

# The Study of Recovery and Reproducibility of Extractable Organofluorine in Sediment Samples Using Uncustomed Combustion Ion Chromatography

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## 1 Introduction

Organofluorine compounds are widely used because of their unique physicochemical properties (water and oil repellency, heat resistance). Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid are registered as persistent organic pollutants (POPs), but in recent years, their analogues have been found to have similar properties, and registration of these analogues as POPs is being considered. Moreover, per- and polyfluoroalkyl substances (PFAS) are formed by reactions of the precursors. As the properties of fluorine compounds become better understood, increasing numbers of compounds will need to be investigated. However, it is difficult to assess 4000–5000 individual compounds, and measurement of extractable organofluorine (EOF) is attracting attention as a method for comprehensive evaluation. By measuring EOF, the collective risks associated with PFAS, including unknown organofluorine compounds, can be assessed. Combustion ion chromatography (CIC) is used to measure EOF, but few studies have examined the recovery rates and extraction reproducibility of fluorine determination in solid samples using CIC<sup>1</sup>. Therefore, in this study, we investigated the recovery and reproducibility of EOF in sediment samples using CIC. Before evaluating the extraction method, the blank reduction in CIC was worked. The recovery rate and reproducibility were examined by adding PFOA to sediment samples and measuring the EOF in the sediment samples (Figure 1).

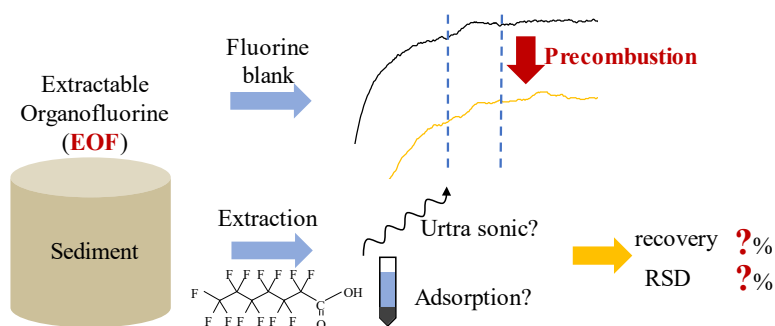


Figure 1: The outline of this study.

## 2 Materials and Methods

**CIC blank:** Fluorine in the CIC blanks was detected by performing the measurements with nothing in the sample boat. Measurements were conducted using Methods 1–6 in Figure 2. Before measuring the blanks, the sample loop volume was changed from 100 to 200  $\mu\text{L}$  to increase the sensitivity. The oxygen and argon used for CIC were high purity (> 99.999%) because fluorine has also been reported in blank samples containing cylinder gas<sup>2</sup>. Water was used as the absorbing solution. Fluorine contamination may occur in parts of the absorber and in the main body of the CIC composed of fluorocarbon resin. However, in this study, these parts were not replaced because of the difficulty involved. The chromatography used in this study is not a model designed for fluorine analysis but for chlorine and bromine analysis; therefore, we assessed whether fluorine analysis is possible using this model.

**Accuracy of PFOA determination in organic solvents by CIC:** Before measuring EOF, the accuracy of the CIC measurements was evaluated. PFOA powder dissolved in methanol was measured by CIC and LC/MS, and the concentrations obtained by each method were compared. For CIC, 50  $\mu\text{L}$  of the PFOA solution was added to the sample boat, and the sample was combusted at 1000°C. The fluorine gas produced was absorbed in 10 mL water, and 200  $\mu\text{L}$  solvent was injected into the ion chromatography and measured. The PFOA concentration was converted to a fluorine concentration. Calibration curves were prepared by combusting the PFOA solution under the same

conditions as those used for the samples. Studies have reported that the accuracy of quantification differs between burning the inorganic fluorine solution or injecting it directly into the chromatography because of the PFOA combustion efficiency and adsorption/desorption on the parts<sup>1</sup>.

