



# National Institute of Standards & Technology

## Report of Investigation

### Reference Material 8446

#### Perfluorinated Carboxylic Acids and Perfluorooctane Sulfonamide in Methanol

This Reference Material (RM) is a solution of perfluorinated carboxylic acids (PFCAs) and perfluorooctane sulfonamide (PFOSA) in methanol intended primarily for use in the calibration of chromatographic instrumentation. A unit of RM 8446 consists of four 2 mL ampoules, each containing approximately 1.2 mL of solution. Two of the ampoules contain PFCAs in Methanol, and the other two ampoules contain PFCAs and PFOSA in Methanol.

**Reference Mass Fractions of PFCAs and PFOSA:** The reference mass fraction values are given in Table 1 for the PFCAs in Methanol and in Table 2 for the PFCAs and PFOSA in Methanol. The values are based on results obtained from the gravimetric preparation of the solution and analytical results determined by using liquid chromatography. Reference values are noncertified values that are the best estimates of the true values; however, the values do not meet the NIST criteria for certification and are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods [1].

**Expiration of Value Assignments:** The values for **RM 8446** are valid, within the measurement uncertainty specified, until **31 January 2024**, provided the RM is handled and stored in accordance with the instructions given in this report (see "Instructions for Use"). This report is nullified if the RM is damaged, contaminated, or otherwise modified.

**Maintenance of RM:** NIST will monitor this RM over the period of its validity. If substantive technical changes occur that affect the value assignment before the expiration of this report, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Coordination of the technical measurements leading to the value assignments of this RM was under the direction of J.L. Reiner and L.C. Sander of the NIST Chemical Sciences Division.

Consultation on the statistical design of the experimental work and evaluation of the data were provided by N.A. Heckert and J.H. Yen of the NIST Statistical Engineering Division.

Analytical measurements were performed by J.M. Keller, J.L. Reiner, and M.M. Schantz of the NIST Chemical Sciences Division.

Support aspects involved in the issuance of this RM were coordinated through the NIST Office of Reference Materials.

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Report Issue Date: 18 March 2014

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## INSTRUCTIONS FOR USE

**Handling:** This material contains perfluorinated compounds, many of which have been reported to have toxic and/or carcinogenic properties, and should be handled with care. Use proper disposal methods.

**Storage:** Sealed ampoules, as received, should be stored in the dark at temperatures below 30 °C.

**Opening of Ampoule:** Open ampoules carefully to prevent contamination or injury. The ampoules are pre-scored and should **NOT** be opened using a file. Sample aliquots, minimum sample size of 50 µL, for analysis should be withdrawn at 20 °C to 25 °C **immediately** after opening the ampoules and should be processed without delay for the reference values in Tables 1 and 2 to be valid within the stated uncertainties. Because of the volatility of methanol, reference values are not applicable to material stored in ampoules that have been opened for more than 5 min, even if they are resealed.

## PREPARATION AND ANALYSIS<sup>(1)</sup>

**Preparation:** The PFCAs and PFOSA used in the preparation of this RM were obtained from 3M (St. Paul, MN), ABCR (Karlsruhe, Germany), Fisher Chemical (Fairlawn, NJ) and Sigma Aldrich (St. Louis, MO). The solution was prepared at NIST by weighing and mixing the individual perfluorinated compounds and methanol. The weighed components were added to the methanol and mixed until completely dissolved and homogenized. Four molar equivalents of sodium hydroxide, based on the total mass of the perfluorinated compounds, were added following the addition of all compounds. The total mass of this solution was measured, and the mass fractions were calculated for the components. This bulk solution was then chilled to approximately -5 °C, and 1.2 mL aliquots were dispensed into 2 mL amber glass ampoules that were then flame sealed.

