spiked on Different Support Materials Using SFE (CO₂ at 276 bar, 40 °C, 4 mL/min, 20 min) (*n* = 2)

support material	carbosulfan recovery (%)	imidacloprid recovery (%)
stainless steel beads	99.8	93.8
glass beads	101	94.8
sea sand	86.6	30.9

dioxide, prior to extraction of real samples. These experiments were performed by loading, into the extraction vessel, 100 μ L of stock solutions either on sea sand (0.1–0.3 mm diameter, Merck), on stainless steel beads (500 μ m, Anval, Torshälla, Sweden), or on glass beads (0.2 mm diameter, Kebo Lab, Spånga, Sweden). The support material volume was 2 mL, filling up the extraction vessel to about one-third. The sample solvent was allowed to evaporate at low pressure before the real extraction step.

For the subsequent rinsing step, the analytes were eluted with 1.5 mL of acetonitrile. In all experiments 100 μ L of the internal standard (nonanophenone) solution was pipetted into the collection vials of the SFE unit to compensate for any variation of the volume. The vials were, after the extraction, gently shaken before LC analysis.

Liquid Extraction. For comparison, a validated in-house method based on liquid extraction was used. An amount of 10 g of dust was shaken with 50.0 mL of acetone (for carbosulfan) or acetonitrile (for imidacloprid) at 10 °C overnight. The extracts were transferred to tubes and centrifuged at 8000 rpm for 40 min. Internal standard was added, and the final LC analysis of the extracts was performed as described.

The values obtained with this validated method were considered as the true values. All SFE recovery values given in the text refer to the values obtained with this conventional method.

RESULTS AND DISCUSSION

Establishing Conditions for Efficient Trapping.

An efficient trapping is vital for subsequent work. To investigate the collection efficiency at different temperatures, carbosulfan was extracted from stock solution by varying the trap temperature between 10 and 80 °C. In the same way imidacloprid was studied at 40, 80, and 110 °C. A high temperature, still without analyte degradation, is of interest to use because it might prevent solvent condensation when there is a need for modifier. No differences in recoveries were found at different trapping temperatures for the two investigated compounds.

Rinsing of the trap with acetonitrile was performed at different temperatures (40–60 °C). In all cases both carbosulfan and imidacloprid were quantitatively eluted with 1.5 mL of solvent pumped at 1.0 mL/min. Further experiments were performed with an elution volume of 1.5 mL of acetonitrile and with the elution temperature set to 40 °C.

Extractions from Support Materials. The insecticides were spiked on different support materials (e.g., stainless steel beads, sea sand, and glass beads) as described previously. Extractions were performed at 40 °C and 276 bar (0.90 g/mL) for 20 min, with the flow rate set to 4 mL/min. The results are shown in Table 1.

It is obvious that analyte extractability is dependent on the support material chosen. High recoveries are reached for the two most inert materials. If only sea sand was considered, the poor recovery might have been attributed to low analyte solubility, but the results with stainless steel beads and glass beads show that it is most probably due to differences in analyte–matrix interactions. One explanation may be that sea sand,

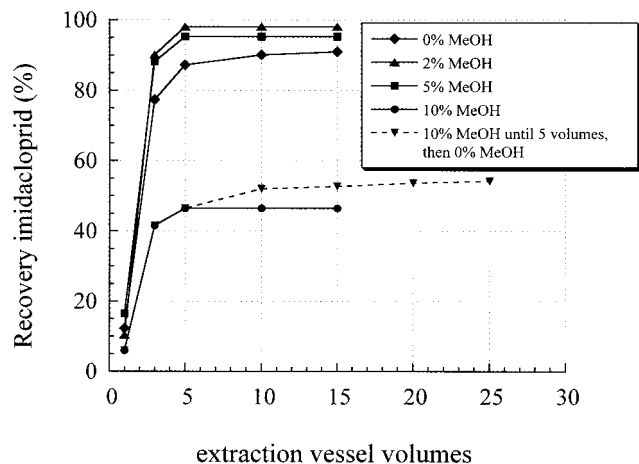


Figure 2. Recovery of imidacloprid spiked on stainless steel beads using different amounts of methanol as modifier to supercritical carbon dioxide. Conditions: pressure, 276 bar; extraction temperature, 40 °C (density, 0.90 g/mL); flow rate, 4 mL/min; trap temperature, 80 °C. Each datapoint is the mean of two measurements.

being less homogeneous than the other two support materials, offers the possibility of several types of interactions, for example, with highly charged cations. Decreased recoveries of analytes applied on sea sand compared to stainless steel or glass beads have also been observed by Järema et al. (1998) for the extraction of the drug clevidipine.

