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Influence of ageing on the supercritical fluid extraction of pollutants in soils

V. Camel[a], A. Tambuté[b], M. Caude[a,*]

[a]*Laboratoire de Chimie Analytique de l'Ecole Supérieure de Physique et Chimie Industrielles de Paris, 10 Rue Vauquelin, 75231 Paris Cedex 05, France*

[b]*Direction des Recherches et Etudes Techniques, Centre d'Etudes du Bouchet, BP No. 3, Le Bouchet, 91710 Vert-le-Petit, France*

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Abstract

Soil samples were contaminated with several solutes, two means of contamination being evaluated to obtain homogeneous samples, in order to simulate real samples. The soils were allowed to age and periodically sampled. Letting the samples dry in a hood for less than 1 day resulted in a dramatic decrease in the recoveries, owing to evaporation of the spiking solvent. The extraction became generally more difficult as the ageing time increased, but the nature of both the solute and the soil had a strong influence on the results. Hence, a phosphonate and a phosphate were always quantitatively extracted, whereas aromatics were strongly retained in a very organic soil. Increasing the temperature, at constant pressure, greatly enhanced the extraction of all the investigated solutes. Similar results were obtained by adding methanol (10%, v/v) to the supercritical carbon dioxide; however, in that event, the dynamic time must be chosen with care, otherwise part of the extracted solutes is eluted from the trap by the polar modifier.

1. Introduction

For several years, considerable applications of supercritical fluid extraction (SFE) have been reported. Owing to the unique properties of supercritical fluids, this new technique has many advantages over classical extraction methods such as liquid–liquid extraction, namely speed of extraction, selectivity, safety, the possibility of direct coupling to chromatographic techniques [1–3] and mainly reduce the volumes of hazardous solvents. Indeed, the need for alternative extraction methods is emphasized by current efforts by the US Environmental Protection Agency to reduce by 95% the use of methylene chloride as an extraction fluid for environmental sample preparation in the next few years [4].

Supercritical carbon dioxide (CO_2) has proved to be efficient in removing selected pollutants from different environmental matrices [5], e.g., herbicides from soils [6,7], polychlorinated biphenyls (PCBs) from river sediments [8,9], polycyclic aromatic hydrocarbons (PAHs) from urban air particulate matter or soil [8,10] and total petroleum hydrocarbons (TPHs) from soils [11]. Unfortunately, supercritical CO_2 behaves as a non-polar extractant; so its extraction strength is insufficient for the quantitative recovery of many

* Corresponding author.

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polar analytes from adsorptive samples. As an example, phosphonates and phosphates in soil were not quantitatively extracted with pure CO_2 [12]. This problem may be partially overcome by the addition of a polar solvent (modifier) to the supercritical CO_2, either directly to the matrix itself or to the fluid via an additional pump. Thus, methanol-modified supercritical CO_2 gives much better recoveries for phosphonates and phosphates [12]. Methanol was also a good modifier during the SFE of organochlorine and organophosphorous pesticides from soils [13].

In some particular cases, a reactive modifier can be added to the matrix prior to the SFE. Some applications reported the in situ chemical derivatization of herbicides in soil and sediment using either trimethylphenylammonium hydroxide and boron trifluoride in methanol [14], or a mixture of tetrabutylammonium hydroxide and methyl iodide [15]. Also, the extraction of PAHs from urban dust and a marine sediment was greatly enhanced by the addition of a mixture of hexamethyldisilane and trimethylchlorosilane (2:1) to the CO_2, due to derivatization of the matrix [16].

Occasionally, other supercritical fluids have been preferred to CO_2 because of their higher solvation power. For example, N_2O gave better recoveries than CO_2 during the extraction of chlorinated dibenzofurans in municipal fly ash [17] or the extraction of amines from contaminated soils [18]; also, using $CHClF_2$ (Freon-22) or N_2O as the extractant greatly improved the recoveries of PCBs from sediment material, PAHs from petroleum waste sludge and PAHs from railroad bed soil [19]. However, the use of these fluids is not always possible. N_2O can oxidize some organic matrices, so we must take care with this supercritical fluid in order to avoid explosion hazards [20]. Despite its higher polarity, the use of $CHClF_2$ is also not recommended because of the negative environmental effects of Freons, particularly with ozone. For these reasons, CO_2 remains the most widely used extraction fluid.

The nature of the matrix to be extracted is of prime importance. For example, soils with a high organic content are known to usually retain polar solutes more strongly [21]. Numerous interactions may exist simultaneously between a solute molecule and a complex matrix. Spiking analytes on to heterogeneous matrices, such as soils, may not be a reliable means of representing the extraction behaviour of native analytes.

The purpose of this study was to investigate the reliability of employing SFE to extract pollutants from soil samples. The investigated solutes were two irritants (*o*-chlorobenzylidenemalonitrile and dibenzo[*b*,*f*]-1,4-oxazepin), and products related to toxic compounds, tributyl phosphate {a simulant, for the volatility, of a chemical warfare agent [O-ethyl,S-(2-diisopropylaminoethyl) methylphosphonothiolate or VX]}, pinacolyl ethyl methylphosphonate [a derivative of a chemical warfare agent (pinacolyl methylphosphonofluoridate or soman)], benzophenone (a final degradation product of the 3-quinuclidinyl benzylate or BZ) and methyl salicylate {a simulant, for the volatility, of a chemical warfare agent [bis(2-chloroethyl) sulfide or yperite]}. We also investigated two derivatives of the latter compound in order to determine the influence of the hydroxyl group on the retention.

