

SEPARATION CONDITIONS AND PERCENTAGE RECOVERY OF DIOXIN-LIKE PCBs, PCDDs AND PCDFs THROUGH POWER-PREP BY FLUID MANAGEMENT SYSTEMS

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Introduction

The environmental contamination by highly toxic polychlorinated, -biphenyls (DL-PCBs), -dibenzo-p-dioxins (PCDDs), -dibenzofurans (PCDFs) and organic pesticides among general population is of major debate¹⁻². Due to the public awareness and complicated procedures of analyzing aforementioned chemicals, a much precise methods with special emphasis on rapid determinations and cost effective method should be developed³. Since the traditional (the method currently used for analyzing organic chemicals) clean up and analysis of organic pollutants are rather time consuming and very expensive. Nevertheless, analysis of these organic pollutants is compulsory in environmental and biological samples that include human tissue (e.g., human blood). In this particular instance, speedy and cost reducing methods should be focussed for the future generation³.

The rapid spread of new technology has raised the level of concern about electric and magnetic field interference and has greatly increased the consequences of that interference. Consequently, the Fluid Management Systems (FMS) instruments employed for the sample preparation and purification of environmental and pharmaceutical samples in recent past. Particularly high speed automated sample clean-up system for dioxins, PCBs and pesticide analysis have been introduced for the environmental analysis. High-speed sample

processing Power-Prep workstation attained greater attention in order to swift analysis of organic pollutants. These instruments were designed to automate the extraction and cleanup of toxic compounds such as dioxins, PCBs, pesticides, and PAHs from environmental, biological and food samples. Using these systems it is possible to conduct from 1 to 10 samples in less than 1 hour, thereby, achieving high recoveries and excellent precision for all target compounds.

In the present investigation, we conducted PCDD/DF and DL-PCBs analysis in FMS with silicagel, alumina and carbon columns with different mixtures of elution solvents such as hexane (HEX), dichloromethane (DCM) and Toluene (TOL) in order to find out the best condition and adaptability of FMS for the environmental analysis.

Materials and Methods

Preparation of standard solution and analysis:
The ¹³C₁₂-labeled standard solutions (viz., 17 isomer/congeners of 2,3,7,8-chlorine substituted dioxins, furans along with 1,2,3,4-TCDD, 1,3,6,8-TCDD/TCDF of PCDD/DFs and 14 dioxin like PCBs [4 non-ortho, 8 mono-ortho and 2 di-ortho]) were spike in the n-hexane and these hexane layer were spiked in silicagel column, alumina column and activated carbon column for separation test. The silicagel cartridge consists of 44% H₂SO₄ silica (5 g) and silicagel (2.7 g). The alumina cartridge packed

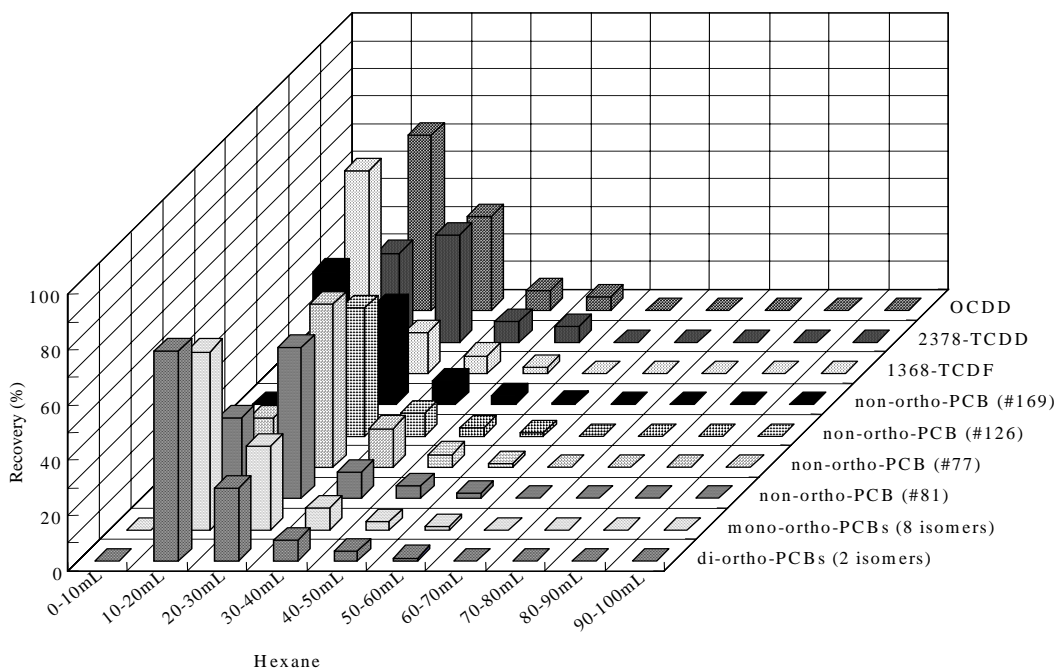
with 12 g of alumina, whereas, activated carbon cartridge packed with 0.36-g active carbon powder. The test was conducted in silicagel, alumina and active carbon separately as well as sequential basis that established for traditional dioxin analysis determinations.

