



PFOS/PFOA analysis – Why do my Laboratory Results Not always agree for PFOS and which number is Correct?

BACKGROUND

In June 2009, ALS became the first NATA accredited laboratory for PFOS/PFOA analysis in Australia. Six years down the track and there are now several laboratories accredited to perform PFOS/PFOA and PFC analysis.

Over the years there have been a number of differences between laboratory results and a recent proficiency trial confirmed differences still exist. One issue is that industry practitioners are unsure which results are correct. This EnviroMail™ intends to provide good science and logic to explain why results may be different such that industry can make decisions and understand which numbers are most likely to be accurate for your needs.

PAST INTERLAB DISCREPANCIES

ALS has often discussed the fact that there are branched and linear Isomers of PFOS in the environment. Analytically these chemicals have different responses during instrumental testing. In the early days of PFOS analysis some laboratories only reported linear PFOS however now most laboratories report the aggregate of linear and branched PFOS.

ISOTOPE DILUTION METHODS?

PFC analysis by LC/MS/MS is prone to matrix interferences. Stable isotope labelled analogues of PFOS and PFOA ($^{13}\text{C}_4$ or $^{13}\text{C}_8$) can be added to each sample to normalise response to matrix. Internal standardisation uses the response ratio of native to labelled compound in standards to provide for normalisation of responses in the presence of matrix. Isotope dilution takes a different approach, using relative ratios of natural to enriched isotope to directly determine concentration of the target analyte. While there may be some misunderstanding of the difference between the two uses of stable isotopes of PFOS, during analysis, all labs actually use internal standardisation as opposed to Isotope Dilution.

WHAT DO PROFICIENCY TRIALS SHOW?

ALS has participated in a number of proficiency trials on PFOS/PFOA. The first finding of ALS investigations following the most recent trial is the difference in the ways laboratories appear to calculate results.

- Some Laboratories quantify using standards that contain both linear and branched PFOS
- Some Laboratories quantify using standards that contain only linear PFOS
- Some correct for recoveries
- Some labs do not correct for recoveries (as per NEPM)

Overleaf provides further insights into which results might be correct however the big question is 'were proficiency samples spiked with the typical PFOS profile seen in the environment or were they spiked with Linear PFOS'. In the proficiency trial cited below, the answer is linear PFOS and of course the labs that calibrate using linear PFOS (only) will therefore appear to have better proficiency accuracy.

The question to the expert is 'do samples in the Environment only contain linear PFOS?' There are lots of views. ALS has analysed many thousands of samples over the last six years. Data follows overleaf from select major projects.

WHAT WILL PROFICIENCY TESTING BRING?

The good news about proficiency trials is that these facilitate discussion, investigation, knowledge sharing, corrective action and dissemination of information to ultimately move laboratory data quality closer to the true value (as opposed to consensus value) and precision should improve for laboratories over time. This will in turn deliver better comparison of data for industry if the same principles of calibration are in use. Proficiency will drive agreement between laboratories over time.

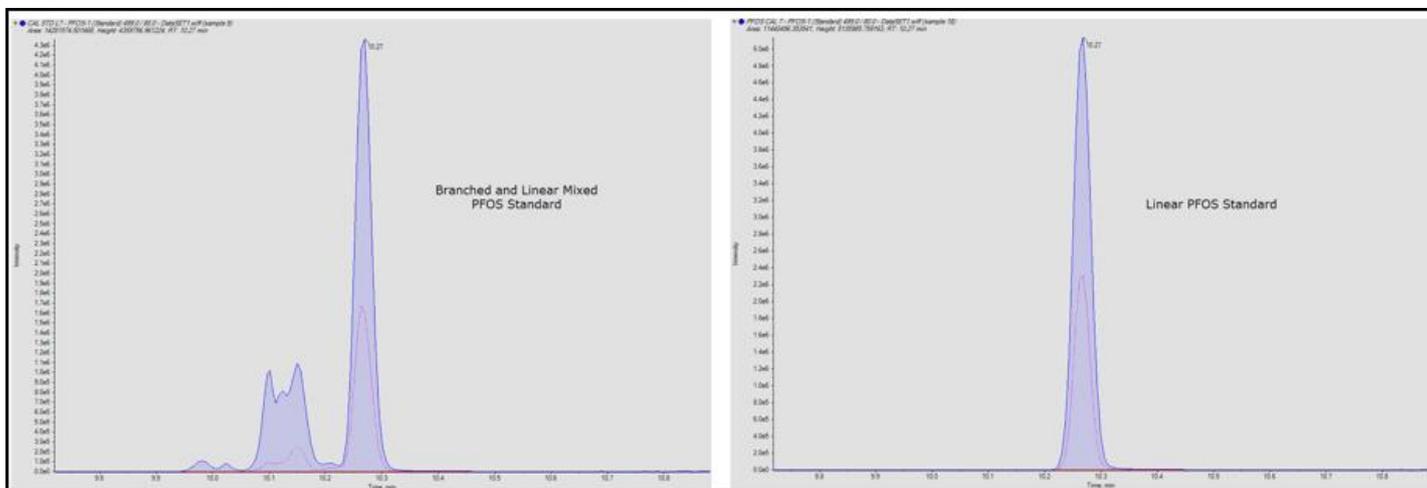
WHAT IS THE REAL DISTRIBUTION OF LINEAR AND BRANCHED PFOS OUT THERE?

