STUDY OF EXTRACTION PROCESS UTILIZING SUPERCRITICAL FLUID FOR CHLORINATED AROMATIC HYDROCARBONS

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ABSTRACT

The supercritical fluid extraction (SFE) of chlorinated aromatic hydrocarbons is investigated by governing a variety of interrelated parameters, including pressure, temperature and velocity of fluid. Based on supercritical fluid extraction technology to extract chlorinated aromatic hydrocarbons, the optimum extraction parameters are established and compared with the results of Soxhlet. The result shows the optimal extraction parameters at 250 bar of pressure, 40 degree centigrade of temperature, and 2.0 mL/min for the fluid flow rate. For the influence of solvent experiment, the high recovery of 2-5 rings chlorinated aromatic hydrocarbons is applied to n-Hexane and Dichloromethane by the ratio 1:1 and Dichloromethane. Furthermore, it is found that SFE has a higher recovery percentage than Soxhlet for 2 rings chlorinated aromatic hydrocarbon. Regarding to the time consuming, the SFE with 1-5 rings chlorinated aromatic hydrocarbons are found to be the faster than Soxhlet. Additionally, the recovery percentage of compounds are between 67.55~89.27％ and 71~112.8％ for 8270 Phenols Mix and TCL Polynuclear Aromatic Hydrocarbons Mix, respectively. Based on these results, the SFE is proved to be a better and feasible extraction technology for volatile and semi-volatile organic compounds.

KEYWORDS: Supercritical fluid extraction, chlorinated aromatic hydrocarbons, recovery, soxhlet extraction

1. Introduction

Supercritical fluid has the similar function as diffusive gas and solute liquid. In general, the supercritical fluid has faster permeability and solubility rather than liquid. Indeed, by comparing traditional industrial solvent with supercritical carbon dioxide or other supercritical fluid, the supercritical fluid is identified as the most environmental friendly use solvent. Also, accrued pollutant can be much more reduced as carbon dioxide or recycled and reused after cooling the pressure down. Due to the development of the supercritical fluid extraction technology, pernicious elements can be removed from pollutant that is called green chemistry from the viewpoint of sustainable environment. The implementation of supercritical fluid extraction (SFE) in environmental analysis has been well documented by [1]. For the determination of 2,3,7,8 TCDD in sediment samples, [2] used both static and dynamic SFE technologies with nitrous oxide at 2% solution of methanol in nitrous oxide. The supercritical fluid is becoming an acceptable alternative to conventional liquid solvents for the rapid analytical-scale extraction of environmental samples. Moreover, a single stage solvent extraction using either methanol or 2-propanol can successfully remove between 65 to 75% of DDT, DDD and DDE, while large extraction stage up 6 can remove more than 99% [3].

By comparing SFE with Soxhlet, the result of extract organochlorines from matrices including high level fate showed that SFE is powerful alternative for extraction since the solution for applying the trait of gas such as temperature and pressure that reached the critical point and easily penetration into smallest pores such fly ash. Another advantage specification for SEF is to shorten the extraction time [4]: 24 hours requirement to extract PCDDs from a matrix of fly ash by Soxhlet equipment and over 15 hours for clean-up as well as quantization, only 2.5 hours by SFE.

Supercritical fluid extraction recoveries are controlled by many variables including pressure, temperature, solvent, velocity of fluid, extractor geometry, restrictor sizes, modifiers, and sample matrix composition. The case, analysis of chlorinated dibenzofurans in municipal fly ash reported by [5] indicated that the optimum timing for extracting 25 to 30 mg of samples is less than 120 min., 400 atm and 45 degree centigrade.

The main objective of this study is to investigate a variety of interrelated parameters such as pressure, temperature and velocity of fluid, and compare the soxhlet extraction for determining the feasibility technique for supercritical fluid extraction.

