# Analytical Methods

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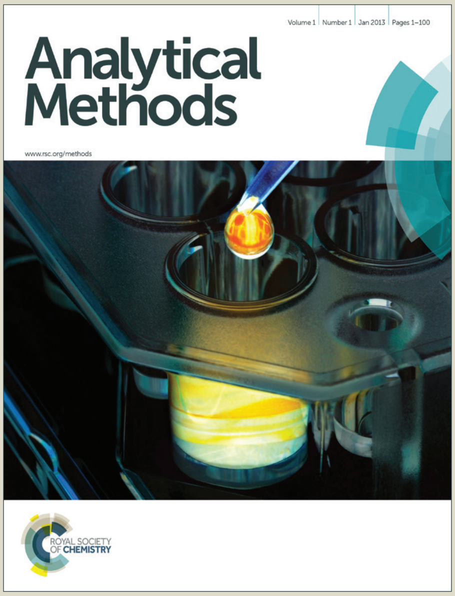

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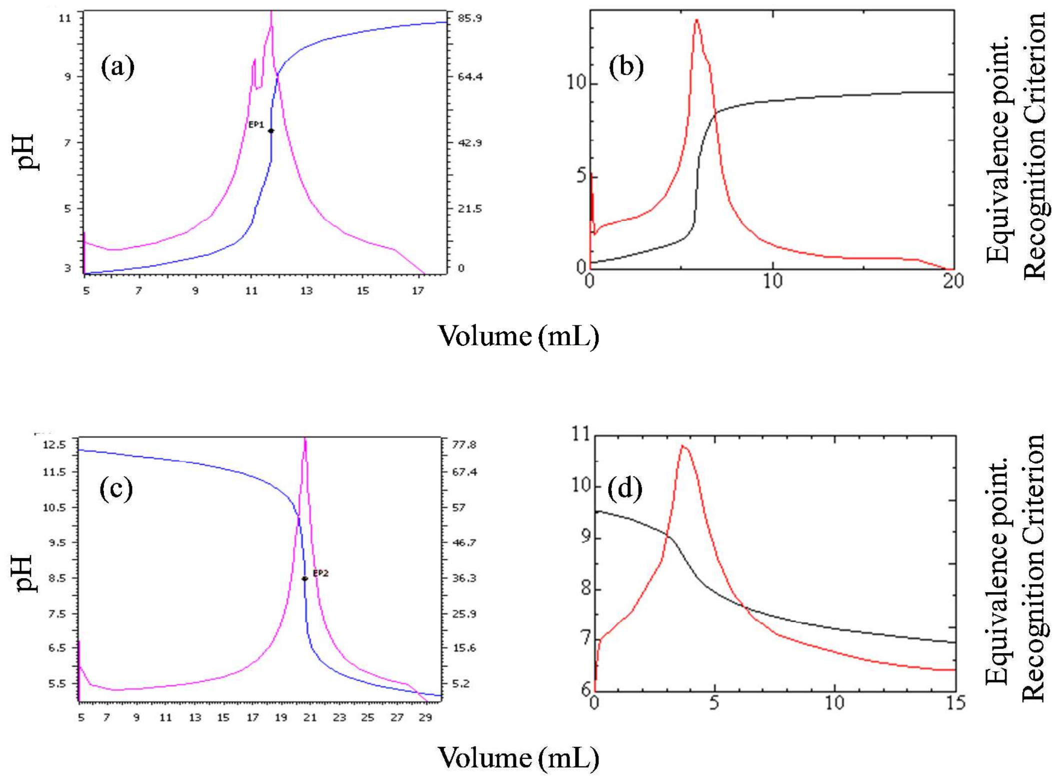

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TECHNICAL NOTES

# Evaluation of perfluorooctanoic acid purity based on potentiometric titration

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Reliable purity evaluations of perfluorooctanoate (PFOA), surfactants, are desired for accurate quantifications because purity is essential for preparation of calibration solutions. To meet this requirement, PFOA monohydrate homogenized was prepared for improvements of repeatability, and was diluted in aqueous NaOH for measures of poor solubility on titration analyses, which is commonly used for purity evaluations of chemicals. Purity based on the titration technique was determined by subtracting the mass fractions of impurities related to PFOA analyzed by using a LC/MS from those of purity expressed as acids analyzed by neutralization potentiometric titration using a potentiometric titrator. To validate obtained result, another analytical result based on the mass balance technique was determined by subtracting the mass fractions of every impurity. From the results in this study, this titration technique can help evaluating reliable purity of analytes similar to PFOA.

