

PURITY EVALUATION OF PERFLUOROOCCTANOIC ACID USING NEUTRALIZATION TITRIMETRY

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Introduction

Perfluoroalkylcarboxylic acids (PFCAs) have been widely used for manufacturing materials and for daily use due to functional physicochemical properties¹. However, among PFCAs, perfluorooctanoic acid (PFOA) has been known to be persistent and toxic^{2,3}. Therefore, in US EPA, the PFOA Stewardship Program has been started to extinct use of PFOA itself, and guidelines of drinking water on PFOA in UK, Germany, etc. have been prepared. Because use of calibration solution having accurate concentration is important to estimate concentration levels of PFCAs properly, quality assurances of measurements using certified reference materials (CRMs) are required. Particularly, in calibration solution CRMs, purity evaluation of chemicals used for preparation of solution is essential to calculate prepared concentration. On purity evaluation of perfluoro compounds, a few reports related to LC/MS and ¹⁹F-NMR measurements were available in the publication^{4,5}. However these techniques did not satisfy requirements for reliable purity evaluation of PFOA, because some impurities such as water and non-volatiles are difficult to evaluate in LC/MS and NMR spectra of main component may overlap impurities that structures are similar to main component. Then, we applied to titrimetry to evaluate purity, because titrimetry is regarded as one of primary methods of measurement having the highest metrological properties and obtained values are considered to be traceable to the SI⁶. In this paper, the SI traceable purity of linear PFOA was evaluated by titrimetry using a potentiometric titrator (PT), and evaluated purity was validated with LC/MS and water content measurements.

Materials and methods

Linear PFOA (lot KWJ8163) was purchased from Wako Pure Chemical Industries. Perfluoroheptanoic and –nonanoic acids (PFHA and PFNA) were purchased from Fluorochem. CRM 3001-a (potassium hydrogen phthalate) used for calibrations of purity expressed as acids on PT measurements was obtained from NMIJ/AIST. Aqueous NaOH solutions (0.05 and 0.01 mol/L, Wako Pure Chemical Industries) were used on PT measurements. A standard solution of water in propylene carbonate (Aquamicron® Water Standard 0.2 mg), which is traceable to NIST SRM

2890 for validation on coulometric Karl-Fischer titrator (KFT) measurements was obtained from Mitsubishi Chemical. CRM 3001-a was diluted in Milli-Q water by gravimetric preparation⁷, and this solution (0.1 mol/kg) was used as a calibration solution of acid. Influence of carbonic acid dissolved in Milli-Q water used for preparation was separately estimated by using 0.01 mol/L aqueous NaOH solution. PFOA (414 to 419 mg) was also diluted in 0.05 mol/L aqueous NaOH solution (60 g). In addition, 0.05 mol/L aqueous NaOH solution without PFOA was used as a blank. Moreover, to estimate influences of the aqueous NaOH solution as a blank during PT measurements, both aqueous NaOH solutions with and without PFOA were measured alternately. Neutralization titrimetry of calibration solution of acid, PFOA solutions, and blank was carried out using a Titlando 809 (Metrohm Japan) equipped with a unitrode electrode. Drift rate of 30 mV/min, drip rate of 5 mL/min, and 10 μ L minimum volume of cylinder were applied. After evaluation of purity of PFOA expressed as acids, purity of PFOA (kg/kg) was determined by subtracting impurities related to PFOA estimated with LC/MS from the purity of PFOA expressed as acids. A LC/MS (Shimadzu LCMS-2010A) with electrospray negative ionization mode connected an L-column ODS (150 mm \times 1.5 mm i.d., particle size 3 μ m, CERI) was used to measure isomers and congeners of PFOA. Water content in PFOA was measured by using an AQ-7 (Hiranuma Sangyo) at room temperature under a dried-air atmosphere⁸. Non-volatiles in PFOA were measured gravimetrically by using a hand-made vacuum evaporator (VE)⁹.

Results and discussion:

In titrimetry, purity of PFOA expressed as acids is evaluated by measuring equivalent volume of calibration solution of NMIJ CRM 3001-a (0.1 mol/kg). Namely, titrimetry is closely related to gravimetric preparation and amount-of-substance concentration of PFOA⁶. A microbalance MC5 (Sartorius) with a readability of 1 μ g was used to weigh PFOA, because accuracy of weighing directly affects that of measurement values. In addition, it was clarified that a reproducibility of PT measurements was improved with increase of the concentration of PFOA. Therefore, PFOA solutions were prepared by using not Milli-Q water but aqueous NaOH solution. Figure shows comparison data of PFOA solutions prepared in Milli-Q water and in aqueous NaOH solution on PT measurements. Apparently, peak shape of titration curve became sharp, and therefore reliable equivalent volume could be measured. As a result, the concentration of PFOA (average value; $n = 5$) was obtained as 0.0023 mol/g, and then purity of PFOA expressed as acids was obtained as 0.9607 kg/kg by multiplying molar mass of PFOA. Next, impurities related to PFOA were measured with LC/MS and quantified using response factors or calibration curves, because these impurities behaved as acids and led overestimation of purity of PFOA expressed as acids. Branched PFOA and PFHA were identified with LC/MS, and quantified as 0.0009 kg/kg (average value; $n = 5$) and 3.030×10^{-5} kg/kg (average value; $n = 3$), respectively. Thus, purity of PFOA based on titrimetry was determined with 0.9598 kg/kg

(Table). On the other hand, uncertainty on purity evaluation was independently estimated on titrimetry and chromatography based on the publication¹⁰. On titrimetry, uncertainties of measurement for PFOA and carbonic acid, deviation of weighing, uncertainties of molar mass¹¹ and CRM used¹², uncertainty of cylinder that relates to volume, variation of density that depends to temperature, and variation of concentrations of solutions were considered. On chromatography (LC/MS), uncertainties of measurement for branched PFOA and PFHA, tolerance of response factors, and variation of calibration curves were considered. From the estimation of above parameters, uncertainty on purity evaluation based on titrimetry was determined with 0.0034 kg/kg (Table), and one of the main sources of uncertainty was measurement arising from PT.

