Determination of Perfluorooctane Sulfonates (PFOS) in the Coating of Nonstick Cooker by HPLC/MS/MS

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Abstract：A novel and rapid method based on high performance liquid chromatography-tandem mass spectrometry (HPLC/MS/MS) with accelerated solvent extraction (ASE) was developed for quantitative detection of trace perfluorooctane sulfonates (PFOS) in the coating of nonstick cooker. PFOS residue was extracted from the coating of nonstick cooker by acetonitrile with ASE. The extract was filtrated through membrane with 0.2 μm diameter. The filtration liquid was injected into HPLC and determined using acetonitrile and 10 mmol/L ammonium acetate solution with the volume ratio of 4:1 as mobile phase. PFOS was detected using electrospray ionization (ESI) on a tandem mass spectrometer in multiple reaction monitoring mode. Qualitative analysis of PFOS could be performed using the retention time of the mass chromatogram and the relative abundance of two daughter ions of PFOS, and quantitative analysis was conducted using external standard method. The linear calibration curve was obtained in the range of 0.002 - 0.1 μg/mL with a linear correlation coefficient (R^2) of 0.999. The recovery for PFOS was 95.63 - 101.75% with relative standard deviation of 1.57 - 3.59%. And the detection limit for PFOS was 0.4 μg/m^2 with the signal-to-noise ratio of 10, which would meet the restriction requirement for PFOS content in nonstick cooker in the EU directives. With high accuracy and sensitivity, the sample treatment is simple and rapid, and the method could be used for PFOS inspection in the coating of nonstick cooker.

Keywords: High performance liquid chromatography-tandem mass spectrometry (HPLC/MS/MS), perfluorooctane sulfonates (PFOS), coating, nonstick cooker, accelerated solvent extraction (ASE)

1 Introduction

Perfluorooctane sulfonate (PFOS, the molecular structural formula as indicated in Fig. 1), one of the most well-known perfluorinated compounds, has been widely used in industry and consumer products including stain- and water-resistant coatings of cookers, fabrics and carpets, oil-resistant coatings for paper products approved for food contact, fire-fighting foams, mining and oil well surfactants, floor polishes, insecticide formulations, textiles, detergents, fabric finishing agent, etc, owing to the thermal and chemical stability of its chemical structure for over 50 years.

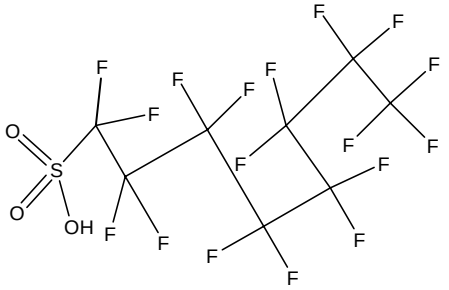

Fig. 1 The molecular structural formula of PFOS

The release of PFOS to the ambient environment can occur via all kinds of pathway because of their vast usage. Different levels of PFOS have been detected in a variety of wildlife across the globe and in human beings[1]. Also because of its stability, PFOS is environmentally persistent and bioaccumulative[2] with multiple toxicities reported in experimental animals and humans, such as endocrine disruption, thyroid and liver carcinogenicity, development alteration, and genotoxicity, etc[3, 4].

Recently the concerns about environmental behavior, toxicology and current pollution of PFOS have been becoming a hotspot of international authorities. In 2000, the Environmental Protection Agency (EPA)[5] stated PFOA and PFOS withdrawal to avoid environmental pollution. In 2002, the Organisation for Economic Co-operation and Development[6] reported that these substances are bio-persistent, tend to accumulate in different tissues of living organisms and are toxic to mammalians. On December 27th, 2006, EU legislation established restriction directive (2006/122/EC) to strictly limit the use and marketing of chemicals containing PFOS as well as products containing these substances[7], which was put into effect on June 27th, 2008. The directives prescribe that the PFOS may not be placed on the market or used as a substance or constituent of preparations in a concentration equal to or higher than 0.005 % by mass, nor in semi-finished products, articles or parts with concentration equal to or higher than 0.1 % by mass, and nor for textiles and other coated materials with PFOS equal to or higher than 1 μg/m^2 of the coated material.

