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Quantification of extractable total per- and polyfluoroalkyl substances (PFASs) in water using persulfate preoxidation and chemical defluorination with sodium biphenyl Monyratanak Lim¹, Nguyen Cong-Hau¹, Yunho Lee^{1,*}



¹ School of Environment and Energy Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, Republic of Korea * E-mail address (corresponding author): yhlee42@gist.ac.kr

Abstract

Total oxidizable precursor (TOP) assay is a promising method for enhancing the selectivity towards total PFAS, and optimization of the solid phase extraction (SPE) washing step was crucial in minimizing interferences from inorganic fluoride and non-PFAS organofluorine compounds present in simulated water samples after TOP assay (60 mM $K_2S_2O_8$ and 150 mM NaOH), thus contributing to the overall quality and precision of environmental monitoring with an average removal rate of 95%. The low LOD for SBP defluorination was estimated at 0.016 µg F/L and exhibited high recoveries for most of the PFASs in the simulated water samples. The results of SBP defluorination with TOP assay showed lower concentration than those without TOP assay, implying the necessity of TOP assay to enhance the selectivity. Ultimately, the integration of the TOP assay preoxidation technique with the SBP assay contributes to the development of a reliable analytical method and affordable for the analysis of total PFAS concentrations in water samples. Moreover, the proposed TOP assay preoxidation technique with the SBP assay does not require high-standard analytical instruments and can be applied in many laboratories for preliminary PFAS detection and monitoring processes. Consequently, the proposed TOP assay coupled with SPE preconcentration and SBP defluorination will be used to quantify total PFAS





Results and Discussion



Figure 1. Fluoride recoveries of the defluorination reactions between SBP and individual terminal and precursor PFASs. ACN spiked with PFASs at concentration levels of 500 µg/L (a) and Mixed (b). Fluoride recovery (%) is calculated by the ratio between fluoride concentrations obtained from the SBP assay and theoretically calculated from the chemical structure of each PFAS. (c) The SPE recoveries were determine by the targeted LC/MS analysis with TOP assay preoxidation using the simulated water sample at each 1 µg/L in UW. The bar heights represent the averages of triplicate experiments with the error bars indicating the standard deviations.

2. Optimization of SPE washing step to minimize the inorganic fluoride interferences and TOP assay efficiency to eliminate non-PFAS organofluorine compounds



Figure 2. (a) The simulated water sample was prepared by separately spiking TFA, BF_4^- (NaBF₄), PF_6^- (NaPF₆), and F^- (NaF) at 5 μ g/L in UW and the mixed 4 compounds at 2 µg/L/each in UW. The SPE recoveries for each compound were calculated by quantifying them using the SBP assay. The simulated water sample was prepared by separately

spiking non-PFAS organofluorine (b) non-PFAS organofluorine at 2.5 mg/L in UW. The recoveries of the fluoride for each compound were applied to different concentrations

of TOP assay and measured by the IC without the SPE. (c) non-PFAS organofluorine at 25 µg/L of CIP (%F= 5.73 %, 1.43 µgF/L), BFB (%F= 10.85 %, 2.71µgF/L), FLX

(%F=18.42 %,4.06 µgF/L), and ToF (%F= 5.47 %, 1.36 µgF/L) in UW. The recoveries of the fluoride for each compound were measured by the HPLC-UV and compared

between without TOP assay and with TOP assay 60 mM. The bar heights represent the averages of triplicate experiments with the error bars indicating the standard deviations.

Objectives

- To integrate the TOP assay and SPE to improve the selectivity of PFASs
- To compare the SBP assay with the advanced instrument combustion ion chromatography (CIC)
- To quantify total PFAS monitoring in several river basins



Figure 3. Concentrations determined by LC/MS, CIC, and SBP assays, both without and with TOP for (a) IW and (b) RW samples. All concentrations are expressed as µgF/L. The LC/MS results indicate the summed concentration of target PFAS. The bar heights represent the averages of triplicate experiments, with the error bars indicating the standard deviations.



Methodology

in both samples.

Conclusion

The study presents a method for analyzing total PFAS concentrations in environmental samples, focusing on the optimization of preoxidation, solid-phase extraction, and derivatization steps. The TOP assay was used for preoxidation, followed by WAX SPE cartridges for sample preconcentration. The study also explored the efficiency of the SBP assay towards various PFAS terminals and precursors. The integration of the TOP assay's pre-oxidation technique with the SBP assay enhanced selectivity towards total PFAS and minimized non-PFAS organofluorine compounds. This comprehensive approach contributes to the development of a reliable and accurate analytical method for the analysis of total PFAS concentrations in environmental samples, ultimately supporting the assessment of PFAS contamination levels and environmental monitoring.

Part 1: Persulfate peroxidation and solid phase extraction



Part 2: Defluorination and pre-column derivatization HPLC-UV for sodium biphenyl (SBP)



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