



Variation in concentration of perfluorooctanoic acid in methanol solutions during storage



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HIGHLIGHTS

- Perfluorooctanoate in methanol solutions decreased with length of storage.
- Methyl perfluorooctanoate and methyl formate increased with length of storage.
- Methyl perfluorooctanoate increased with increase in methyl formate.
- Methyl perfluorooctanoate increased when perfluorooctanoate decreased.
- Variation in the solutions stored around 5 °C was smaller than that at room temp.

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ABSTRACT

Perfluoroalkyl carboxylic acids (PFCAs) including perfluorooctanoic acid (PFOA) have been widely recognized as persistent environmental contaminants. For accurate quantification of PFCAs, their stability in calibration solutions is important because they are criteria of quantification. To examine stability of PFCAs in methanol, we monitored PFOA and its related compounds around 4 years. Interestingly, perfluorooctanoate was varied randomly, and methyl perfluorooctanoate (MePFOA) and methyl formate were observed when perfluorooctanoate decreased. Moreover, no detection of both methyl esters was in methanol solutions immediately after preparation. In each of prepared methanol solution of perfluorohexanoic, perfluoroheptanoic, and perfluorononanoic acids, their corresponding methyl esters and methyl formate were observed. Furthermore, MePFOA was observed even in the solutions stored around 4 months and thereafter MePFOA increased with increase in methyl formate. Therefore, PFCAs including PFOA should be used immediately after preparation when methanol is used as a solvent.

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1. Introduction

Perfluoroalkyl acids have been included among the group of perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs), and they have been widely used in the manufacture of materials and for daily use due to their physicochemical properties that make them suitable for various functions (Kissa, 2001). PFCAs and PFSAs have been given more attention than other environmental contaminants such as PCBs and dioxins because of their ubiquitous presence in the environment (Kennedy et al., 2004; de Voogt and Saez, 2006; Houde et al., 2006; Senthilkumar et al., 2007). Parts of PFCAs and PFSAs are potential to persist and spread in the environment.

On the other hand, there are also some reports of instability and decomposition assessments of PFCAs and PFSAs in stock and aqueous solutions. Among PFCAs (C8, 9, 10, 11, and 13), only C13 on

methanol solution showed instability at room temperature, though long-term stability (more than 300 d) was observed for all PFCAs around 4 °C (Risha et al., 2005). Short half-lives of PFCAs and PFSAs in aqueous solutions with ultrasonic treatment (Moriwaki et al., 2005) and ultraviolet irradiation (Chen and Zhang, 2006; Chen et al., 2007) have also been reported. Moreover, mixture of trifluoroacetic acid and other chemicals (cyclopentene or 1,4-quinodimethane) easily led to ester products under mild condition (below 40 °C) (Peterson and Allen, 1962; Davis et al., 1962), because esterification and silylation of fluoro-carboxylic acids were easier than those of carboxylic acids due to mainly their lower pK_a (Sheppard and Sharts, 1969). Additionally, Wellington Laboratories announced that methanolic solution of PFCAs will lead to formation of methyl esters (Certificate of analysis/documentation from Wellington Laboratories). Therefore, to reliably quantify on PFCAs, further investigation for stability of PFCAs in calibration solutions during storage must be needed.

In this study, we investigated behavior of perfluorooctanoic acid (PFOA), which is the most popular PFCAs as environmental

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contaminants (Kissa, 2001; Kennedy et al., 2004), in prepared solutions during storage with their related compounds. We evaluated not only PFOA using a LC/MS but also esters as non-ionic compounds using a GC/MS. Effects of temperature and storage period will be also discussed.

2. Materials and methods

2.1. Chemicals

PFOA (lot TSH9252), perfluorohexanoic acid (PFHxA, lot ALR0187), and perfluorohexane (lot TLP0953) were obtained from Wako Pure Chemical Industries (Osaka, Japan). Methyl perfluorohexanoate (MePFHxA), methyl perfluoroheptanoate (MePFHpA), methyl perfluorooctanoate (MePFOA), LC/MS grade acetonitrile (ACN), Infinity Pure grade methanol (MeOH), Analytical grades ammonium acetate used as the buffer, sodium carbonate (lot CDG6899), sodium bicarbonate (lot CDH6255), and sodium tetraborate (lot JWK7655) were also obtained from Wako Pure Chemical Industries. Perfluoroheptanoic acid (PFHpA, batch H3002) and perfluorononanoic acid (PFNA, batch H7568) were obtained from Fluorochem (Old Glossop, England, UK), and then methyl perfluorononanoate (MePFNA) was obtained from Matrix Scientific (Columbia, SC, USA). The EP (Nacalai 1st) grade of methyl formate (lot FHM01) was obtained from Nacalai Tesque (Kyoto, Japan). NMIJ CRM 4220-a [potassium perfluorooctane sulfonate (K-PFOS) in MeOH; NMIJ, National Metrology Institute of Japan; CRM, certified reference material, Tsukuba, Japan] was used for an internal standard (IS) for quantification of PFOA. Sulfuric acid (lot 404U1014) and fluoride ion (lot K93888C) were obtained from Kanto Chemical (Tokyo, Japan) and Kishida Chemical (Osaka, Japan), respectively.