Due to the hazard and international restrictions of PFOS, developing accurate and quick analytical inspection method for PFOS in industry commodities would be a critical step for risk assessment and trade safeguard. With the established solid phase extract (SPE) or methyl tert-butyl ether (MTBE) extract pretreatment methods[8], the known analytical and detection methods for PFOS include high performance liquid chromatography-tandem mass spectrometry (HPLC/MS/MS)[9-11], high performance liquid chromatography-photoionization mass spectrometry (HPLC/APPIMS)[12, 13], high performance liquid chromatography-mass spectrometry (HPLC/MS)[14, 15], high performance liquid chromatography-hybrid quadrupole time of flight mass spectrometer (HPLC/Q-ToF MS/MS)[16, 17], gas chromatography-mass spectrometry(GC/MS)[18, 19], nuclear magnetic resonance (NMR)[20, 21], liquid chromatography-fluorescence detector(LC/FLD)[12], liquid chromatography-diode array detector(LC/DAD)[22], ion exclusion chromatography(IEC)[23, 24], combustion ion chromatography(CI)[25], etc., among which HPLCP/MS/MS is the widely used method offering both good sensitivity and peak identification.

There have been some reports about the detection of PFOS pollution in environment[9] such as air[19], water[13, 14, 20, 26, 27], activated sludge[28], analysis of PFOS levels in biological wildlife and humans such as blood[29-32], fish and seashee[33], Arctic biota[17], and inspection of PFOS content in textiles and leather[15, 34, 35], etc.

But there lacks the research for the quick analysis method of PFOS in the coating of nonstick cooker, neither the analysis inspection standard. While considering the solid appearance of the coating of nonstick cooker, some other pretreatment methods should be aimed because the normally used pretreatment methods, such as SPE or MTBE extract method, are mainly dealt with liquid preparations.

Here a novel and rapid method based on HPLC/MS/MS with accelerated solvent extraction (ASE) was developed for quantitative detection of trace PFOS in the coating of nonstick cooker. PFOS residue was extracted from the coating of nonstick cooker by acetonitrile with ASE, and the PFOS level was determined by HPLC using electrospray ionization (ESI) coupled with tandem mass spectrometer in multiple reaction monitoring mode, to offer a reliable and economical approach for analysis of trace PFOS in the coating of nonstick cooker, according with the restriction for PFOS content in nonstick cooker in the EU directives.

2 Materials and Methods

2.1 Reagents

PFOS was obtained from Sigma-Aldrich Chemical Co. (CAS 1763-23-1, purity≥96%，Sigma-Aldrich Chemical Co., Milwaukee, WI, USA). Ammonium acetate was purchased from Dima-Tech Inc (HPLC grade, National City, California, USA), and acetonitrile from Fisher Scientific (HPLC grade, Waltham, Massachusetts, USA). Milli-Q water was used for preparation and detection during test.

2.2 Instrumentation

The sample was tested on Waters 2695-Micromass Quattro micro^{TM} API high performance liquid chromatography coupled with tandem mass spectrometry (HPLC/MS/MS), equipped with autosampler and workstation. And the pretreatment was conducted with Accelerated Solvent Extractor ASE300 (DIONEX company, Sunnyvale, California, USA).

2.3 Standard solutions preparation

100.0 mg PFOS standard was weighed accurately and dissolved with acetonitrile into a 100 mL volumetric flask, after shaking up to make up PFOS standard solution of 1000 μg/mL, and different concentrations of PFOS standard solutions were achieved by diluting with acetonitrile. PFOS was embodied as perfluorooctane sulfonate anion ($C_8F_{17}O_3S^-$) in these solutions and as the quantitative substance.

2.4 Sample pretreatment

After cutting into little pieces, the coatings of nonstick cookers with total area of 50 cm^2 were extracted in Accelerated Solvent Extractor by acetonitrle. The extraction temperature was set at 175 ℃, pressure 1500 psi, equilibrium time 7 min, and repeated for twice. Then the extraction was cooled to room temperature and evaporated to dry, and the residuals were dissolved in 1.0 mL acetonitrile to be prepared for detection after filtrating through membrane with 0.2 μm diameter.

2.5 HPLC/MS/MS analysis conditions

High performance liquid chromatography was performed using Atlantis T3 C18 column with 2.1 mm × 150 mm i.d. 5.0 μm. The mobile solvent used was acetonitrile and 10 mmol/L ammonium acetate solution with the volume ratio of 4:1. The flow rate was 0.2 mL/min and the injection volume was 10 μL.

