

PERFLUORINATED CARBOXYLIC ACIDS AND SULFONIC ACIDS IN WASTE SAMPLES

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Abstract

An analytical method of perfluorinated compounds (PFCs) in waste samples contained matrix components was developed. Target compounds were perfluorinated carboxylic acids (C4-C14, PFCAs) and perfluorinated sulfonic acids (C4, C6, C8, C10, PFSAs). The analysis was performed by using LC/MS/MS with negative electrospray ionization.

Ion suppression of target compounds was confirmed in the automotive shredder residue sample due to the presence of matrix components coeluted from SPE cartridge. To reduce matrix components, the clean up step was added in the sample preparation before the elution from SPE cartridge. Consequently, recovery rates of internal standard were improved. The concentrations of target compounds in the cinder, soot & dust, night soil and sewage sludge samples were closer to limits of quantification. On the other hand, the target compounds, except PFHxS(C6) and PFDS(C10), in the automotive shredder residue sample were detected. Additionally, PFOA(C8) and PFOS(C8) were predominant PFCs in the automotive shredder residue sample.

Introduction

Perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS) and their homologue, PFCAs and PFSAs, have attracted attention in the world due to their persistence, bioaccumulation and toxicity¹. Furthermore, they have been widely observed in wildlife², human blood³ and various environmental media such as water⁴ and atmosphere⁵. Therefore, PFOS and perfluoro-1-octanesulfonyl fluoride (PFOSF) were added as persistent organic pollutants (POPs) under Stockholm Convention and were globally-regulated⁶. The manufacture and use of PFOS are expected to reduce. However, it is considered that products which have been already stocked widely by our living are finally accumulated in final landfill sites. Investigation of PFCs in waste samples which are carried in to final landfill sites is needed for identification of source and countermeasure for PFCs pollution control. On the other hand, it is reported that analysis of matrix samples such as human blood samples is difficult due to the matrix effects⁷. It is considered that waste samples also contain many matrix components which affect the ionization efficiency of target compounds (ion suppression) in LC/MS/MS analysis. In this study, the experiments to confirm ion suppression and to reduce matrix components were carried out. Additionally, various waste samples were analyzed by using the modified method.

Material and method

Standards

Standard solution of PFCAs and PFSAs mixture (PFAC-MXB) contained Perfluorobutanoic acid (PFBA), Perfluoropentanoic acid (PFPeA), Perfluorohexanoic acid (PFHxA), Perfluoroheptanoic acid (PFHpA), Perfluorooctanoic acid (PFOA), Perfluorononanoic acid (PFNA), Perfluorodecanoic acid (PFDA), Perfluoroundecanoic acid (PFUnDA), Perfluorododecanoic acid (PFDoDA), Perfluorotridecanoic acid (PFTrDA), Perfluorotetradecanoic acid (PFTeDA), Perfluorobutane sulfonate (L-PFBS), Perfluorohexane sulfonate (L-PFHxS), Perfluorooctane sulfonate (L-PFOS), and Perfluorodecane sulfonate (L-PFDS) were purchased from Wellington laboratories. Internal standard solution of PFCAs and PFSAs mixture (MPFAC-MXA) contained Perfluoro-n-[¹³C₄]butanoic acid (MPFBA), Perfluoro-n-[1,2-¹³C₂]hexanoic acid (MPFHxA), Perfluoro-n-[1,2,3,4-¹³C₄]octanoic acid (MPFOA), Perfluoro-n-[1,2,3,4,5-¹³C₅]nonanoic acid, (MPFNA), Perfluoro-n-[1,2-¹³C₂]decanoic acid (MPFDA), Perfluoro-n-[1,2-¹³C₂]undecanoic acid (MPFUdA), Perfluoro-n-[1,2-¹³C₂]dodecanoic acid (MPFDoDA), Sodium perfluoro-1-hexane[¹⁸O₂]sulfonate (MPFHxS), and Sodium perfluoro-1-[1,2,3,4-¹³C₄]octanesulfonate (MPFOS) were purchased from Wellington laboratories. The purity of standard solution was higher than 98%.

