Comparison of the extraction of phenolic and nitroaromatic pollutants using supercritical and enhanced-fluidity liquid methanol–CO_2 mixtures

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Abstract

The extraction of eleven phenols and nitroaromatics from an octadecyl polysiloxane stationary phase material is investigated using both supercritical fluid and enhanced-fluidity liquid conditions. Carbon dioxide and extraction fluid mixtures consisting of 10 and 20 mol% methanol in CO_2 are tested at 25, 45 and 65°C. Characteristic properties of the matrix, analytes and extraction fluids are examined in order to explain trends and controlling factors in extraction yields. As expected, the higher solvent strength of the methanol–CO_2 mixtures greatly reduces the volume and time required for efficient extraction compared to CO_2 alone. The effect of temperature is markedly less important than composition for the mixtures and matrix studied and the state of the extraction fluid, either liquid or supercritical, is irrelevant for the majority of analytes. The enhanced-fluidity liquid technique appears to be a viable alternative to supercritical fluid extraction for the extraction of polar analytes from more complex matrices.

Keywords: Environmental analysis; Extraction methods; Enhanced-fluidity liquids; Phenols; Nitroaromatic compounds; Aromatic compounds, nitro

1. Introduction

Supercritical fluid extraction (SFE) with carbon dioxide is a favorable method for the extraction of organic pollutants from solid matrices. Chemical properties, such as viscosity and diffusion, that are intermediate between those of gases and liquids make supercritical fluids particularly attractive [1–3]. Although CO_2 is a nonpolar solvent, its large quadrupole moment allows some interaction with polar solvents and analytes [2]. Even analytes that

are quite soluble in CO_2 may not be efficiently extracted if interactions with the matrix are strong. Small quantities (generally 1–10 mol%) of organic modifiers have been added either to the extraction fluid [2] or directly to the sample [4]. When a modifier such as methanol is added to CO_2 the critical temperature (T_c) of the resulting mixture is elevated (Table 1), often considerably, limiting the proportion of modifier which may be added if work is to occur in the supercritical region [5,6].

Solid-phase extraction (SPE) of pollutants from water followed by SFE has also shown advantages [7,8]. Primarily, liquid solvent waste was reduced. Selective elution was possible by changing extraction

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Table 1
Critical parameters for CO_2 and methanol–CO_2 mixtures

Composition	T_c (°C)	P_c (atm)
CO_2[a]	31.1	72.9
Methanol–CO_2[b]		
16:84	50	94
33:67	100	152
48:52	150	159

All methanol–CO_2 compositions are given on a mol% basis.
[a] From Ref. [5].
[b] From Ref. [6].

conditions such as pressure, temperature, or modifier to minimize extractable matrix interferences.

The addition of larger proportions (10–20 mol%) of methanol to CO_2 is investigated herein as a means of extending the range of SFE for the extraction of polar pollutants. The main criterion is that the extraction fluid exists as a one-phase liquid or supercritical fluid. Standard SFE equipment was used for all experiments. Partial phase diagrams for methanol–CO_2 are available in the literature [6,9–11]. A more global measurement of methanol–CO_2 phase behavior was recently studied [12]. In general, pressures in excess of 163 atm (1 atm=101 325 Pa) produce one phase mixtures over the 0–100 mol% methanol composition range at temperatures up to 100°C [9,12]. A 10:90 mol% methanol–CO_2 extraction fluid was tested both above (supercritical) and below (liquid) the mixture T_c, while a 20:80 mol% methanol–CO_2 mixture was used below (liquid) the mixture T_c only. When temperatures below the mixture T_c are used, the mixture is a liquid and the term enhanced-fluidity liquid is used to describe its properties [13].

Enhanced-fluidity liquids were previously studied for the extraction of polyaromatic hydrocarbons from sea sand [14,15]. SFE experiments resulted in approximately 20% recoveries while quantitative recoveries were obtained with the enhanced-fluidity liquid mixture of 40:60 mol% methanol–CO_2 at 238 atm and temperatures of 40–90°C for the five analytes studied. A 4-ml volume of the methanol–CO_2 mixture was used to extract the analytes. Experimental advantages, such as reduced restrictor plugging and increased precision for the extraction yields with liquid methanol–CO_2 mixtures were also found. Janicot et al. used liquid mixtures of carbon dioxide and polar modifiers for the extraction of

morphine and other natural products from poppy straw [16]. Both methanol–CO_2 and methanol–water–CO_2 mixtures were used over a 50–100 (w/w) % CO_2 range.

