Australian Government
Department of Industry, Science and Resources

National Measurement Institute

Designing Proficiency Testing Schemes to Assist Laboratories with New Analytical Methodologies

Luminita Antin, Mark Lewin, Raluca Iavetz

Introduction

The design of a proficiency testing (PT) scheme is very important when introducing new programmes, especially for those driven by changes in the regulatory framework. The scheme must be carefully planned to address the requirements of new regulations as well as provide relevant information to support laboratories in developing their methods. A PT scheme (AQA 19-19) was developed by the National Measurement Institute Australia (NMIA) to provide laboratories with feedback on their methods for measurement of per-and poly-fluoroalkyl substances (PFAS) in water, before and after total oxidisable precursor (TOP) assay treatment in accordance with the requirements of the PFAS National Environmental Management Plan (NEMP) Australia and New Zealand.[1]

Study Background

TOP assay is a method designed to assess PFAS contamination in a sample, even when PFAS contaminants cannot be measured or are not targeted analytes. It is a sample pre-treatment aimed at converting oxidisable PFAS (precursors) into measurable perfluoroalkyl carboxylic acids (PFCA). The presence of precursors is indicated by comparing PFCA concentration before and after oxidation, while the maximum chain length of the oxidation products after TOP assay application may be related to the maximum possible perfluorinated chain length of the precursors.

PFAS NEMP 2020 provides nationally agreed guidance on the management of PFAS contamination in the environment and includes options for TOP assay-based measurements and associated quality control criteria.

Study Aims

The outcomes of the study were assessed against the following aims:

- Evaluate laboratories' capabilities in measuring PFAS analytes in water before and after TOP assay pre-treatment.
- Evaluate the oxidative method parameters applied by laboratories, which are currently not standardised.

Study Design

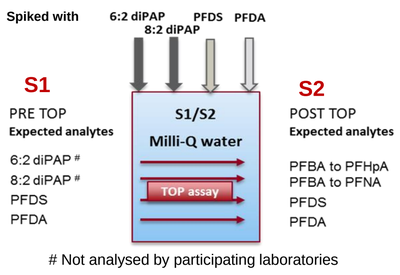
➔Assessment Criteria

- z-Scores and E_n- scores.[2]
- Quality criteria stipulated in PFAS NEMP for assessment of oxidative methods:

Method Assessment
Analyte losses during preparation process
Precursors conversion to PFCA products
Precursors conversion to PFSA products
Oxidation completeness

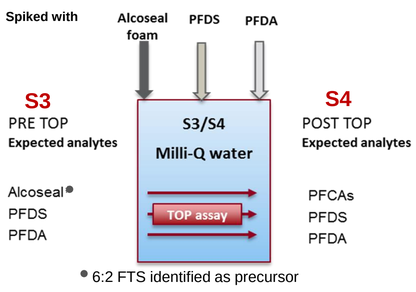
➔Study Samples

S1/S2 Identical Milli-Q Water Samples



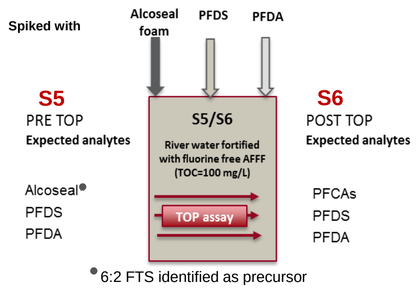
Not analysed by participating laboratories

S3/S4 Identical Milli-Q Water Samples



● 6:2 FTS identified as precursor

S5/S6 Identical River Water Samples (TOC=100 mg/kg)



● 6:2 FTS identified as precursor

Figure 1: Study Design

Sample homogeneity and stability were assessed according to ISO/IEC 17043 requirements.[2]

➔Design Solutions to Assess:

Analyte losses during preparation process

- PFDS and PFDA were added to S1/S2, S3/S4 and S5/S6 as monitoring compounds (Figure 1):
  - ✓ If no analyte losses occur, then the level of PFDA and PFDS pre- and post-TOP assay is expected to be similar.

Precursors conversion to PFCA products

- 6:2 diPAP and 8:2 diPAP were added to S1/S2 as precursors (Figure 1):
  - Participants were expected to report PFBA to PFNA as products of the oxidative pre-treatment.
  - The z-scores for PFBA to PFNA analytes are a reflection of :
    - participants' ability to measure PFCA in water and
    - the performance of their oxidation method.
  - The level of total PFCA in S2 was expected to be higher than in S1.
- Alcoseal firefighting foam was added in S5/S6 (river water) to replicate a real-life scenario, and at the same level in S3/S4 (milli-Q) to investigate the matrix effects (Figure 1):
  - The level of total PFCAs in post-TOP samples was expected to be higher than in pre-TOP samples.
  - The levels of total PFCAs in S4 and S6 were compared and expected to be similar.