2. Materials and Method

2.1 Instrument for Experiment

The instrument applied for supercritical fluid is provided by HP, Model SFE 7680T (Hewlett-Parkard, North Hollywood, CA, USA). **Figure 1** describes the SFE system. The SFE system is comprised of a set of dual-piston pump to provide the largest pressure till 380 bar, thermostatic extraction chamber to heat till 150 degree centigrade, 7 mL of thimble by hand-lock, variable tor, and analytic trap of Octadecy-lbonded silica (ODS). The liquid carbon dioxide goes into thimble by pressure with high pressure pump and both of temperature and pressure for fluid reach the threshold limit value (TLV) or the value for experiment to set up after pre-heater then carbon dioxide goes through extraction chamber with the status by supercritical fluid and takes along sample extract. Carbon dioxide after restrictor with supercritical status is step-down as gas which has no solubility right now, and therefore sample extract can be easily parted from fluid and adsorb on analytic trap. The final step is to apply an appropriate solvent and fixed flow rate to rinse analytic trap in order to collect rinsing solvent into 1.8 mL of vial, then the collected fluid can directly apply GC/FID and GC/MS for analysis.

2.2 Production procedure for Quartz Sand

The diameter of quartz sand (Mesh #25 to 30) after sieving procedure is 0.7 to 1.1 millimeter and 1.1 to 1.4 millimeter for this research. Wash particle and impurity on the surface of quartz sand with deionised water, apply acetone and n-Hexane solvent to remove out survival water and dissolve adsorbent elements on the surface after baking under 105 degree centigrade with 24 hours then bake continuously as storage for future requirement.

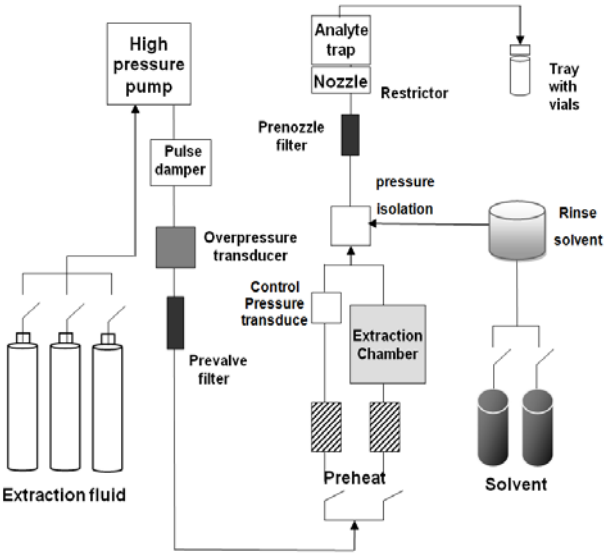

Figure 1. SFE 7680T system**.**

2.3 Methods for Experiment

First of all, put a set of glass wool into the location that fluid flows in the bottom of thimble then place around 1 gram of Na_2SO_4 into glass wool also get 1 gram of clean quartz sand (Mesh, #25 to 30) into 7ml of thimble. Add standard solution (Semi-volatile Internal Standard Mix, or 8270 Phenols Mix, or TCL Polynuclear Aromatic Hydrocarbons Mix. The standard solution were purchased from SUPEICO (Bellefonte, Pennsylvania, USA)) into quartz sand then finally place a set of glass wool, the height of filler has to fit for both of spiral caps, stopper both of spiral caps tightly then keep thimble into extraction chamber and set up the extraction parameter for future extraction.

3. Results and Discussion

3.1 Extractive effect against pressure and temperature

The most important parameters influencing supercritical fluid extraction are pressure and temperature. Therefore, this present paper research aims to understand the impact of recovery with chlorinated aromatic hydrocarbons by supercritical fluid extraction against pressure and temperature. For this purpose, the temperature and pressure were set at 25 and 40 degree centigrade, and 250 and 360 bars, respectively. From the results given in **Table 1**, it can be observed that the recovery is increasing with a fixed temperature of 25 degree centigrade and raising pressure from 250 to 360 bars.

Recovery presented a reduction with fixed temperature for 40 degree centigrade and raising pressure from 250 to 360 bars so that recovery won't be effectively advanced with fixed temperature as 40 degree centigrade and raising pressure. This is mainly caused by the molecular distance shortens and permutation more close together as density increases, hence viscosity coefficient raises and the strength of flow ascends. On the contrary, the recovery decreases because of the low diffusion coefficient of fluid which fluid cannot quickly pass through matrix under such density condition also decrease the contact ratio with sample extract [6-7].