The results confirm that carbosulfan is sufficiently soluble in supercritical carbon dioxide. For imidacloprid complete recovery was not accomplished (94%) even with inert stainless steel beads in the extraction vessel, which indicates slight solubility problems or, alternatively, adsorption to the support matrix. Hence, to increase the extractability of imidacloprid, methanol was added as modifier. The trap temperature was now increased from 40 to 80 °C to prevent the condensation of methanol in the trap. This trap temperature has previously been found to be sufficient for up to at least 5% of methanol in the extraction fluid (Järema et al., 1998). In Figure 2 the recovery of imidacloprid using different concentrations of methanol in carbon dioxide is plotted versus extraction fluid volume (expressed as the number of extraction vessel volumes being swept with fresh supercritical fluid).

It is evident that a concentration of 2% methanol is sufficient to give 100% recovery of imidacloprid, whereas higher concentrations (10%) decreased the recovery. A visual inspection of the content in the extraction vessel after the extraction step showed that the steel beads were still wet, indicating that all of the methanol had not been dissolved in the CO₂. This was checked by another extraction, by pumping modifier until 5 extraction vessel volumes were swept by the extracting fluid and then continuing the extraction without modifier for another 20 extraction vessel volumes. This experiment, shown with broken lines in Figure 2, indicates that the rest of the methanol containing some amounts of analyte dissolves in the CO₂ when the extraction proceeds without any modifier. The recovery increases by some percentage units. However, the total recovery is still low. The reason could be that the high extraction efficiency with 10% methanol, combined with condensation of methanol on the trap, leads to a large loss of extracted analytes to the waste during the initial part of the extraction procedure.

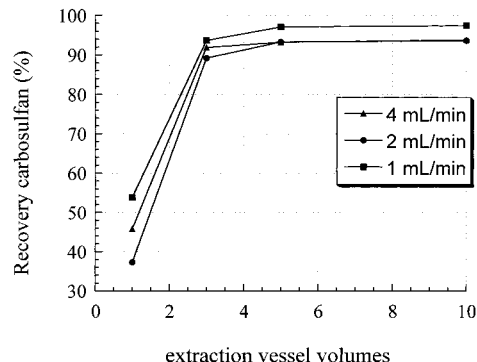


Figure 3. Recovery of carbosulfan from 20 mg of dust. Conditions: extracting medium, supercritical carbon dioxide; pressure, 138 bar; extraction temperature, 40 °C (density, 0.75 g/mL); trap temperature, 40 °C. Each datapoint is the mean of two measurements.

Extraction of Process Dust Waste Samples. Extraction of Carbosulfan. Initial extraction experiments of carbosulfan from dust showed no difference in recovery when a lower pressure (e.g., 138 bar, 40 °C) was chosen. Further extractions were therefore performed at 138 bar and at three different flow rates (1, 2, and 4 mL/min) with the other parameters as in the extractions from support materials. For each curve a fractionated extraction/elution procedure was run for a total amount of 70 mL of extraction fluid, corresponding to 10 extraction vessel volumes. The results are shown in Figure 3.

The recovery at 1 mL/min was ~98% compared to ~94% at 4 mL/min. The lower recovery is probably attributed to problems during the collection process, due to the large flow of gaseous carbon dioxide through the trap.

Extraction of Imidacloprid. A. Varying the Extraction Conditions with 2% Methanol as Modifier. When imidacloprid was extracted from support materials (276 bar, 40 °C, 4 mL/min) as reported above, it was found that using 2% methanol as modifier gave full recovery. For extractions of imidacloprid from the dust waste using the same conditions, a recovery of 59% (RSD = 10%, $n = 5$) was obtained within 30 min, which corresponds to a fluid volume of 15 extraction vessel volumes.

Further experiments showed that the recovery seemed to be virtually independent of the flow rate and that static extraction had no positive effect on the recovery in this case. Recoveries with a 10 min static/20 min dynamic procedure ($n = 2$) were in fact 7% lower than those from the dynamic procedure described above with other experimental conditions identical. These results indicate that a considerable portion of the pesticide is hard bound into the interior of the dust particles. Using 2% methanol as modifier is not sufficient to break the strong interaction between this part of the sample and the target substance. For the more loosely bound portion, which corresponds to ~60% of the total amount of analyte, the kinetics is fast as revealed by the similar recoveries at different flow rates. The seed pellets, from which the dust originates, contain the pesticide together with a binding component, normally a polymer material. It seems to be probable that the pesticides present in the interior of this polymer material will suffer from low diffusion constants and from strong adsorption to the matrix.

