TRACE ANALYSIS OF ORGANIC FLUORINE IN HUMAN BLOOD USING COMBUSTION ION CHROMATOGRAPHY FOR FLUORINE (CIC-F)

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Introduction

A number of polyfluorinated compounds (PFCs) have been identified in the environment. Mass balance analysis combining individual PFCs and total organic fluorine (TOF) is expected to provide useful information on potential discharges of unknown PFCs into the environment. PFCs are present at parts-per-billion to parts-per-quadrillion levels in biota or water. However, limit of quantitation of TOF using general type of combustion ion chromatography (CIC) has been in sub-parts-per-million levels, because of high background levels arising from instrumental blanks. In this study, possible sources of contamination of blank were identified and eliminated to improve the sensitivity of the method. The method developed in this study is capable of detecting TOF at parts-per-billion (μg as fluorine per litter: μg-F/L) to parts-per-trillion (ng-F/L) levels in blood and water samples, respectively. Several human blood and water samples were analyzing using this method for validation and the results were discussed based on mass balance analysis of PFCs.

Materials and Methods

Individual PFCs in human blood was determined based on ion-pair extraction. Nevertheless, several modifications have been done to enable accurate separation of inorganic fluorine (IF), extractable organic fluorine (EOF) into a non-polar solvent (Hexane) (fraction 2) and an ion pairing solvent (fraction 1) (Figure 1). The final residue 2 was supposed to contain IF and non-extractable fluorine. Bulk analysis of blood sample was also carried out to calculate total fluorine (TF).

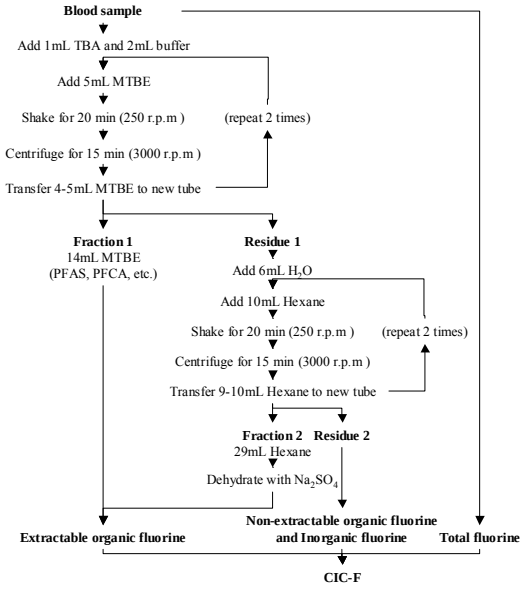

Figure 1. Schematic outline of the analytical procedures for total fluorine, organic fluorine, or inorganic fluorine in blood samples.

Concentrations of TF and EOF were determined using recently developed combustion ion chromatography for fluorine (CIC-F). Although PFCs are present at parts-per-billion to parts-per-quadrillion levels in biota and surface waters, current methods to measure TOF have high detection limits in the order of parts-per-million. The sensitive method for measuring TOF using general type of combustion ion chromatograph has a detection limit in the order of sub-parts-per-million because of high background levels arising from instrumental blanks. The schematic

diagram of the CIC-F is shown in Figure 2. The extracts were set on a silica boat and put into a furnace at 900–1000°C. Combustion of samples in a furnace converted organofluorine and inorganic fluorine compounds into hydrogen fluoride (HF). The HF was absorbed into sodium hydroxide solution. Concentrations of F^- in the solution were analyzed using ion chromatography. The total time for analysis is approximately 20 min per sample.[3]

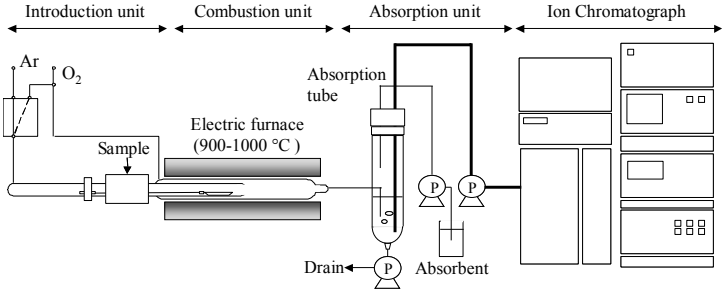

FIGURE 2. Combustion Ion Chromatograph for Fluorine (CIC-F)

Results and Discussion

Removal of Inorganic Fluorine in Extracts. Removal of inorganic fluorine in a solvent is crucial for the measurement of organic fluorine. We examined the removal capability by ion-pair extraction and hexane extraction with fluoride (F^-) solutions (Figure 1). Sodium fluoride was used as the standard and the concentration of F^- were 1, 10, 100 mg-F/L (ppm). Concentrations of inorganic fluorine in each fraction were analyzed using combustion ion chromatography (Table 1). The results indicated that inorganic fluorine was not detected in all extracts from ion-pair extraction and hexane extraction. Therefore, the extracts from ion-pair extraction and hexane extraction were sufficiently free of inorganic fluorine. The recoveries of PFCs (perfluoroalkyl sulfonates (PFASs; C3–C8), perfluorocarboxylic acids (PFCAs; C5–C10), and some fluorinated telomer alcohols (FTOHs)) were 73.4–104%.

