**SCIENCE HUB DATA**

**An ultra-sensitive method for the analysis of perfluorinated alkyl acids in drinking water using a column switching high-performance liquid chromatography tandem mass spectrometry**

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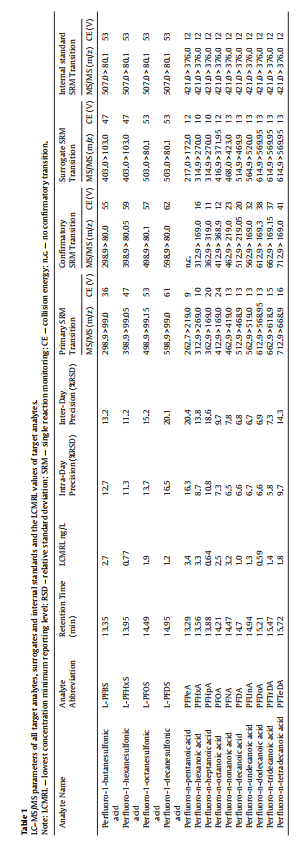
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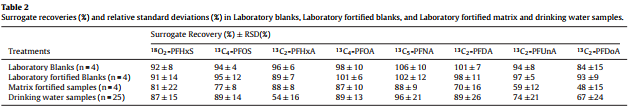
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**Recoveries in Fortified Laboratory Blanks.** Recoveries of the target and internal standard were calculated using the equation (SI-1).

Eq. (SI-1)

Where Cmeasured is measured concentration in the standards fortified water; Sconc is set concentration (7.5 pg/g).

**Recoveries in Fortified Matrix Samples.** Recoveries of the target chemicals in the fortified matrix samples were calculated using the equation (SI-2).

Eq. (SI-2)

Where Cmeasured is measured concentration in the standards fortified matrix sample; Cbackground is the background concentration in unfortified matrix samples; Sconc is set concentration (7.5 pg/g).

**Surrogate recovery.** Surrogate recovery in the drinking water samples was calculated using the equation (SI-3).

Eq. (SI-3)

Where Aes is area of each surrogate standard in the extract; Aei is area of respective internal standard in the extract; Acs is area of each surrogate standard in the calibration solution; and Aci is area of respective internal standard in the calibration solution

**Concentrations in drinking water.** Concentration calculations for each analyte in drinking water are based on the internal standard procedure using the equation (SI-4).

Eq. (SI-4)

Where Cex is the concentration of a compound in the analyte; Vex is extract volume in ml; Ws is sample weight in g.

Further, density of water, 0.9976 g/mL at 73 ºF was used to convert sample weight (g) to volume (ml).

**Table SI 1.** List of Target PFAAs and mass labelled PFAAs mix and their CAS numbers

|  |  |  |  |
| --- | --- | --- | --- |
| **Compound Names** | **Abbreviation** | **CAS** | **Purity** |
| ***Target PFAAs mix (PFAC-MXB)*** |  |  |  |
| Perfluoro-n-butanoic acid | PFBA | 375-22-4 | > 98% |
| Perfluoro-n-pentanoic acid | PFPA | 2706-90-3 | > 98% |
| Perfluoro-n-hexanoic acid | PFHxA | 307-24-4 | > 98% |
| Perfluoro-n-heptanoic acid | PFHpA | 375-85-9 | > 98% |
| Perfluoro-n-octanoic acid | PFOA | 335-67-1 | > 98% |
| Perfluoro-n-nonanoic acid | PFNA | 375-95-1 | > 98% |
| Perfluoro-n-decanoic acid | PFDA | 335-76-2 | > 98% |
| Perfluoro-n-undecanoic acid | PFUnA | 2058-94-8 | > 98% |
| Perfluoro-n-dodecanoic acid | PFDoA | 307-55-1 | > 98% |
| Perfluoro-n-tridecanoic acid | PFTrDA | 72629-94-8 | > 98% |
| Perfluoro-n-tetradecanoic acid | PFTeDA | 376-06-7 | > 98% |
| Perfluoro-n-hexadecanoic acid | PFHxDA | 67905-19-5 | > 98% |
| Perfluoro-n-octadecanoic acid | PFODA | 16517-11-6 | > 98% |
| Potassium perfluoro-1-butanesulfonate | L-PFBS | 374-73-5 | > 98% |
| Sodium perfluoro-1-hexanesulfonate | L-PFHxS | 29420-49-3 | > 98% |
| Sodium perfluoro-1-octanesulfonate | L-PFOS | 1763-23-1 | > 98% |
| Sodium perfluoro-1-decanesulfonate | L-PFDS | 335-77-3 | > 98% |
| ***Stable isotope labelled PFAAs (MPFAC-MXB) for Surrogates:*** | | **Isotopic Purity** | **Purity** |
| Perfluoro-n-[13C4]butanoic acid | MPFBA | > 99% | > 98% |
| Perfluoro-n-[1,2-13C2]hexanoic acid | MPFHxA | > 99% | > 98% |
| Perfluoro-n-[1,2,3,4-13C4]octanoic acid | MPFOA | > 99% | > 98% |
| Perfluoro-n-[1,2,3,4,5-13C5]nonanoic acid | MPFNA | > 99% | > 98% |
| Perfluoro-n-[1,2-13C2]decanoic acid | MPFDA | > 99% | > 98% |
| Perfluoro-n-[1,2-13C2]undecanoic acid | MPFUdA | > 99% | > 98% |
| Perfluoro-n-[1,2-13C2]dodecanoic acid | MPFDoA | > 99% | > 98% |
| Sodium perfluoro-1-hexane[18O2]sulfonate | MPFHxS | > 94% | > 98% |
| Sodium perfluoro-1-[1,2,3,4-13C4]octane sulfonate | MPFOS | > 99% | > 98% |
| ***Stable isotope labelled PFAAs for Internal Standards:*** |  | **Isotopic Purity** | **Purity** |
| Perfluoro-n-[13C8] octanoic acid | M8PFOA | > 99% | > 97.9% |
| Sodium perfluoro-1-[13C8] octanesulfonate | M8PFOS | > 99% | > 98% |