To compare SFE and enhanced-fluidity liquid extraction efficiencies with polar analytes, a series of phenols and nitroaromatics were tested. These environmental pollutants originate from a variety of sources including the paper and lumber industries, [17–19] and the synthesis of insecticides, fungicides and herbicides [17,20]. Seven of the eleven analytes tested are currently listed on the US Environmental Protection Agency (EPA) priority pollutant list [21].

Several groups have investigated the extraction of phenols from spiked matrices using CO_2 and supercritical methanol–CO_2 mixtures [22–24]. Lopez-Avila et al. extracted base/neutral/acidic compounds, including ten of the eleven analytes studied here, from spiked sand, florisil, alumina and silica gel. Methanol, acetone and toluene were tried as modifiers and were added directly to the sample. Recoveries were less than 60% for all matrices with the exception of sand where yields of 50–100% were noted.

The experiments described above primarily involved the extraction of samples that were spiked just prior to extraction and often directly in the extraction vessel. Analytes can be more readily removed from spiked samples than from native samples. Studies have shown that more than 24 h is necessary for most organic solutes to equilibrate with solid matrices [25]. For example, Hawthorne et al. showed that native naphthalene on urban air particulate extracted five times slower than naphthalene that was "spiked" onto the air particulate and allowed to age for 15 h [26].

In this study, phenols and nitroaromatics were adsorbed onto an octadecyl polysiloxane stationary phase material using a four week mixing and equilibration period that simulates native adsorption reasonably well. A comparison of extraction recoveries with CO_2 and mixtures consisting of 10 and 20 mol% methanol in CO_2 at liquid and supercritical fluid conditions is made. The relative contributions of temperature and composition to extraction yield are considered and the solvent strengths of various extraction fluids are compared. Characteristic physical and/or chemical properties of the matrix and

analytes are also discussed in order to explain trends in extraction yields.

2. Experimental

2.1. Materials

2,4-Dinitrophenol, stabilized with 10–15% water, and 4,6-dinitro-2-methylphenol, stabilized with 11% water, were obtained from ChemServices (West Chester, PA, USA). Phenol, 2-chlorophenol, o-cresol, m-cresol, nitrobenzene, 2,4-dimethylphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol were purchased from Aldrich (Milwaukee, WI, USA). p-tert.-Butylphenol (internal standard) and biphenyl (GC time reference compound) were also obtained from Aldrich. All were specified at 98% or higher purity and were used as received. J.T. Baker HPLC grade methanol (100.0% purity, Phillipsburg, NJ, USA) and Fisher Optima grade methylene chloride (99.9% purity, Fairlawn, NJ, USA) were used as extraction fluid modifiers and solvents. SFE/SFC grade CO_2 without a helium pad was purchased from Air Products and Chemicals (>99.9999% purity, Allentown, PA, USA). Polygosil octadecyl (ODS) polysiloxane stationary phase material was obtained from Keystone Scientific (Bellefonte, PA, USA). The ODS-bonded porous silica had a 63–200 μm particle size distribution, an average pore size of 60 Å and a carbon loading of 12.1%.

The ODS was washed with methanol and methylene chloride and then dried with nitrogen prior to use. The ODS was saturated with methylene chloride and spiked at the 15 μg/g level with a 2 mg/ml stock solution of 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol and pentachlorophenol and at the 10 μg/g level with a 2 mg/ml stock solution of the other eight analytes. The higher spiking level was used because these three analytes exhibit higher limits of detection than the others by GC–flame ionization detection (FID). The spiked sample was stored in the refrigerator and mixed daily for two weeks before slowly evaporating the solvent with nitrogen. The dry sample was then sealed in a bottle and mixed daily for two additional weeks to allow uniform adsorption of analytes onto the ODS and diffusion into the inner pore sites.