TABLE 1. Concentrations of inorganic fluorine (fluoride) and recoveries of PFCs in each fractions using ion-pair extraction and hexane extraction methods (mg-F/L, ppm).

	Ion-pair extraction Fr.1	Hexane extraction Fr.2
1 mg-F/L (ppm)	n.d.	n.d.
10 mg-F/L (ppm)	n.d.	n.d.
100 mg-F/L (ppm)	n.d.	n.d.
Recovery (%)	73.4 – 104	–

n.d. denotes found below limit of detection of total fluorine (<0.025 ppm)

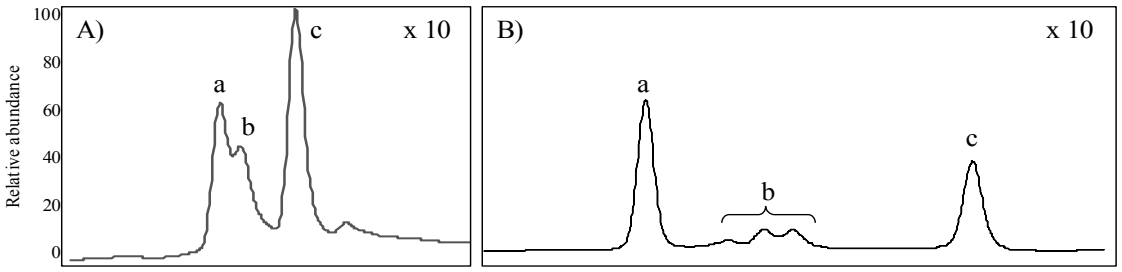

FIGURE 3. Chromatograms of fluoride and organic acids obtained with (A) column A and (B) column B. (a) is fluoride; (b) and (c) are some unknown organic acids.

Co-elution of Fluoride and Organic Acids. Co-elution of fluoride and some of the organic acids has interfered with accurate and sensitive measurements of fluoride. The separation of fluoride and some of the organic acids were examined with two types of columns having different ion-exchange capacities. Column A was unable to resolve fluoride and some of the organic acids (Figure 3). However, the peaks were fully separated by using column B (310 μeq/column), having approximately 10 times higher ion-exchange capacity than that of column A (30 μeq/column) that operated at the identical conditions.

Instrumental and Gas Blanks. Several experiments were conducted to check for the contamination sources of organic and inorganic fluorine in instrumental blanks. Fluoride was detected in sodium hydroxide solution absorbing combustion gases (Ar and O_2) without injection (Figure 4). This result suggested that the source of contamination is in the CIC instrument or gases. Normal grade gases were changed to high purity gases (Ar: 99.9999%, O_2: 99.9995%). Tubings in the ion chromatograph, gas lines, valves for gas bottle, and gas regulator, made of polytetrafluoroethylene, were replaced with stainless steel and polyetheretherketone (PEEK) or polyethylene tubings. Furthermore, a gas purifier containing activated carbon was placed into the gas line to remove trace levels of organofluorine compounds in gases. Following these modifications, backgrounds levels of fluorine in instrumental and gas blanks decreased considerably (Figure 4). The limit of detection (LOD) of organic fluorine was evaluated for each sample based on the maximum blank concentration, the concentration factors, and the injection volume of sample. The LODs for water and blood samples were 1 ng-F/L (ppt) and 1 μg-F/L (ppb), respectively. The LODs can be decreased by increasing the volume of sample taken for analysis or by reducing the background levels.

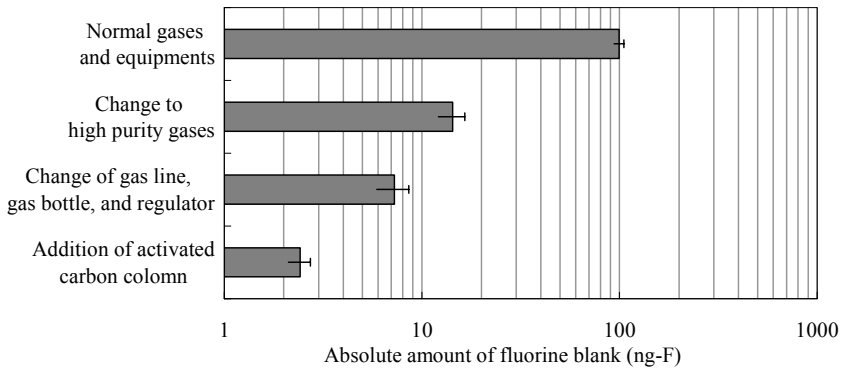

FIGURE 4. Absolute amount of fluorine in CIC instrumental blanks (n=4).

