

Full Length Research Paper

Extraction of chlorinated aromatic hydrocarbons using supercritical fluid

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This study aims to examine a variety of interrelated parameters including pressure, temperature and velocity of fluid using Supercritical Fluid Extraction (SFE) of chlorinated aromatic hydrocarbons. The optimum parameters for the supercritical fluid extraction of chlorinated aromatic hydrocarbons were determined and compared with the 'soxhlet' extraction. The results revealed that the optimal conditions for extraction are a pressure of 250 bars and a temperature of 40°C and a fluid flow of 2.0 ml/min. Moreover, in an experiment on the effect of solvent, the high recovery of chlorinated aromatic hydrocarbons for 2 to 5-rings were applied to n-hexane and dichloromethane in the ratio 1:1 and dichloromethane alone. Additionally, SFE was found to have higher recovery percentage than Soxhlet for chlorinated aromatic hydrocarbon with 2 rings. The SFE with chlorinated aromatic hydrocarbons with 1 to 5 rings was faster than soxhlet extraction. Furthermore, the recovery percentage of the 8270 phenols mix and the TCL polynuclear aromatic hydrocarbons mix is 68 ~ 89% and 71 ~ 113%, respectively. These results demonstrate that the SFE is a better method for extracting volatile and semi-volatile organic compounds.

Key words: Optimal extraction, supercritical fluid extraction, solvent, recovery, soxhlet extraction.

INTRODUCTION

Supercritical fluid characteristics are similar to those of diffusive gas and solute liquid. Generally, supercritical fluid can infuse faster than liquid and has great solubility. Indeed, comparing traditional industrial solvent with supercritical carbon dioxide or another supercritical fluid indicates that the supercritical fluid is the most environmentally friendly solvent. A wide variety of solvents is available for use as supercritical fluids including carbon dioxide, nitrous oxide, ethane, propane, n-pentane, ammonia, fluoroform, sulphur hexafluoride and water. Carbon dioxide is currently the solvent of choice, as it can easily reach supercritical conditions and has clear advantages (for example low toxicity, inflammability and high purity) over other fluid (Zougagh

et al., 2004). The development of supercritical fluid extraction technology has enabled the removal of pernicious elements from pollutants. This green chemistry helps to sustain the environment. The implementation of supercritical fluid extraction (SFE) in environmental analysis has been extensively well documented (Hawthorne and Miller, 1987; Leazer et al., 2009; Liang et al., 2010). In 1989, Onuska and Terry used both static and dynamic SFE with nitrous oxide and a 2% solution of methanol in nitrous oxide for the determination of 2, 3, 7 and 8 TCDD in sediment samples. Supercritical fluid is becoming an acceptable alternative to conventional liquid solvents for use in the rapid analytical-scale extraction of environmental samples. Additionally, a single-stage solvent extraction using either methanol or 2-propanol can successfully remove between 65 to 75% of DDT, DDD and DDE, while a large extraction stage up 6 can remove more than 99% (Endalkachew et al., 1996). Supercritical fluid extraction