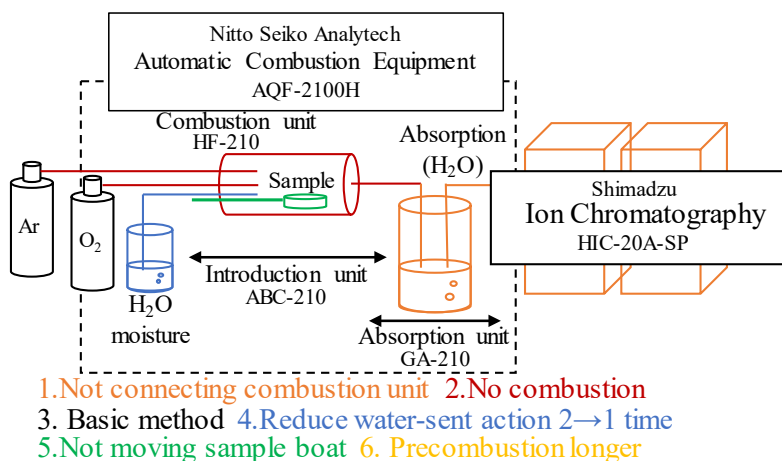


Figure 2: CIC systems and conditions for blank fluorine measurement. The colors of the parts of the CIC and the conditions match.

**EOF extraction methods:** Sediment was collected from Osaka Bay and freeze-dried. The extraction was conducted following an established method<sup>3</sup> (Figure 3A). First, 3 g sediment sample (for EOF measurement) and 0.5 g sediment sample in PFOA solution (for quality assurance) were placed in polypropylene (PP) centrifuge tubes. Then, sodium hydroxide/methanol (8:2 methanol:water) was added, and the sample was sonicated. Methanol was added, the solution was shaken, the solid–liquid phase was separated by centrifugation, and the liquid phase was concentrated in a rotary evaporator and passed through an ENVI-Carb cartridge. The resulting liquid was passed through an SPE-WAX cartridge. The liquid phase was eluted in 0.1% ammonium hydroxide/methanol using the SPE-WAX method and measured by CIC. The recovery rates were compared under different conditions of this method, such as the temperature at which the samples were passed through the sonicator and ENVI-Carb cartridge. Since recent studies have shown that ultrasonic waves decompose PFOA, recovery was also assessed in the absence of ultrasonic waves. In addition, since solids precipitated before the solution passed through the ENVI-Carb cartridge, the solution was rapidly passed through the cartridge to prevent precipitation. The recovery rate was also measured by LC/MS under similar conditions because many studies have confirmed the recovery rate by LC/MS<sup>1,3</sup>. Water was used as the absorbing solution for CIC. Calibration curves were generated based on PFOA solutions prepared in the concentration range of 160–3200 µg-F/L and burned in the same manner as the samples. The water used in this study was ultrapure Milli-Q water.

### 3 Results

**CIC blank:** Figure 4A shows the resulting chromatograms. No peaks were observed when only the absorber or ion chromatography were measured (condition 1). When the combustion unit was connected to the ion chromatography, there were no fluorine peaks unless heat was applied (condition 2). The peak in condition 3 remained the same size when the number of times ultrapure water was added for humidification was reduced (condition 4) or when the sample boat was not moved (condition 5). However, the peak became smaller after increasing the duration of air baking before measurement (condition 6).

**Accuracy of PFOA determination in organic solvents by CIC:** The concentrations of the PFOA solution measured by CIC and LC/MS were 106% and 91%, respectively. This indicated that CIC can quantify PFOA in organic solvents, and that the PFOA solution used to check the EOF recovery rate had a value close to the theoretical value.

**EOF extraction methods:** Figure 4B shows that the best fluorine recovery was obtained using ultrasonication and passing the extracted solution through a cartridge before it returned to room temperature, which resulted in a 68.6% recovery rate. When the extract was at room temperature, the recovery and variability were both 44.6% by CIC and 55.7% for LC/MS. In the absence of ultrasonication, the recovery rate was 45%. In the absence of sediment, the recovery rate was 90.7% with a variability of only 7.6%. The EOF in sediment only, without PFOA, had a mean concentration of 25.1 ng-F/g with a residual standard deviation (RSD) of 49.2%.

