

Modified Sample Clean-up for Combined POPs Using Automated Multi-Column Fractionation and Analytical Optimization

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Introduction

Continued interest in Persistent Organic Pollutants (POPs) such as polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs) and biphenyls (PCBs) means that there is a demand for reliable sample processing with short turn-around times and a high degree of precision and reproducibility. Traditionally open column chromatography clean up of these samples has involved acidified or acid-base-neutral silica, alumina and carbon columns. The automated systems developed have mostly limited themselves to collecting two fractions, with PCDD/Fs and co-planary PCBs eluting in one fraction and the mono- and di-ortho PCBs in a second fraction.¹

In the work presented here, we have developed a method to include not only PCDD/Fs and PCBs, but also organochlorine pesticides and polychlorinated naphthalenes. A total of three fractions were collected. The method enables laboratories to optimize their workflow so as to collect as many analytes as possible within the same clean up step.

Materials and methods

Automated Column Chromatography Clean Up

The system consists of a control module, valve modules, pump modules, and sample processing modules. A small computer has been included in the system which controls the elution programs. Programming of the various columns, solvent flows and volumes is done via a plumbing schematic. The system uses flows typically between 5 and 10 mLs/min. Columns used are acid-base-neutral silica with silver nitrate, florisil and carbon.

The system used hexane, dichloromethane and toluene for elution. Total solvent use for the data shown here is 500-600 mLs. 1 g soil extracts were used for testing the methods. The silver nitrate part of the silica column was used to remove any sulfur from the soil. The sulfuric acid and sodium hydroxide impregnated parts of the silica column were used to oxidize and reduce any organic interferences. The florisil was optimized so as to fractionate all PCBs and retain all PCDD/Fs and PCNs which were subsequently eluted onto the carbon. Hexane eluted through the silica and florisil columns was collected as Fraction # 1, containing all PCBs, BDE-209, some of the other PBDEs (partial) and some of the Organochlorine Pesticides. Dichloromethane was then eluted through the florisil and carbon columns and collected as Fraction # 2. This fraction contained the remaining PBDEs and the other non-acid labile OCPs. Finally the carbon column was eluted in the reverse direction with toluene, collecting PCDD/Fs and the PCNs as Fraction # 3.

Concentration

Samples were reduced in volume in a 6 position evaporator: pre-heated for 20 min at 45-55 °C, followed by heating under nitrogen at ~ 6-8 psi. The evaporator has built-in sensors that automatically shut off the nitrogen flow when the sample reaches ~ 0.5 mLs of volume. Further nitrogen blow down in a vial evaporator reduced the final sample volume to 10 uL. Recovery standards were then added.

Analysis

Samples were analyzed for PCDD/Fs and PCBs on a high resolution Thermo DFS GC/MS with a Trace 1310 GC containing a 60 m DB-5 like column. Temperature programs used were ~ 55 min for PCDD/Fs and ~ 35 min for PCBs. PBDEs and OCPs were analyzed on a Thermo Quantum ULTRA TSQ with a Trace Ultra GC with dissimilar injection ports (PTV & Split/Splitless).

Results and Discussion

Results are shown for PCDD/Fs (Figure 1), PCBs (Figure 2), PBDEs (Figure 3) and PCNs (Figure 4). Recoveries found were excellent across all individual congeners and compound classes. Florisil was shown to be very effective for optimizing PCBs in an environmental matrix. Florisil turned out to be also very efficient at fractionating the PCNs together with the PCDD/Fs. The data for PCNs was limited by the number of commercially available congeners. When analyzing PBDEs activated copper would be a suitable alternative to the use of silver nitrate which could increase recoveries. OCP recoveries (not shown) could benefit from using small amount of sample, as increasing amounts of acidified silica gel necessary for larger sample amounts (e.g., 10 g) could result in decreased recoveries.

The data shown demonstrates the feasibility to extend sample clean up and fractionation beyond the traditional compounds classes of PCDD/Fs and PCBs. Fully automated open column chromatography can now be used to add PBDEs, PCNs, and OCPs to the analysis at little extra cost. The use of florisil columns as an alternative to alumina shows promising results for fractionating these five compound classes into three fractions. An added advantage is that all PCBs elute in the same Fraction (# 1). The degree of deactivation of the florisil sorbent is critical to achieve the right amount of fractionation.