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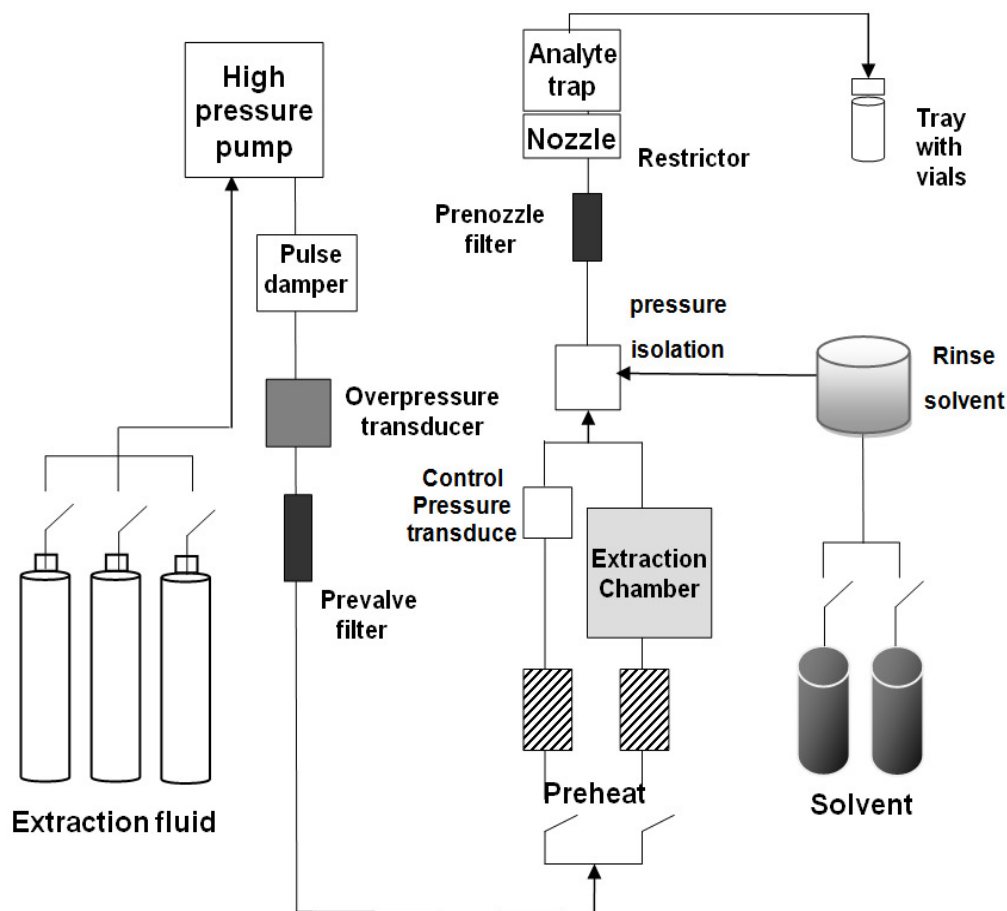


Figure 1. SFE 7680T system.

has been shown to provide a powerful alternative to traditional solvent extraction methods, particularly in removal of contaminants from solid samples (Kumoro and Hasan, 2007; Majors, 2007; Ozcan et al., 2009). This method exploits the properties of the gas at temperatures and pressures near the critical point. That allows easy penetration into the smallest pores of particles such as fly ash. Another advantage of SFE is that it shortens the extraction time (Onuska and Terry, 1991): extracting PCDDs from a matrix of fly ash using soxhlet equipment takes 24 h and clean-up and quantization takes 15 h; in contrast; SFE takes only 2.5 h.

SFE results in a dramatic decrease in extraction times and avoids the use of large quantities of organic solvents that are often toxic (Becnel and Dooley, 1998). Supercritical fluid extraction recovery rates are controlled by various variables including pressure, temperature, solvent, velocity of fluid, extractor geometry, restrictor sizes, modifiers and sample matrix composition. An analysis of chlorinated dibenzofurans in municipal fly ash by Onuska and Terry (1993) indicated that the optimal conditions for extracting 25 to 30 mg of samples is 120 min at 400 atm and 45°C. The main objective of this

study is to investigate various interrelated parameters such as pressure, temperature and velocity of fluid, and to compare supercritical fluid extraction with soxhlet extraction for evaluating their performance.

MATERIALS AND METHODS

Experimental apparatus

An Hewlett-Packard SFE 7680T (Hewlett-Packard, North Hollywood, CA, USA) was used in this study. Figure 1 presents the SFE system. The SFE system comprises a set of dual-piston pumps to provide the highest pressure of 380 bar, a thermostatic extraction chamber to heat to 150°C, a 7 ml thimble by hand-lock, variable tor and an analytic trap of octadecyl-bonded silica (ODS). The liquid carbon dioxide enters the thimble under pressure that is applied using a high-pressure pump and both the temperature and the pressure of the fluid reach the threshold limit values (TLV), and then the carbon dioxide goes through the extraction chamber and becomes a supercritical fluid. Supercritical carbon dioxide that has gone through the restrictor is stepped-down as an insoluble gas. Therefore, a sample can be easily extracted from the fluid and adsorbed by the analytic trap. High purity CO₂ was passed through the extraction vessel at various oven temperatures and densities. The gases of carbon dioxide (CO₂) used in the experiments were of

