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RESEARCH ARTICLE

OPTIMIZATION OF SOLVENT FOR THE EXTRACTION OF PERFLUOROCTANOIC ACID(PFOA) FROM A POLYTETRAFLUOROETHYLENE RESIN

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ABSTRACT

The optimization of the extraction conditions of perfluorooctanoic acid (PFOA) from a polytetrafluoroethylene (PTFE) fine resin powder was investigated in this work. A PTFE resin containing a high concentration of PFOA was used for the optimization. From the optimization results, the effective extraction solvents were determined to be methanol and acetone, and their PFOA-analyzed concentrations were 9840 ng/g and 9520 ng/g with relative standard deviation (RSD) values of 4.1% and 2.6%, respectively, based on three measurements. Conversely, the PFOA could not be extracted using hexane as the solvent. The reproducibility of the PFOA analysis in PTFE fine resin powder by the extraction with methanol was investigated. As a result, the recovery for the spiked PFOA in the PTFE resin was 108±6% (N=5). Conclusively, the developed method for the extraction of PFOA in the PTFE fine resin powder was considered satisfactory.

KEYWORDS

PFOA, PTFE resin, LC/MS/MS, Extraction, Optimization.

1. INTRODUCTION

In recent years, perfluorinated organic compounds (PFCs), such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS), have been widely used as water repellents, fire extinguishers, fluoropolymer processing, and surfactants. PFCs accumulate in the environment due to their low degradability; consequently, they cause significant environmental pollution, which is attracting global concern (Olsen et al., 2003; Saito et al., 2004; Olsen et al., 2007; Haukas et al., 2007; Dreyer et al., 2009; Takagi et al., 2012). Therefore, the regulation and control of PFCs globally are highly necessary. In particular, PFOA was officially added to the persistent organic pollutants Convention in 2019 (Stockholm Convention On Persistent Organic Pollutants, United Nations Nations Unies, 2019) and the Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) regulation. The standard concentration of PFOA and its salts was set to a very low level of 25 ng/g, due to the revision of the restricted substances in Annex XVII in July 2020 (European Chemicals Agency, ANNEX XVII TO REACH-Conditions of restriction).

Thus far, PFOA has been applied as an auxiliary agent or surfactant in the fabrication of fluoroplastics, including polytetrafluoroethylene (PTFE). Additionally, PFOA may be detected in the by-products obtained from PTFE resin owing to the scission of the main chain under exposure to radiation. Therefore, the determination of the PFOA content in each product and the evaluation of the satisfaction degree of the regulation value for the products are imperative.

So far, the determination of the PFOA content from bulk samples containing PTFE polymers, packaging materials and textiles using pressurized liquid extraction (PLE) have been reported (Larsen et al., 2005; Gang et al., 2009; Gang et al., 2009). Also, the determination of the PFOA content from particulate activated carbon has been reported, and the CEN/TS 15968:2010 method for the determination of PFOS in coated and impregnated solid particles has been presented by the European Committee for Standardization (Comite Europeen de Normalisation, 2010; Takemine et al., 2013). However, there is little information on the optimization of solvents, which have been extensively studied from polar

to non-polar solvents, for the extraction conditions of PFOA from products such as PTFE resins. In this study, we investigate the optimization of the extraction conditions of PFOA from a PTFE fine resin powder and the relationship between the extraction solvent and the PFOA efficiency to develop a standard analysis method for PFOA.

2. EXPERIMENTAL

2.1 Reagents and chemicals

A mixed standard solution of PFC-MXA (2 µg/mL), manufactured by Wellington Laboratories, was used as the PFOA standard solution. Immediately before use, the standard solution was diluted with methanol in six steps so that the concentrations of the PFOA solution were in the range of 0.050–2.0 ng/mL. A standard solution of MPFOA (PFOA-¹³C₄ internal standard, 50 µg/mL), purchased from Wellington Laboratories, was used by the PFOA-¹³C₄ internal standard solution. The PFOA-¹³C₄ internal standard solution was diluted with methanol to a concentration of 1.0 ng/mL immediately before use. A portion (100 µL) of the PFOA-¹³C₄ internal standard solution was added to 1 mL of the PFOA standard solution, and a nitrogen stream was supplied to adjust the volume to 1 mL to obtain the standard solution for the calibration curve. Methanol, toluene, and hexane (residual pesticide test grade) were obtained from Kanto Chemical Co. Acetonitrile and formic acid (LC/MS analytical grade) were obtained from Kanto Chemical Co. Acetone (residual pesticide test grade) and ammonium acetate (special reagent grade) were manufactured by Fuji Film Wako Pure Chemical Co. Mill-Q water was used for the experiments. PTFE resin powders (A) and (B) containing relatively high and low concentrations of PFOA were purchased from an anonymous company. The obtained PTFE resin powders were freeze-pulverized into fine particles, which were filtered through a 500 µm mesh before use.