We studied the effect of ageing (up to 60 days) for soil samples spiked using two techniques. The nature of the soil was also taken into account. The extraction conditions (pressure, temperature, addition of methanol to the CO_2) were changed to improve the recoveries.

2. Experimental

2.1. Reagents and chemicals

Ethyl salicylate (ES) and methyl 2-methoxybenzoate (MMYB) were obtained from Aldrich (Strasbourg, France) (purity 99%). Methyl salicylate (MS), methyl 2-methyl benzoate (MMB), tributyl phosphate (TBP), *o*-chlorobenzylidenemalonitrile (CB), dibenzo[*b*,*f*]-1,4-oxazepin (CR), 2-cyanodibenzo[*b*,*f*]-1,4-oxazepin (CR-CN), pinacolyl ethyl methylphosphonate (PEMP) and 2-methylcyclohexyl ethyl methylphosphonate (MCEMP) were synthesized

in our laboratory. Trimethyl phosphate (TMP) was obtained from Janssen Chimica (Noisy le Grand, France) (purity 97%). Benzophenone (B) was obtained from Prolabo (Paris, France) (purity 99%) and 2-chloro-5-nitrobenzophenone (ClNB) from Leune (Paris, France) (purity 99%). The structures and normal boiling temperatures of all the solutes and their related toxic compounds are illustrated in Fig. 1. Some of them were solids (CB, CR, CR-CN, B, ClNB) and others liquids (ES, MMYB, MS, MMB, PEMP, MCEMP, TBP, TMP) at room temperature.

Individual stock solutions of each solute at 1000 or 5000 ppm (μl l^{-1} for liquids, mg l^{-1} for solids) were prepared either in methanol (HPLC grade) or in diethyl ether (extra-pure grade) in order to spike the soil samples. They were kept in a refrigerator to avoid any degradation. However, as chemical degradation has been observed

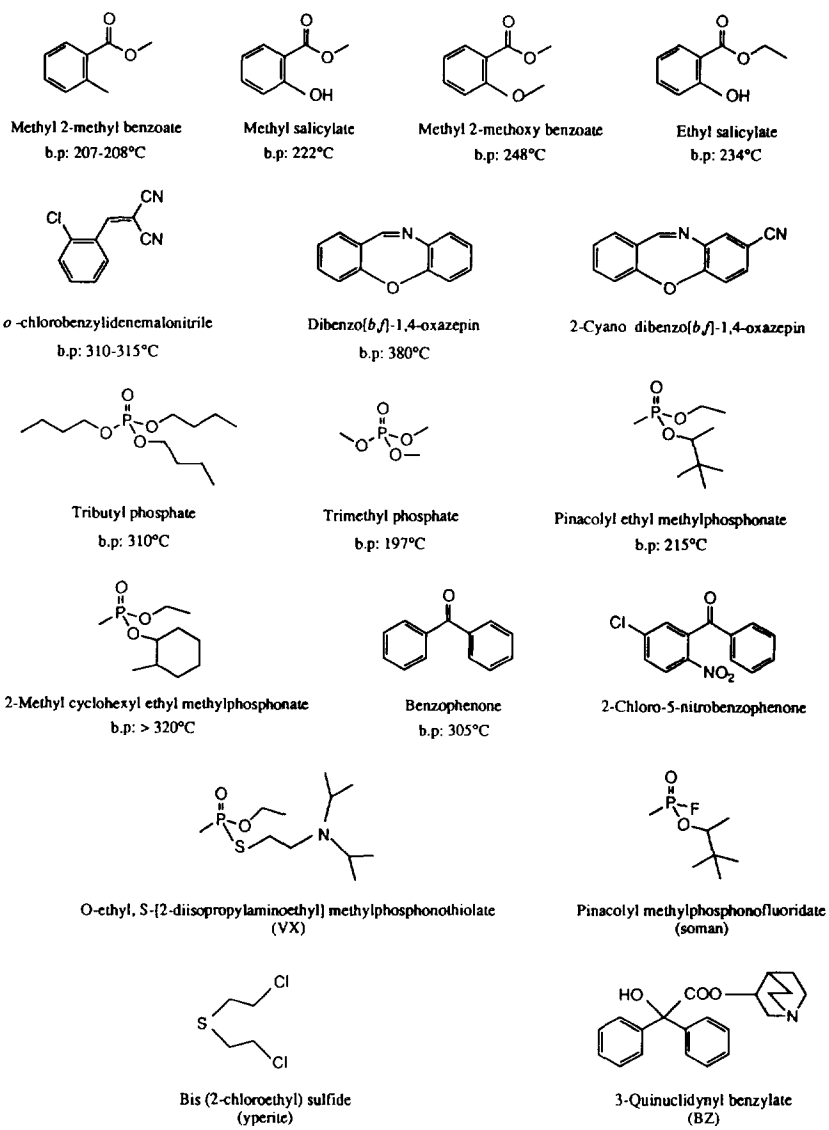


Fig. 1. Structures of the investigated compounds and of their related toxic compounds (b.p. = normal boiling temperature).

for CB in methanol, acetonitrile (gradient grade) was used as the solvent for the three related compounds CB, CR and CR-CN.

SFC-grade carbon dioxide (purity N 48; Alphagaz, Saint Quentin en Yvelines, France) was used as the supercritical fluid.