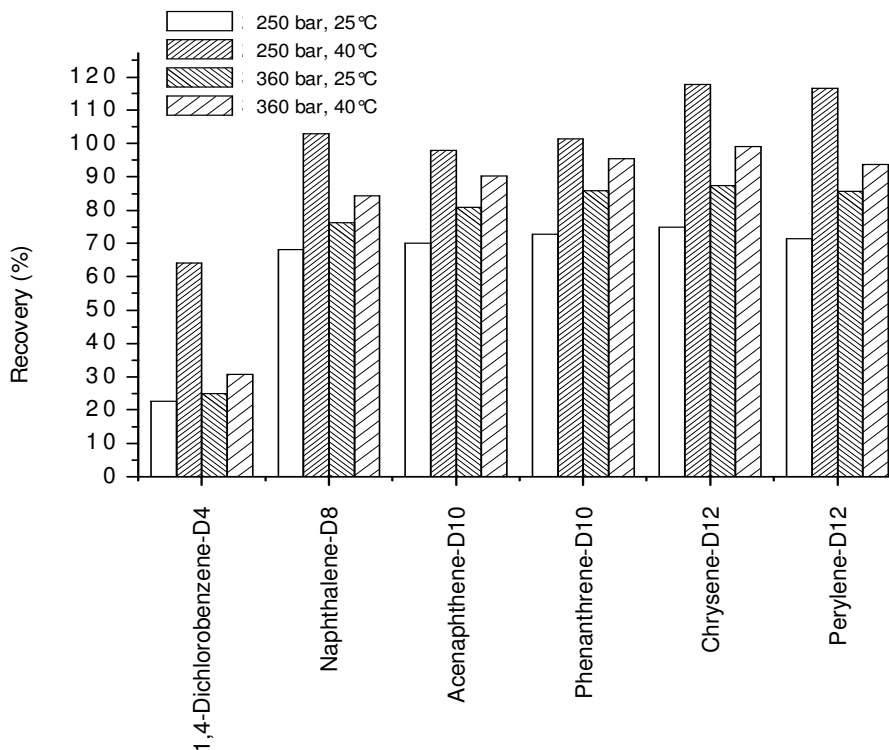


Figure 2. Recovery percentage of chlorinated aromatic hydrocarbons for different pressures and temperatures.

99.99% purity. The final step is the supercritical fluid which was depressurized, collected on a Propak-Q solid trap (Hewlett-Packard). The application of a suitable solvent at a fixed flow rate was used to rinse the analytic trap. The rinsing solvent is collected in a 1.8 ml vial, and then GC/FID and GC/MS can be used directly to analyze the collected fluid. The other chemical solvents which include n-hexane, acetone, dichloromethane and toluene (for Soxhlet extraction) were purchased from local market.

Preparation of quartz sand

The diameters of quartz sand (Mesh #25 to 30) after sieving were 0.7 to 1.1 mm and 1.1 to 1.4 mm. Particles and impurities were washed from the surface of quartz sand using deionized water. Acetone and n-hexane solvent were used to remove the remaining water. Dissolve elements were adsorbed on the surface of quartz sand. Then, the sand was baked at 105°C for 24 h continuously before it was stored for future use.

Experimental method

For achieving the objectives, the followings are the steps of experiment method carried out in this study. First, the glass wool was placed in the bottom of the thimble where the fluid flows. Then 1 g of Na₂SO₄ and 1 g of clean quartz sand were placed around on glass wool and placed (mesh, #25 to 30) into a 7 ml thimble. The standard solution was added by gastight syringes [which were semi-volatile internal standard mix, 8270 phenols mix, or TCL polynuclear aromatic hydrocarbons mix purchased from SUPEICO (Bellefonte, Pennsylvania, USA)] and then more glass wool was placed in the thimble. The stoppers were pushed tightly into the

caps, then the thimble was placed in the extraction chamber and the extraction parameters were set for extraction. The effect of the extraction pressure (250 and 360 bar), the temperature (25 and 40°C), the CO₂ flow rate (2 and 4 ml/min), static (10 min) and dynamic extraction times (10 min), and extraction solvent were investigated and optimal operating conditions were found out.