The recovery rises with fixed pressure of 250 bars and the raising of temperature from 25 to 40 degree centigrade. The recovery is also presented low range of raise with fixed pressure as 360 bars and raising form 25 to 40 degree centigrade. It can be concluded that the best recovery for pressure and temperature has to be applied at 250 bars and 40 degree centigrade. Density and temperature of fluid showed an inverse ratio with fixed pressure, i.e. high temperature and low density of fluid increase diffusion coefficient and make it quick pass through matrix. Accordingly, the advance desorption rate for the recovery sample extract is advanced with the raising of temperature. For organic material with high molecular weight and low vapour pressure such as PAHs of 5 to 6-ring compounds, vapour pressure of such organic material will be advanced with raising temperature and effectively interrupt the bonding between organic and matrix [8-9]. Study done by [10] compares the concentration of pressure at 200, 400, 500 bar for a constant temperature 140˚C. The results show that temperature is the governing parameter rather than pressure, due to the similarity of their extraction concentration. The element influencing the recovery is the temperature as reported in literature. Advancing either vapour pressure or desorption rate of sample extract will positively influence the effect of recovery.

Table 1. Recovery percentage of chlorinated aromatic hydrocarbons for different pressures and temperatures.

Extraction solvent：Dichloromethane Flow rate：2.0 mL/min
Standards：Semi-volatile Internal Standard Mix, 50 ng/μL × 500 μL

Recovery(%)	250 bar 25℃	250 bar 40℃	360 bar 25℃	360 bar 40℃
1,4-Dichlorobenzene-D4	22.6	64.1	25.0	30.6
Naphthalene-D8	68.2	103.0	76.2	84.4
Acenaphthene-D10	70.1	97.9	80.9	90.3
Phenanthrene-D10	72.8	101.3	85.9	95.5
Chrysene-D12	75.0	117.7	87.3	99.1
Perylene-D12	71.5	116.7	85.6	93.7

3.2 Extractive effect against flow rate

In this phase, the pressure and temperature are set to 250 bars and 40 degree centigrade as the result from the last phase to research extractive effect against flow rate. The comparative result is plotted in **Figure 2**. 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.

By speculation, extraction flow rate is much higher and stagnation time fluid within extractive trap is shortened to cause incomplete contact with fluid and sample extraction also extractive efficiency is influenced seriously. The main cause that influences the efficiency of the dynamic extraction procedure is the speed of flow rate. Owing to the requirement by dynamic extraction to be provided, the coordination between the speed of flow rate and extractive timing will indirectly influence the actual volume to pass through extractive trap. This is not only sustained but also stable and flash fluid in order to pass through solid matrix and also enough flow volume to pick extractive analysis samples to collected trap. In other words, recovery is presented as positive correlation with the speed of flow and sample extract during process of dynamic extraction.

3.3 Extractive effect against solvent

In general, PAHs is non-polar material as its molecular structure with high symmetrization and shorter dipole moment. Non- or weak-polar organic solvent such as n-Hexane, Acetone, Toluene and Dichloromethane has the highest dissolution [11], so that apply three kinds of solvent to extract, n-Hexane, Dichloromethane and the co-solvents as ratio 1:1 by n-Hexane and Dichloromethane, for this phase to study the impact of recovery with different solvent. The results showed in **Table 2 and Figure 3** present the recovery for low and high-ring compound. From these results, it is more indicated to apply extraction co-solvents with co-solvents as ratio 1:1 by n-Hexane and Dichloromethane and Dichloromethane; meanwhile, higher recovery for high-rings is applied to Dichloromethane. The study done by [12] point out the most outstanding extractive effect for PAHs of high molecular weight to be applied with Dichloromethane.