Power-Prep system consists of high-speed sample processing device in which it can control by computer monitor. The computer controlled liquid chromatography system performs simultaneous sample processing automatically. This system performs the entire extraction and cleanup automatically including sample loading, washing, elution and fraction collection. FMS's powerful windows-based monitoring and control software offers a rich set of features and flexibility. It includes functions to develop and optimize methods. Input parameters include flow rates, volumes, column

modules, sample processing modules. The Power-Prep modules are mounted vertically on a portable cabinet. It is a self-contained system that also provides storage for solvent bottles, waste and collectors.

Results and Discussion

The results obtained based on the silicagel column and hexane was shown in Figure 1. Mono and di-ortho PCBs with higher chlorinated ones, non-ortho PCBs such as CB-126, CB-169, higher chlorinated dioxins and higher chlorinated dibenzofurans along with 1,3,6,8-TCDF were mostly eluted in 10-20 mL hexane and almost 90% were eluted with in 40 mL hexane (Figure 1). Collectively, 10-20 mL and 20-30 mL but with in 60 mL separation was complete using silicagel and hexane alone. The percentage recovery was also found to >80%.



selection, sample size, solvent selection and fraction collection. Each Power-Prep system contains multiple quick connect modules consisting of: power supply module, control module, pump & pressure modules, valve drive

Figure 1. Separation conditions of PCBs and PCDD/DFs in silicagel column with HEX.

The separation conditions of PCDD/DFs and

dioxin-like PCBs in alumina column were shown in Figure 2. The recovery standard of 1,2,3,4-TCDD was found 100% in all the fractions and thus its indicates complete recovery in alumina fractionation. The 30 mL of HEX didn't separate any dioxins/furans and PCBs but the 50% DCM:HEX 50:50 (v:v) at the 10-20 mL to 30-40 mL were separated dioxins and PCBs. While dioxins and furans take long elution time of upto 40 mL whereas, dioxin-like PCBs get separated with in 20 mL of elution solvent. Indicatably, 2,3,7,8-TCDD and OCDD elution found late with complete separation was noticed at 60 mL of DCM:HEX.

were separated in 50% DCM:HEX and minor fractions at 10% TOL (15 mL each) with in 10-20 mL. In order to completely separate mono- and di-ortho PCBs, the TOL percentage was increased respectively, 10, 20, 25, 30%. The non-ortho PCBs separated only at reverse TOL while increased separation conditions of mono-/di-ortho PCBs was observed at 30% TOL. We also conducted mono- and di-ortho PCBs separation with 10% and 25% TOL with 15, 20, 30 mL volume, respectively. The results were more or less similar to the 10% TOL separation however slight improvement in separation conditions were noticed. On the whole, the best

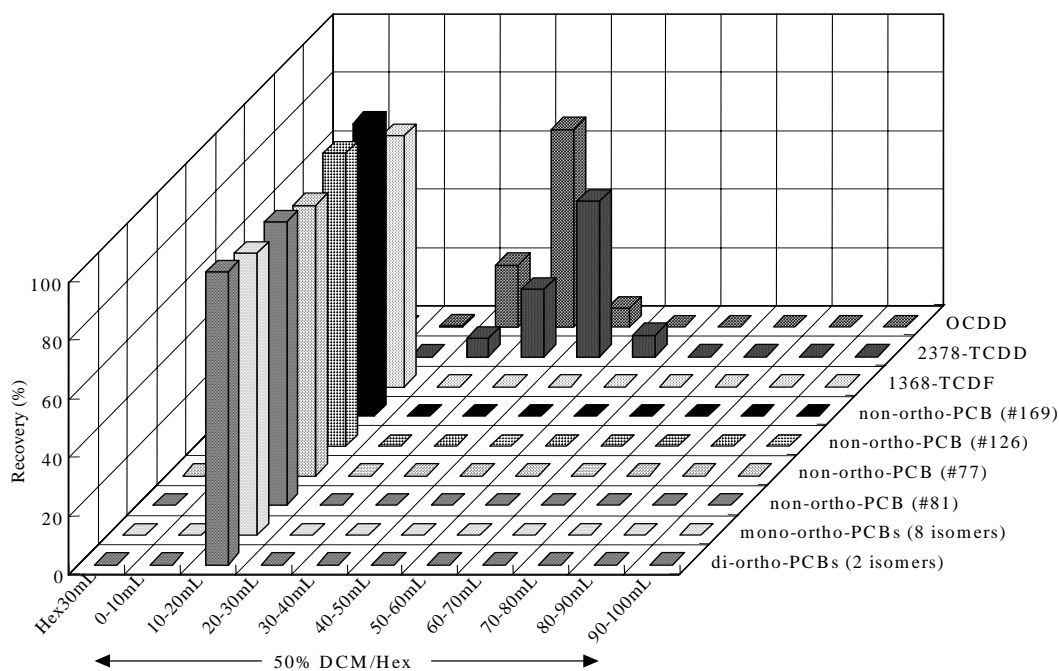


Figure 2. Separation conditions of PCBs and PCDD/DFs in alumina column with HEX and 50% DCM:HEX.