2.2. Soxhlet extractions

A micro Soxhlet extractor equipped with a 30-ml flask and water-cooled condenser was purchased from Ace Glass (Vineland, NJ, USA). A 1.00 g sample of spiked ODS was extracted with 15 ml methylene chloride. A 10–15 min solvent recycle time was used. The extraction was allowed to proceed at the boiling point of the solvent for 4 h until the ODS changed from yellow to white in color. For two of the five replicates, the solvent was replaced after 4 and 8 h; the extraction was then continued to 24 h. No analytes were detected in the extractant for the 4–8 h or 8–24 h fractions. Therefore, three further replicate extractions were performed for 4 h each.

2.3. Supercritical fluid and enhanced-fluidity liquid extractions

All extractions were performed using an ISCO SFX 220 automated supercritical fluid extractor and model 260D syringe pump (Lincoln, NE, USA). Extractions with CO_2 were performed by filling the syringe pump directly from the CO_2 gas cylinder. Binary fluids required two syringe pumps for mixture preparation. On a mole fraction basis, an appropriate volume of methanol was added to the empty extraction pump. The second pump, acting as a pure CO_2 reservoir, was operated in the constant pressure mode. An appropriate volume of CO_2 at a given density was then transferred to the extraction pump while maintaining constant pressure at the CO_2 pump. The methanol–CO_2 mixture was pressurized to 238 atm in the extraction pump and allowed to equilibrate for at least 12 h prior to use to ensure complete mixing.

The homogeneity of the mixture was evaluated based on the volume of methanol collected from the extraction chamber following the extraction. The design of the extractor is such that the extraction vessel and surrounding chamber are both pressurized during an extraction. High pressure seals are located on the chamber cap assembly and are not needed on the extraction vessel itself. At the conclusion of the dynamic step, the analyte valve (connecting the extraction vessel and restrictor) closes and the vent

valve (connecting the extraction vessel to atmospheric pressure via a length of stainless-steel tubing) opens, releasing the remaining pressure inside the extraction chamber. Any methanol which vented through the tubing at this time was collected into a large test tube and measured in a graduated cylinder. Volumes of 0.4 ml and 0.7 ml methanol consistently vented for 10:90 and 20:80 mol% methanol–CO_2 mixtures, respectively.

The 2.5-ml stainless-steel extraction vessel was equipped with a 2-μm frit above and a 0.5-μm frit below the 0.50 g ODS sample with the flow of extraction fluid down through the vessel. All extractions were performed at 238 atm and either 25, 45 or 65°C. A 1-min holding time was used to allow pump equilibration after filling the extraction chamber. A dynamic extraction step of chosen volume followed. The flow-rate was maintained at approximately 0.5 ml/min, measured as liquid flow at the syringe pump, via 25–40 cm lengths of 30 μm I.D. fused-silica tubing (Polymicro Technologies, Phoenix, AZ, USA).

The collection solvent was 5 ml methylene chloride containing 10 μg p-tert.-butylphenol (internal standard) and biphenyl (GC time reference compound). The collection vial was chilled in an ice water bath for 3–5 min prior to the dynamic step, but was then removed and mounted on the side of the extractor. Minor restrictor plugging during the CO_2 extractions was alleviated by lifting the restrictor out of the cold solvent or by warming the collection vial in a room temperature water bath for a few seconds. Extracts were concentrated to approximately 25 μl with nitrogen before transferring to autosampler vials and refilling to 1 ml. This step was used to minimize the amount of methanol present in the extract for GC analysis but was done with all extracts so that analyte losses due to the evaporation step were constant.

Fraction collection experiments were performed in triplicate by replacing the collection vial after a selected volume had passed through the extraction vessel. Vials were changed after 1, 2, 3, 4, 6, 8 and 12 ml for extractions with pure CO_2 and after 0.5, 1, 1.5, 2, 4, 8 and 12 ml for extractions with methanol–CO_2. An appropriate extraction volume was then chosen to maximize recoveries and five replicate extractions were done.