**Liquid Chromatographic Analysis:** Aliquots from ampoules selected by a stratified random sampling were analyzed by using liquid chromatography tandem mass spectrometry (LC-MS/MS). An internal standard solution containing <sup>13</sup>C- labeled PFCAs and PFOSA was added to each sample for quantification purposes. Calibration solutions consisting of weighed amounts of the perfluorinated compounds and internal standard compounds in methanol were chromatographically analyzed to determine analyte response factors.

**Reference Mass Fractions for PFCAs in Methanol:** Each reference value is a weighted mean of average mass fractions, with one average from gravimetric preparation and two averages from chromatographic measurements [2,3]. The expanded uncertainty is the half-width of a symmetric 95 % parametric bootstrap confidence interval [4], which is consistent with the ISO/JCGM Guides [5,6]. The effective coverage factor, *k*, is 2. Since two methods were used for each compound, the measureand is the average mass fraction for each compound listed. The reference values are metrologically traceable to the SI unit of milligram per kilogram.

Table 1. Reference Mass Fractions for PFCAs in Methanol in RM 8446

PFCA	Compound	Mass Fractions (mg/kg)
PFHxA	Perfluorohexanoic acid	59.1 ± 1.4
PFHpA	Perfluoroheptanoic acid	76.0 ± 7.2
PFOA	Perfluorooctanoate acid	54.8 ± 2.2
PFNA	Perfluorononanoic acid	63.0 ± 1.4
PFDA	Perfluorodecanoic acid	58.1 ± 4.0
PFUnA	Perfluoroundecanoic acid	62.8 ± 6.5
PFDoA	Perfluorododecanoic acid	59.5 ± 7.0
PFTriA	Perfluorotridecanoic acid	62.9 ± 2.8
PFTA	Perfluorotetradecanoic acid	58.0 ± 3.8

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<sup>(1)</sup>Certain commercial equipment, instruments, or materials are identified in this report to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

**Reference Mass Fractions for PFCAs and PFOSA in Methanol:** Each reference value is a weighted mean of average mass fractions, with one average from gravimetric preparation and two averages from chromatographic measurements [2,3]. The expanded uncertainty is the half-width of a symmetric 95 % parametric bootstrap confidence interval [4], which is consistent with the ISO/JCGM Guides [5,6]. The effective coverage factor,  $k$ , is 2. Since two methods were used for each compound, the measureand is the average mass fraction for each compound listed. The reference values are metrologically traceable to the SI unit of milligram per kilogram.

Table 2. Reference Mass Fractions for PFCAs and PFOSA in Methanol in RM 8446

	Compound	Mass Fractions (mg/kg)
PFBA	Perfluorobutanoic acid	43 ± 11
PFPeA	Perfluoropentanoic acid	60.9 ± 0.9
PFOSA	Perfluorooctane sulfonamide	66.9 ± 1.7

#### REFERENCES

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- [2] Dersimonian, R.; Laird, N.; *Meta-analysis in clinical trials*; *Controlled Clin. Trials*, Vol. 7, pp. 177–188 (1986).
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- [4] Efron, B.; Tibshirani, R.J.; *An Introduction to the Bootstrap*; Chapman & Hall (1993).
- [5] JCGM 100:2008; *Evaluation of Measurement Data - Guide to the Expression of Uncertainty in Measurement*; (GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology (JCGM) (2008); available at [http://www.bipm.org/utis/common/documents/jcgm/JCGM\\_100\\_2008\\_E.pdf](http://www.bipm.org/utis/common/documents/jcgm/JCGM_100_2008_E.pdf) (accessed March 2014); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at <http://www.nist.gov/pml/pubs/index.cfm> (accessed March 2014).
- [6] JCGM 101:2008; *Evaluation of Measurement Data – Supplement 1 to the “Guide to the Expression of Uncertainty in Measurement” - Propagation of Distributions using a Monte Carlo Method*; JCGM (2008); available at [http://www.bipm.org/utis/common/documents/jcgm/JCGM\\_101\\_2008\\_E.pdf](http://www.bipm.org/utis/common/documents/jcgm/JCGM_101_2008_E.pdf) (accessed March 2014).

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