

# DETERMINATION OF DIOXINS/FURANS (PCDD/Fs), DIOXIN-LIKE POLY-CHLORINATED BIPHENYLS (dlPCBs), POLYBROMINATED DIPHENYL ETHERS (PBDEs) AND POLYCHLORINATED NAPHTHALENES (PCNs) IN CLEAN WATER USING THE CAPE TECHNOLOGIES CLEANUP TECHNIQUE

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## Introduction

The analysis of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), dioxin-like polychlorinated biphenyls (dlPCBs), polybrominated diphenyl ethers (PBDEs) and polychlorinated naphthalenes (PCNs) is very challenging. Very laborious multi-stage sample preparation methods prior to instrumental detection<sup>1,2</sup> using gas chromatography-high resolution mass spectrometry (GC-HRMS) are required in order to detect these analytes at the sub-picogram levels needed to reach regulatory limits and health guidelines. All of the desired components of a compound group must be quantitatively extracted from the sample matrix. Target compounds must then be separated and purified by removing co-extractables and interferences through the cleanup procedure. Traditional open column cleanup for dioxin analysis involves acid/base/neutral silica, alumina and carbon columns. Similar procedures and reagents are used to cleanup extracts for other compound groups such as dlPCBs and PCNs<sup>3</sup>. The classical cleanup procedure can take up to three days for a set of 10 samples for each group of compounds (PCDD/F, PBDEs, PCNs, dlPCBs) excluding glassware cleaning time and background contamination checks. Traditional cleanup methods are time-consuming, laborious and costly. Many laboratories analyze PCDD/Fs, PCBs, PBDEs and PCNs separately, or combine only two of the groups together because of difficulties in collecting compounds in one sample extract<sup>4,5,6</sup>.

Yang et al<sup>7</sup> were able to analyze PCDD/Fs, dlPCBs, PBDEs and PCNs together in one run for fish tissue using disposable coupled acid silica and carbon columns provided by CAPE Technologies. This cleanup technique produced high quality and consistent results within one day. It is less laborious and costly than classical open column methods. In this study, the CAPE Technologies cleanup technique is investigated for determination of dioxins and dioxin-like compounds in aqueous samples.

## Materials and methods

Known amounts of <sup>13</sup>C<sub>12</sub>-labeled PCDD/F, dlPCB, PBDE and PCN standards and native PCDD/F, dlPCB, PBDE and PCN standards were spiked into water sample prior to extraction. Ten 2-L water samples were extracted with C18 based solid phase extraction (SPE) on a solid phase extraction manifold (J.T. Baker, Avantor Performance Materials, PA, USA). A mixture of acetone and hexane was used to elute the target compounds. Water extracts were concentrated to approximately 0.5mL. The CAPE Technologies immunoassay sample preparation kit (Cape Technologies, South Portland, ME, USA) was used for the sample cleanup for all samples. Acid silica columns and 2% ultra-clean carbon columns used with the kit were also purchased from CAPE Technologies. The columns were pre-rinsed with dichloromethane and hexane. Concentrated water extracts were loaded onto the coupled acid silica and carbon columns (AS-C). Target compounds were eluted from the silica column with hexane to transfer the compounds onto the carbon column. Twenty millilitres of hexane, 10mL hexane:dichloromethane (15:85) and 10mL dichloromethane were used to elute mono-ortho PCBs/PBDEs from the carbon column in the forward direction (non-planar fraction – F1). The carbon column was then reversed and non-ortho PCBs, PCDD/Fs and PCNs were eluted with 30mL toluene in the second fraction (planar fraction – F2). Fraction 1 was evaporated to dryness and Fraction 2 was evaporated nearly to dryness. Both fractions were quantitatively transferred into GC auto sampler vials and injection standards were added for analysis by GC-HRMS. Detailed analytical procedures are listed in the respective analytical methods E3418, E3430 and E3431 which can be obtained from: [LaboratoryServicesBranch@ontario.ca](mailto:LaboratoryServicesBranch@ontario.ca)