2.4. Extract analysis

Analyses were performed on a Hewlett-Packard 5890 Series II Plus gas chromatograph equipped with a split-splitless injection port and a FID system. An HP 7673 autosampler was used for a splitless injection of 1 μl. A 30 m×0.25 mm I.D. (1 μm film thickness) SPB-5 fused-silica capillary column (Supelco, Bellefonte, PA, USA) was used. The initial oven temperature of 40°C was held for 1 min after which the temperature was increased by 30°C/min to 100°C and held for 2 min. Finally, the temperature was increased by 10°C/min to 250°C and held for 1 min. This allowed baseline separation of all components. The electronic pressure control feature provided pressure programming of the helium carrier gas from 14 to 21 p.s.i. (1 p.s.i.=6894.76 Pa) after an initial pressure pulse upon injection. The splitless purge valve was turned on at 0.6 min. The injector and FID system were maintained at 290 and 300°C, respectively. Instrument control and data acquisition and analysis were accomplished via HP 3365 Chem-Station software installed on a 486 computer.

Quantitation was achieved by analyzing standards prepared by serial dilution from the phenol and nitroaromatic stocks. At least four standards across the concentration range of 1.5–18 μg/ml, 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol and pentachlorophenol, and 1–12 μg/ml of the other eight analytes were prepared and analyzed with each batch of extracts. Linear curve fits with correlation coefficients (r^2) >0.99 were consistently found for 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol and pentachlorophenol, and r^2>0.999 for the other eight components.

3. Results and discussion

3.1. Chemical and surface properties that affect the extraction process

Extracting an analyte from a solid matrix often involves many interrelated physical and chemical interactions [1,2,27,28]. These factors include the ability of the extraction fluid to interrupt matrix–analyte interactions (adsorption), solubility of the analyte in an adsorbed liquid layer, such as water,

diffusion of the fluid into and out of the inner pore sites of the matrix and the solubility of the analytes in the bulk extraction fluid. While all of these factors are important with native samples, analyte solubility in the bulk fluid is clearly of prime importance with spiked samples which are extracted immediately after spiking [28]. Kinetic studies of adsorption of analytes on soils and sediments have shown that a period of no less that two weeks is needed for the analyte to reach equilibrium with the adsorptive media. The spiking procedure used here allowed four weeks of interaction between the spiked analytes and the octadecyl polysiloxane surface before experiments were performed. Matrix–analyte interactions should more closely simulate those of native samples.

The ODS should be a simplified "model surface" for describing native solids such as soils and sediments because both hydrophobic sites (C_{18} chains) and hydrophillic sites (Si–OH) are present. The ODS is nearly ideal in that the pore size and particle size distribution are quite uniform. Therefore, unlike native matrices, variation in extraction yield among the samples should not result due to differences in pore distribution. Also the pore size (average of 60 Å) in the ODS was much larger than the hydrodynamic radii of the analytes. All analytes should have had equivalent access to the interior pore structure. Accordingly, analyte adsorption to the C_{18} chains and to any exposed silanols of the underlying silica should predominately control matrix–analyte interactions. In this study, the effect of the matrix on the extraction process is controlled and well defined. This allows a better understanding of the influence of the extraction fluids and analytes on the extraction mechanism.

3.2. Solubility data available for test analytes

All of the analytes tested are soluble in liquid methanol [17]. Phenol and methanol have the same Hildebrand solubility parameter ($\delta = 14.52$ $cal^{1/2}\, cm^{3/2}\, mol^{-1}$) at 25°C [29]. Liquid CO_2 has a Hildebrand solubility parameter (δ) of 7.0–7.5 $cal^{1/2}\, cm^{3/2}\, mol^{-1}$ at 25°C and 238 atm, [30]. The solubility of phenol in liquid CO_2 at 25°C has been reported as 3% (w/w) [31]. This corresponds to

approximately 28 mg phenol/ml CO_2 at 25°C and 238 atm (the pressure used here for extractions). For a 0.50 g ODS extraction, the maximum concentration of phenol present was 5 μg, well below the solubility limit. Two of the analytes studied, 2-chlorophenol and nitrobenzene, are miscible with liquid CO_2, [31]. These compounds were consistently extracted within the first 2 ml during the fraction collection experiments, indicating weak adsorption to the ODS and high solubility in all of the extraction fluids tested.