Precursor conversion to PFSA products

- PFDS was added to S1/S2, S3/S4 and S5/S6 (Figure 1). PFDS was the only PFSA present in the study samples. No precursor conversion to PFSA should take place for AFFF samples:
  - The level of PFSA in post-TOP samples was expected to be similar to that of pre-TOP samples.

Oxidation completeness

- Alcoseal firefighting foam was added to S3/S4 and to S5/S6 (Figure 1).
  - Participants were expect to report measurable precursors in pre-TOP samples and to convert it to PFCA in post-TOP samples.
  - Insignificant amounts of measurable precursors were expected to be reported in post-TOP samples.

Outcomes

➔Participants' Capabilities in Measuring PFAS Analytes in Water Before and After Oxidation Pre-treatment

- 91% of the reported results returned satisfactory z-scores.
- 73% of the E_n-scores were satisfactory.
- 97% of the results were reported with an associated estimate of expanded uncertainty.
- The magnitude of the reported expanded uncertainties was within the range 1.3% to 500% of the reported value.

➔Assessment of the Oxidative Methods Used by Participants:

Analyte losses during preparation process

- The level of PFDA in post-TOP samples decreased. The decrease was consistent among the three sample pairs at approximately 14% (Figure 2).
- The PFDS decrease between pre- and post-oxidation samples was neither substantial nor consistent.

Figure 2: S2 vs S1 Change in PFDA Results

Precursors conversion to PFCA products

- The between-laboratory coefficient of variation for PFDA in S1 and for PFBA to PFNA analytes in S2 was in good agreement with the set performance coefficient of variation.
- The results reported for Total PFCA in S2 were in excellent agreement with each-other, indicating a comparable conversion of the spiked precursors to PFCAs by participating laboratories.
- With one exception, all participants reported results for Total PFCA in post-TOP greater than or equal to the results reported for Total PFCA in the pre-TOP (Figure 3).
- No matrix effects were evident between the milli-Q water and river water samples: a reasonable consensus was found between the results reported by participants for Total PFCA in S4 (milli-Q) and S6 (river water).

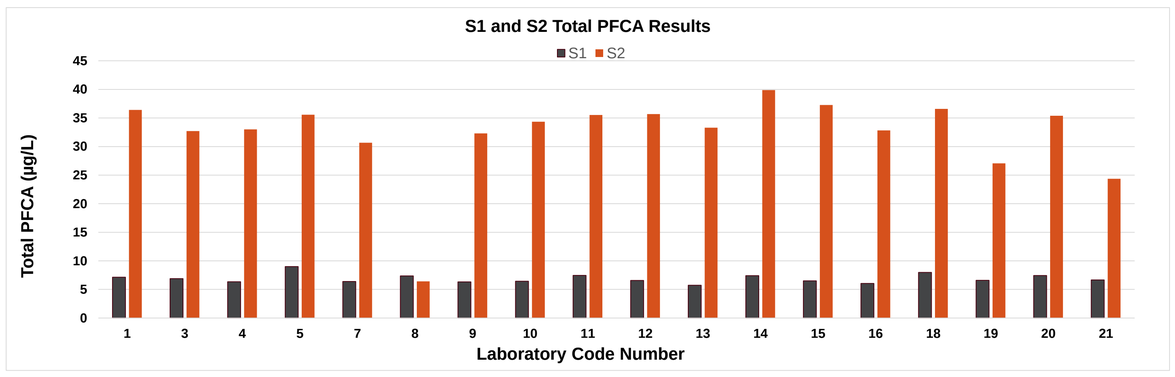


Figure 3: S1 and S2 Total PFCA Results

Precursors conversion to PFSA products

- There was no conversion of the precursors to PFSA products.
- The total level of PFSA in post-TOP and pre-TOP samples was similar, except for two laboratories (Figure 4).