## Introduction

Perfluoroalkyl carboxylic acids (PFCAs) 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.[1] However, selected PFCAs including perfluorooctanoate (PFOA) have also been known to be persistent and/or toxic.[2,3] The United States Environmental Protection Agency has initiated a PFOA Stewardship Program to ultimately eliminate PFOA usage and emissions.[4] In addition, guidelines for PFOA in drinking water in the UK and Germany have been prepared.[5] Therefore, accurate quantifications of PFOA are essential to assess its concentration levels.

In accurate quantifications, the use of calibration solutions with reliable concentrations is important. Moreover, evaluating reliable purity of PFOA used for solution preparation is essential as it affects the final concentration. According to our previous report,[6] the purity of PFOA varied due to different ambient conditions during sample handling because PFOA is a hygroscopic substance.[1] Namely, the reliability of purity of PFOA is required on the quality assurance of analyses.

Primary techniques on measurements are skill with the best metrological properties, which are often chosen for development of certified reference materials (CRMs). The Consultative Committee for Amount of Substance (CCQM) of the International Committee for Weights and Measures (CIPM) has identified several methods as having the potential to be primary techniques on measurements, using techniques such as gravimetry, coulometry, isotope dilution mass spectrometry, freezing point depression technique, and titrimetry.[7,8] For purity evaluations of chemicals, property values that are traceable to the International System of Units (SI) are obtained preferably by the freezing point depression technique.[9] However, this technique did not satisfy requirements for reliable purity evaluation of linear PFOA because this compound is detergent, hygroscopic and water as an impurity was repeatedly adsorbed and desorbed under different ambient conditions during sample handling.[6]

Then, we focused on the titrimetry regarded as one of primary techniques on measurements[7,8] to evaluate reliable purity of PFOA because PFOA is a monovalent acid. However, some problems must be solved to achieve accurate titration on purity evaluation, such as hygroscopicity[6] and poor solubility[1] of PFOA. We have found the conditions to prepare the homogenous linear PFOA with stable purity by referring to our previous report.[6] Moreover, we have changed the titration solvent from water to aqueous NaOH to improve poor solubility. In addition, analytical results based on the neutralization potentiometric titration using a potentiometric titrator (PT) were compared with the results based on the mass balance technique[10,11] in combination with LC/MS, Karl-Fischer titrator (KFT), etc. for validation. In this paper, the optimization of the neutralization potentiometric titration is described.

## Experimental section

### Chemicals

Linear PFOA for Environment Analysis (lot: TSH9252) and linear PFOA for Chemical Analysis (lot: PEH6950) were obtained from Wako Pure Chemical Industries (Osaka, Japan). Structures of main component in these reagents were confirmed using a nuclear magnetic resonance (fluorine-19) at JEOL (Tokyo, Japan). The procedure for homogenization of both PFOA is detailed in elsewhere.[6] Aqueous NaOH solutions (0.05 and 0.01 mol $L^{-1}$) used for PT analyses, Infinity Pure grade acetonitrile (ACN), ACN for LC/MS Analysis and Analytical grade ammonium acetate as the buffer were also obtained from Wako Pure Chemical Industries. Perfluoroheptanoate (PFHpA) and perfluorononanoate (PFNA) were obtained from Fluorochem (Old Glossop, England, UK). Homogenization of PFNA is also described elsewhere.[6] CRM 3001-a (potassium hydrogen phthalate, KHP) used for calibrations of purity expressed as acids on PT analyses was obtained from the National Metrology Institute of Japan (Tsukuba, Japan). Acetone for Residual Pesticide/PCB Analysis used for prewashing the experimental items and methanolic KOH solution (0.1 mol $L^{-1}$) for PT analyses were obtained from Kanto Chemical (Tokyo, Japan). Hydranal-Aqualyte RS-A and Aqualyte CN were used as the catholyte and anolyte for KFT, respectively, and were obtained from Sigma-Aldrich Japan (Tokyo, Japan). A standard solution of water in propylene carbonate (Aquamicron Water Standard 0.2 mg) that was traceable to NIST SRM 2890 was used as the verification standard and was obtained from Mitsubishi Chemical (Tokyo, Japan).