RESULTS

Effect of pressure and temperature on extraction

The most important parameters that affect supercritical fluid extraction are pressure and temperature. Therefore, this study elucidates the effect of pressure and temperature on the supercritical fluid extraction of chlorinated aromatic hydrocarbons. For this purpose, the temperature and pressure were set to 25 and 40°C, and 250 and 360 bars, respectively. The extraction temperature should exceed 32°C to maintain CO₂ in the supercritical state. The temperature was set at 40°C and to compare with the results for room temperature at 25°C. Additionally, for studying the difference between the method 3562 of US EPA and the maximum pressure (360 bar) equipped on the experimental system, the pressure was set at 250 and 360 bars. The results given in Figure 2 reveal that the percentage of compounds recovered at 25°C is 22.6 and 25% at 250 and 360 bars. A comparison of a 1-ring chlorinated aromatic hydrocarbon

Table 1. Recovery percentage of chlorinated aromatic hydrocarbons for different flow rate.

Extraction solvent: Dichloromethane		
Standards: Semivolatile Internal Standard Mix, 50 ng/μL \times 500 μL		
Pressure: 250 bar		
Chamber temperature: 40 $^{\circ}$C		
Recovery (%)	Flow rate (2.0 ml/min)	Flow rate (4.0 ml/min)
1,4-Dichlorobenzene-D4	64.1	11.1
Naphthalene-D8	103.0	83.1
Acenaphthene-D10	97.9	91.0
Phenanthrene-D10	101.3	95.5
Chrysene-D12	117.7	98.5
Perylene-D12	116.7	94.4

(1, 4 dichlorobenzene-D4) with a 2-ring chlorinated aromatic hydrocarbons (naphthalene-D8) indicates that the recovery percentage of compounds at 25 $^{\circ}$ C is 68.2 and 76.2% at 250 and 360 bars, respectively. The recovery percentage of compounds with same condition, 71.4 \pm 1.9 and 83.7 \pm 3.6% for 3-ring chlorinated aromatic hydrocarbons (acenaphthene-D10 and phenanthrene-D10); 75 and 87.3% for 4-ring chlorinated aromatic hydrocarbons (chrysene-D12); 71.5 and 85.6% for 5-ring chlorinated aromatic hydrocarbons (perylene-D12). The recovery increased with pressure from 250 to 360 bars at a fixed temperature of 25 $^{\circ}$ C.

Effect of flow rate on extraction

In this phase of the study, the pressure and temperature were set to 250 bars and 40 $^{\circ}$ C, based on the results of the previous phase to determine the effect of flow rate on extraction. The results given in Table 1 reveal that in flow rates of 2.0 and 4.0 ml/min, the recovery percentage is 64.1 and 11.1% for 1-ring chlorinated aromatic hydrocarbon; the corresponding values are 103 and 83.1% for 2-ring chlorinated aromatic hydrocarbons, 99.6 \pm 2.4 and 93.3 \pm 3.1% for 3-ring chlorinated aromatic hydrocarbons; 117.7 and 98.5% for 4-ring chlorinated aromatic hydrocarbons; and 116.7 and 94.4% for 5-ring chlorinated aromatic hydrocarbons. Notably, the recovery decreases as the extraction flow rate increases from 2.0 to 4.0 ml/min.

Effect of solvent on extraction

PAHs are non-polar materials. Their molecular structures are highly symmetrical and their dipole moments are short. Non- or weakly polar organic solvents such as n-hexane, acetone, toluene and dichloromethane can dissolve the most PAHs (Butler and Crossley, 1981), so

three solvents n-hexane, dichloromethane and n-hexane and dichloromethane co-solvents in a ratio of 1:1 are used in this phase to investigate the effect of solvent on recovery. Table 2 and Figure 3 present the recovery of low and high-ring compounds. Extraction using co-solvents n-hexane and dichloromethane in the ratio 1:1 is the most effective recovery. Dichloromethane yields a higher recovery of high-ring compounds.