References:

1. Focant, JF, Shirkhan, H, Patterson Jr, DG (2009) *Organohalogen Compounds*, **71**, 2438-2443.

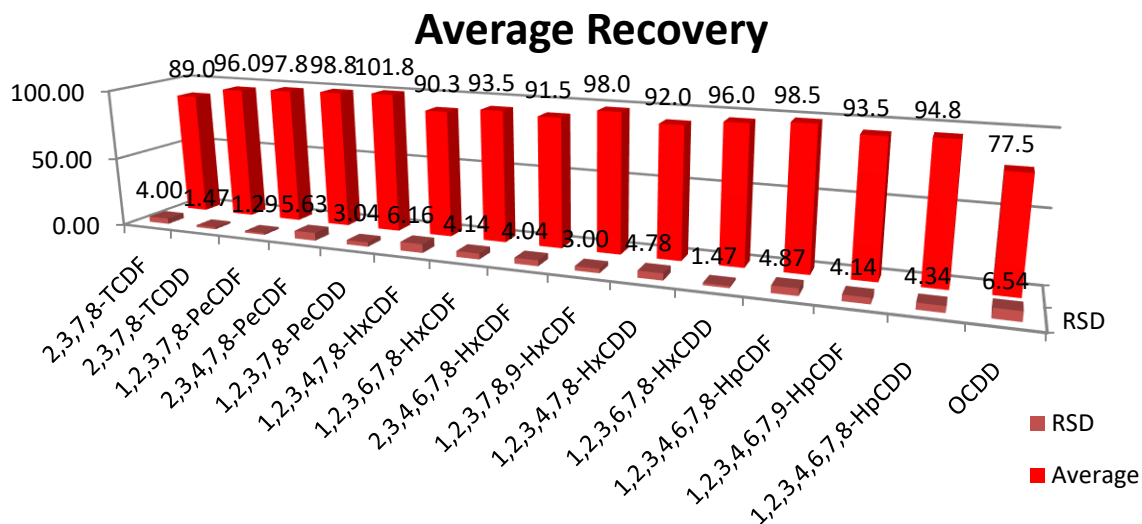


Figure 1. PCDD/Fs Labeled Recovery in a Soil Matrix.

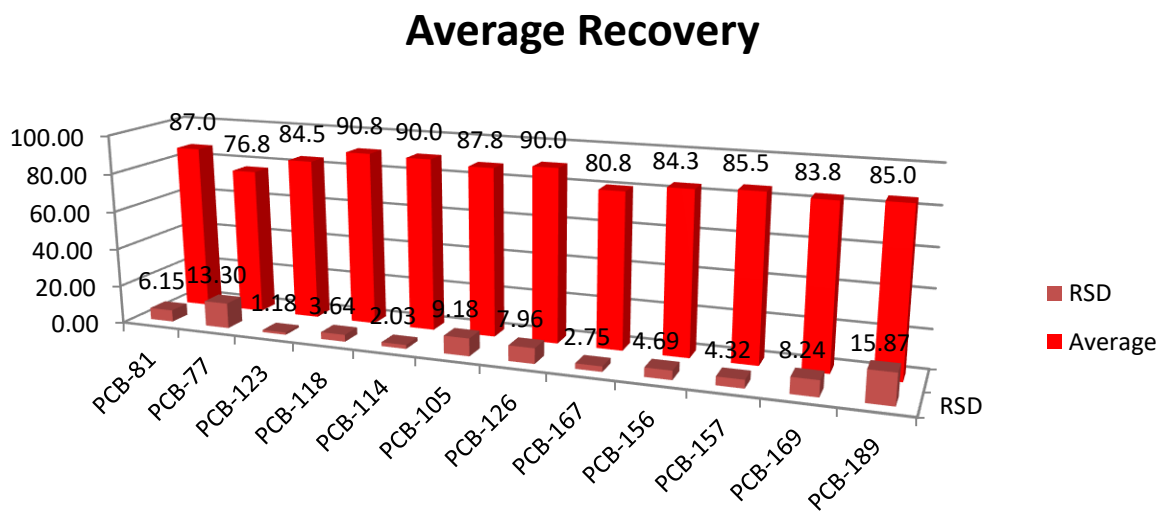


Figure 2. PCBs Labeled Recovery in a Soil Matrix.