### Neutralization potentiometric titration

The neutralization potentiometric titration was carried out using a Titlando 809 (Metrohm, Herisau, Switzerland) equipped with a unitrode electrode. For analyses of PFOA solutions, purity of PFOA expressed as acids was evaluated by analyzing equivalent volume of calibration solutions of CRM 3001-a. KHP (purity expressed as acids: 0.99991 kg $kg^{-1}$) was diluted in 1 L of Milli-Q water (Nihon Millipore Integral 3, Tokyo, Japan), and this solution (preparation concentration: approximately 0.05 mol $L^{-1}$, $c_{\mathrm{KHP}}$) was used as the calibration solution of acid. The $c_{\mathrm{KHP}}$ was calculated using Equation 1:

$$c_{\mathrm{KHP}} = \frac{P_{\mathrm{KHP}} \times m_{\mathrm{KHP}}}{M_{\mathrm{KHP}} \times v_{\mathrm{water}}} \qquad (1)$$

where $P_{\mathrm{KHP}}$ is purity expressed as acids, $m_{\mathrm{KHP}}$ is mass of KHP, $M_{\mathrm{KHP}}$ is molar mass of KHP, and $v_{\mathrm{water}}$ is volume of Milli-Q water. Next, 0.01 mol $L^{-1}$ aqueous NaOH solution was used as the burette solution. Concentration of the aqueous NaOH solution ($c_{\mathrm{NaOH}}$, mol $g^{-1}$) was calculated using Equation 2:

$$c_{\mathrm{NaOH}} = \frac{c_{\mathrm{KHP}} \times v_{\mathrm{KHP}}}{m_{\mathrm{NaOH}}} \qquad (2)$$

where $v_{\mathrm{KHP}}$ is volume of the calibration solution of acid consumed in the neutralization potentiometric titration, and $m_{\mathrm{NaOH}}$ is mass of the aqueous NaOH solution. Moreover, homogenous PFOA (as a monohydrate, 49.4–50.7 mg) was diluted in Milli-Q water (0.05 mol $L^{-1}$). Finally, concentration of PFOA in Milli-Q water ($c_{\mathrm{PFOA}}$, mol $g^{-1}$) was calculated using Equation 3:

$$c_{\mathrm{PFOA}} = \frac{c_{\mathrm{NaOH}} \times m_{\mathrm{NaOH}}}{m_{\mathrm{PFOA}}} \qquad (3)$$

where $m_{\mathrm{PFOA}}$ is mass of the aqueous PFOA solution. Purity of PFOA expressed as acids (kg $kg^{-1}$) was calculated by multiplying $c_{\mathrm{PFOA}}$ by molar mass of PFOA. Drift rate of 30 mV $min^{-1}$, drip rate of 5 mL $min^{-1}$, and 10 µL minimum volume of cylinder were applied. Mass of solutes and solvents was respectively monitored using a MC 5 microbalance (readability 1 µg, Sartorius, Gottingen, Germany) and a LC 5101S balance (readability 1 mg, Sartorius), which had been calibrated by the Japan Calibration Service System (JCSS), by which metrological traceability in Japan has been assured.[12]