2.2 Determination of the optimal organic extraction solvent

The extraction of PFOA from a PTFE resin powder (A) was performed with reference to CEN/TS 15968:2010 (Comite Europeen de Normalisation, 2010). Approximately 0.5 g of the PTFE powder (A) was weighed in a 50

mL centrifuge tube, and 50 mL of an organic solvent was added for the extraction of PFOA from PTFE. Next, the suspension was subjected to ultrasonic irradiation at 60 °C for 2 h for the extraction. The extraction temperature of 60 °C was sourced from the CEN/TS 15968:2010 method. A different temperature of 20 °C was also tested to examine the effect of relatively low temperatures. After the extraction, 25 µL of each extract was added to 1 mL of the PFOA-¹³C₄ internal standard solution (1 ng/mL) in a Spitz tube (10 mL). Thereafter, the solution was adjusted to 10 mL with methanol to obtain an analytical solution, which was subjected to liquid chromatography with tandem mass spectrometry (LC/MS/MS) analysis.

2.3 Recovery Test

To evaluate the precision of the developed method, a recovery test was performed with the PTFE fine resin powder (B) containing the PFOA in a relatively low concentration. The PTFE resin powder (approximately 0.5 g) was weighed into a 50 mL centrifuge tube, and 250 µL of the PFOA standard solution (100 pg/µL) and 50 mL of methanol were added. Subsequently, the suspension was sonicated for 2 h at 60 °C for the extraction. After the extraction, a 1 mL portion of the extraction methanol was added to 100 µL of the PFOA-¹³C₄ internal standard solution (1 ng/mL) in Spitz tubes (10 mL). Afterward, the solution was evaporated to dryness under a mild nitrogen stream at room temperature. Finally, the residue was dissolved in 1.0 mL of methanol. The sample was subjected to LC/MS/MS analysis. The recovery test data were the average values obtained with more than five samples.

2.4 Analysis of PFOA by LC/MS/MS

The LC section of an Agilent 1260 HPLC and the MS/MS section of a Sciex QTRAP5500 were utilized for the LC/MS/MS measurement in this study (Furukawa et al., 2009). The separation column was an InertSustain C18 (2.1 × 150 mm, 3 µm; GL Sciences Inc.), and the column temperature was 40 °C. The mobile phases for the gradient measurement were A: 55% + B: 45% (0 min) and A: 5% + B: 95% (13 min), with an aqueous solution of A: 0.5 mM ammonium acetate containing 0.1% formic acid and B: acetonitrile. The flow rate was 0.2 mL min⁻¹, and the injection volume was 20 µL. For the MS/MS operating conditions, the negative ESI mode was employed, and the multiple reaction monitoring (MRM) transitions were from m/z 413 to m/z 169 for the quantitative ion of PFOA and m/z 417 to m/z 372 for the quantitative ion of PFOA-¹³C₄ (internal standard).

3. RESULTS AND DISCUSSION

It was described in the previous work that the pressurized liquid extraction (PLE) of PFOA was used for the analysis of the PFOA content in the bulk samples containing PTFE polymers, packaging materials and textiles (Larsen et al., 2005; Gang et al., 2009). Although intensive conditions using PLE for the determination of PFOA were needed for bulk samples (sample size: more than 500 µm), little information on mild extraction conditions of PFOA has been reported for the fine PTFE powder. Hence, the optimization of the extraction of PFOA from a PTFE fine resin powder under mild conditions was studied for the determination of PFOA using LC/MS/MS. To optimize the extraction conditions of PFOA from the PTFE fine resin powder, the effects of the organic solvent and temperature on the extraction efficiency were investigated. First, suitable organic solvents were explored for the extraction of PFOA from the PTFE fine resin powder (A).

Various organic media such as methanol; methanol containing 1%, 5%, and 10% formic acid; acetone; acetonitrile; toluene; and hexane were evaluated for the extraction. Figure 1 shows the effect of the organic solvent on the concentration of the PFOA extracted from the PTFE resin powder. As shown in Figure 1, methanol was the most effective solvent for the extraction of PFOA, and the analyzed concentration was 9840 ng/g with a relative standard deviation (RSD) of 4.1% (N=3). Methanol was adopted as the extraction organic solvent in the CEN/TS 15968 procedure (Comite Europeen de Normalisation, 2010). When acetone was used as the extractant, the PFOA-extracted concentration was 9520 ng/g with an RSD of 2.6% (N=3). The result was similar to that obtained with methanol.