**Table SI 2.** LC-MS/MS parameters

|  |  |  |
| --- | --- | --- |
| **LC: Nexcera (Shimadzu Co. Ltd., Japan)** | | |
| Mobile Phase | Pump A | Deionized water |
|  | Pump B | Methanol |
|  | Pump C | 0.1% NH4OH in Pre-clean Methanol |
|  | Pump D | Deionized water |
| Flow rate | Ternary Gradient (A/B/C Pump) | 0.25 mL/min |
|  | Sample Loading (D Pump) | 1 mL/min |
| Column | Scrubber column (Pump A) | OASIS HLB 2.1 x 20 mm |
|  | Scrubber column (Pump B) | OASIS WAX 2.1 x 20 mm |
|  | Scrubber column (Pump C) | Ghost Trap DS 7.6 x 30 mm |
|  | Scrubber column (Pump D) | OASIS HLB 2.1 x 20 mm |
|  | Pre-concentration column | OASIS WAX 2.1 x 20 mm |
|  | Analytical column | Inertsustain C18 2.1 x 50 mm |
| Auto sampler | Injection Volume | 3 mL |
| **MS: LCMS-8080 (Shimadzu Co. Ltd., Japan)** | | |
| Interface Parameter | Interface HV | - 4.5 kV |
|  | Probe Temperature | 300 °C |
|  | HSID Temperature | 200 °C |
|  | Nebulizer Gas (Air) | 2 L/min |
|  | Heating Gas (Air) | 12 L/min |
|  | Curtain Gas (N2) | 3 L/min |
|  | Exhaust Gas | ON |

**Table SI 3.** Quality control and acceptance criteria

|  |  |  |
| --- | --- | --- |
| **Prior to analysis** |  | Criteria |
| Initial precision and recovery (IPR) | LFB-NIES (n=7) | <= +/- 30% a |
| Procedure blank | Procedure blank (n=7) | <= LCMRL |
| **For all batches** |  |  |
| Initial Calibration | Calibration Point | >= 5 point |
| r2 | >= 0.99 |
| Deviation at each point | <= +/- 30% |
| Calibration Verification | Cal 5 | <= +/- 20% |
| Blank Analysis for Instrument | LRB-NIES | <= LCMRL |
| Cal 0 | <= LCMRL |
| Blank Analysis for Method | LRB-EPA | <= LCMRL |
| Frequency of Blank analysis in a sequence | After every tenth sample | <=LCMRL |
| Ongoing Precision and recovery standard (OPR) EPA | LFB-EPA Recovery | <= +/- 30% a |
| Quality Control Sample | LFM-EPA | <= +/- 30% a |

a Except for PFPeA, PFHxA and PFHpA for these <= +/- 40%;

Z

**Table SI 4.** Lowest Concentration Method Reporting Level (LCMRL) values and Blank concentrations in the procedural blanks analyzed at extraction laboratory and analytical laboratory