### Impurity analysis

Every impurity predicted was evaluated using a LC/MS (Shimadzu LCMS-2010A; Kyoto, Japan) for isomers and homologues of PFOA, a KFT (Hiranuma Sangyo AQ-7; Mito, Japan) for water content, and a vacuum evaporator (custom-built) for non-volatiles. LC separation was carried out using 30% ACN in 10 mmol aqueous ammonium acetate under isocratic mode. The column used was a L-column ODS (150 mm × 1.5 mm i.d., particle size 3 µm, Chemicals Evaluation and Research Institute, Tokyo, Japan). The column temperature and flow rate were set at 40 °C and 100 µL $min^{-1}$, respectively. Five microliters of PFOA ACN solution was injected for each run. Conditions of the quadrupole MS have been described elsewhere.[6,13] The amounts of the isomer/homologue impurities were estimated using a LC/MS, and the response factors for estimating the ratio of each impurity in MS (peak areas of anions in MS chromatogram / mass of analyte of PFCAs) were corrected with the PFHpA, PFOA, and PFNA. In case of obtaining authentic standards (e.g. PFHpA), the amounts of the homologue impurities were estimated by standard addition method using a LC/MS (0.0003, 0.0025, 0.0036, and 0.0129 mg $kg^{-1}$; ACN solutions prepared by the gravimetric preparation[14]). In this study, the isomer and homologue impurities that were detected using a LC/MS were assumed to be its acids when calculating the amount-of-substance concentration of PFOA. The water content in PFOA was analyzed using a coulometric KFT equipped with a diaphragm at room temperature under a dried-air atmosphere (dew point: below –30 °C) in a glove box. Conditions of this coulometric KFT have been described elsewhere.[15] Aliquots of PFOA (10.0–10.1 mg) were introduced into the KFT vessel following instrument equilibration. PFOA was analyzed in quadruplicate after verification using a standard solution of water. Non-volatiles such as inorganic salts were determined using a custom-build apparatus equipped with a vacuum pump and platinum boats. PFOA (10.1–10.8 mg) was analyzed in triplicate. Conditions of vacuum evaporator have been described elsewhere.[6] The boiling point of PFOA under vacuum conditions was estimated based on the Antoine Equation and literature value.[16] The mass of non-volatiles was monitored using a SC 2 microbalance (readability 0.1 µg, Sartorius, Gottingen, Germany) calibrated by the JCSS.[12]

### Purity evaluation

We have performed two methods, the titration and mass balance techniques, to evaluate reliable purity of PFOA. For the titration technique, after evaluation of purity of PFOA expressed as acids, the purity (mass fraction: kg $kg^{-1}$) of PFOA was determined by subtracting impurities of PFOA estimated using a LC/MS from the purity of PFOA expressed as acids, because these impurities behaved as acids and led overestimation of the purity of PFOA expressed as acids. For the mass balance technique, the purity (kg $kg^{-1}$) of PFOA was determined by subtracting every impurity estimated using a LC/MS, a KFT, and a vacuum evaporator from 1 kg $kg^{-1}$. Finally, both purities were compared, and confirmed to be identical within the limits of uncertainty.

## Results and discussion

### Titration using water as the solvent

Table 1 shows results of PFOA (lot: TSH9252) solutions prepared in Milli-Q water. Relative measurement standard deviation of the analytical solutions was 0.03 ($n$ = 5). This deviation seems to be because that $c_{\mathrm{PFOA}}$ was lower due to poor solubility and results of the measurement affected carbon dioxide which behaved as acids in water.

**Table 1** Analytical conditions and results of potentiometric titration on perfluorooctanoate (PFOA) solutions prepared using Milli-Q water and aqueous NaOH

| | Solvent used for analytical solutions | |
|---|---|---|
| | Milli-Q water | 0.05 mol L$^{-1}$ Aqueous NaOH |
| Amount of PFOA | 40 mg | 400 mg |
| Calibration solution | 0.05 mol L$^{-1}$ CRM 3001-a in Milli-Q water | 0.1 mol L$^{-1}$ CRM 3001-a in Milli-Q water |
| Burette solution | 0.01 mol L$^{-1}$ Aqueous NaOH | 0.1 mol L$^{-1}$ CRM 3001-a in Milli-Q water |
| Relative measurement standard deviation ($n$ = 5) | 0.03 | 0.002* |
| Remark | - | Titration of aqueous NaOH with and without PFOA was performed alternately, and the difference of both results was evaluated as the purity. |

[a] * combines deviation arising from both results of aqueous NaOH with and without PFOA.