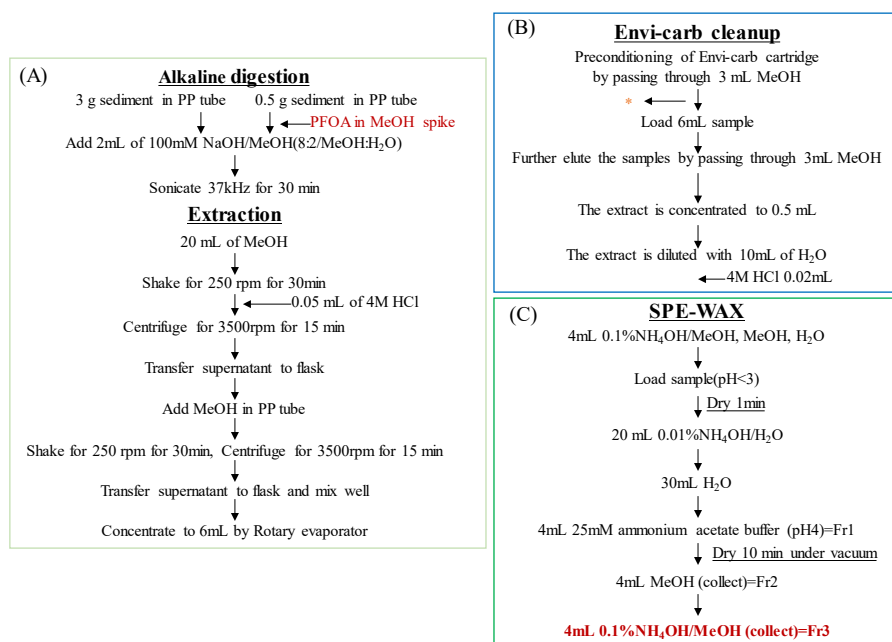


Figure 3: The EOF extraction procedure. \* indicates the point where the influence of ultrasonication is checked.

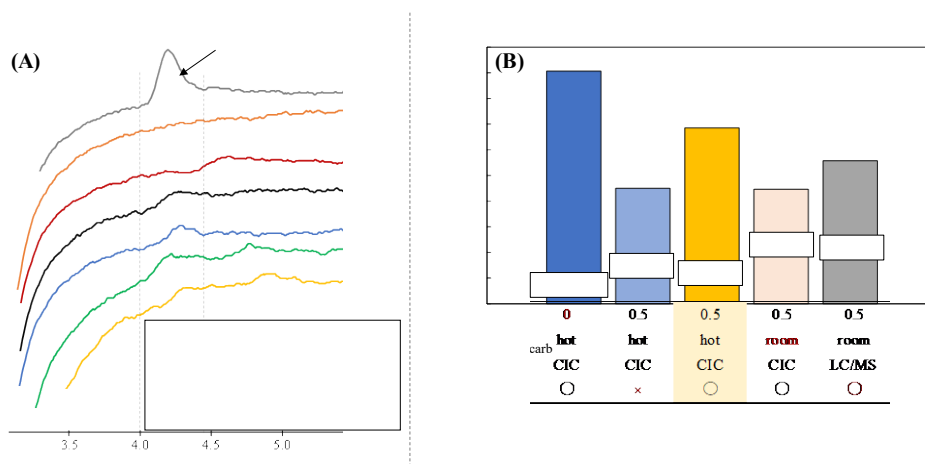


Figure 4: The study results. (A) Chromatograms of the fluorine blanks under each condition. (B) The recovery rate and RSD obtained by PFOA extraction.

#### 4 Discussion

**CIC blank:** In Figure 4A, since no fluorine was detected in condition 1, in which there was no connection to the combustion chamber, or in condition 2, in which there was no heating, it is thought that the fluorine detected in condition 3 using the basic method was derived from fluorine attached to the combustion tub. The fluorine compounds attached to the combustion tube during storage are desorbed upon overheating, resulting in some fluorine detected in the blank. Therefore, according to the results obtained under condition 6, it is important to desorb most of the fluorine compounds adhering to the sample prior to measurement by increasing the durations of baking before measurement. In addition, since fluorine compounds adhere to the quartz cotton that is packed in the end of the combustion tube, the empty baking time should be increased to reduce the contribution of fluorine from the quartz cotton. When a blank was inserted between sample measurements, the number of blanks did not increase for low concentration samples, so it is unlikely that the fluorine compounds adhering to the combustion tube originated from the sample, and the possibility that the effect of the blank increased during sample measurements is small.