Waste samples and Sample preparation

Waste samples were cinder, soot & dust, night soil, sewage sludge and automotive shredder residue from incineration treatments, sewage treatment plants and recycling facilities.

Each waste sample was spiked with 20 μL of MPFAC-MXA (each 100 ng/mL in methanol) as an internal standard. The sample was extracted by ultrasonic extraction for 15min with 10 mL of methanol. After the extraction, the sample was centrifuged at 3000r/min for 10min. The extracted layer was fractionated to a new vial. The operation of extraction was repeated three times. The combined extraction was concentrated to approximately 5 mL under nitrogen stream. The concentrated solution was diluted to 100 mL of distilled water. After the dilution, 10 μL of formic acid was added to the solution. The solution was loaded to Solid Phase Extraction cartridge (Presep PFC- II, Wako Pure Chemical Industries). The target compounds were eluted with 5 mL of 0.1% ammonium hydroxide in methanol. The eluted solution was concentrated to 1 mL under nitrogen stream.

Experiment to confirm ion suppression in the automotive shredder residue sample

To confirm and compare matrix in the final solution qualitatively, the solution of the cinder and automotive shredder residue samples were analyzed by liquid chromatography (LC)-tandem mass spectrometer (MS/MS) using Xevo TQ (Waters) coupled with ACQUITY UPLC (Waters). The analysis was conducted using negative electrospray ionization with single scan mode (scan range 100–2000 m/z). 10 mM ammonium acetate and acetonitrile were used for LC mobile phase. Analytical column was ACQUITY UPLC BEH (C18, 2.1 \times 50 mm, 1.7 μm , Waters). Separation of instrument blank was performed using a retention gap column (ACQUITY UPLC BEH (C18, 2.1 \times 10 mm, 1.7 μm , Waters)).

To confirm ion suppression of target compounds, 10 μL of PFAC-MXB (each 2000 ng/mL in methanol) was spiked into the final solution of automotive shredder residue sample, its solution diluted ten times of methanol and diluted a hundred times of methanol. These solutions and standard solution were analyzed by the LC/MS system described above, using the same LC conditions and negative electrospray ionization with multiple reaction monitoring mode. The intensity ratio was calculated by dividing the peak area of the sample solution by the peak area of the standard solution. The peak area of the sample solution was calculated by subtracting the peak area before spiking PFAC-MXB from the peak area after spiking.

Experiment to reduce matrix components in the automotive shredder residue sample

To reduce matrix components which cause ion suppression of target compounds, a clean up step was added in the sample preparation before the elution from SPE cartridge. The clean up step was performed by washing SPE cartridge (Presep PFC- II) with 20 mL of 40/60, 50/50, 70/30, 80/20, 90/10 and 100/0 methanol/water. The analysis was performed by LC/MS/MS.

Analysis of waste samples using the modified method

The cinder, soot & dust, night soil, sewage sludge and automotive shredder residue samples were analyzed by using the method added the clean up step. The clean up step was performed by washing SPE cartridge with 20 mL of methanol.

Results and discussion

Experiment to confirm ion suppression in the automotive shredder residue sample

Figure 1 shows the total ion chromatogram (TIC) of the cinder and automotive shredder residue samples. The intensity of the automotive shredder residue sample was relatively higher than the cinder sample. The automotive shredder residue sample contained matrix components which eluted at the same retention time of PFCs. Figure 2 shows the intensity ratio of target compounds spiked into the solution of automotive shredder residue sample. If ion suppression was not observed, the intensity ratio should be 100%. The intensity ratio in the solution which was not diluted was below 100%. Especially, the intensity ratios of PFDA(C10) and PFDoDA(C12) were less than 60%. Furthermore, the intensity ratio reached 100% as the solution was diluted.