Table 2. Modifier Effects on the Recovery of Imidacloprid from Dust Waste Samples (SFE Conditions: 138 bar, 40 °C, 4 mL/min, 20 min Dynamic Extraction)

modifier conditions	% recovery (%RSD based on triplicate extractions)						
	methanol/CO ₂	acetonitrile/CO ₂	acetone/CO ₂	tetrahydrofuran/CO ₂	water/CO ₂	5% triethylamine in methanol/CO ₂	5% ethanolamine in methanol/CO ₂
2% ^a	47 (7)	26 (46)	15 (26)	17 (7)	14 (8)	44 (3)	51 (12)
5% ^a	69 (5)	58 (12)	38 (5)	45 (4)	12 (9)	56 (3)	66 (20)
1.6 mL ^b	35 (26)	36 (35)	47 (3)	43 (5)	8 (6)	59 (6)	67 (23)

^a Mixture of modifier and supercritical carbon dioxide added continuously to the extraction cell. ^b Pure modifier pumped into the extraction cell and, shortly after, 20 min continuous addition of supercritical carbon dioxide to the extraction cell.

B. Varying Type and Concentration of Modifier. From the results above it seems to be clear that some matrix modifications are needed to increase the recovery. The predominance of amorphous or crystalline regions in a polymer affects the permeability to the supercritical fluid. Usually the permeability decreases when the crystalline degree increases. Changing the temperature might change the degree of crystallinity, making the pesticides more difficult to extract (Nerin et al., 1997). Organic solvents are known to be able to swell a matrix, which might enable the fluid to extract the target substance. Recent results concerning vitamin extraction from milk powder have shown that ethanol added to the extraction cell could break the lactose shells, increasing the recovery of vitamins A and E toward 100% (Turner and Mathiasson, 2000).

Obviously 2% methanol was not sufficient to achieve acceptable recoveries when the dust matrix was extracted. Accordingly, higher concentrations of methanol as well as other modifiers were investigated. Because the purpose was to investigate differences in the extraction efficiencies of imidacloprid with various types and concentrations of modifier, a relatively short extraction time and moderate conditions were utilized (138 bar, 40 °C, 4 mL/min, 20 min dynamic extraction) in order to observe the recovery enhancements by modifiers. (Extraction with pure CO₂ under these conditions gave a recovery of 7.5% with RSD = 8%, $n = 3$.)

Furthermore, to facilitate the release of adsorbed imidacloprid molecules from the matrix, two amines (triethylamine and ethanolamine) were added to the modifier methanol. Amines such as triethylamine are commonly used in supercritical fluid or liquid chromatography to improve the chromatographic peak shapes by masking the residual silanols present on the stationary phase. To avoid modifier condensation, the trap temperature was set to at least 10 °C above the boiling point of the modifier. The results of experiments using different modifiers are shown in Table 2.

As expected, high concentration and increased solvent strength were beneficial for the extraction of the polar imidacloprid. Methanol at 5% was most efficient with a recovery of ~70%. The addition of basic compounds such as triethylamine and triethanolamine did not improve the recovery. An interesting point was that direct addition of acetone or tetrahydrofuran gave higher recoveries than continuous addition of 2% of modifier. (Addition of 1.6 mL of modifier directly corresponds to the same amount of modifier using 2% modifier continuously during a 20-min dynamic extraction step.) When water was used as modifier, low recoveries were obtained throughout the experiments, and this can be explained by the low solubility of water in the supercritical carbon dioxide, resulting in a two-phase system in the extraction vessel with the analytes remaining mainly in the water phase. Even if the

analytes can be extracted from the aqueous phase, this will need a larger volume of extracting fluid. An increase of the extraction time might in this case be beneficial.

A visual inspection of the extracts obtained using methanol with 5% ethanolamine (v/v) as modifier revealed a flocculate precipitation when acetonitrile was used as the collection solvent. This could be explained by carbamate formation, which tends to occur when organic bases react with CO₂ (Ashraf-Khorassani et al., 1990; Bartle et al., 1991). The filtering step introduced in the case here led to losses due to coprecipitation.