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Target Analytes** |  | **Blank Concentration, ng/L** | | | | | | | |
| **LCMRL, ng/L** | **NIES** | | | | **EPA** | | | |
| **Batch 1** | | **Batch 2** | | **Batch 1** | | **Batch 2** | |
| **Replicate 1** | **Replicate 2** | **Replicate 1** | **Replicate 2** | **Replicate 1** | **Replicate 2** | **Replicate 1** | **Replicate 2** |
| PFBS | 2.7 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL |
| PFHxS | 0.77 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL |
| PFOS | 1.9 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL |
| PFDS | 1.2 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL |
| PFPeA | 3.4 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL |
| PFHxA | 3.3 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | 5.72 | 4.28 | <LCMRL | <LCMRL |
| PFHpA | 0.64 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL |
| PFOA | 2.5 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL |
| PFNA | 3.2 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL |
| PFDA | 1.0 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL |
| PFUnA | 1.3 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL |
| PFDoA | 0.59 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL |
| PFtriDA | 1.4 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL |
| PFteDA | 1.8 | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL | <LCMRL |

**Table SI 5.** Percent recoveries of target analytes in laboratory fortified blanks and matrix fortified blanks

|  |  |  |
| --- | --- | --- |
| **Target Analytes** | **Laboratory fortified blanks (n=8)** | **Matrix fortified Samples (n=4)** |
| PFBS | 100±15 | 126±28 |
| PFHxS | 90±16 | 109±30 |
| PFOS | 99±7 | 107±7 |
| PFDS | 74±29 | 56±33 |
| PFPeA | 139±13 | 128±5 |
| PFHxA | 114±10 | 131±17 |
| PFHpA | 110±13 | 110±22 |
| PFOA | 97±12 | 111±5 |
| PFNA | 107±8 | 109±7 |
| PFDA | 108±7 | 110±7 |
| PFUnA | 105±14 | 88±9 |
| PFDoA | 96±8 | 83±13 |
| PFtriDA | 85±17 | 73±14 |
| PFteDA | 87±15 | 73±6 |

**Table SI 6.** Summary of Calibration curve % Relative Standard Deviation (%RSD) of 14 analytes

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Target Compound** | **LCMRL, ng/L** | **MS/MS** | **r2** | **Range** | **% Relative Standard Deviation (n=4)** | | | | | | |
| **Cal1** | **Cal2** | **Cal3** | **Cal4** | **Cal5** | **Cal6** | **Cal7** |
| **0.5** | **2.5** | **5** | **15** | **25** | **50** | **100** |
| PFBS | 2.7 | 298.9>99.0 | 0.999 | C2-C7 | ----- | 5.7 | 3.0 | 1.9 | 5.0 | 3.6 | 0.7 |
| PFHxS | 0.77 | 398.9>99.05 | 0.999 | C1-C7 | 7.5 | 3.6 | 6.8 | 4.2 | 4.8 | 2.6 | 1.8 |
| PFOS | 1.9 | 498.9>99.15 | 0.999 | C1-C7 | 12.7 | 12.1 | 8.3 | 6.4 | 4.5 | 3.0 | 5.0 |
| PFDS | 1.2 | 598.9>99.0 | 0.999 | C1-C7 | 10.7 | 4.8 | 7.6 | 3.0 | 5.2 | 4.8 | 6.6 |
| PFPeA | 3.4 | 262.7>219.0 | 1.000 | C1-C7 | 9.4 | 6.0 | 2.4 | 0.7 | 1.8 | 2.7 | 1.8 |
| PFHxA | 3.3 | 312.9>269.0 | 1.000 | C1-C7 | 7.6 | 1.5 | 2.5 | 4.4 | 4.6 | 1.2 | 2.4 |
| PFHpA | 0.64 | 362.9>169.0 | 0.998 | C1-C7 | 13.2 | 3.7 | 2.1 | 4.4 | 3.0 | 2.0 | 3.5 |
| PFOA | 2.5 | 412.9>169.0 | 1.000 | C1-C7 | 5.5 | 3.9 | 2.6 | 4.6 | 2.1 | 4.3 | 5.3 |
| PFNA | 3.2 | 462.9>419.0 | 0.999 | C1-C7 | 14.6 | 8.0 | 8.2 | 4.2 | 2.7 | 4.8 | 6.2 |
| PFDA | 1.0 | 512.9>468.9 | 1.000 | C1-C7 | 8.1 | 4.8 | 3.8 | 5.6 | 4.2 | 7.2 | 3.5 |
| PFUnA | 1.3 | 562.9>519.0 | 1.000 | C1-C7 | 3.6 | 4.1 | 5.8 | 5.2 | 2.6 | 5.8 | 3.8 |
| PFDoA | 0.59 | 612.9>568.95 | 0.999 | C1-C7 | 7.6 | 6.7 | 9.6 | 2.2 | 4.4 | 4.5 | 4.4 |
| PFtriDA | 1.4 | 662.9>618.9 | 1.000 | C1-C7 | 10.2 | 7.4 | 8.5 | 4.9 | 5.0 | 4.9 | 5.2 |
| PFteDA | 1.8 | 712.9>668.9 | 0.999 | C1-C7 | 17.1 | 5.9 | 7.1 | 5.3 | 4.2 | 5.1 | 5.3 |