Thus, it was confirmed that many matrix components were coeluted from the SPE cartridge and caused ion suppression of target compounds in the automotive shredder residue sample.

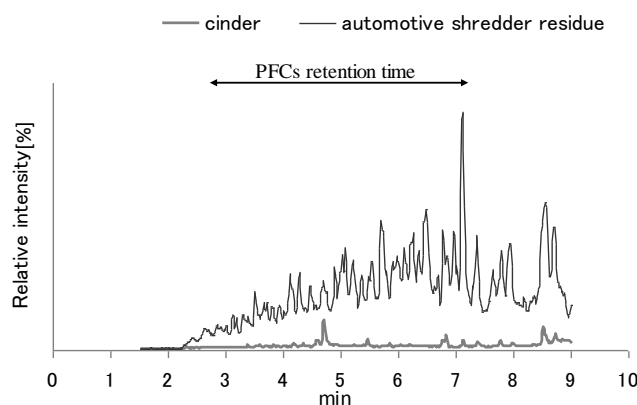


Figure 1. Total ion chromatogram (TIC)

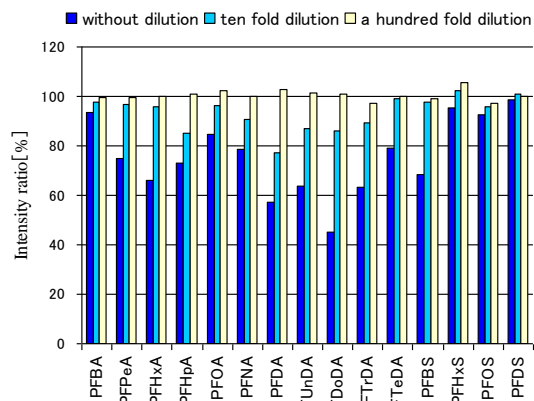


Figure 2. Intensity ratio of target compounds

Experiment to reduce matrix components in the automotive shredder residue sample

Figure 3 shows the results of recovery rates of internal standard in the automotive shredder residue sample when the clean up step was added. The recovery rates ranged from 32 to 65% in 40/60 methanol/water, 32 to 64% in 50/50 methanol/water, 37 to 77% in 70/30 methanol/water, 30 to 81% in 80/20 methanol/water, 36 to 109% in 90/10 methanol/water and 41 to 98% in methanol. In case it was not washed, the recovery rates ranged from 19 to 40%. The recovery rates were improved as the percentage of methanol was increased. This suggests that over 90 percent methanol is suitable solvent as the clean up step.

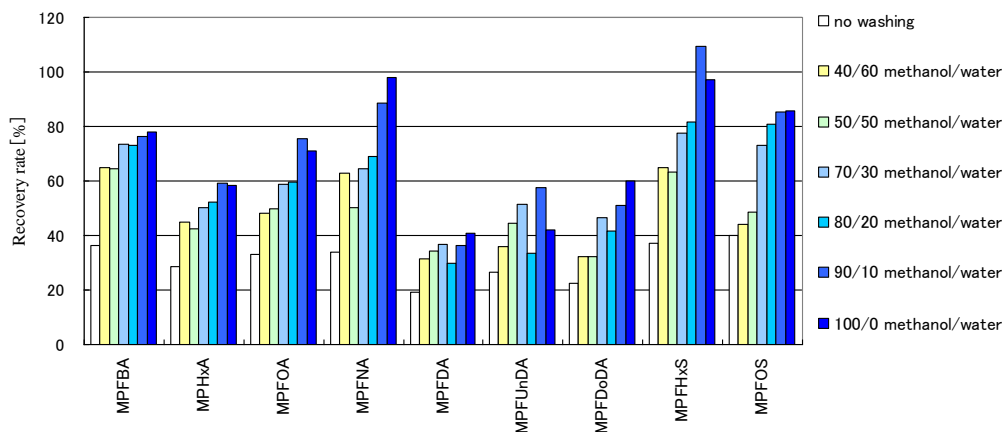


Figure 3. Washing effect on recovery rate of internal standard

Analysis of waste samples using the modified method

Table 1 shows the concentrations of PFCs in waste samples. The concentrations of PFCs in the cinder, soot & dust, night soil and sewage sludge samples were closer to limits of quantification (PFCAs:0.03 $\mu\text{g}/\text{kg}$, PFSA:0.06 $\mu\text{g}/\text{kg}$). On the other hand, the target compounds, except PFHxS(C6) and PFDS(C10), in the automotive shredder residue sample were detected. The maximum concentration in the automotive shredder