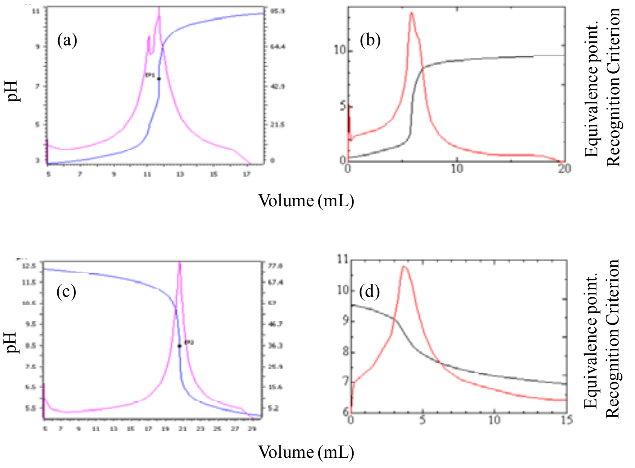

**Fig. 1** Titration curves of perfluorooctanoate solutions. (a) is data of solution prepared in Milli-Q water, (b) is data of solution prepared in methanol, (c) is data of solution prepared in aqueous NaOH solution with back-titration, and (d) is data of solution prepared in methanolic KOH with back-titration.

Fig. 1(a) shows data of the analytical solutions on PT analyses. Apparently, peak shape of titration curve was doublet, and became broad. Therefore, determination of reliable equivalent volume of burette solution was difficult. As supplement, when methanol was used as the solvent for non-aqueous titration, a titration curve was also broad as shown in Fig. 1(b). Then, to avoid these problems, solvent for the titration and effect of carbon dioxide were investigated.

### Titration using aqueous NaOH as the solvent

Next, we selected aqueous NaOH as the solvent to apply to back-titration method (Fig. 2). In this case, both the calibration and burette solutions represented 0.1 mol L$^{-1}$ CRM 3001-a in Milli-Q water (Table 1). The 0.05 mol L$^{-1}$ aqueous NaOH solutions without PFOA were used as the blank. Concentration of aqueous NaOH solution as the blank ($c_{\mathrm{blank}}$, mol g$^{-1}$) was calculated using Equation 4:

$$c_{\mathrm{blank}} = \frac{c_{\mathrm{KHP}} \times v_{\mathrm{KHP}}}{m_{\mathrm{blank}}} \qquad (4)$$

where $m_{\mathrm{blank}}$ is mass of the blank. Moreover, PFOA (414–419 mg) was diluted in 0.05 mol L$^{-1}$ aqueous NaOH solution (60 g) by the gravimetric preparation.[14] Furthermore, to compensate for influences of the aqueous NaOH solution as the blank during PT analyses, both aqueous NaOH solutions with and without PFOA were analyzed alternately. Concentration of PFOA in aqueous NaOH solution ($c_{\mathrm{PFOA\_back}}$, mol g$^{-1}$) was calculated using Equation 5:

$$c_{\mathrm{PFOA\_back}} = \frac{c_{\mathrm{blank}} \times m'_{\mathrm{blank}} - c_{\mathrm{KHP}} \times v'_{\mathrm{KHP}}}{m'_{\mathrm{PFOA}}} \qquad (5)$$

where $m'_{\mathrm{blank}}$ is mass of aqueous NaOH solution used for preparation of PFOA solutions, $v'_{\mathrm{KHP}}$ is volume of the calibration solution of acid consumed in neutralization potentiometric titration during analyses of PFOA solutions, and $m'_{\mathrm{PFOA}}$ is mass of aqueous NaOH solutions with PFOA. For carbon dioxide, concentration of carbon dioxide dissolved in Milli-Q water was estimated by standard addition method[17,18] with titrator using aqueous NaOH (0.01 mol L$^{-1}$) and KHP (20 mg, 40 mg, and 60 mg). KHP was respectively added in Milli-Q water by the gravimetric preparation[14], and then titration of these KHP solutions with different concentrations was performed ($n$ = 3 in each concentration). Concentration of carbon dioxide could be calculated by using intercept given by linear regression of a calibration curve arising from obtained results.[17,18] Apparently, peak shape of titration curve became sharp, and then reliable equivalent volume of burette solution could be analyzed as shown in Fig. 1(c). Moreover, repeatability of PT analyses was improved in spite of back-titration method (Table 1). In addition, it seemed that deducting effect of carbon dioxide was better for reliable measurements because carbon dioxide in water behaved as weak acids. Similar to Fig. 1(b), when methanolic KOH was used as the solvent on the back-titration method, a titration curve was worse as shown in Fig. 1(d). As these results, applied titration technique using aqueous NaOH as the solvent has good advantages because determination of reliable equivalent volume of burette solution became easy and thereafter the measurement standard deviation was improved. From the results in the titration technique, $c_{\mathrm{PFOA\_back}}$ (average value; $n$ = 5) was obtained as 0.0023 mol g$^{-1}$. And then, purity of PFOA expressed as acids was obtained as 0.9607 kg kg$^{-1}$ by multiplying molar mass of PFOA