Application of Mass Balance Analysis.

Eighteen sample of human plasma from the United States and occupationally exposed human blood samples from Japan were subjected to CIC-F analysis. Concentrations of individual PFCs and TF are shown in Figure 5. The plasma samples from the US showed a concentration of approximately 20 ppb for total PFCs; PFC concentrations in occupationally exposed individual were thirty times higher than those of general population. TF concentrations were similar between occupationally exposed and general population samples, but the contributions from organic and inorganic fluorine were different (Figure 6). Distribution of PFOS and PFOA to TF were 10% and 6%, respectively, in the general population in the US. Approximately 85% of the total fluorine was unknown fluorinated chemical, including IF. However, occupationally exposed sample contained majority of TF as PFOA and PFOS (80–90%). Less than 20% of the TF were unknown in occupationally exposed sample. It suggests less proportion of inorganic fluorine in blood, which was thought to be a major portion of fluorine in environmental matrixes.

In conclusion, analysis of contribution of individual PFCs to total fluorine, using mass balance approach, is important to understand residues in environmental matrixes and bioaccumulation of all fluorinated chemicals including the unknowns.

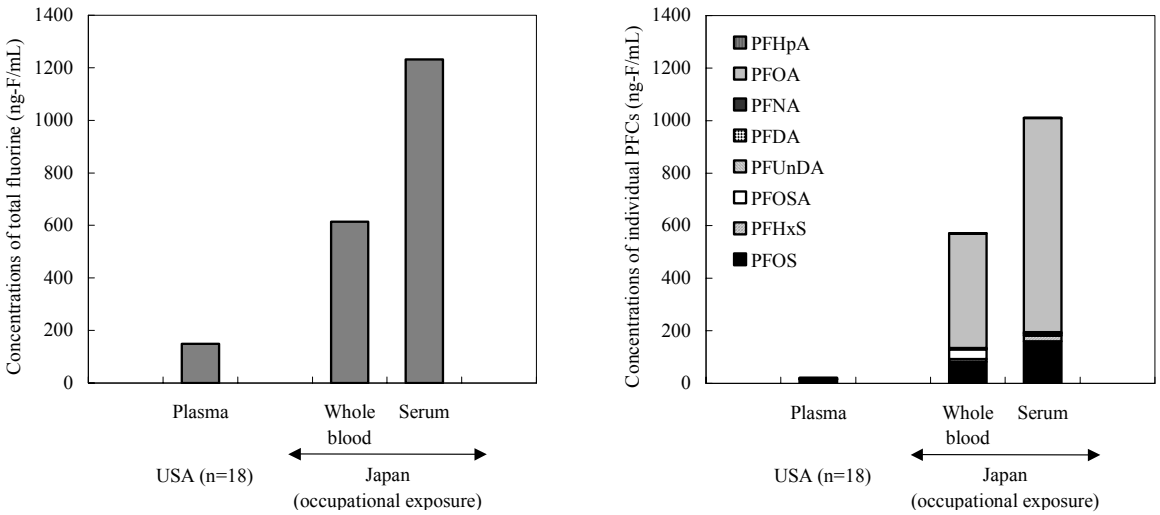

FIGURE 5. Concentration of individual PFCs and TF in human blood.

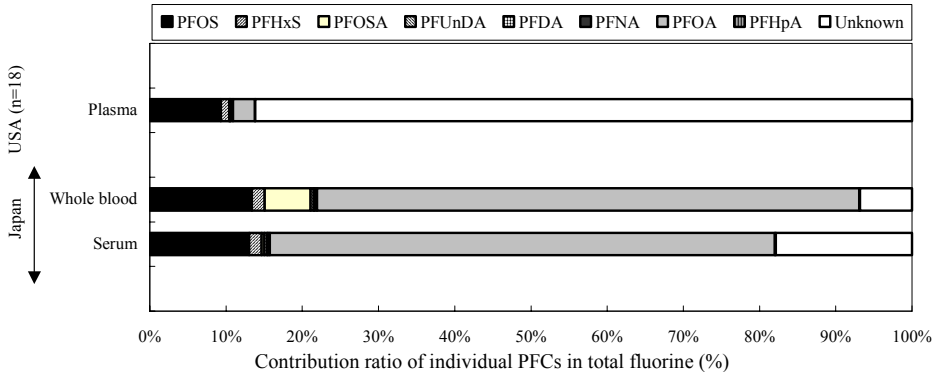

FIGURE 6. Contribution of individual PFCs to TF in human blood.

References

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2. Hansen KJ, Clemen LA, Ellefson ME, Johnson HO. *Environ Sci Technol* 2001; 35: 766.
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