residue sample was 7.8 µg/kg-wet (PFOA). In the composition of PFCs, PFOA(C8) and PFOS(C8) were predominant PFCs in the automotive shredder residue sample (Figure 4).

Table 1 Concentrations of PFCs in waste samples

| Samples | PFBA | PFPeA | PFHxA | PFHpA | PFOA | PFNA | PFDA | PFUnDA | LOD of PFCAs | LOQ of PFCAs |
|-----------------------------|-------|-------|-------|-------|-------|-------|-------|--------|--------------|--------------|
| cinder | <0.03 | 0.062 | <0.03 | <0.03 | 0.044 | <0.03 | <0.03 | ND | 0.01 | 0.03 |
| soot & dust | <0.03 | <0.03 | 0.03 | <0.03 | <0.03 | <0.03 | ND | ND | 0.01 | 0.03 |
| night soil | 0.077 | <0.03 | 0.034 | <0.03 | 0.035 | <0.03 | <0.03 | ND | 0.01 | 0.03 |
| sewage sludge | ND | <0.03 | <0.03 | <0.03 | <0.03 | <0.03 | ND | ND | 0.01 | 0.03 |
| automotive shredder residue | 0.5 | 0.16 | 0.79 | 1.3 | 7.8 | 4.4 | 0.67 | 1.5 | 0.05 | 0.15 |

| | PFDoDA | PFTTrDA | PFTeDA | L-PFBS | L-PFHxS | L-PFOS | L-PFDS | LOD of PFASs | LOQ of PFASs |
|-----------------------------|--------|---------|--------|--------|---------|--------|--------|--------------|--------------|
| cinder | ND | ND | <0.03 | ND | ND | ND | ND | 0.02 | 0.06 |
| soot & dust | ND | ND | ND | ND | ND | ND | ND | 0.02 | 0.06 |
| night soil | ND | ND | ND | ND | ND | ND | ND | 0.02 | 0.06 |
| sewage sludge | ND | ND | ND | ND | ND | ND | ND | 0.02 | 0.06 |
| automotive shredder residue | 0.37 | 0.87 | 0.43 | 4.4 | ND | 5.7 | ND | 0.1 | 0.3 |

Unit: µg/kg-wet

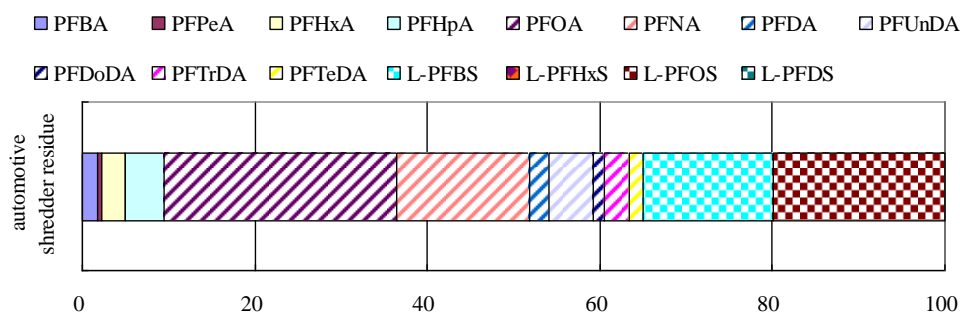


Figure 4. Composition of PFCs in automotive shredder residue sample

Acknowledgment

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