**EOF extraction methods:** The results with versus without ultrasonic treatment and with versus without sediment are shown in Figure 5A. The intermediate concentration was collected at point A shown in the figure. When sediment is present, the concentration at the intermediate point has less fluorine when ultrasonic treatment is used, suggesting that PFOA is mineralized<sup>4</sup>. However, when comparing the final concentrations, the reduction in the fluorine amount was greater under the condition without ultrasonic treatment, indicating that ultrasonication improves recovery. Ultrasonication likely improves the recovery rate when using ENVI-Carb and SPE-WAX cartridges. When

ultrasonication was used, but no sediments present, there was a slight decrease in the concentration at the midpoint. The difference in PFOA mineralization in the presence versus absence of sediment, when using ultrasonication, is thought to be related to sulfate in the sediment. There are reports that PFOA mineralization using ultrasonication is greater when sulfate is added as a catalyst, and that PFOA is transformed to hydrogen fluoride (HF) by sulfate radicals<sup>4</sup>. However, even in the absence of sediment and ultrasonication, the concentration at the midpoint decreased. This may be due to adsorption. PFOA is reported to adsorb on glass and PP labware. In this study, PFOA may have adsorbed on the PP centrifuge tubes<sup>5</sup> while the sample was left standing, thus becoming resistant to sonication.

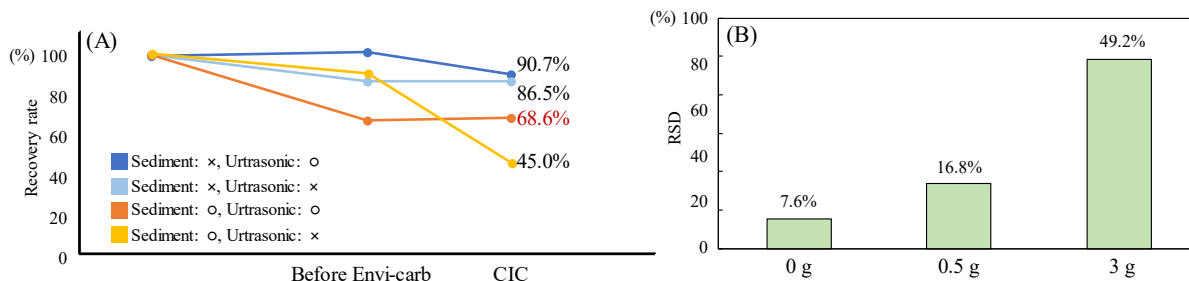


Figure 5: (A) The recovery rate before ENVI-Carb and the final PFOA extraction. (B) The RSD depends on the amount of sediment present.

The EOF level in the sediment without PFOA was 25.1 ng-F/g. This is similar to the EOF concentration in sediment from Lake Ontario (17–40 ng-F/g)<sup>3</sup>. Therefore, our results are reasonable. The RSD values for each sediment mass used, shown in Figure 5B, indicate that the variation increases with the sediment mass, suggesting that the large variability was due to the presence of sediment particles, and that operational improvements are needed, such as changing the temperature at which the solution passes through the ENVI-Carb cartridge, the liquid-to-solid ratio during extraction, and the centrifugation conditions.

## 5 Conclusions

By reducing blanks and improving extraction methods, it is possible to measure EOF by CIC, without using a chromatograph model designed for fluorine analysis. The main cause of fluorine blanks in CIC is considered the release of overheated fluorine from the combustion tube. Regarding the accuracy of EOF extraction, the recovery rate of PFOA was approximately 70% due to PFOA adsorption to the experimental apparatus and mineralization caused by ultrasonic irradiation. Nevertheless, this accuracy is somewhat acceptable. However, the reproducibility of the method needs to be improved, as the presence of sediments causes large variation in the reproducibility..

## 6 Acknowledgments

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## 7 References

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