2.2. Preparation of solutions for storage

PFOA (2.5 mg) was weighed and dissolved in MeOH (50 g) by the gravimetric preparation method (ISO 6142, 2001; Ishikawa et al., 2008). MeOH is the most popular solvent on calibration solutions of PFOA. The mass was measured using a MC 5 microbalance for solute (Sartorius, Gottingen, Germany) and an AX 205 for solvent (Mettler Toledo, Schwerzenbach, Switzerland) calibrated by the JCSS (Japan Calibration Service System). (JCT 20302, 2012 from National Institute of Technology and Evaluation) PFOA-methanol solution of (50 mg kg⁻¹) was encapsulated into amber glass ampoules (approximately 30 ampoules). This procedure on ampoule containing approximately 1 g (1.4 mL) of solution was repeated under the same conditions for another five times at certain interval of times. One of the advantages of this scheme is that sensitivity correction of instruments is not required because all the measurements are made in the same period. Ampoules from each of the periods were used to clarify behavior of amounts of

perfluorooctanoate, MePFOA and methyl formate. Amber glass ampoules were stored at room temperature (23–25 °C), except parts of them were also stored around 5 °C. All the ampoules were kept under dark for 0 d to around 4 years. Table 1 summarizes a list of prepared solutions in this study.

As a supplement, solute (each of 20–80 mg of PFHxA, PFHpA, or PFNA) was weighed and dissolved in MeOH (20–60 g) by the gravimetric preparation method, and then each solution (500–1000 mg kg⁻¹) was made into glass vial. Solutions on a supplement were tightly capped and stored under dark around 5 °C.

2.3. Preparation of solutions for GC and LC measurements

For LC/MS measurements, an IS [net amount is approximately 1 g (1.4 mL)] was used to quantify amounts of perfluorooctanoate. For GC/MS measurements, methanol solutions of MePFOA (0, 0.8, 4.5, 24 mg kg⁻¹) and methyl formate (0, 0.16, 1.3, 23 mg kg⁻¹) for calibration curves were prepared by the gravimetric preparation method.

Three ampoules stored at room temperature in each of the six periods were randomly selected (18 ampoules selected in total) and were subjected to measurements. The 0.2 mL (0.15–0.16 g) of selected ampoule was divided and added into an IS in each. Obtained mixture solution was subdivided into three, and measured using a LC/MS. Remained 1.2 mL (0.87–0.90 g) of the selected ampoule was subdivided into three, and measured using a GC/MS with solutions of MePFOA and methyl formate for calibration curves. Three ampoules stored around 5 °C in each of the three periods were also randomly selected (9 ampoules selected in total) and were similarly subjected to measurements using LC/MS and GC/MS.

2.4. Measurements of perfluorooctanoate using a LC/MS

A LC/MS (Shimadzu LCMS-2010A, Kyoto, Japan) was used to quantify amounts of perfluorooctanoate. PFOA and an IS (K-PFOS) were separated isocratically using 10 mmol ammonium acetate/water and 80% ACN as the mobile phase at a flow rate of 200 µL min⁻¹ with a Shodex JJ-50 2D column (150 mm × 2.0 mm, 5 µm, Showa Denko, Tokyo, Japan). A 50 µL portion of mixture solutions was injected (*n* = 3 for each solution). Conditions of quadrupole MS were as follows. Electrospray probe voltage was held at 3.0 kV (negative). Nebulizer and dry gas flows (both nitrogen) were kept at 1.5 L min⁻¹ and 0.1 MPa, respectively. Curved Desolvation Line (CDL) and block heater temperatures were both held at 200 °C. The MS parameters were optimized to transmit [M-H]⁻ ions for PFOA and [M-K]⁻ ions for K-PFOS using electrospray negative ionization mode. The ions were monitored using scan mode (*m/z* 100–600). In this study, PFOS anion was used as an IS for quantification of perfluorooctanoate because stability of K-PFOS-methanol solutions has been confirmed (Hanari et al.,

Table 1
List of methanol prepared solutions.

Solute	Prepared concentration (mg kg ⁻¹)	Vessel	Storage temperature	Preparation date	Period of storage
PFOA	50	Glass ampoule	Room temp, 5 °C	July-08	48 months
PFOA	50	Glass ampoule	Room temp	January-09	42 months
PFOA	50	Glass ampoule	Room temp, 5 °C	August-10	23 months
PFOA	50	Glass ampoule	Room temp	March-11	16 months
PFOA	50	Glass ampoule	Room temp, 5 °C	March-12	4 months
PFOA	50	Glass ampoule	No storage	July-12	0 month
PFHxA	950	Glass vial	5 °C	July-08	48 months
PFHpA	1050	Glass vial	5 °C	November-08	44 months
PFNA	550	Glass vial	5 °C	August-08	47 months

PFOA, perfluorooctanoic acid; PFHxA, perfluorohexanoic acid; PFHpA, perfluoroheptanoic acid; PFNA, perfluorononanoic acid.

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