2.2. Soil samples

Three types of soil were used: a sand (a sandy loam soil: 83.4% sand, 13.7% silt, 2.9% clay, 0.4% moisture, 0.98% organic matter, surface area 1.6 $m^2 g^{-1}$); a podzol (91.9% sand, 5.4% silt, 2.7% clay, 1.1% moisture, 6.93% organic matter, surface area 0.4 $m^2 g^{-1}$) obtained from the French National Institute of Agronomic Research (INRA, Olivet, France); and an organic soil (9.6% sand, 59.6% silt, 30.8% clay, 25.8% organic matter) collected next to our laboratory (fine gravels were removed, then the soil was allowed to dry at room temperature for 1 week and sieved). For the sand and the podzol, the surface area was determined by the adsorption of liquid nitrogen at −195°C, using the Brunauer–Emmett–Teller (BET) method.

Contamination of the soil samples was performed using two different spiking methods.

In the "spot" method, approximately 5.5 g of soil were weighed in a cupel; 0.2 or 0.5 μl (for liquids) or 0.2 or 0.5 mg (for solids) of the solute(s) to be extracted (0.2 ml of the 1000 ppm solution or 0.1 ml of the 5000 ppm solution) were added directly to the soil and mixed with a spatula. This resulted in a contamination level of either 36 or 91 ppm. Then the sample was kept for an appropriate period of time (ageing time) in a hood at room temperature before its extraction.

In the "slurry" method, 300 g of dry soil were weighed into a flask; 10 μl (for liquids) or 10 mg (for solids) of each solute were mixed with 50 ml of diethyl ether, and the solution obtained was added to the soil. Then the flask was placed in a rotary evaporator for 1 h at 60°C in order to remove the diethyl ether gently. Assuming that the contamination was homogeneous, the contamination level was 33 ppm for each solute. The contaminated soils obtained were kept at room temperature and aliquots (5.5 g) were periodically sampled and extracted.

2.3. Supercritical fluid extraction

All SFE experiments were carried out using an HP 7680A supercritical fluid extractor (Hewlett-Packard France, Les Ulis, France). Approximately 5.5 g of soil were placed in the 7-ml thimble. The sample was typically extracted with CO_2 at 200 bar, 40°C (density 0.84 g ml^{-1}), and 1 ml min^{-1} of liquid CO_2 as the flow-rate in the dynamic mode. The nozzle was maintained at 45°C to prevent plugging. Extracted solutes were usually trapped on an octadecylsilica (ODS, 30–40 μm particle diameter) column maintained at 30°C. After the extraction, the trap was rinsed with 0.9 ml of methanol to elute the extracted solutes (one rinse was sufficient).

Each experiment was done in triplicate to give an average extraction recovery and a relative standard deviation (R.S.D.). In addition, blank extractions of the empty vessel were conducted between two experiments to clean the system. No memory effect was observed.

If insufficient recoveries were obtained after a typical dynamic extraction of 15 min with supercritical CO_2 (40°C, 200 bar, 1 ml min^{-1}), additional extractions were usually performed with methanol–supercritical CO_2 mixtures. Addition of methanol was made either directly to the sample (the soil was put back in the cupel and mixed with methanol; the sample was placed in the cell again and another extraction was performed), or continuously using an auxiliary pump (Hewlett-Packard Model 1050).

In some experiments, the gaseous CO_2 leaving the trap was collected in methanol using two successive vials, in order to dissolve the solutes that might be entrained out of the trap. Each vial contained 5 ml of solvent maintained at −14°C using a cryostat. After the extraction, the solutions were sonicated for a few minutes to remove the dissolved carbon dioxide, then 1.5 μl of each

vial content was analysed using gas chromatography, after the addition of an internal standard.

2.4. Gas chromatographic analysis

The extracts were analysed by gas chromatography with flame ionization detection (GC–FID) using a Varian Model 3400 instrument equipped with a Varian Model 8200 autosampler, a split–splitless injector and a 25 m × 0.25 mm I.D. fused-silica capillary column (CP-Sil-5 CB, 0.25 μm film thickness; Chrompack). Helium was used as the carrier gas (1 ml min^{-1}) and as the FID make-up gas (30 ml min^{-1}). The injector and detector temperatures were 250 and 300°C, respectively. Samples (1.5 μl) were injected with a splitting ratio of 1:25 using the solvent flush technique (methanol was used as the rinse solvent). A good separation of all the solutes was achieved using the following column temperature programme: 80°C for 4 min, ramped at 5°C min^{-1} to 120°C (maintained for 2 min) and at 5°C min^{-1} to 180°C (maintained for 15 min). The elution order of analytes was: trimethyl phosphate, methyl 2-methylbenzoate, methyl salicylate, pinacolyl ethyl methylphosphonate, ethyl salicylate, methyl 2-methoxybenzoate, 2-methylcyclohexyl ethyl methylphosphonate, *o*-chlorobenzylidenemalonitrile, benzophenone, tributyl phosphate, dibenzo[*b*,*f*]-1,4-oxazepin, 2-cyanodibenzo[*b*,*f*]-1,4-oxazepin and 2-chloro-5-nitrobenzophenone.

Quantification was based on the addition of an appropriate internal standard directly to the trap rinse solution: trimethyl phosphate for tributyl phosphate; ethyl salicylate for methyl salicylate, methyl 2-methylbenzoate and methyl 2-methoxybenzoate; 2-cyanodibenzo[*b*,*f*]-1,4-oxazepin for *o*-chlorobenzylidenemalonitrile and dibenzo[*b*,*f*]-1,4-oxazepin; 2-methylcyclohexyl ethyl methylphosphonate for pinacolyl ethyl methylphosphonate; and 2-chloro-5-nitrobenzophenone for benzophenone. Calibration graphs were obtained using a Shimadzu Model C-R5A integrator. Excellent correlation coefficients were obtained ($R > 0.9992$).