The tandem mass spectrometer settings were as following: ES- source, ionization mode ES-, capillary voltage 3.0 kV, cone voltage 55.0 V, extractor voltage 3.0 V, RF lens voltage 1.5 V, source temperature 120 ℃, desolvation temperature 350 ℃, multiple reaction monitoring(MRM), parent ion m/z 499, daughter ion m/z 80 and 99, coll energy 45 eV for monitoring ion of m/z 499>80, and coll energy 38 eV for monitoring ion m/z 499>99.

3 Results and Discussion

3.1 Optimization of HPLC/MS/MS conditions

Different chromatographic columns, instrument conditions and mobile solvents were applied to detect PFOS, and the total ion chromatograms were indicated in Fig. 2.

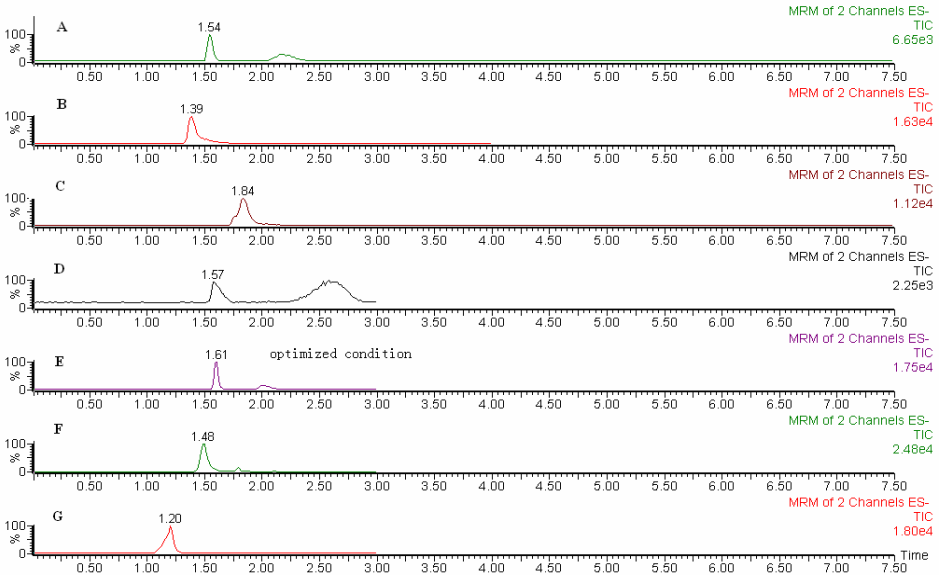

Fig.2 HPLC/MS/MS total ion chromatogram of PFOS standard.

After considering the shape and height of the chromatogram peak, the effect from peaks of other impurities and the retention time, the fine chromatogram was focused on Fig.2 (E) with the relevant optimized conditions described in 2.5 for HPLC/MS/MS. The corresponding total ion and daughter ions chromatograms of PFOS standard were shown in Fig. 3. $C_8F_{17}O_3S^-$(m/z 499) was selected as the parent ion and FSO_3^-(m/z 99) and SO_3^-(m/z 80) as the daughter ion of PFOS in HPLC/MS/MS method, and the retention time and abundance ratio could identify PFOS qualitatively to prevent false positive estimation.