(Table 2). This result was overestimated acids because impurities of PFOA behaved as acids. Consequently, impurities of PFOA were analyzed using a LC/MS and identified as branched PFOA isomers and PFHpA homologue. These were quantified using response factors or calibration curves arising from standard addition method. Branched PFOA isomers and PFHpA homologue were 0.0009 kg kg$^{-1}$ (average value; $n$ = 5) and $3.030\times10^{-5}$ kg kg$^{-1}$ (average value; $n$ = 3), respectively (Table 2). Thus, the purity of PFOA based on the titration technique was determined to be 0.9598 kg kg$^{-1}$.

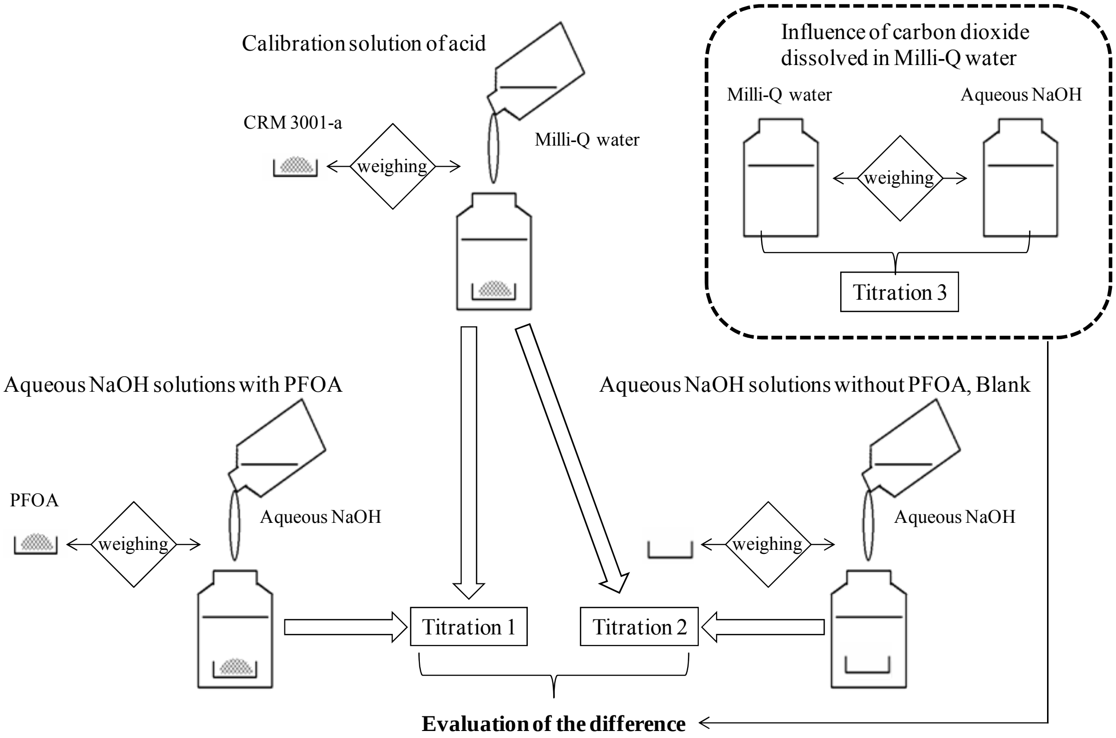

**Fig. 2** Sumary of neutralization potentiometric titration with back-titration method. Purity of perfluorooctanoate (PFOA) expressed as acids was evaluated using the difference arising from results of Titrations 1 and 2, and separately considered results of Titration 3. CRM 3001-a represents certified reference material of potassium hydrogen phthalate used for calibrations of purity expressed as acids.