Comparison of supercritical fluid extraction with soxhlet extraction

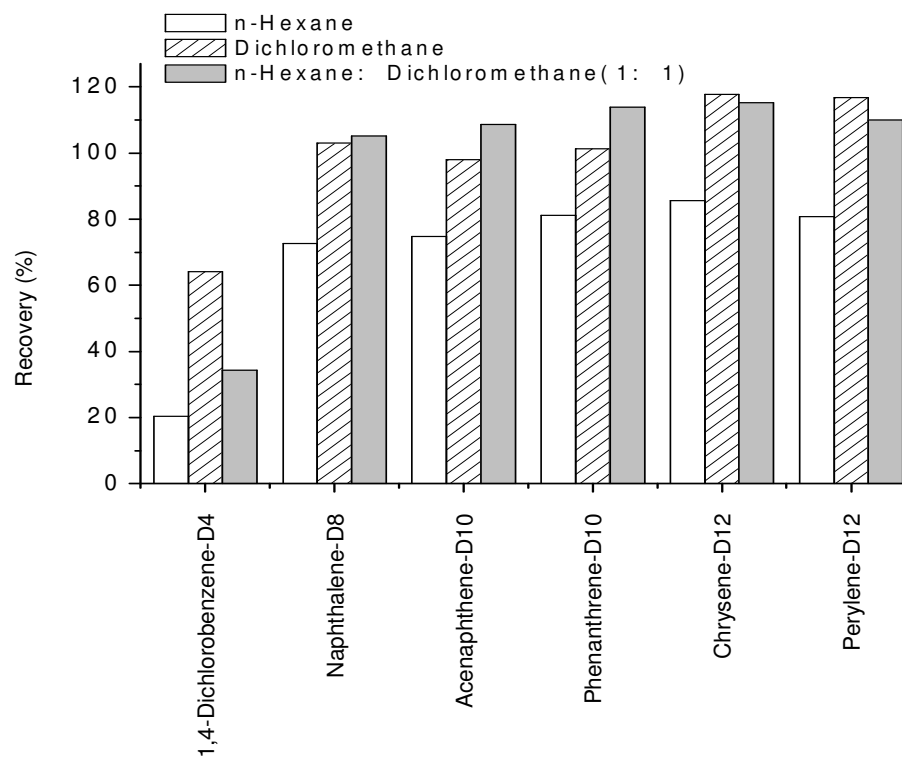
The disposal of a semi-volatile internal standard mix by traditional soxhlet extraction and supercritical fluid extraction is evaluated to identify a potential supercritical fluid extraction approach. Table 2 and Figure 4 present the results obtained using soxhlet extraction. The results reveal that the recovery of low-ring compounds by either SFE or soxhlet is low. The recovery of 2-ring chlorinated aromatic hydrocarbons by SFE is compared with that by soxhlet extraction using three solvents. The recovery of 3 to 5-ring chlorinated aromatic hydrocarbons by soxhlet extraction is high for a single extraction solvent like n-hexane. Furthermore, the recovery of low to high-ring compounds by SFE is high when a single extraction solvent, dichloromethane, or co-solvents n-hexane and dichloromethane in the ratio 1:1 are used.

Extraction of different target compounds

In this phase, dichloromethane is applied as an extraction solvent to investigate the effect of target compound on recovery by supercritical fluid extraction. Figure 5a shows that the recovery of all compounds from 8270 phenols mix is from 68 to 89%. The recovery of all compounds from TCL poly nuclear aromatic hydrocarbons mix is 71 to 113% as displayed in Figure 5b.

Table 2. Comparison of supercritical fluid extraction and soxhlet extraction for the different solvent used.