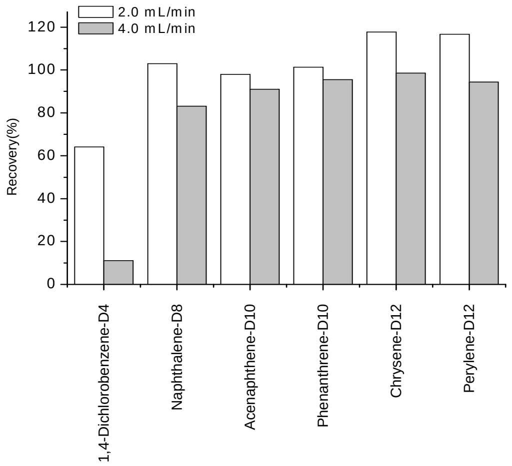

Figure 2. Recovery percentage of chlorinated aromatic hydrocarbons for different flow rate

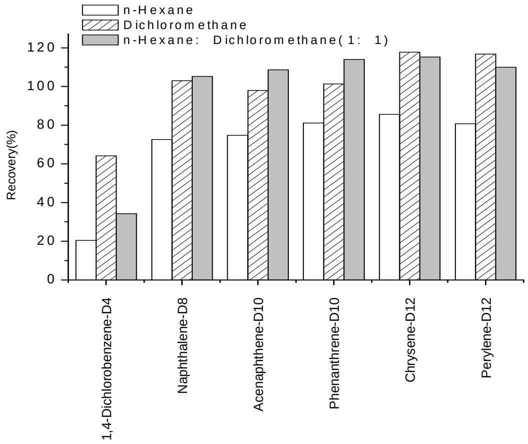

Figure 3. Recovery percentage of chlorinated aromatic hydrocarbons for different solvent by SFE.

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

Method	SFE			Soxhlet		
Recovery(%)	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

3.4 Comparison of supercritical fluid extraction and Soxhlet extraction

The method to dispose of semi-volatile internal standard mix by traditional soxhlet extraction and supercritical fluid extraction is assessed for determining a possible technique of supercritical fluid extraction. The results for Soxhlet are shown in **Table 2 and Figure 4** which illustrate the comparison of recovery application. The results presented recovery for low-ring compounds are lower to apply either SFE or Soxhlet. The result presented higher recovery for 2-ring chlorinated aromatic hydrocarbon by SFE after comparison with Soxhlet to apply three kinds of solvents for extraction. High recovery for 3 to 5-ring chlorinated aromatic hydrocarbons by Soxhlet has a single-apply extraction solvent, n-Hexane. Additionally, high recovery for low to high-ring compounds by SFE has a single-apply extraction solvent, Dichloromethane or co-solvents as the ratio 1:1 by n-Hexane and Dichloromethane.

From the results of this study, it can be concluded that, supercritical fluid extraction is better than Soxhlet extraction. By the comparison of the extract time, within an hour by supercritical fluid extraction can be fulfilled, over 18 hours by Soxhlet extraction is required with same result. Furthermore, for a low volume of solvent i.e. less than 20ml of organic solvent, the supercritical fluid extraction is needed to acquire effective sample extraction, however, over 300ml requires the Soxhlet extraction.

3.5 Extraction for different target compounds

For this phase, Dichloromethane is applied as extraction solvent to research the impact of recovery by supercritical fluid extract different target compounds. Recovery of all compounds to extract 8270 Phenols Mix is from 67.6% to 89.3% which is presented in **Figure 5a**. Average recovery is to estimate dimension of molecular weight is not the main element to influence recovery under appropriate temperature and pressure for extraction. Recovery of all compounds to extract TCL Polynuclear Aromatic Hydrocarbons Mix is from 71% to 112.8% as **Figure 5b**, especially higher recovery by PAHs of high-ring compound, lower recovery by Benzo (A) pyrene. By speculation, the interactions between Benzo (A) pyrene and matrix were much stronger and extract hardly, however recovery of 5 and 6-ring chlorinated aromatic hydrocarbons are very high.