**Table 2** Summary of analytical results (kg kg$^{-1}$) obtained by each analytical method on perfluorooctanoate (PFOA)

| | Acids | Impurities behaved as acids | Impurities except acids | Analytical method |
|---|---|---|---|---|
| Purity expressed as acids | 0.9607<br>(0.0034) | - | - | Neutralization titrimetry* |
| Perfluoroheptanoate (PFHpA) | - | $3.030 \times 10^{-5}$<br>($5.811 \times 10^{-6}$) | - | Standard addition method using LC/MS*,** |
| Branched PFOA | - | 0.0009<br>(0.0003) | - | Quantification by response factor using LC/MS** |
| Water content | - | - | 0.0407<br>(0.0003) | Coulometry** |
| Non-volatile content | - | - | 0<br>($4.600 \times 10^{-6}$) | Gravimetry** |

[a] Value in parentheses is its associated uncertainty. * and ** are related to titration and mass balance techniques, respectively.

On the other hand, uncertainty of the purity was independently estimated on titration technique and chromatography (LC/MS). For the titration, uncertainties due to titration of PFOA and carbon dioxide, deviation of weighing, uncertainties of molar mass[19] and used CRM[20], uncertainty of cylinder that relates to volume, variation of density that depends on temperature, and variation of concentrations of blank solutions were considered. For LC/MS, uncertainties due to analyses of branched PFOA isomers and PFHpA homologue, tolerance of response factors, and/or variation of calibration curves arising from standard addition method were considered. From the estimation of above parameters, standard uncertainty of purity based on the titration was determined to be 0.0034 kg kg$^{-1}$ (Table 2), and the main sources of uncertainty was measurement standard deviation arising from PT and concentration of blank solutions (Table 3).

**Table 3** Contribution of factor of neutralization titrimetry on uncertainty.

| Method (Uncertainty) | Factor | Contribution (%) |
|---|---|---|
| Titrimetry (0.0034) | Measurement standard deviation | 27.57 |
| | Weighing | 0.06 |
| | Molar mass | ≒ 0 |
| | CRM | 0.88 |
| | Cylinder | 18.79 |
| | Density | 0.18 |
| | Concentration of blank solutions | 52.51 |
| | | 100.00 |

[a] Contribution was calculated based on the equation 5.

### Results of impurities

Each impurity (branched PFOA isomers, PFHpA homologue, the water mass fraction, and non-volatiles) was separately analyzed using a LC/MS, a KFT, and a vacuum evaporator. For impurities related to PFOA, these were described as above. For KFT, observed water was 0.0407 kg kg$^{-1}$ (average value; $n$ = 4, Table 2). No notable non-volatiles were detectable compared to the blank.

Next, uncertainty on impurities was independently estimated on LC/MS, KFT, and vacuum evaporator. Uncertainty arising from LC/MS was described as above. For KFT, measurement standard deviation and deviation of weighing were considered in the uncertainty calculation. Standard uncertainty of the water mass fraction from KFT was estimated to be 0.0002 kg kg$^{-1}$. For vacuum evaporator, standard uncertainty of microbalance used was considered. From the estimation of above parameters, uncertainty on impurity analysis was determined to be 0.0003 kg kg$^{-1}$ (Table 2).

### Purity validation

Purity of PFOA based on the titration technique was determined to be (0.9598 ± 0.0034) kg kg$^{-1}$. To validate the purity based on the titration technique, purity based on the mass balance technique was obtained as (0.960 ± 0.001) kg kg$^{-1}$ from the results in impurity analysis. Eventually, both values were identical within the limits of uncertainty. As supplementary data, purity evaluation of homogenous PFOA (lot: PEH6950) and PFNA could be performed similarly by the titration and mass balance techniques (data not shown). Each result from another PFOA and PFNA was also comparable within the limits of uncertainty.

## Conclusions

Reliable purity of PFOA could be evaluated based on the titration technique regarded as primary techniques on measurements for the first time. The use of this result can provide the SI traceable analytical results. Also, a technique of reliable purity evaluation based on potentiometric titrimetry is applicable to not only inorganics[21,22] and clinical substances[23,24] but also PFCAs.

## Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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