3. Results and discussion

A preliminary study was first conducted to check the efficiency of the collection step. Freshly contaminated samples were extracted at 40°C, 200 bar and 1 ml min^{-1} CO_2. After only 15 min (30 min for pinacolyl ethyl methylphosphonate), quantitative recoveries were obtained for all the solutes. Indeed, we expected the extraction to be easy, because the spiking solvent was initially present in the cell, and also the solutes did not have time to diffuse inside the matrix. In fact, these results underline the efficiency of the collection on an octadecylsilica column maintained at 30°C.

However, we noticed an entrainment effect with the more volatile solutes, methyl salicylate and methyl 2-methylbenzoate, for extraction times longer than 20–30 min (this was confirmed by collecting the CO_2 leaving the trap in methanol using two successive vials maintained at −14°C). Additional experiments showed that losses could be avoided by using a silica gel column, owing to hydrogen bonding between the solutes and the silanol groups of the silica.

3.1. Extraction of soil samples contaminated using the "spot" method

After their contamination, soil samples were kept in the hood at room temperature for a certain period of time. Several experiments were conducted to investigate the effect of the spiking solvent on the recovery. Because the nature of either the matrix, the solute or the solvent can have a strong influence on the results, several combinations were studied.

Sand–CB or CR–acetonitrile

Firstly, sand samples were contaminated with 0.5 mg of *o*-chlorobenzylidenemalonitrile or dibenzo[*b*,*f*]-1,4-oxazepin dissolved in acetonitrile, and allowed to dry in the hood at room temperature for about 1–3 days. Mean recoveries vs. extraction time are illustrated in Fig. 2. A 30-min extraction with pure CO_2 gave recoveries of only 30% for *o*-chlorobenzyl-

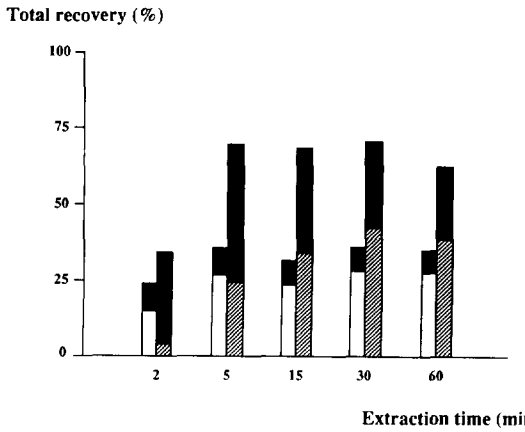


Fig. 2. Recoveries for *o*-chlorobenzylidenemalonitrile (CB) and dibenzo[*b*,*f*]-1,4-oxazepin (CR) from aged spiked sand samples (1–3 days) for several extraction times. CB: (□) 1st extraction; (■) 2nd extraction (addition of 0.2 ml methanol). CR: (▨) 1st extraction; (▩) 2nd extraction (addition of 0.2 ml methanol). Extraction conditions: $T_{cell} = 40°C$, $P = 200$ bar, 1 ml min^{-1} of liquid CO_2, $T_{nozzle} = 45°C$, $T_{trap} = 30°C$ (ODS), 0.2 min static followed by the dynamic period specified, spiking of 0.5 mg of each solute in acetonitrile.

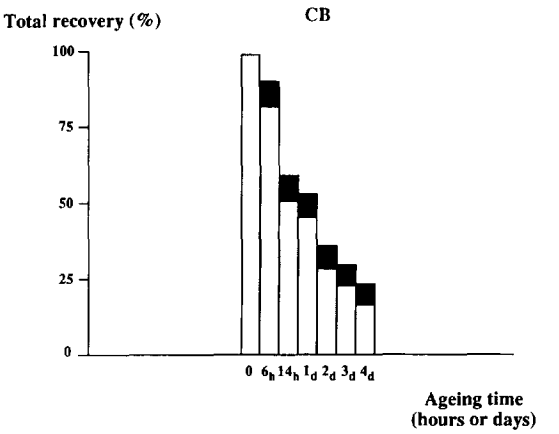


Fig. 3. Influence of the ageing time (up to 4 days) on the recovery of *o*-chlorobenzylidenemalonitrile (CB) added to sand samples using the "spot" method. (□) 1st extraction; (■) 2nd extraction (addition of 0.2 ml of methanol). Extraction conditions: $T_{cell} = 40°C$, $P = 200$ bar, 1 ml min^{-1} of liquid CO_2, $T_{nozzle} = 45°C$, $T_{trap} = 30°C$ (ODS), 0.2 min static followed by 15 min dynamic, spiking of 0.5 mg of CB in acetonitrile.

idenemalonitrile and 43% for dibenzo[*b*,*f*]-1,4-oxazepin. Apparently, no more solute could be extracted with longer extraction times (60 min) under these conditions (40°C, 200 bar, 0.84 g ml^{-1}). Extracting the samples at a higher temperature or pressure (density) would certainly result in improved recoveries, but the purpose of this study was simply to determine the role of the spiking solvent.

Each sample was re-extracted under the same conditions after the addition of methanol (0.2 ml) directly to the soil. As can be observed in Fig. 2, this solvent enhanced the extraction, especially for dibenzo[*b*,*f*]-1,4-oxazepin. This could result from hydrogen bonds between dibenzo[*b*,*f*]-1,4-oxazepin molecules and methanol. However, high relative standard deviations were obtained: 5–12% for dibenzo[*b*,*f*]-1,4-oxazepin and ca. 25% for *o*-chlorobenzylidenemalonitrile, probably because of differences in ageing times between triplicate samples (1–3 days). This was confirmed by performing 15-min extractions of aged samples (up to 4 days) contaminated with *o*-chlorobenzylidenemalonitrile (Fig. 3). The recoveries decreased after 6 h, but this time better relative standard deviations were obtained between the triplicate samples (2.4–18.5%). As no trace of any degradation product was detected by gas chromatography, part of the *o*-chlorobenzylidenemalonitrile may be either strongly bound to the matrix or, more probably, transformed into polar compound(s) that is (are) either difficult to extract or to determine using gas chromatography (as the normal boiling temperature of *o*-chlorobenzylidenemalonitrile is 310–315°C, the decrease in recoveries cannot be attributed to evaporation losses).