The separation conditions of PCDD/DFs and dioxin-like PCBs using active carbon column were shown in Figure 3. PCDD/DFs and non-ortho PCBs were eluted only in reverse TOL while, majority of mono and di-ortho PCBs

suited condition of FMS power prep instrument was summarized in Figure 4. In this study, the blank run also carried out with each batch and the results suggested there is a mono-ortho PCBs such as CB-118. Furthermore no contamination was noticed in any fractions of silicagel, alumina and active carbon powder columns. With considering the observations reported in this study the FMS seems to a highly reproducible and most reliable.

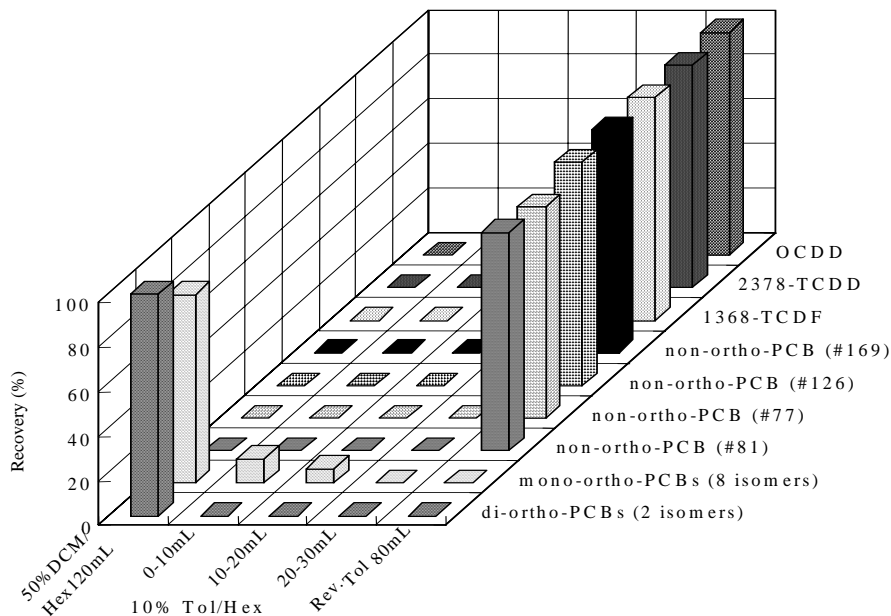


Figure 3. Separation conditions of PCBs and PCDD/DFs in active carbon column with 50% DCM:HEX, 10% TOL and reverse TOL.

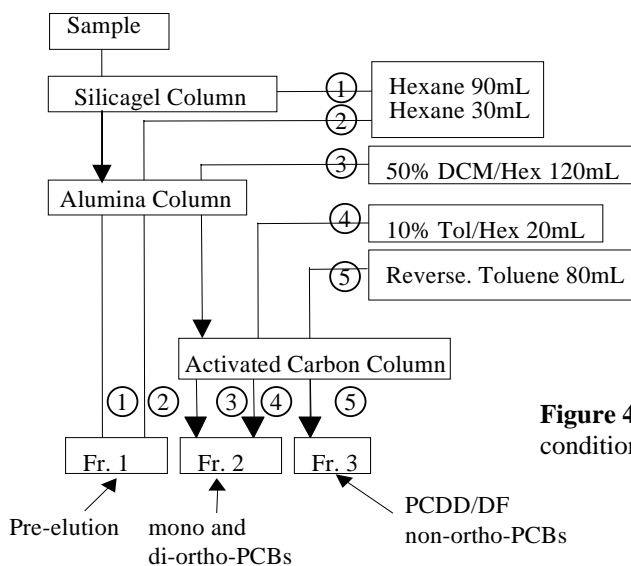


Figure 4. The best suited operation and flow condition of FMS.

References

1. Senthil Kumar, K., Kannan, K., Paramasivan, O.N., Shanmugasundaram, V.P., Nakanishi, J., Masunaga, S. (2001) Environ Sci Technol 35: 3448
2. Senthil Kumar, K., Kannan, K., Giesy, J.P., Masunaga, S. (2002) Environ Sci Technol 36: 2789
3. Shibayama, M., Takasuga, T., Hayashi, A., Inoue, T. (2003). J Environ Chem 13: 17-29 (in Japanese)