## Results and discussion

Using the C18 based SPE disk extraction and CAPE Technologies cleanup technique described in the methods and materials section, all four groups of compounds, PCDD/Fs, dlPCBs, PBDEs and PCNs were successfully separated into two fractions.  $^{13}\text{C}_{12}$  isotopically labeled compounds were quantitatively recovered for each group. The average percent recoveries are shown in Figure 1. Using coupled AS-C columns, the  $^{13}\text{C}_{12}$  labeled PCDD/F recoveries ranged from 50% to 70%;  $^{13}\text{C}_{12}$  labeled dlPCB recoveries ranged from 50% to 70%;  $^{13}\text{C}_{12}$  labeled PBDE recoveries ranged from 50% to 110%; and  $^{13}\text{C}_{12}$  labeled PCN recoveries ranged from 20% to 80%.  $^{13}\text{C}_{12}$  labeled PCN 42 and PCN 27 have relative low recovery due to loss during sample concentration due to their higher volatility.

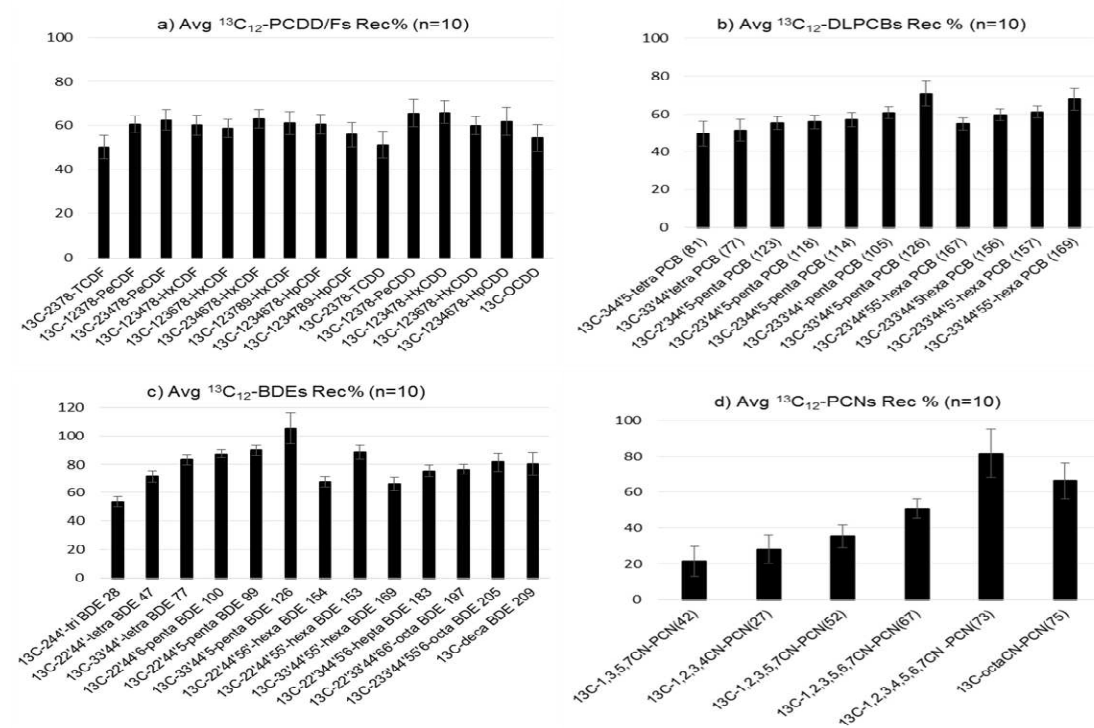
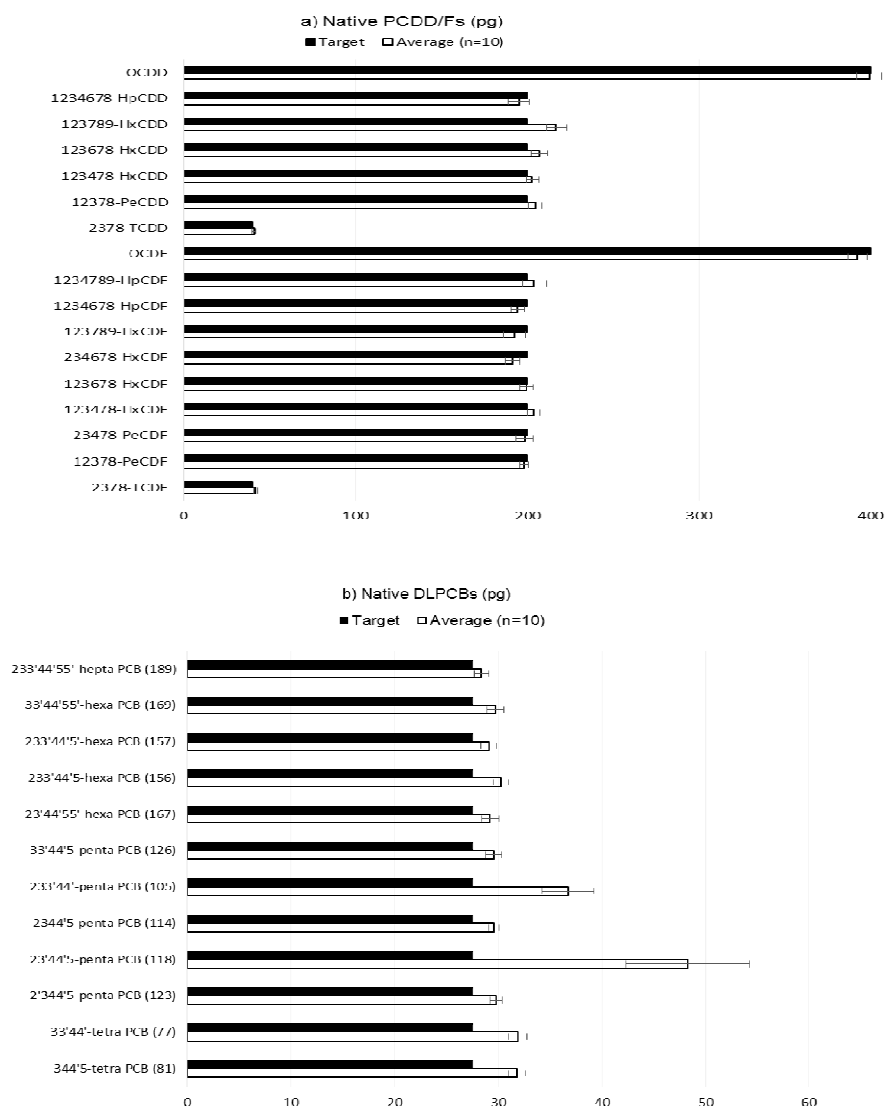