Organic soil–MMB, MS and MMYB–methanol

The next study was conducted to investigate the effect of ageing for other solutes. This time, organic soil samples were contaminated with methyl 2-methylbenzoate, methyl salicylate and methyl 2-methoxybenzoate using the "spot" method (methanol was used as the spiking solvent), and kept at room temperature in the hood for a given time (up to 4 days) before their extraction. As can be observed in Fig. 4, quan-

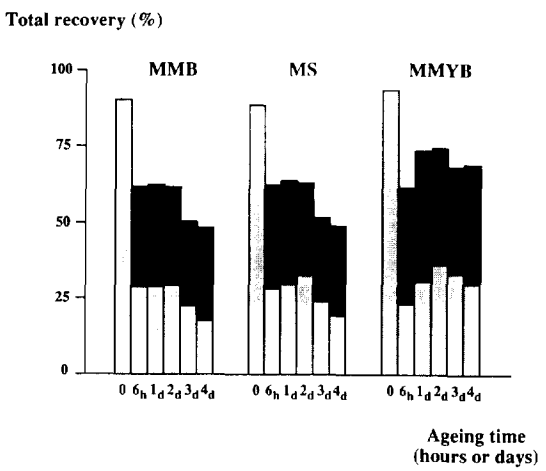


Fig. 4. Influence of the ageing time (up to 4 days) on the recovery of methyl 2-methylbenzoate (MMB), methyl salicylate (MS) and methyl 2-methoxybenzoate (MMYB) added to organic soil samples using the "spot" method. (□) 1st extraction; (■) 2nd extraction (addition of 0.2 ml of methanol). Extraction conditions: $T_{cell} = 40°C$, $P = 200$ bar, 1 ml min^{-1} of liquid CO_2, $T_{nozzle} = 45°C$, $T_{trap} = 30°C$ (ODS), 0.2 min static followed by 15 min dynamic, spiking of 0.2 μl of each solute in methanol.

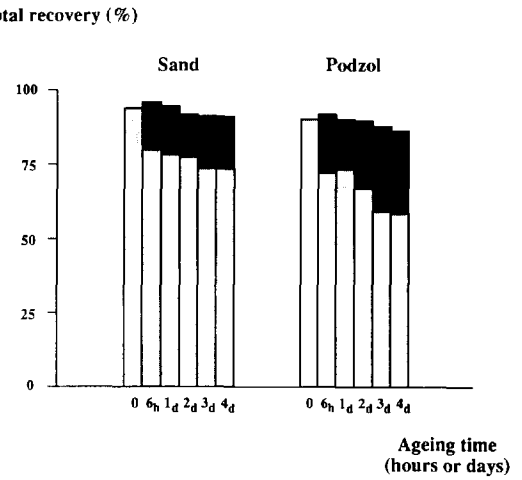


Fig. 5. Influence of the ageing time on the recovery of benzophenone (B) added to sand or podzol samples using the "spot" method. (□) 1st extraction; (■) 2nd extraction (addition of 0.2 ml of methanol). Extraction conditions: $T_{cell} = 40°C$, $P = 200$ bar, 1 ml min^{-1} of liquid CO_2, $T_{nozzle} = 45°C$, $T_{trap} = 30°C$ (ODS), 0.2 min static followed by 15 min dynamic, spiking of 0.2 μl in methanol.

titative extractions could be obtained for the three solutes immediately after their spiking. However, letting the samples dry in the hood (even for only 6 h) led to lower recoveries. This phenomenon can be explained either by the strong adsorption of the solutes molecules on the active sites of the matrix (the partitioning of the solutes is controlled by the "chemistry of the system"), or by the evaporation of methanol (methanol enhances the solute extraction).

Improved recoveries could be obtained after the addition of 0.2 ml of methanol directly to the soil samples and the performance of another extraction. Hence the low recoveries observed after the first extraction are mainly attributable to the absence of methanol.

Sand or podzol–B–methanol

In a similar study, we contaminated sand and podzol samples with 0.5 mg of benzophenone (methanol as the spiking solvent) and allowed them to dry in the hood (up to 4 days). Once extracted with pure CO_2 for 15 min, each sample was re-extracted after the addition of methanol (0.2 ml) directly to the soil. As illustrated in Fig. 5, benzophenone was easily extracted. Quantitative recoveries (around 90%) were obtained for freshly contaminated samples. Letting the samples dry resulted in slightly lower values, especially for podzol. However, 15-min extractions with pure CO_2 under moderate conditions (40°C, 200 bar, 1 ml min^{-1}) gave better results than for the solutes we studied earlier: 73% for sand and 58% for podzol after 4 days of ageing. In addition, high recoveries could be obtained after the second extraction, 91% and 86%, respectively. All the above results underline the fact that the spiking solvent enhances the extraction. Letting the solvent evaporate leads to two cases, depending on the solute nature. For non-polar compounds (i.e., highly soluble in pure supercritical carbon dioxide), quantitative extractions will still be obtained under the same conditions. In contrast, for the others, lower recoveries will be obtained. In fact, the latter case seems more frequent. To overcome the solute retention inside the matrix, a modifier can be added; however, a large solvent volume will lead to losses if

small columns are used to trap the analytes (owing to an elution effect inside the trap).