Ortho-substitution on phenol, in general, increases solubility in liquid CO_2 at room temperature [32]. Methyl substitution in any position also improves the solubility of phenols. However, the addition of chloro and nitro groups in positions other than ortho tends to lower solubility, [32]. This results because the intramolecular hydrogen bonding present with ortho-substitution is no longer possible, and thus the polarity increases considerably. While nitrobenzene was readily extracted with CO_2, 2,4-dinitrophenol was not recovered without the addition of methanol. The methyl substituent in the ortho-position of 4,6-dinitro-2-methylphenol may enhance solubility such that the analyte can be recovered to some extent with CO_2 alone. Analyte solubilities are expected to increase further with the addition of methanol to CO_2. Due to preferential clustering interactions of cosolvents such as methanol around polar analytes, the 10:90 and 20:80 mol% methanol–CO_2 solutions have solvent strengths markedly closer to that of pure methanol than that of CO_2. For example, when Kamlet–Taft solvent strength parameters were measured for the 20:80 mol% methanol–CO_2 liquid mixture, the α and β parameters that measure hydrogen-bond acidity and hydrogen-bond basicity, respectively, were approximately 80% those of pure methanol and the π^* parameter was approximately 50% that of pure methanol [33]. Therefore, for the trace levels of analytes extracted, solubility in methanol–CO_2 mixtures should not be a factor in the extraction process.

3.3. Soxhlet extraction results

To allow direct comparison of SFE and enhanced-fluidity liquid extraction with the most common competing liquid extraction, the ODS was also

Table 2
Soxhlet extraction and collection efficiency results

Analytes	Soxhlet extraction (% recovery[a])	Collection efficiency (% recovery[a])	Boiling point (°C)	pK_a^b
Phenol	67± 5	86±15	182	10.0
2-Chlorophenol	66± 6	81±18	175–176	8.6
o-Cresol	68± 4	86±15	191	10.2
m-Cresol	68± 2	89±13	203	10.1
Nitrobenzene	73± 6	80±17	210–211	
2,4-Dimethylphenol	71± 2	87±13	212	10.6
2,4-Dichlorophenol	76± 3	90±14	209–210	7.9
2,4,6-Trichlorophenol	86± 4	101±10	246	6.2
2,4-Dinitrophenol	84±10	128±26	–	4.1
4,6-Dinitro-2-methylphenol	72± 2	102± 7	–	4.7
Pentachlorophenol	70±3	106±14	310	4.5

[a] Average % recovery for five replicates±the 95% confidence intervals.
[b] From [34].

extracted by Soxhlet using methylene chloride as the solvent. Table 2 summarizes the % recoveries, relative to the spiking levels, for the 4-h micro Soxhlet extractions. Because none of the analytes was recovered from the fractions collected after 4 h, the extraction was considered exhaustive. Soxhlet results ranged from a low value of 66% for a more volatile analyte such as 2-chlorophenol, to high values of 84 and 86% for 2,4-dinitrophenol and 2,4,6-trichlorophenol, respectively. These data will be compared later to the results of the SFE and enhanced-fluidity liquid extractions.

3.4. Collection efficiency of analytes

Effective trapping of analytes in the collection solvent and minimal evaporative loss during the concentration step are crucial for high extraction recoveries. Losses during the extraction and evaporation steps were considered together because both steps were used with all extracts. Methylene chloride collection solvent was spiked with analytes such that the final concentration was 10 or 15 μg. The solvent was then chilled in an ice water bath for 3–5 min prior to use. Next, 3 ml of 20:80 mol% methanol–CO_2 at 238 atm and 65°C was purged through the solvent. After concentrating with nitrogen and refilling to 1 ml, the solution was analyzed by GC. The peak areas for the analytes in the collection solvent were compared to the peak areas for analyte solutions with the original spiked concentrations (10 or

15 μg) to obtain the % recoveries for the analyte collection process. Table 2 shows that recoveries of 80–90% were common for the more volatile components. Hawthorne et al. reported a collection efficiency of 77% for phenol using supercritical CO_2 and 3 ml methylene chloride [27]. When the temperature of the solvent was controlled to a constant 5°C, collection efficiency improved to 98% for phenol. Cooling due to the expansion upon depressurization of the extraction fluid may be somewhat less for the enhanced-fluidity liquid mixtures relative to supercritical fluids and may account for the collection efficiencies of 80–90% obtained in this study.