Figure 1:  $^{13}\text{C}_{12}$  isotopically labeled target compounds: a)  $^{13}\text{C}_{12}$ -PCDD/F, b)  $^{13}\text{C}_{12}$ -dlPCB, c)  $^{13}\text{C}_{12}$ -PBDE and d)  $^{13}\text{C}_{12}$ -PCN recoveries (%) in clean water.

The native PCDD/F, dlPCB, PBDE and PCN amounts reported in total picograms are compared with the spiked amounts as shown in Figure 2. Native PCDD/F amounts agree very well with the spiked amounts where recoveries ranged from 96% to 109%. Native dlPCB amounts were slightly higher than the spiked amounts. The dlPCB recoveries ranged from 103% to 116%, except for PCB 118 and PCB 105 at 175% and 133%, respectively. This is mainly due to background levels present in the laboratory. Native PBDE amounts agree with the spiked level; recoveries ranged from 97% to 136% except BDE 209 with a recovery of 167%, indicating background contribution of BDE 209 in the laboratory as it was widely used in numerous industrial products, such as fabrics and electronics as flame retardant. Native PCN recoveries ranged from 95% to 128% except PCN 54 and PCN 70 with recoveries of 139% and 160%, respectively.

The CAPE Technologies cleanup technique using coupled AS-C column is an effective method for the determination of dioxin and dioxin-like compounds in clean aqueous samples. This cleanup technique significantly reduces the cleanup time from three days to one day. Sample extracts were cleaned using separate disposable columns which eliminated cross contamination between sample batches. Also, this technique uses

much less solvent than that used in the classical three-stage dioxin procedure. The CAPE Technologies cleanup technique is easy to use, simple, fast and inexpensive when compare to classical methods. It can be used as an effective cleanup method for the simultaneous sample preparation of PCDD/Fs, dlPCBs, PBDEs and PCNs for clean aqueous samples.



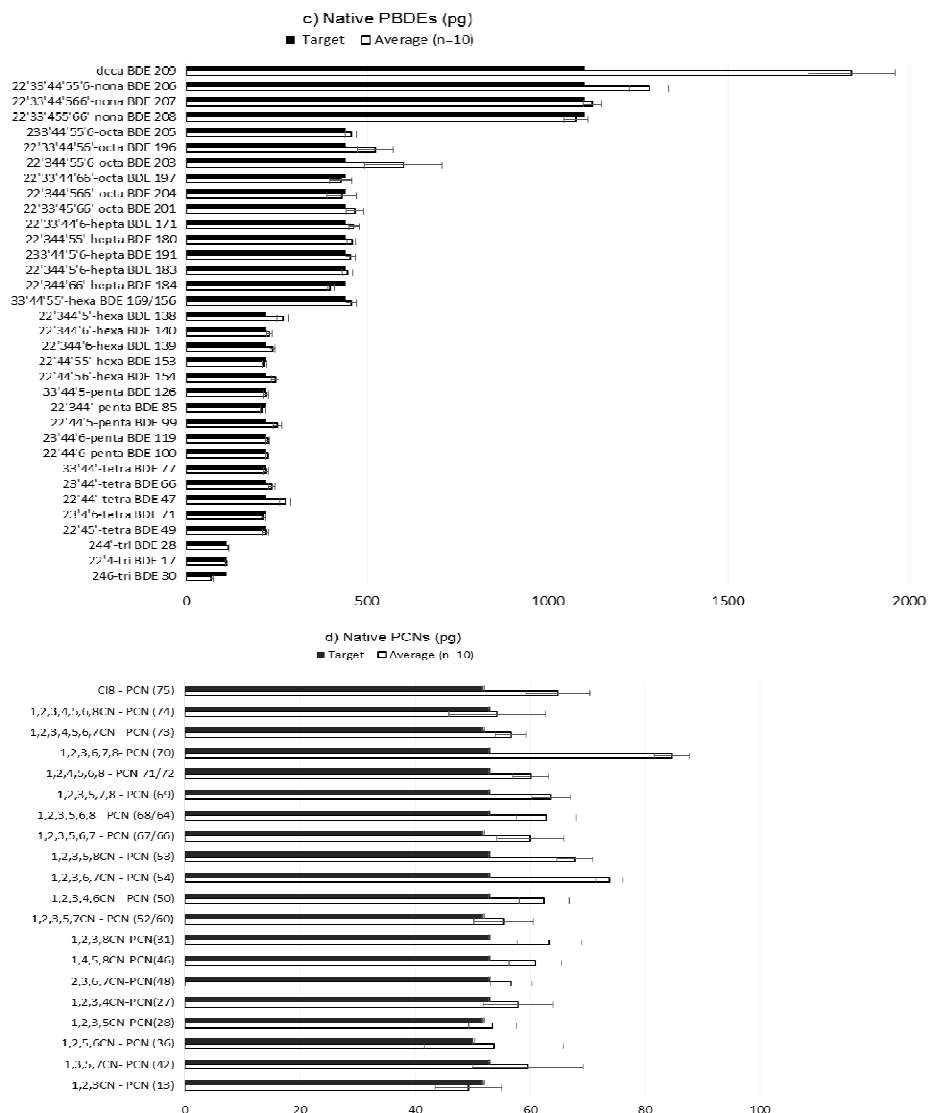


Figure 2: Average native compounds amount (pg) compared with the spiked amount: a) PCDD/Fs, b) dI PCBs, c) PBDEs and d) PCNs in clean water.

**References**

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