In order to simulate real soil samples, we further contaminated larger amounts of soil (300 g) according to the "slurry" method described earlier.

3.2. Extraction of soil samples contaminated using the "slurry" method

Influence of ageing time on the recoveries

Organic soil–MS and TBP–diethyl ether. Similar experiments were conducted with organic soil samples contaminated using the "slurry" method with methyl salicylate and tributyl phosphate (organic soil A). Extraction conditions were the same as above (Table 1). The results are illustrated in Fig. 6a. Whereas tributyl phosphate was still quantitatively extracted, methyl salicylate remained strongly retained on the matrix. Good relative standard deviations could be obtained between samples, showing the homogeneity of the contamination.

Organic soil–all investigated solutes–diethyl ether. Finally, the same protocol was used to contaminate the organic soil with all eight solutes investigated. Two kinds of soil samples were obtained (organic soils D_1 and D_2). Assuming the contamination was homogeneous, soil D_1 would contain 33 ppm of each solute. Soil D_2 would differ from soil D_1 in that benzophenone was ten times more concentrated (330 ppm) (we wanted to see if, with such a high concentration, the ODS trap would be overloaded, thus leading to inefficient collection).

The results obtained for D_1 are illustrated in Fig. 6b. Whereas pinacolyl ethyl methylphosphonate and tributyl phosphate could be quantitatively extracted for all samples, the mean recoveries decreased with ageing time for the other solutes, showing the progressive retention of the solute molecules on less accessible active sites. The fact that only aromatics were retained in the organic soil was probably due to $\pi-\pi$ interactions between these solutes and the organic matter of the soil [22]. Pinacolyl ethyl methylphosphonate and tributyl phosphate have neither a polar group nor an aromatic ring; as a consequence, they were easily extracted from the organic soil.

No trace of *o*-chlorobenzylidenemalonitrile could be detected in the extracts. Instead, one of its retro-synthesis product (*o*-chlorobenzaldehyde or CB*) was found. As this compound could not be detected for soil samples previously contaminated using the "spot" method, we believe that the higher temperature (60°C) used during the "slurry" contamination method enhanced the degradation of *o*-chlorobenzylidenemalonitrile. Thus, the following reaction seemed to take place:

Table 1
Experimental conditions for successive extractions

Successive extraction	Static period (min)	Dynamic period (min)	Volume of modifier added to the soil (μl)	Modifier added to the CO_2
1st	0.2	15	0	None
2nd	0.2	15	0	3% CH_3OH
3rd	0.2	15	0	5% CH_3OH
4th	5	15	500	None
5th	0.2	15	0	20% CH_3OH

$T_{cell} = 40°C$, $P = 200$ bar, 1 ml min^{-1} CO_2 liquid, $T_{trap} = 30°C$, $T_{nozzle} = 45°C$.

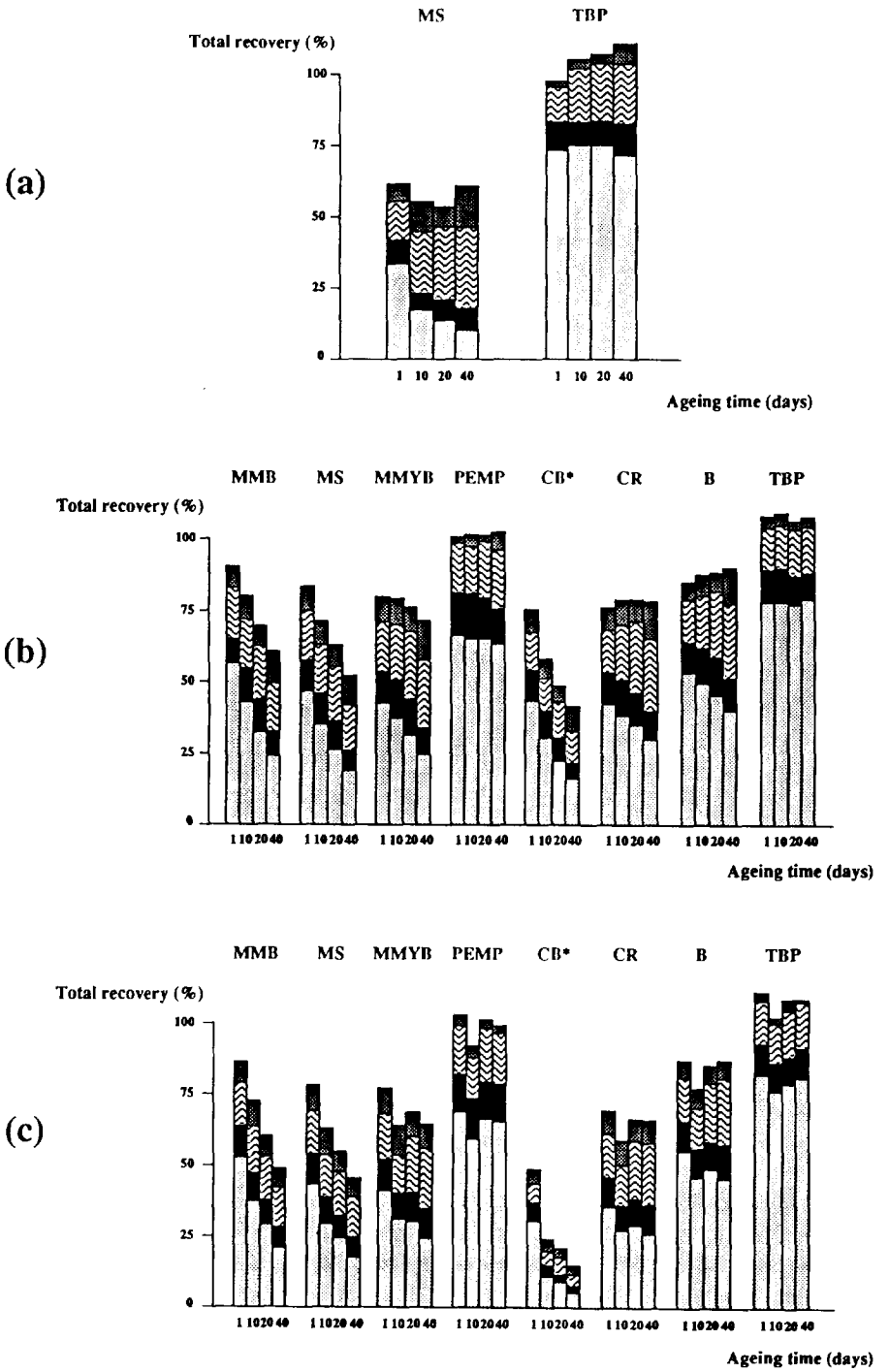
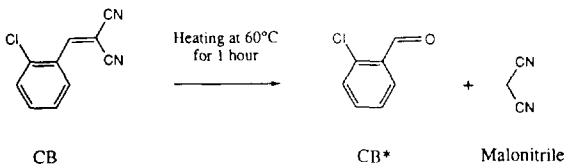