3.5. Extractions using CO_2 and methanol–CO_2

3.5.1. Effect of extraction fluid composition and extraction temperature

Plots of % recovery vs. extraction fluid volume were prepared for each analyte at the nine conditions tested (see Table 3). Fig. 1 shows the extraction of 2,4-dimethylphenol and 2,4-dichlorophenol at 45°C and 238 atm for the three mixture compositions studied (CO_2, 10:90 mol% methanol–CO_2 and 20:80 mol% methanol–CO_2). An initial rapid rise was followed by a plateau where little or no additional concentration was detected. Similar curves were observed for the other analytes. The steepness of the curves describes the extraction fluid's solvent strength. This is both the fluid's ability to interrupt

Table 3
Summary of extraction conditions[a]

Conditions	Temperature (°C)	Fluid state	Extraction volume (ml)	Average time (min)[b]	Flow rate (ml/min)[c]
CO_2	25	Liquid	12	23.2±0.4	0.52
	45	Supercritical	10	19.6±0.5	0.51
	65	Supercritical	10	22.1±1.1	0.45
10:90 mol% CH_3OH-CO_2	25	Liquid	6	12.3±0.9	0.49
	45	Liquid	4	7.9±0.1	0.51
	65	Supercritical	4	8.5±0.9	0.47
20:80 mol% CH_3OH-CO_2	25	Liquid	3	6.4±0.1	0.47
	45	Liquid	3	5.6±0.2	0.54
	65	Liquid	3	6.6±0.2	0.46

[a] All extractions were performed at 238 atm.
[b] Average time for five replicates ±95% confidence interval.
[c] Calculated from the extraction volume and average time.

matrix–analyte adsorptive interactions and the solubility of the analytes in the bulk extraction fluid for removal from the vessel. As expected, the methanol–CO_2 mixtures are of greater solvent strength than pure CO_2 for the polar analytes, resulting in extraction profiles for the analytes which are greatly enhanced.

From the concentration vs. volume plots for all components at each composition and temperature, an optimum extraction volume was chosen on the plateau of the curves. For example, the optimum volumes chosen for pure CO_2, 10:90 mol% methanol–CO_2 and 20:80 mol% methanol–CO_2 as extraction fluids at 25°C were 12 ml, 6 ml and 3 ml, respectively (see Table 3). A minimum extraction volume of 3 ml was used so that the 2.5-ml vessel was swept at least once during the dynamic step. In Table 3, the dynamic extraction time was monitored directly on the extractor. The average flow-rate was then calculated.

Table 4 shows the average % recoveries±95% confidence interval for five replicates at 238 atm and 45°C for CO_2, 10:90 mol% methanol–CO_2 and 20:80 mol% methanol–CO_2. The % recovery relative to the Soxhlet data is given in parentheses. For the first eight analytes, the advantage of methanol addition is apparent by recoveries consistently equivalent to or better than those obtained by Soxhlet. Lower recoveries of 2,4-dinitrophenol, 4,6-dinitro-2-methylphenol and pentachlorophenol, relative to the other phenols and nitroaromatics, were previously

reported by Lopez-Avila [4]. For an extraction from spiked florisil, 2,4-dinitrophenol and 4,6-dinitro-2-methylphenol were not recovered at all and only 2% of pentachlorophenol was extracted with the addition of methanol directly to the sample. In this study, 2,4-dinitrophenol was not detected with pure CO_2 but extraction improved considerably with the addition of methanol (29 and 45% recoveries, relative to Soxhlet, for 10:90 and 20:80 mol% methanol–CO_2, respectively). Recoveries of 4,6-dinitro-2-methylphenol and pentachlorophenol ranged from 45 to 96%, relative to Soxhlet.