In the case of acetonitrile high RSD values were obtained in all experiments, indicating incomplete penetration of the modifier into the sample matrix in some of the three subsamples.

C. Effect of Pressure (Density) and Temperature. Experiments were undertaken to study the combination of temperature and pressure using 5% methanol as modifier. For other systems it has been demonstrated that by increasing the temperature, the extraction rate was profoundly increased (Langenfeld et al., 1995; Yang et al., 1995). Also, the pressure (density) of the extracting fluid is normally of great importance in the determination of the solubility of the analyte in the bulk fluid.

At 40 °C, two different pressures were tested, that is, 138 bar (0.75 g/mL) and 276 bar (0.90 g/mL), and the recoveries obtained after a 20 min extraction were 67 and 73%, respectively. At 80 °C, at same pressures, that is, 138 bar (0.37 g/mL) and 276 bar (0.75 g/mL), the recoveries were 29 and 91%, respectively. Increasing the extraction time to 3 h at the mildest SFE condition (138 bar, 40 °C) gave still not more than 75% recovery. These results showed that an increase in temperature and density is required to reach satisfactory recoveries.

The interactions between the analyte and the matrix can preferably be investigated by performing sequential extractions at different conditions (Bjorklund et al., 1999), and such an extraction profile is shown in Figure 4. SFE conditions were 138 bar and 40 °C for 20 min, 276 bar and 40 °C for 20 min, and 276 bar and 80 °C for 20 min.

From Figure 4 it can be seen that by the use of harsher SFE conditions imidacloprid molecules that are strongly bound to the dust matrix will be more easily released. By a sequential extraction it is obviously possible to extract the total amount of imidacloprid from the dust. If the purpose is to reuse the expensive pesticide and/or to decrease the amount of imidacloprid to a safer level before disposal, a process using mild conditions, for example, lower temperature, may be more economical even if complete recovery is then not achieved. A lower temperature will also give better selectivity toward coextraction of unwanted polymeric compounds often present in the dust, resulting in higher purity of the target compounds in the extract.

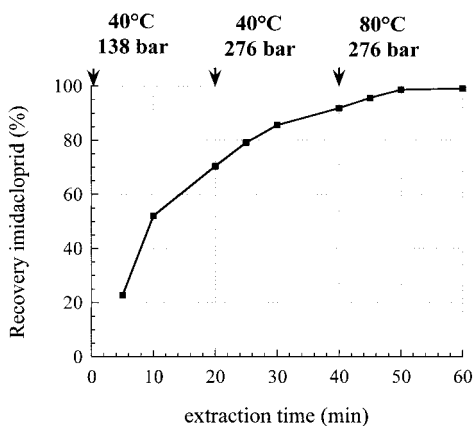


Figure 4. Extraction profile of imidacloprid from 100 mg of dust, using sequentially stronger SFE conditions. Conditions: extracting medium, methanol-modified (5%) supercritical carbon dioxide; flow rate, 4 mL/min; trap temperature, 80 °C. Each datapoint is the mean of two measurements.

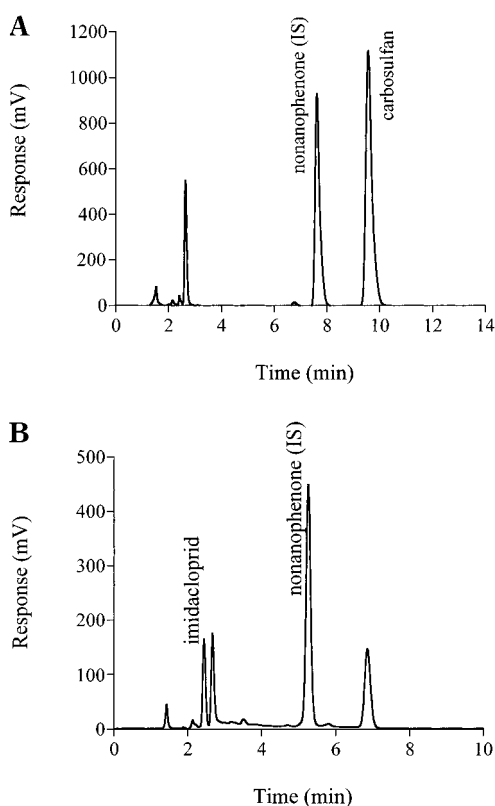


Figure 5. LC-UV chromatograms of extracts after (A) SFE (carbon dioxide, 138 bar, 40 °C, 1 mL/min) of dust containing carbosulfan and (B) SFE (methanol-modified (5%) carbon dioxide, 276 bar, 80 °C, 4 mL/min) of dust containing imidacloprid. LC conditions were as described under Experimental Procedures.