Method	SFE			Soxhlet		
	n-Hexane	Dichloromethane	n-hexane: dichloromethane (1:1)	n-Hexane	Dichloromethane	n-Hexane: dichloromethane (1:1)
1,4-Dichlorobenzene-D4	20.4	64.1	34.3	47.5	62.0	-
Naphthalene-D8	72.6	103.0	105.2	65.7	60.5	21.8
Acenaphthene-D10	74.8	97.9	108.6	81.9	72.1	66.6
Phenanthrene-D10	81.1	101.3	113.9	98.6	92.1	88.5
Chrysene-D12	85.6	117.7	115.2	106.8	112.4	91.9
Perylene-D12	80.7	116.7	109.9	102.8	116.1	86.5

**Figure 3.** Recovery percentage of chlorinated aromatic hydrocarbons for different solvent by SFE.

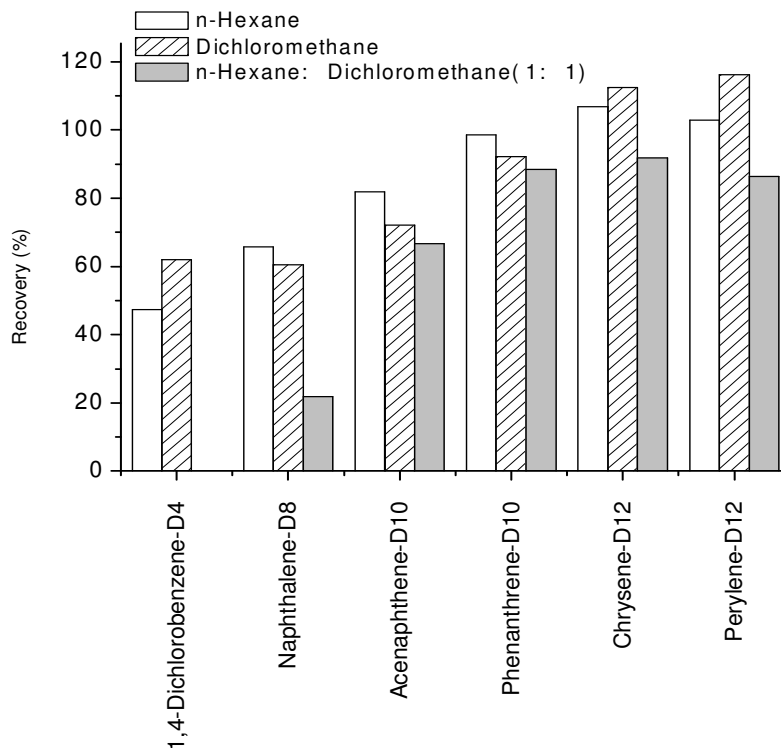


Figure 4. Recovery percentage of chlorinated aromatic hydrocarbons for different solvent by Soxhlet.

DISCUSSION

Effect of pressure and temperature on extraction

As shown in Figure 2, the recovery at a fixed temperature for 40°C decreased as the pressure increased from 250 to 360 bars, mainly because the inter-molecular distance declined and the permutation became closer as the density increased. Therefore, the viscosity coefficient increased and the strength of the flow increased. The recovery decreased because of the decreasing of diffusion coefficient of the fluid which cannot rapidly pass through the matrix under such density conditions which also decrease the contact with the sample (Reindl and Höfler, 1994; Seidel and Lindner, 1995). When fixing pressure at 250 bars, the recovery increases with temperature from 25 to 40°C. At a fixed pressure of 360 bars, the recovery is low while comparing with the results obtained in 250 bars. The best recovery is at a pressure and temperature of 250 bars and 40°C. The density and temperature of the fluid varied inversely at a fixed pressure that is a high temperature and a low density of fluid are associated with a high diffusion coefficient and the rapid passing of the fluid through the matrix. Therefore, the increase rate of desorption in the recovery of sample extract increased with temperature. For an organic substance of high molecular weight at a low vapor pressure such as the PAHs of 5 to 6-ring

compounds, the vapor pressure of such organic substance will be advanced with raising temperature and effectively interrupt the bonding between organic and matrix (Hawthorne and Miller, 1994; Marín et al., 1998). Windal et al. (1998) compared the concentrations at pressures of 200, 400 and 500 bar at a constant temperature of 140°C. Their results indicated that temperature and not pressure is the governing parameter because of the similarity between the extraction concentrations.