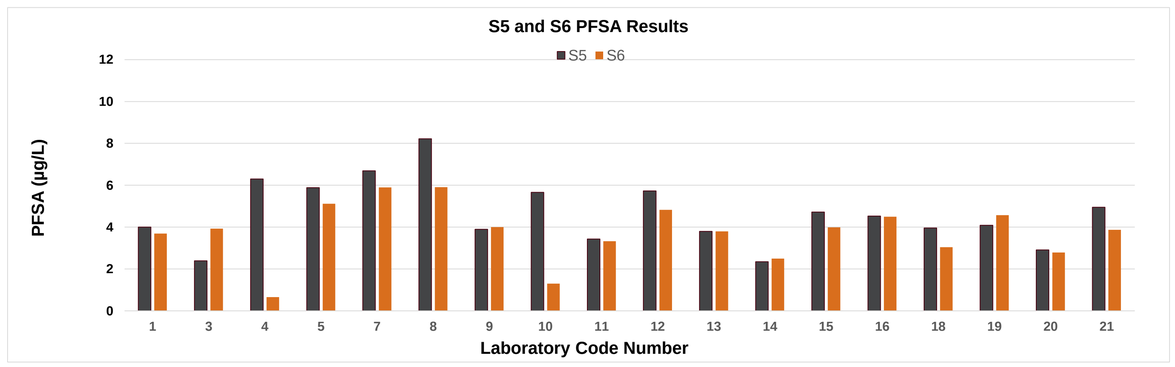


Figure 4: S5 and S6 PFSA Results

Oxidation completeness

- All laboratories identified 6:2 FTS as major precursor in S3 and S5 for Alcoseal spiked sample.
- All participants but four used an oxidative sample pre-treatment that resulted in insignificant measurable precursors (Figure 5).

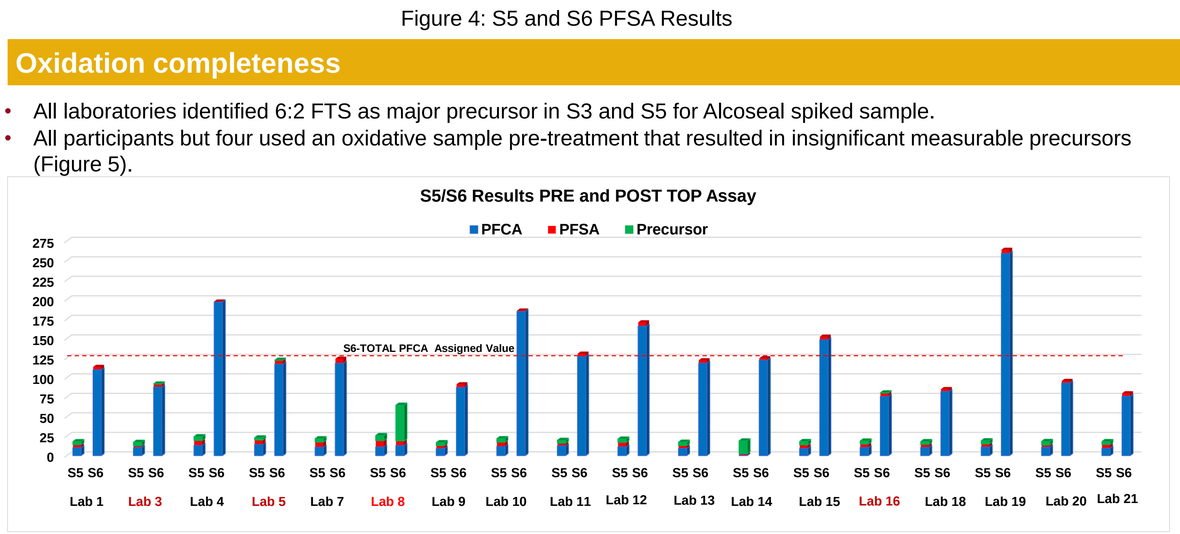


Figure 5: S5 and S6 Results pre- and post-TOP Assay

Conclusions

A new PT scheme designed to assess laboratories' implementation of the TOP assay sample pre-treatment in accordance with Australian regulatory requirements was introduced. Some laboratories are still reporting small or large relative uncertainties that are potentially unrealistic for routine PFAS measurements. Although most participants complied with NEMP quality criteria requirements, and could convert precursors into measurable PFAS, monitoring compound results suggest some analyte losses during the oxidative process.

References

1. PFAS National Environmental Management Plan Version 2.0, 2020
2. ISO/IEC 17043:2010, Conformity assessment – General requirements for proficiency testing

Acknowledgements

NMI colleagues Geoffrey Morschel, Jenny Xu, Hamish Lenton, Danny Slee, Luke Baker, Gabriela Saveluc, Isaac Schipp.
Participants in the NMI PT program whose results are presented in this poster.