Fig. 6. Influence of the ageing time on the recovery of solutes added to organic samples using the "slurry" method. (a) Organic soil A; (b) organic soil D_1; (c) organic soil D_2. (□) 1st extraction; (■) 2nd extraction; (▨) 3rd extraction; (▩) 4th extraction. Extraction conditions: as in Table 1.



However, we cannot be certain that all the *o*-chlorobenzylidenemalonitrile was degraded, because no quantitative recoveries of *o*-chlorobenzaldehyde could be obtained. The other degradation product, malonitrile, was not present in the extracts; this might be due to its strong adsorption on the active sites of the matrix.

Similar results were obtained for D_2 (Fig. 6c), showing that the contamination level of B was still acceptable for the trap. Lower recoveries were observed for *o*-chlorobenzaldehyde, perhaps because less *o*-chlorobenzylidenemalonitrile had been degraded or because a stronger retention in the matrix took place.

The above results underline the homogeneity and the reproducibility obtained with such a contamination method.

A visual observation could be made whenever 0.5 ml of methanol was added directly to the organic soil samples: the extracts became yellow (for sand samples the colour was also visible, but it was less pronounced). This indicates that the addition of a modifier may entail the co-extraction of solutes and materials from the matrix (this could lead to a lower solubility of the investigated solutes in the supercritical fluid). Fortunately, in our study, they did not interfere with the solutes during the gas chromatographic analysis.

Effect of extraction conditions on recoveries

In order to improve the extraction recoveries of all the solutes from D_1 (ageing time ca. 55–60 days for the following experiments), we investigated the effect of changing either the density, the temperature or the nature of the fluid. The results are illustrated in Fig. 7.

Increasing the density at 40°C (0.95 instead of 0.84 g ml^{-1}) had no significant influence on the recoveries. On the other hand, elevating the temperature from 40° to 100°C resulted in enhanced recoveries, despite the fact that the density was lowered (0.74 g ml^{-1}). This positive effect of the temperature has already been observed during the extraction of native PAHs [10,23] and PCBs from sediments [8,9]. It probably results from an increase of the analytes' volatility (for the volatile compounds) or/and an easier desorption of the solute molecules from the active sites of the matrix. The distribution constant of a solute between the matrix and the fluid is defined as the ratio

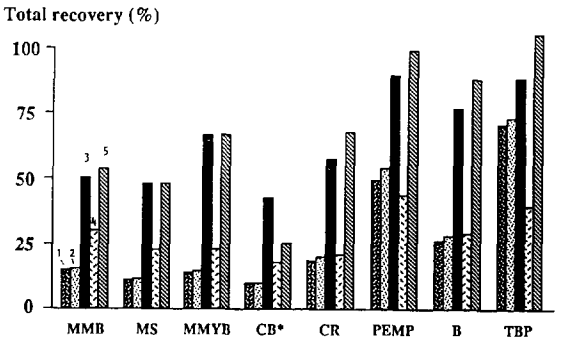


Fig. 7. Influence of the extraction conditions on the recovery of solutes added to organic soil samples using the "slurry" method (ageing time 55–60 days). (1) CO_2, 40°C, 200 bar, 0.84 g ml^{-1}, 15 min; (2) CO_2, 40°C, 383 bar, 0.95 g ml^{-1}, 15 min; (3) CO_2, 100°C, 379 bar, 0.74 g ml^{-1}, 15 min; (4) CO_2 + 10% CH_3OH, 40°C, 200 bar, 15 min; (5) CO_2 + 10% CH_3OH, 40°C, 200 bar, 3 × 5 min. Extraction conditions: 1 ml min^{-1} of liquid CO_2, T_{nozzle} = 45°C, T_{trap} = 30°C (ODS), 0.2 min static.

$$K = C^{M}/C^{SF}$$

where C^{M} and C^{SF} are the concentrations in the matrix and in the supercritical fluid, respectively. It is well known that K depends strongly on the temperature T, according to

$$\log K = -\Delta G/RT$$

where ΔG is the free energy and R the gas constant. As a consequence, an increase in temperature would lead to a decrease in K and, thus, to a higher solute concentration in the fluid.