The factor that affects the recovery is the temperature as reported in the literature. Increasing either the vapor pressure or the desorption rate of a sample extract improves the effect of recovery.

Effect of flow rate on extraction

The dynamic extraction stage continuously provides fresh CO₂ to the extraction cell and plays the role of carrier to replace the mixtures remaining in the extraction cell. Hence, CO₂ flow rate becomes an important factor which affects the fluid volume passing through the extraction cell (Cheng et al., 2008). The results given in Table 1 reveal that in flow rates of 2.0 and 4.0 ml/min, it can be noticed that the recovery presents a reduction with the increasing of the extraction flow rate from 2.0 to 4.0 ml/min. The extraction flow rate is speculated to be much

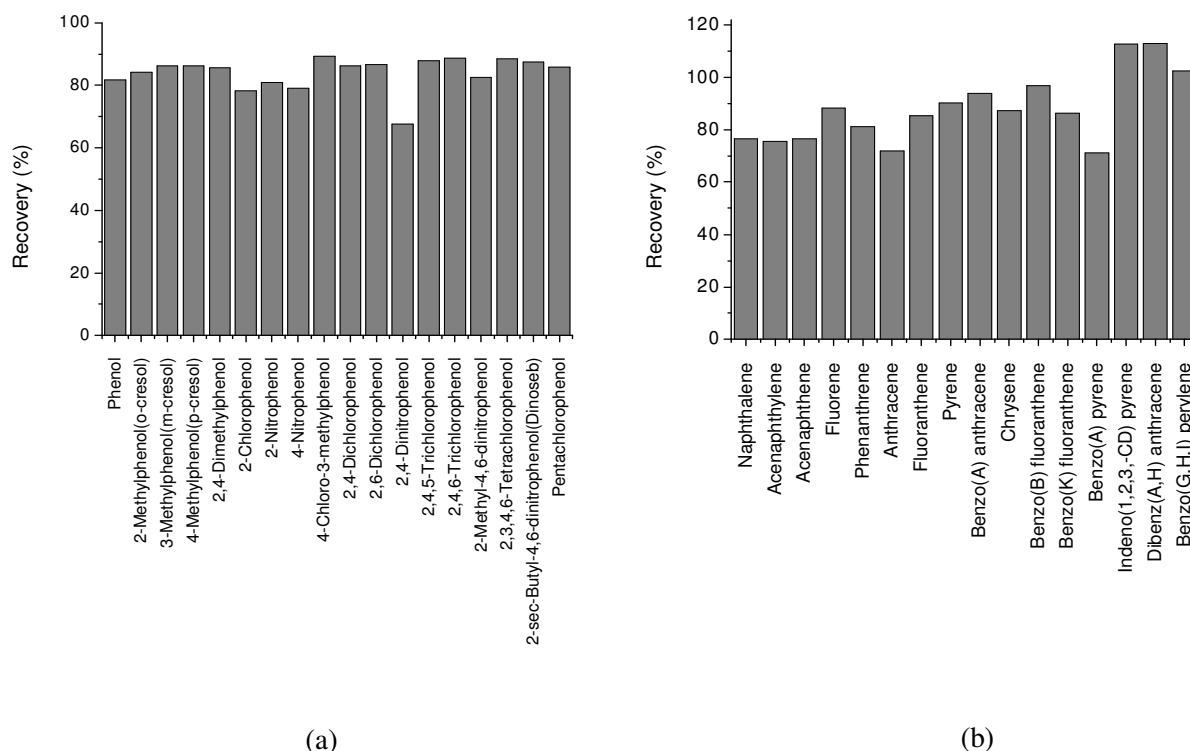


Figure 5. Recovery percentage of different target compounds. (a) 8270 phenols mix. (b) TCL polynuclear aromatic hydrocarbons mix.

higher and the stagnation time of the fluid within extractive trap is shorter, causing incomplete contact of the extractives with the fluid, and the efficiency of sample extraction is also seriously affected. The main factor that influences the efficiency of the dynamic extraction procedure is the flow rate. As the dynamic extraction required a sustained, steady and fresh for the fluid to pass through the solid matrix and need to provide sufficient volume of fluid to take extractives to collection trap. The flow rate and the extraction time indirectly influence the actual volume of the fluid passes through an extractive trap. Restated recovery is positively correlated with the flow rate and the extraction time.