The trends were in good agreement with the results on the efficiency of PFOA extraction from granular activated carbon (Takemine et al., 2013). Conversely, in the case of toluene, the concentration of PFOA was 3280 ng/g with an RSD of 34.3% (N=3), and the values were significantly lower than those observed for methanol and acetone. Furthermore, the extraction of PFOA using hexane was difficult. Since the structure of PFOA has a hydrophilic carboxylic acid group, a polar organic solvent may be effective for its extraction from PTFE. However, when acetonitrile was used, the concentration of PFOA was considerably low (5950 ng/g with an RSD of 5.1% (N=3)). Similar results have been reported by Takemine,

although the reason could not be elucidated (Takemine et al., 2013). This may be attributed to the low affinity between acetonitrile and PFOA.

In the case of methanol containing 1% formic acid, recommended by the Ministry of Environment, the concentration of the extracted PFOA was 8781 ng g⁻¹ with an RSD of 3.8% (N=3) (Waste Management and Recycling Department, 2011). For methanol with 5% formic acid, the concentration was 8668 ng/g with an RSD of 3.8% (N=3), and with 10% formic acid, it was 8845 ng/g with an RSD of 4.2% (N=3). The concentration was approximately 10% lower than that extracted with methanol only. We expect that the relatively low pH due to the addition of formic acid increases the extraction efficiency of PFOA due to the decrease in the dissociation of PFOA. However, the result suggested that the physical factors: the formic acid mixture and pH, had little influence on the extraction efficiency of PFOA. Consequently, the formic acid concentration did not noticeably affect the extraction efficiency of PFOA. This may suggest that the inclusion of trace water in the extract weakens the affinity between the extract and the PTFE particle surface, accounting for the moderately negative effect on the extraction efficiency of PFOA, due to the hydrophobicity of the PTFE powder surface.

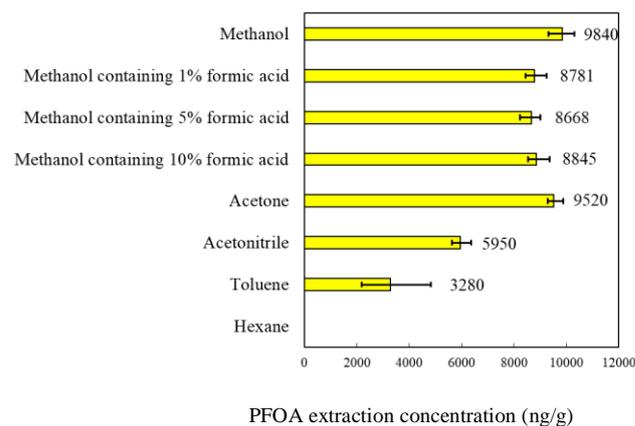


Figure 1: Relationship between the concentration of PFOA extracted from PTFE powder resin (A) and the type of organic solvent used for the extraction. With hexane as the extractant, the PFOA concentration was less than the limit of quantitation.

Next, the influence of temperature on the extraction of PFOA in PTFE was investigated with methanol as the extractant. When the extraction temperature was 20 °C, the concentration of PFOA was 8950 ng/g, which was 9% lower than that obtained at 60 °C. After the first extraction, the second and third extractions were carried out for the same PTFE samples. The analytical values were 560 ng/g, and values less than the limit of quantitation were obtained for the second and third extractions. The reproducibility of the PFOA analysis in PTFE resin powder by the combination of extraction with methanol and LC/MS/MS was investigated. In this study, the PTFE samples (B) were spiked with 50 ng/g PFOA to evaluate the recovery rate. The PFOA quantitation limit for this study was 1.0 ng/g.

Firstly, the PFOA content of the PTFE powder resin (B) was determined in the extraction with methanol method at 60 °C, and the content value of PFOA was 16 ng/g (N=2). Next, 50 ng/g PFOA was spiked into the PTFE sample (B) to evaluate the recovery. As a result of the spike recovery test, the average PFOA content in the spiked PTFE resin was 69.8±3.7 ng/g with an RSD of 5.3% (N=5). The recovery for the spiked PFOA was 108±6% (N=5). The developed extraction method could be considered satisfactorily for the determination of PFOA in PTFE resin powder.

4. CONCLUSIONS

In this study, we examined the optimization of the extraction conditions of PFOA from PTFE fine resin powder. It could be found from the result that the condition of extraction with methanol at 60°C was the most effective. It was also found that when acetone was used as the extraction solvent, it almost had the same performance as that obtained with methanol. This result shows that the extraction using acetone can be applied into the determination of the PFOA content in the PTFE-contained grease, which can not be mixed with methanol.

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