The key reason ALS believes there is variation in laboratory test data is relatively simple – Calibration. ALS investigations have identified bias in instrumental responses between linear and branched PFOS Isomers using LC/MS/MS analysis.

So, if your lab uses only linear PFOS in calibration they should have a high bias for results for real samples with a normal distribution of branched and linear PFOS. If your lab uses a standard of normal distribution of Linear and Branched PFOS then they will have a lower bias when testing proficiency trials if only linear PFOS is spiked.

Figure 1 shows the linear and branched PFOS standards. In LC/MS/MS, the ion fragment m/z 80 is the so-called quantitation ion used by most labs. A second ion fragment with a mass of 99 can be used as a confirmatory ion by ratio with the quantitation ion. Figure 1 shows that the relative abundance of 80 and 99 ion fragments is different in aggregate for linear and branched PFOS standards. In fact, the abundance of the ion 80 is around 40% greater for the same quantity of a branched standard versus the linear standard. If the mixture (with similar levels of branched and linear isomers) has an overall difference of 40% area, then the individual differences in responses for linear & branched are clearly even greater! ALS has a solution to this problem internally and will adopt protocols that provide tighter accuracy and precision in the unlikely event that linear only PFOS is found in environmental samples (see overleaf).

Figure 1. Mixed linear/branched PFOS standard (left) and linear standard (right). The blue trace is the quantitation ion and the pink is the qualifier ion. Note that the abundance of ion 80 increases with increased branching. The ion ratios suggest that the linear peak in the mixed standard is not purely linear.



WHAT DOES THIS MEAN?

Proficiency results are useful in assessing quality, however the key piece of information that must be considered is do proficiency samples contain a typical profile of PFOS found in the environment or manufactured linear standards. The answer is that a recent proficiency spiking of PFOS utilised a linear standard. If a lab analysed the proficiency samples using a linear standard they should get good results but the big question is does this mean your real world sample results are as accurate? The page overleaf contains the PFOS profile from several major projects or PFC containing products tested by ALS. As can be clearly seen, the profiles of PFOS mixtures (branched and linear) are much closer to the 'branched and linear mixed standard' used by ALS. Which results will be the most accurate in this scenario? The answer is the lab using the standards best matched to real samples.