Analytical Aspects. It is obviously possible to completely extract nonpolar as well as polar pesticides from the dust using an appropriate combination of pressure and temperature and in the latter case also modifier. This can be of value if supercritical fluids are to be used in a remediation procedure and also if the pesticides need to be determined quantitatively for environmental or quality reasons.

Chromatography. Chromatograms of extracts obtained after SFE are shown in Figure 5.

Extracts of carbosulfan contained lower amounts of unwanted coextractants in the chromatograms com-

pared to these obtained from conventional solvent extraction. In the case of imidacloprid, the use of a modifier and a relatively high extraction temperature led to significant extraction of matrix compounds. The chromatograms of SFE extracts using the optimized conditions were almost identical to those of the conventional method. With respect to unwanted coextractants when using different modifiers, methanol and acetonitrile were the modifiers that gave imidacloprid extracts with fewer coextractants. However, the resolution between the analytes and possible interfering peaks was in all cases sufficient to permit relevant quantitation based on peak area.

Quantitation. The SFE procedures described above can be used for analytical determinations. In the case of carbosulfan, for multiple extractions of 20 mg of dust sample using supercritical CO₂ at final optimized analytical conditions (138 bar, 40 °C, 1 mL/min, 30 min dynamic, trap temperature = 40 °C), a recovery of 98.9% with an RSD value of 2.3% ($n = 10$) was obtained.

In the case of imidacloprid, further optimization was performed in an attempt to reduce the extraction time, by excluding the first and second steps in Figure 4. The third step with the SFE conditions 276 bar and 80 °C was thus performed in duplicate for 20, 30, and 40 min in a dynamic extraction mode. The recoveries obtained were 91, 95, and 98%, respectively. Multiple extractions of imidacloprid from 100 mg of dust were then performed with extraction time set to 40 min (276 bar, 80 °C, 4 mL/min, 5% methanol as modifier, trap temperature = 80 °C), which gave a recovery of 97.0% with an RSD value of 3.6% ($n = 10$). Judging from these results, a thermal degradation rate at 80 °C seems to be low, due to the high recoveries of imidacloprid obtained and the fact that the size of additional peaks remained unchanged throughout the entire investigation. High extraction temperature is thus not expected to give any problems. The risk of clogging in the restrictor due to coextraction of the polymeric matrix was found to be negligible. One aspect, however, to carefully consider in analytical extractions is the capacity of the collecting device. This is especially important when solid trap devices are used (Hartonen et al., 1997). Because the concentration of analytes in dust may be high (up to 20%), this may in some cases lead to fractionated extraction—eluting procedure to prevent analyte breakthrough in the trap.

To investigate if the few percent up to 100% missing in the obtained recoveries when using the final SFE conditions were due to inefficient trapping, the dust samples were taken from the extraction vessels after the completion of the SFE and treated with 2 mL of acetone or acetonitrile. These liquid extractions were performed in triplicate as described above under Procedures, Liquid Extraction. It was found that 0.35% carbosulfan (RSD = 30%, $n = 3$) and 2.9% imidacloprid (RSD = 16%, $n = 3$) were still in the matrix after SFE treatment. This confirms that the trapping procedure is sufficient. However, the small deviations from 100% recovery are in the case of carbosulfan less than the analytical error in the final LC determination. For imidacloprid the deviations are of the same order and can be tolerated in the quantitation.

Conclusions. This pilot study shows that the SFE technique is efficient for extracting nonpolar as well as polar pesticides from process dust waste remaining from seed pellet production. It seems to be possible to extend

the methodological approach toward pesticides other than those in the study, which can be of value if supercritical fluids are to be used in a remediation procedure.

Nonpolar compounds such as carbosulfan can be efficiently extracted using relatively small volumes of pure supercritical carbon dioxide, whereas polar pesticides such as imidacloprid need a modifier. With a volatile modifier such as methanol, also large-scale SFE ought to be possible without risk for condensation of modifier in the collection device, allowing continuous flow in the system with feedback of the supercritical fluid.

The developed methodology can also be used for analytical purposes, which has been convincingly shown for the two insecticides in this paper.

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