**Table SI 7.** Surrogate recoveries (%) in all the 25 drinking water samples

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Sample ID | 18O2-PFHxS | 13C4-PFOS | 13C2-PFHxA | 13C4-PFOA | 13C5-PFNA | 13C2-PFDA | 13C2-PFUnA | 13C2-PFDoA |
| Sample 1 | 70 | 78 | 69 | 110 | 95 | 102 | 92 | 107 |
| Sample 2 | 99 | 95 | 46 | 92 | 85 | 64 | 41 | 43 |
| Sample 3 | 76 | 102 | 46 | 79 | 109 | 102 | 80 | 69 |
| Sample 4 | 89 | 94 | - | 82 | 82 | 75 | 60 | 54 |
| Sample 5 | 97 | 90 | 53 | 90 | 101 | 108 | 101 | 81 |
| Sample 6 | 75 | 87 | 47 | 69 | 86 | 96 | 84 | 70 |
| Sample 7 | 82 | 84 | 70 | 100 | 110 | 118 | 98 | 102 |
| Sample 8 | 75 | 86 | 48 | 92 | 100 | 91 | 83 | 76 |
| Sample 9 | 73 | 96 | 50 | 81 | 91 | 114 | 93 | 102 |
| Sample 10 | 87 | 98 | 114 | 118 | 168 | 154 | 111 | 115 |
| Sample 11 | 102 | 95 | 49 | 92 | 84 | 91 | 83 | 81 |
| Sample 12 | 117 | 106 | 50 | 90 | 100 | 111 | 109 | 85 |
| Sample 13 | 85 | 89 | 56 | 82 | 93 | 89 | 76 | 65 |
| Sample 14 | 82 | 88 | 58 | 82 | 90 | 92 | 71 | 51 |
| Sample 15 | 90 | 89 | 64 | 108 | 120 | 99 | 60 | 34 |
| Sample 16 | 75 | 76 | 59 | 84 | 91 | 74 | 57 | 47 |
| Sample 17 | 92 | 92 | 37 | 91 | 102 | 84 | 69 | 57 |
| Sample 18 | 87 | 97 | 55 | 87 | 90 | 82 | 57 | 48 |
| Sample 19 | 92 | 85 | 51 | 94 | 102 | 86 | 73 | 60 |
| Sample 20 | 96 | 104 | 48 | 79 | 93 | 72 | 54 | 44 |
| Sample 21 | 94 | 71 | 45 | 91 | 89 | 71 | 49 | 43 |
| Sample 22 | 84 | 104 | 49 | 94 | 113 | 106 | 78 | 57 |
| Sample 23 | 121 | 90 | 53 | 90 | 68 | 19 | 51 | 57 |
| Sample 24 | 98 | 105 | 57 | 82 | 97 | 92 | 79 | 99 |
| Sample 25 | 45 | 37 | 28 | 53 | 47 | 39 | 34 | 36 |

**Table SI 8.** Stability testing data showing the ratio of recoveries of analytes from the cartridges between day 0 and day 28; and the p-values of Kruskal-Wallis followed by Scheffe's test showing no significant differences

|  |  |  |
| --- | --- | --- |
| **Analyte** | **Ratio (day 0/day 28)** | **p-value** |
| PFBS | 0.96 | 0.9271 |
| PFHxS | 0.90 | 0.6281 |
| PFOS | 0.91 | 0.4432 |
| PFDS | 0.93 | 0.9994 |
| PFPeA | 1.22 | 0.0429 |
| PFHxA | 0.86 | 0.0779 |
| PFHpA | 0.82 | 0.0938 |
| PFOA | 0.86 | 0.0643 |
| PFNA | 0.93 | 0.6127 |
| PFDA | 0.94 | 0.8950 |
| PFUnA | 0.88 | 0.4136 |
| PFDoA | 0.86 | 0.6433 |
| PFTriDA | 1.02 | 0.9998 |
| PFTeDA | 1.04 | 0.9960 |