Effect of solvent on extraction

Table 2 and Figure 3 present the recovery of low and high-ring compounds. From these results, it indicated that applying co-solvents at 1:1 of n-hexane and dichloromethane and dichloromethane both obtained better recovery for high-ring compounds. Langenfeld et al. (1994) found that dichloromethane most effectively extracted PAHs of high molecular weight. A comparison of n-hexane and dichloromethane indicates that low to high-ring compounds are more effectively recovered using dichloromethane, and that a lower temperature favors the collection of volatile substances because the

boiling point of dichloromethane is lower than n-hexane. As the viscosity coefficient increases, the temperature decreases and reduces the velocity of bubbles, causing increase contact time for solvent and sample extract. Additionally, the vapor pressure of PAHs decreases as the temperature of the solvent decreases and making vaporization harder.

Comparison of supercritical fluid extraction with soxhlet extraction

Table 2 and Figure 4 present the results obtained using soxhlet extraction. The results presented recovery for low-ring compounds are worse at either SFE or soxhlet while comparing with the results of high-ring compounds. The results of this study demonstrate that supercritical fluid extraction is better than soxhlet extraction. An hour of supercritical fluid extraction yields the same results as more than 18 h of soxhlet extraction. Moreover, supercritical fluid extraction is effective with only a low volume of organic solvent - less than 20 ml, but soxhlet extraction requires more than 300 ml of solvent. The high solvent power of supercritical fluids is becoming a major argument for laboratories engaged in innovative research to develop SFE methods for routine analyses. Thus, a number of laboratories have chosen to replace their conventional methodologies with new, SFE-based

methodologies in order to minimize organic solvent consumption and boost throughput (Zougagh et al., 2004).

Extraction of different target compounds

Figure 5a shows that the recovery of all compounds from 8270 'phenols mix' is from 68 to 89%. The molecular weight does not dominate the recovery at an appropriate temperature and pressure for extraction. The recovery of all compounds from TCL polynuclear aromatic hydrocarbons mix is 71 to 113%, as displayed in Figure 5b. In particular, the recovery of a high-ring compound by PAHs was high and that by benzo (A) pyrene was low. The interactions between benzo (A) pyrene and the matrix were very strong and extraction was difficult. However, the recovery of 5 to 6-ring chlorinated aromatic hydrocarbons was very high. Becnel et al. (1998) indicated that PAH extractions from high organic content soils, recoveries >95% for 2-ring and lighter PAH contaminants and >80% for 3-ring and heavier PAHs were attained using dry SCF-CO₂ at a 200 phase ratio (g of SCF/g of soil), 323 K and 13.8 MPa.

Conclusion

The present study has explored the possibility of using SFE instrument to extract various groups of semi-volatiles (phenols and polycyclic aromatic hydrocarbons) from quartz sand. The results revealed that the optimal conditions for extraction are a pressure of 250 bars and a temperature of 40°C and a fluid flow of 2.0 ml/min. In the experiment on the effect of the solvent, the recovery of 2 to 5 rings chlorinated aromatic hydrocarbons using n-hexane and dichloromethane in the ratio 1:1 and using dichloromethane is high. Additionally, SFE recovers more 2-ring chlorinated aromatic hydrocarbons than does soxhlet. The comparison of the time required by SFE with that required by soxhlet extraction indicates that the SFE more quickly extracts 1 to 5 rings chlorinated aromatic hydrocarbons. The recovery percentages of the compounds are achieved using the 8270 'phenols mix', and the TCL polynuclear aromatic hydrocarbons mix are 67.6 ~ 89.3% and 71 ~ 112.8%, respectively. Based on these results, one can conclude that the SFE is a better method for extracting volatile and semi-volatile organic compounds while comparing to soxhlet extraction.

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