To validate purity based on titrimetry, each impurity (branched PFOA, PFHA, water content, and non-volatiles) was separately measured with LC/MS, KFT, and VE, and then purity obtained by subtracting amounts of the each impurity from 1 was compared. For KFT measurements, observed water content (average value; $n = 4$) was 0.0407 kg/kg. For non-volatile measurements, no notable mass was detectable compared to blank without PFOA. From the results in each measurement, purity of PFOA was obtained as 0.9584 kg/kg. As a result, purity based on titrimetry allowed within uncertainty.

Thus, it can be concluded that purity of PFOA $\{(0.9598 \pm 0.0034) \text{ kg/kg}\}$ evaluated based on titrimetry is reliable. Therefore evaluating purity which is traceable to the SI is possible on not only PFOA but also other isomers/congeners. As an outcome of this study, CRM of PFOA (NMIJ CRM 4056-a) is available at present.

References:

1. Kissa E. (2001); *Fluorinated surfactants and repellents*. Marcel Dekker
2. de Voogt P, Sáez M. (2006); *Trac-Trends Anal. Chem.* 25(4): 326–42
3. Fromme H, Tittlemier SA, Völkel W, Wilhelm M, Twardella D. (2009); *Int. J. Hyg. Envir. Heal.* 212(3): 239–70
4. Arsenault G, Chittim B, McAlees A, McCrindle R, Riddell N, Yeo B. (2008); *Chemosphere* 70(4): 616-25
5. Arsenault G, Chittim B, Gu J, McAlees A, McCrindle R, Robertson V. (2008); *Chemosphere* 73(1): S53-9
6. Milton MJT, Quinn TJ. (2001); *Metrologia* 38(4): 289–96
7. ISO 6142. (2001); *Gas analysis -Preparation of calibration gas mixtures -Gravimetric method*
8. Hanari N, Iwasawa R, Otsuka S, Fujiki N, Matsumoto A, Ihara T, Ishikawa K, Yarita T. (2010); *Accredit. Qual. Assur.* 15(12): 673–9
9. Ishikawa K, Hanari N, Shimizu Y, Ihara T, Nomura A, Numata M, Yarita T, Kato K, Chiba K. (2011); *Accredit. Qual. Assur.* accepted
10. ISO Guide 98-3. (2008); *Uncertainty of measurement -Part 3*

11. Wieser ME, Berglund M. (2009); *Pure Appl. Chem.* 81(11): 2131–56

12. Information on CRMs from NMIJ/AIST available at <http://www.nmij.jp/service/C/crm/>

Figure Titration curves of PFOA solutions prepared in Milli-Q (a) and in aqueous NaOH solution (b).

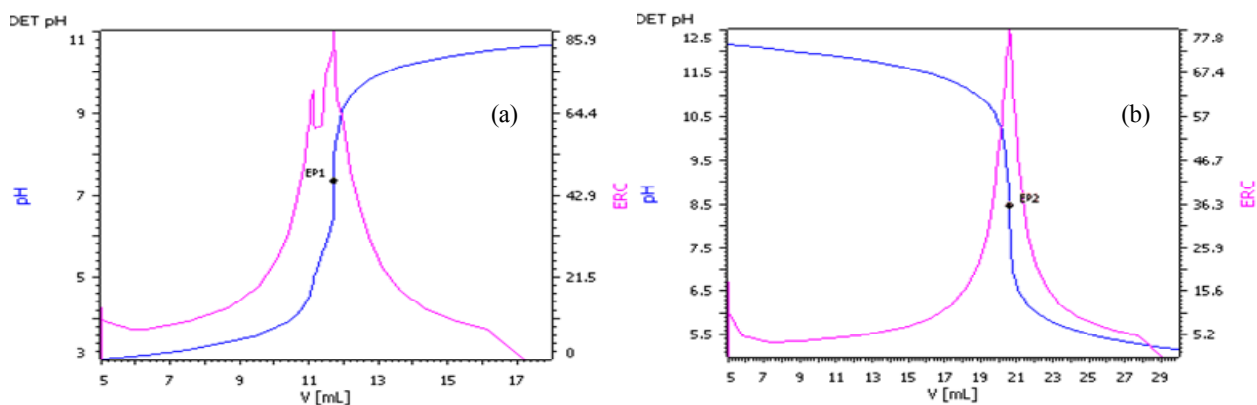


Table Uncertainty budget of purity evaluation of PFOA (kg/kg) based on titrimetry.

Parameter	x_i	$u(x_i)$	Component
Purity estimated with PT	0.9607	0.0034	Measurement
			Weighing
			Molar mass
			CRM
			Cylinder
			Density
			Concentration of solutions
			Impurities estimated with LC/MS
			Response factor
			Calibration curve
Purity based on titrimetry	0.9598	0.0034	