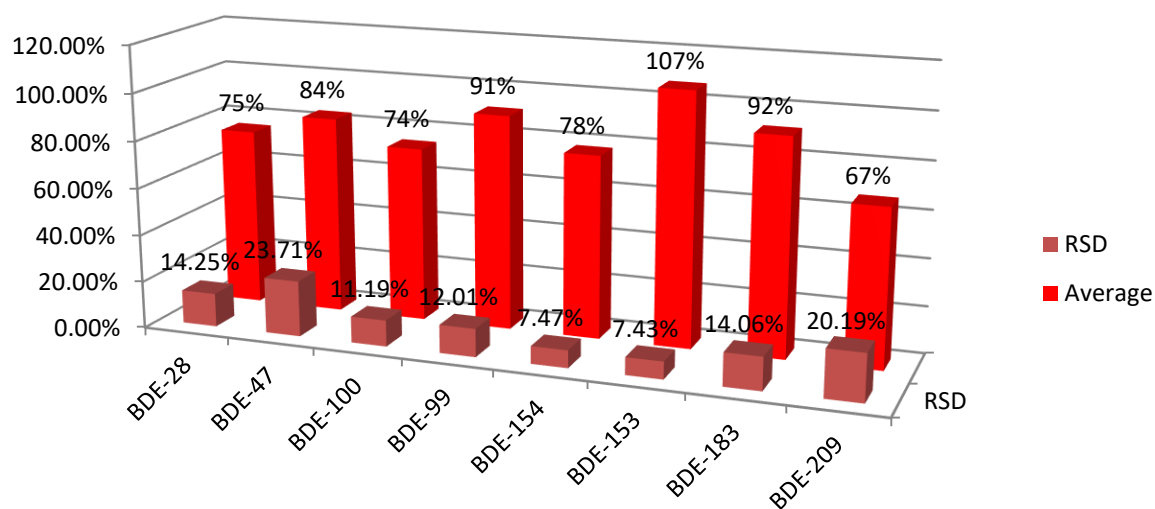


Figure 3. PBDEs Labeled Recovery in a Soil Matrix.

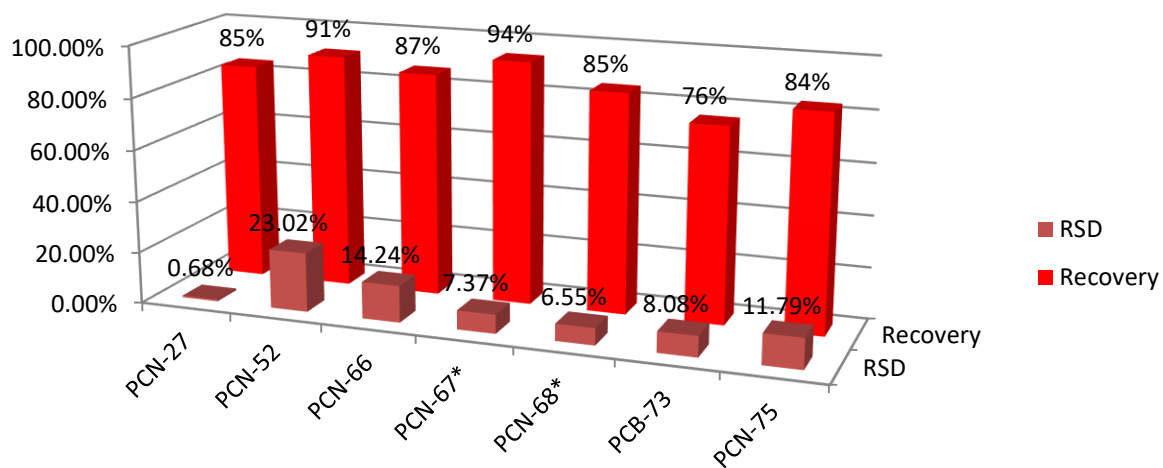


Figure 4. PCNs Labeled Recovery in a Soil Matrix.