Determination of PFOA in the aqueous polymeric dispersion

Sample

Aqueous polymeric dispersion: ASAHIGUARD AG-955

1. Test and control substances

The test substance, perfluorooctanoic acid (PFOA, 98.9 %, lot. C17001401), and the surrogate standard, 9-hydrohexadecafluorononanoic acid (9H-PFNA, 97.8%, lot. C58002501), were purchased from Daikin Fine Chemical (Osaka, Japan). Distilled water was produced in-house and checked for contaminants by LC/MS before use. Distilled water was filtered through a pre-column, Preclean-ORG (GL Sciences Inc. (Tokyo, Japan)) placed between HPLC pump and auto-sampler. HPLC grade methanol (MeOH), reagent grade ethanol (EtOH) and isopropanol (IPA), and reagent grade ammonium acetate were purchased from Kanto Chemical Co., Inc.

In order to avoid contamination, disposable lab ware (tubes, pipettes, etc) was used. 2 mmol/L ammonium acetate solution was prepared by weighing 154 mg of ammonium acetate and dissolving in 1 L of distilled water.

2. Preparation of fortification standards

50 μg/ml and 100 μg/ml PFOA solution was prepared using a solvent (2 / 8 (wt) mixture of distilled water / ethanol). 10 mg/ml 8-2 alcohol solution was prepared using isopropanol (IPA) for solvent for the use of latter section (*2-3)*.

3. Preparation of a surrogate standard

100 ng/ml 9H-PFNA solution was prepared using a solvent (1 / 1 (wt) mixture of distilled water / ethanol).

4. Preparation of calibration standards

0, 0.1, 0.2, 0.4 ml of the 100 μg/ml PFOA solution was diluted by IPA up to 5 ml. 100 μl of the each solution and 9ml of 100 ng/ml 9H-PFNA solution was mixed in a vial. About 1 ml of each solution was filtered through a 0.2 μm filter, Millex-LG (MILLIPORE, U.S.A), into an auto-sampler vial and injected twice into LC/MS conditioned as follows.

5. Extraction of PFOA from the aqueous polymeric dispersion

Before the sampling of the aqueous polymeric dispersion they were shaken well without generating bubbles to homogenize the aqueous polymeric dispersion. 1 ml of the aqueous polymeric dispersion was put in each of four centrifugation vials. Fortification of PFOA and 8-2 alcohol were

conducted as listed in Table 1. Fortification of 8-2 alcohol was conducted for the use of latter section (*2-3*). IPA was added into all vials until total amount with fortification solution was 5 ml. After putting a lid, each of five vials (with the blank) was shaken vigorously and the precipitation was separated by centrifugation at 6000 rpm for 10 minutes.

100 µl of the each supernatant and 9ml of 100 ng/ml 9H-PFNA solution was mixed in a vial. About 1 ml of each solution was filtered through the 0.2 µm filter into an auto-sampler vial and injected into LC/MS conditioned as follows. These procedures were repeated once again for the verification of the reproducibility.

Table 1 Fortification of C8 precursors and PFOA

Sample	Fortification	
	10 mg/ml 8-2 alcohol	PFOA
A	0 µl	0 µl
B	50 µl	100 µl X 50 µg/ml
C	100 µl	100 µl X 100 µg/ml
D	200 µl	200 µl X 100 µg/ml

6. LC/MS analysis

LC/MS analysis was conducted with the conditions listed below.

<Instruments>

(1) LC/MS

HPLC	Agilent Technologies, Model 1100
Mass spectrometer	Agilent Technologies, Model 1100MSD (SL)
(2) LC column	Imtakt (Tokyo, Japan), cadenza CD-C18 2 mm (diameter) X 100 mm
(3) PC	Hewlett Packard Kayak PC Workstation OS: MS-Windows NT 4.0
(4) Software	LC/MSD ChemStation, Rev. A. 08. 03
(5) LC/MS vial	2ml vial for auto-sampler, Chromatography-Convenience 400-C80, Tomsic
	(Tokyo, Japan)

<Analytical conditions>

(1) Column temp.	35 °C
(2) Mobile phase	A: 2 mmol/L ammonium acetate
	B: Methanol
(3) Gradient condition	time/min 0 → 2 → 5 → 15 → 15.01 → 25

	B/% 57 → 57 → 100 → 100 → 57 → 57
(4) Flow rate	0.3 mL/min
(5) Injection volume	5 µL
(6) Retention time	PFOA (4.3 min), 9H-PFNA (2.5 min)

<MS operating parameters>

(1) Ionization mode	Electrospray (ESI) (negative ion mode)
(2) Fragmentor voltage	100 V
(3) Ion monitored	m/z = 413 ($C_7F_{15}COO^-$), 445 ($CF_2H(CF_2)_7COO^-$)
(4) Desolvation temperature	350 °C
(5) Nebulizer gas	N_2
(6) Desolvation	N_2 12 L/min

7. Results

Two calibration curves for standard addition method are plotted and shown in Fig. 1 for the ratio of (peak area of m/z = 413) / (peak area of m/z = 445) as a vertical axis against the amount of PFOA fortification (µg) as a horizontal axis. The coefficients of correlation are more than 0.9990 for both curves, and the amounts of PFOA determined in the aqueous polymeric dispersion are 7.2 ppm and 7.0 ppm (average 7.1 ppm). 7.1 ppm is equivalent to 1.7 x 10^{-5} mol/kg (specific gravity of AG-955 is 1.090).

Two calibration curves for PFOA calibration standards are shown in Fig. 2 for the same axis with Fig. 1. PFOA is not detected (zero count) for 0 µg standard (blank). The coefficients of correlation are more than 0.9995, and the recovery defined as (the slope for the standard addition) / (the slope for the calibration standards) was 95%.

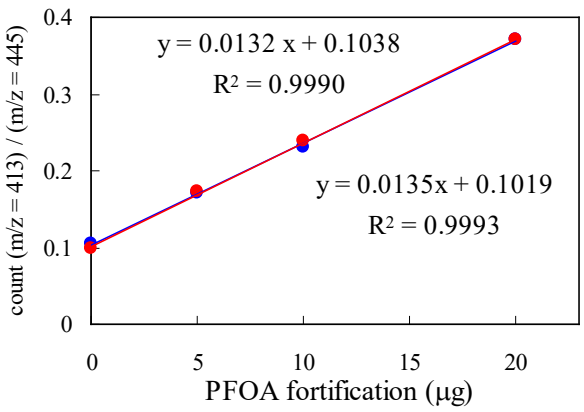

Fig. 1 Calibration curves for AG-955

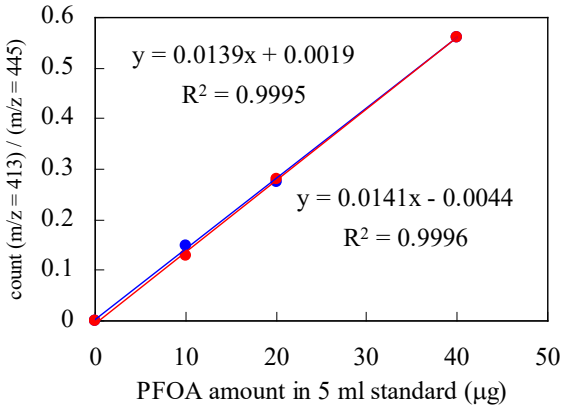

Fig. 2 Calibration curves for PFOA

by standard addition method calibration standards