The pH of the washed ODS in aqueous solution was determined to be 8.9. The pK_a values of the analytes are listed in Table 2 [34]. The acidity of the hydroxyl hydrogen of the phenolics increases with the addition of electron withdrawing nitro and chloro substituents in the ortho- and para-positions due to resonance [35]. Stronger adsorption to Si–OH sites on the ODS is expected for pentachlorophenol, 2,4-dinitrophenol and 4,6-dinitro-2-methylphenol in particular, based on their low pK_a values. This is consistent with the trends in extraction recoveries described above.

3.5.2. Statistical comparison of data

The effect of extraction fluid composition and temperature on the recoveries was studied by using a two-way analysis of variance (ANOVA) with temperature and fluid composition as the independent variables evaluated. The ANOVA calculations were
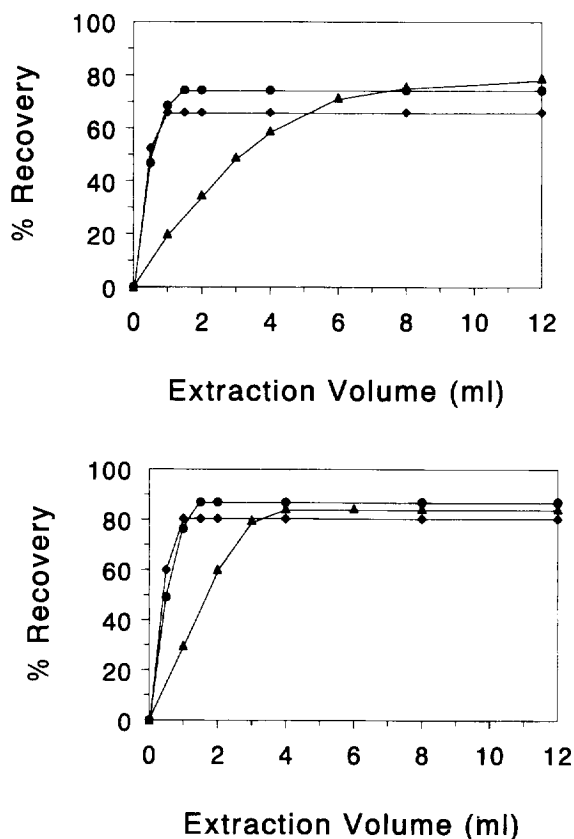
Fig. 1. Effect of extraction fluid composition on the rate of extraction of (upper) 2,4-dimethylphenol and (lower) 2,4-dichlorophenol at 238 atm and 45°C. Data points represent the average % recovery, relative to the spiking level, of triplicate extractions for (▲) CO_2, (●) 10:90 mol% methanol–CO_2 and (◆) 20:80 mol% methanol–CO_2.

accomplished with Systat for Windows, version 5.0 (Systat, Evanston, IL, USA). For all eleven analytes, the methanol–CO_2 compositions had significant effect (>95% confidence level) on the measured extraction yield. No difference was indicated between CO_2 and 20:80 mol% methanol–CO_2 for 2,4,6-trichlorophenol. Higher recoveries were obtained for all other analytes using the methanol–CO_2 mixtures over CO_2 alone. Nitrobenzene, 2,4,6-trichlorophenol, 4,6-dinitro-2-methylphenol and pentachlorophenol did, however, show different means between 10:90 and 20:80 mol% methanol–CO_2. The 10:90 mol% methanol–CO_2 mixtures produced results which were on average 19% higher for these four analytes.

From the ANOVA results, the effect of temperature (over the limited range studied) on the rate and extent of extraction clearly is modest when compared to composition. Six of the eleven analytes showed no temperature dependence in the replicate extractions by ANOVA calculations (95% confidence level). The variation of temperature did affect the extraction of phenol, 2-chlorophenol, 2,4,6 trichlorophenol, 2,4-dinitrophenol and pentachlorophenol. For most of these five compounds, 45°C was an apparent optimum temperature (among 25, 45 and 65°C). However, as Fig. 2 shows, greater extraction yields were observed for pentachlorophenol with increasing temperature using the 10:90 mol% methanol–CO_2 mixture. Also, the rapid rate of extraction was not compromised when using an enhanced-fluidity liquid at 45°C compared to a supercritical fluid at 65°C.