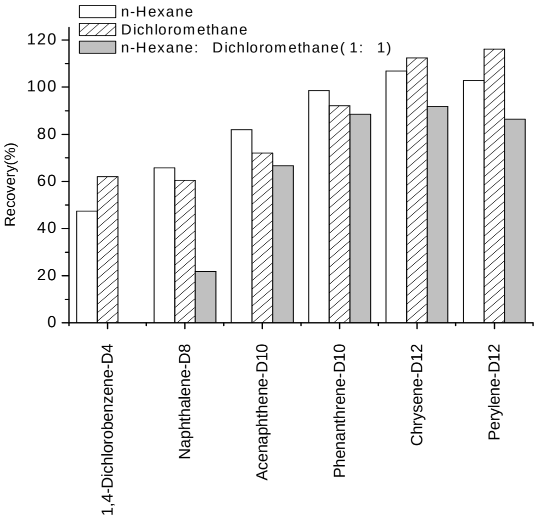

Figure 4. Recovery percentage of chlorinated aromatic hydrocarbons for different solvent by Soxhlet.

4. Conclusion

The present research paper studied the possibility to apply SFE instrument for extraction against different groups of semi-volatiles (phenols and polycyclic aromatic hydrocarbons) from quartz sand. The results show that the optimal condition for extraction such as pressure, temperature and fluid flow rate are 250 bars and 40 degree centigrade and 2.0 mL/min, respectively. For the influence of solvent experiment, the high recovery for 2-5 rings chlorinated aromatic hydrocarbons is applied with n-Hexane and Dichloromethane by the ratio 1:1 and Dichloromethane. Furthermore, SFE has a high recovery percentage than Soxhlet for 2 rings chlorinated aromatic hydrocarbon. The comparison of SFE with Soxhlet for time consuming showed that the SFE can fulfill faster for 1-5 rings chlorinated aromatic hydrocarbons. The recovery percentage of compounds are between 67.55~89.27% and 71~112.8% for 8270 Phenols Mix and TCL Polynuclear Aromatic Hydrocarbons Mix, respectively. Based on these results, the SFE is proved to be a better and feasible extraction technology for volatile and semi-volatile organic compounds.

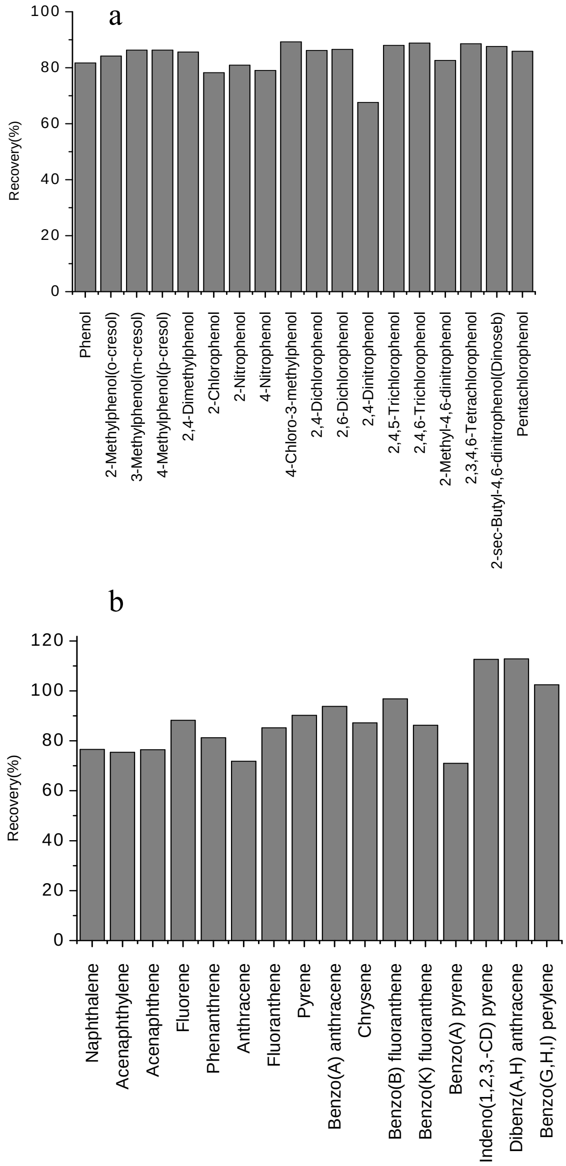

Figure 5. Recovery percentage of different target compounds: (a) 8270 Phenols Mix; (b) TCL Polynuclear Aromatic Hydrocarbons Mix

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