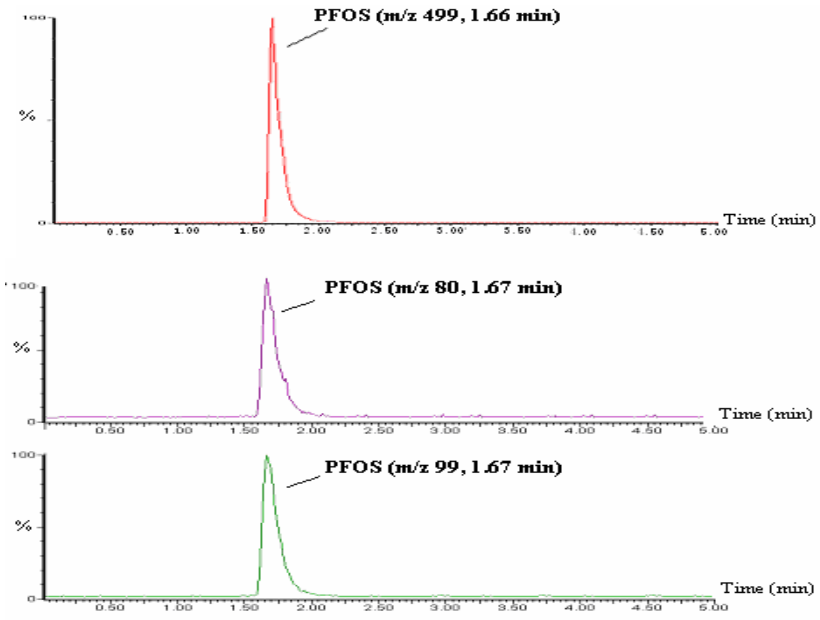

Fig. 3 HPLC/MS/MS total ion and daughter ions chromatograms of PFOS standard.

3. 2 Linearity of calibration

Calibration curve was constructed by plotting the peak areas (X) of daughter ion (m/z 80) of PFOS versus

concentration (Y, μg/mL) at 0.1, 0.05, 0.02, 0.01, 0.005, 0.002 μg/mL respectively, and the values of slope were given along with the intercept and correlation coefficient for the calibration curve. The calibration curves could be used for the quantification of PFOS.

The linearity of the calibration curve of PFOS, Y = 0.0067×X-0.0049, was well correlated with correlation coefficient (R^2) of 0.999 in the concentration range of 0.002-0.1 μg/mL.

3.3 Detection limit

The detection limit for PFOS, estimated under the described conditions at a signal-to-noise ratio of 10, was 0.4 μg/m^2, which is below the restriction content (1 μg/m^2) of PFOS in the coated material in the EU directives.

3.4 Accuracy, precision and recovery

As shown in Fig. 4, the abundance in the HPLC/MS/MS total ion chromatogram of blank sample was low enough to be ignored for the reagent interference and instrument noise during test for the developed method.

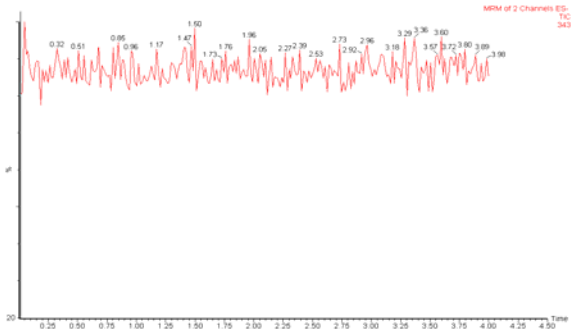

Fig. 4. HPLC/MS/MS total ion chromatogram of blank sample.

To determine the precision and recovery of the method, a blank sample of nonstick cooker coating not containing PFOS was spiked with three different levels of PFOS standard, that were 0.4, 1.0 and 20.0 μg/m^2 respectively, and repeated in eight times for each level. The data obtained were analysed statistically and shown in table 1. The resulting recovery values were in the range of 95.63–101.75%, and the relative standard deviation (RSD) 1.57-3.59%, with a satisfactory recovery and repeatability.

Table 1 The accuracy and recovery tests for PFOS (n=8).

Added amount (μg/m^2)	Found amount (μg/m^2)	Recovery (%)	Relative standard deviation (%)
0.40	0.38	95.94	3.40
1.00	1.02	101.75	3.59
20.00	19.13	95.63	1.57

3.5 Applications

This method has been applied to determine the levels of PFOS in the coatings of five commercial nonstick cookers. These samples were assayed using the procedure described in this study and were analysed in triplicate. Quantification of PFOS was carried out by the integration of the peak in the chromatograph using external standardization method. The contents of PFOS detected in these five commercial nonstick cookers were below our method detection limit, which indicated that they met the restriction requirement in the EU directives.

4 Conclusions

In summary, a novel and rapid quantitative detection approach of detecting trace amount of PFOS in the coating of nonstick cooker was successfully developed unprecedentedly herein using HPLC/MS/MS with ASE pretreatment. The sample treatment is simple and the assay is rapid with good accuracy, precision and recovery obtained for the method, and the detection is sensitive with detection limit down to 0.4 μg/m^2, which could meet the restriction requirement for PFOS content in nonstick cooker in the EU directives. Hence, it is suitable for and

has been applied in routine analysis of PFOS content in nonstick cooker.

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