3.5.3. Additional experimental advantages of enhanced-fluidity liquids

Mild restrictor plugging was encountered during the CO_2 replicates at all three temperatures. No plugging was observed when methanol was present. This could prove advantageous in the extraction of a wet sample, where methanol increases the solubility of water in CO_2 and decreases ice formation. This method is also expected to work well for the extraction or elution of phenols from an ODS extraction disk or cartridge after SPE of a water sample.

Finally, a broader range of temperatures can be utilized with liquids as opposed to supercritical fluids, because exceeding the critical temperature is not necessary. The criteria for an enhanced-fluidity liquid is that the fluid exists in a single phase. Standard SFE equipment is still applicable. Analyte and/or matrix decomposition could be averted while using high solvent strength extraction fluids. High-molecular-mass and low-solubility interferences may be left unextracted by keeping the temperature low.

4. Summary

The goal of this study was to evaluate the use of enhanced-fluidity liquids and supercritical fluids for the extraction of phenolic or nitroaromatic pollutants. ODS was chosen as a simple and uniform matrix and

Table 4
% Recoveries at 238 atm and 45°C with CO_2 and methanol–CO_2 mixtures

Analyte	Supercritical CO_2 10-ml extraction volume	Liquid 10:90 CH_3OH–CO_2 4-ml extraction volume	Liquid 20:80 CH_3OH–CO_2 3-ml extraction volume
Phenol	59±11 (89)[a]	82±8 (123)	82±3 (123)
2-Chlorophenol	59±15 (89)	98±12 (148)	90±5 (136)
o-Cresol	61±11 (89)	80±8 (116)	80±2 (118)
m-Cresol	59±10 (87)	77±8 (114)	77±4 (113)
Nitrobenzene	65±12 (89)	78±10 (108)	71±5 (98)
2,4-Dimethylphenol	62±9 (88)	78±9 (110)	79±3 (111)
2,4-Dichlorophenol	65±10 (85)	89±7 (118)	96±7 (126)
2,4,6-Trichlorophenol	71±9 (82)	103±7 (120)	89±15 (103)
2,4-Dinitrophenol	0	24±21 (29)	38±5 (45)
4,6-Dinitro-2-methylphenol	54±10 (75)	51±19 (71)	41±8 (57)
Pentachlorophenol	32±3 (45)	67±20 (96)	42±5 (59)

[a] Average % recovery, relative to the spiking levels, for five replicates±95% confidence interval.
% Recovery relative to Soxhlet extraction are given in parentheses.

spiked in a manner that allowed adsorption and equilibration to occur. This "model surface" allowed the separation of matrix effects from the properties of the extraction fluids and polar analytes. Efficient extractions were performed in shorter periods of time with liquid methanol–CO_2 mixtures while maintaining many of the attractive features of supercritical fluids. For most of the analytes the extraction yield was unaffected by whether the fluid was in the supercritical or liquid phase region. The extraction fluid composition was the most important variable while the effect of temperature was minimal. This work represents the initial evaluation of enhanced-fluidity liquids for the extraction of polar pollutants. Complex environmental matrices and analytes which are more polar and less soluble in CO_2 are now under investigation.

Acknowledgments

Fig. 2. Effect of extraction temperature on the rate of extraction of pentachlorophenol using 10:90 mol% methanol–CO_2 at 238 atm. Data points represent the average % recovery, relative to the spiking level, of triplicate extractions at (▲) 25°C, (●) 45°C and (◆) 65°C.

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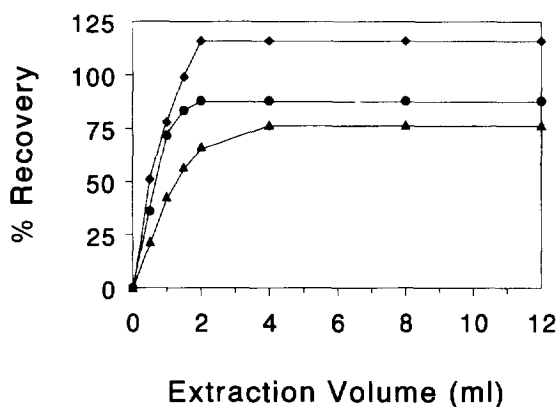
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