Finally, adding 10% methanol (with a second pump) to the supercritical carbon dioxide slightly improved the recoveries of most of the solutes, compared with the results obtained with pure

CO_2 under the same conditions (Fig. 7). For benzophenone, similar results were observed; this was expected because this solute is non-polar. However, the observed recoveries of pinacolyl ethyl methylphosphonate and tributyl phosphate were reduced. This was surprising, as the addition of a modifier is known to have either a positive influence or no effect. We therefore suspected elution of the solutes by the modifier inside the trap during the extraction. To check this assumption, we conducted the same experiments but, this time, we performed three successive 5-min extractions. The gaseous CO_2 was collected using two successive vials filled with 5 ml of methanol at −14°C; they were changed and analysed after each 5-min extraction. The total recoveries for the three successive extractions are illustrated in Fig. 7. Much better values were obtained with this method than after a single 15-min extraction. This clearly demonstrates that during the 15-min extraction, the extracted solutes were partially eluted from the trap by methanol.

Again, employing methanol-modified CO_2 resulted in yellow extracts, because some matrix materials were co-extracted.

4. Conclusions

The supercritical carbon dioxide extraction of several solutes has been investigated. The spiking solvent, whatever its nature (methanol, acetonitrile or diethyl ether), enhanced the extraction. The retention depended on the nature of the soil–solute system. Whereas pinacolyl ethyl methylphosphonate and tributyl phosphate were quantitatively extracted, aromatics remained strongly bound to the matrix (probably owing to $\pi-\pi$ interactions between aromatics and the organic matter).

The addition of methanol to the CO_2 resulted in higher recoveries; however, care must be taken to avoid elution of the extracts by the modifier inside the solid trap. In addition, yellow extracts were obtained because of the co-extraction of soil materials. These two drawbacks can be avoided by increasing the extraction temperature instead of adding modifier to the fluid. This much easier way of obtaining high extraction recoveries should give acceptable results for real samples.

References

[1] L. Myer, J. Tehrani, C. Thrall and M. Gurkin, *Int. Labmate*, 15, No. 7 (1991) 15–19.
[2] J.L. Guinamant, *Analusis*, 20 (1992) m36–m38.
[3] V. Camel, A. Tambuté and M. Caude, *Analusis*, 20 (1992) 503–528.
[4] S.B. Hawthorne, in S.A. Westwood (Editor), *Supercritical Fluid Extraction and its Use in Chromatographic Sample Preparation*, Blackie, Glasgow, 1993, p 39.
[5] V. Camel, A. Tambuté and M. Caude, *J. Chromatogr.*, 642 (1993) 263–281.
[6] S. Ashraf, K.D. Bartle, A.A. Clifford, R. Moulder, M.W. Raynor and G.F. Shilstone, *Analyst*, 117 (1992) 1697–1700.
[7] T.R. Steinheimer, R.L. Pfeiffer and K.D. Scoggin, *Anal. Chem.*, 66 (1994) 645–650.
[8] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller and J. Pawliszyn, *Anal. Chem.*, 65 (1993) 338–344.
[9] H.-B. Lee and T.E. Peart, *J. Chromatogr. A*, 663 (1994) 87–95.
[10] J.M. Levy, L.A. Dolata and R.M. Ravey, *J. Chromatogr. Sci.*, 31 (1993) 349–352.
[11] V. Lopez-Avila, J. Benedicto, N.S. Dodhiwala, R. Young and W.F. Beckert, *J. Chromatogr. Sci.*, 30 (1992) 335–343.
[12] W.H. Griest, R.S. Ramsey, C.-H. Ho and W.M. Caldwell, *J. Chromatogr.*, 600 (1992) 273–277.
[13] J.L. Snyder, R.L. Grob, M.E. McNally and T.S. Oostdyk, *Anal. Chem.*, 64 (1992) 1940–1946.
[14] S.B. Hawthorne, D.J. Miller, D.E. Nivens and D.C. White, *Anal. Chem.*, 64 (1992) 405–412.
[15] V. Lopez-Avila and N.S. Dodhiwala, *J. Agric. Food Chem.*, 41 (1993) 2038–2044.
[16] J.W. Hills and H.H. Hill, *J. Chromatogr. Sci.*, 31 (1993) 6–12.
[17] F.I. Onuska, K.A. Terry and R.J. Wilkinson, *J. High Resolut. Chromatogr.*, 16 (1993) 407–412.
[18] M. Ashraf-Khorassani, L.T. Taylor and P. Zimmerman, *Anal. Chem.*, 62 (1990) 1177–1180.
[19] S.B. Hawthorne, J.J. Langenfeld, D.J. Miller and M.D. Burford, *Anal. Chem.*, 64 (1992) 1614–1622.
[20] D.E. Raynie, *Anal. Chem.*, 65 (1993) 3127–3128.
[21] M.D. Burford, S.B. Hawthorne and D.J. Miller, *Anal. Chem.*, 65 (1993) 1497–1505.
[22] M.H.B. Hayes, in B. Yaron, G. Dagan and J. Goldshmid (Editors), *Pollutants in Porous Media. The Unsaturated Zone Between Soil Surface and Groundwater*, Springer, Berlin, 1984, pp. 126–142.
[23] H.-B. Lee, T.E. Peart, R.L. Hong-You and D.R. Gere, *J. Chromatogr. A*, 653 (1993) 83–91.