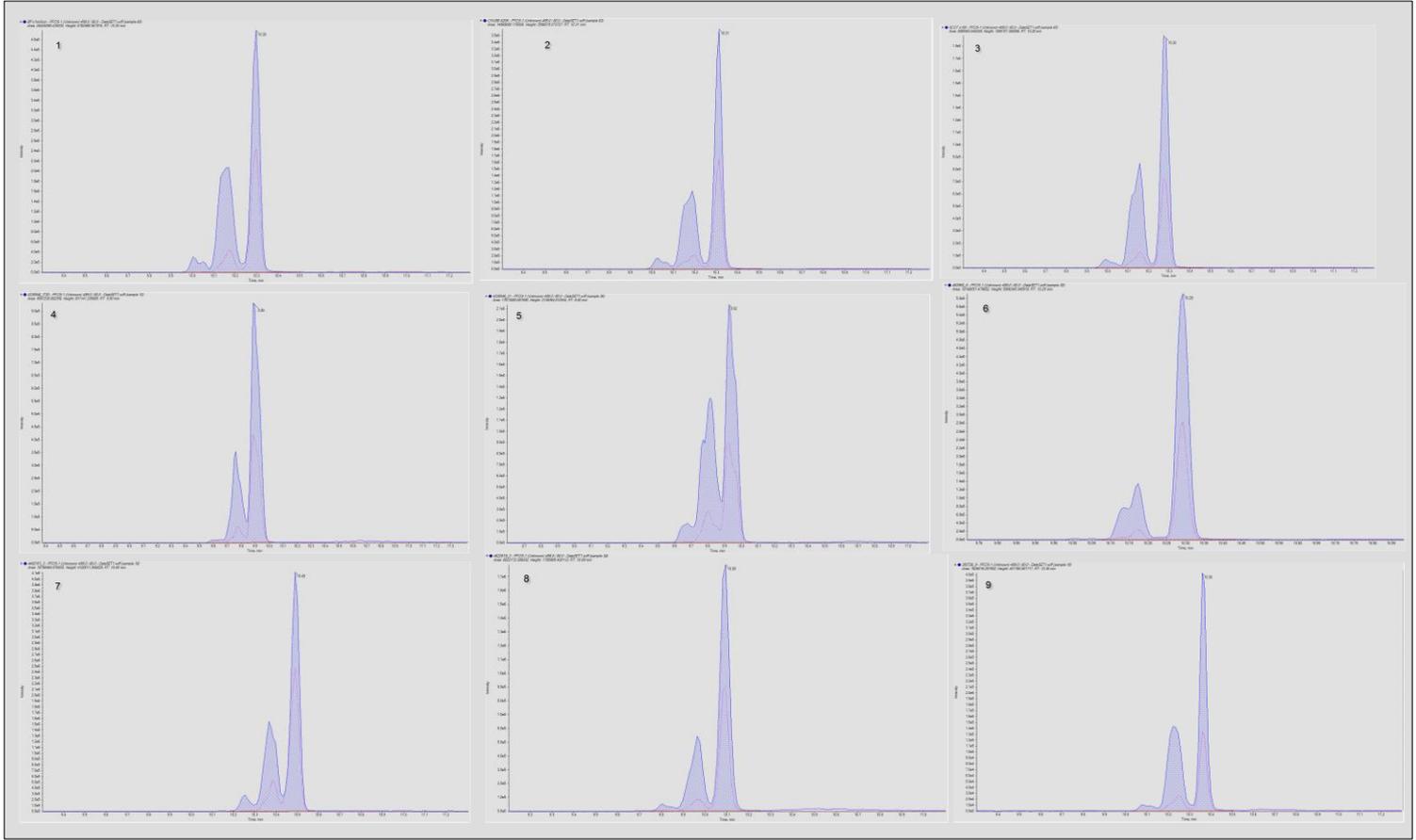
It is important to note that unless the profile of standards to samples is exact (which is virtually impossible to achieve), there will be some level of bias and that an assigned value based upon averages may therefore be significantly misleading and perhaps several labs have positive bias of over 200%.

If a laboratory is quantitating using linear standards, what may this mean for PFOS analysis from this laboratory? According to ALS investigations and research, there could be a systematic high bias for PFOS analysis on real samples containing any branched PFOS. Other laboratories might use linear PFOS standards and it may be appropriate to enquire about your laboratory practices.

The ALS Technical Manager – Marc Centner has considerable experience in this area and can assist you in asking the right questions to explain any discrepancies or understand any systematic bias in your results. (marc.centner@alsglobal.com).

If your laboratory had very good recoveries for Linear PFOS in a proficiency trial that is spiked with linear PFOS this may indicate a significant positive bias in PFOS results for real samples

Figure 2. Chromatograms 1 and 2 show PFOS from actual AFFF products. Chromatogram 3 shows PFOS found in Scotchgard (ca. 1985). The other six chromatograms are from PFOS found in waters on contaminated sites in Western Australia, Victoria, Tasmania and Queensland. Note the variability in environmental samples as discussed but also note that all samples clearly contain branched isomers of PFOS.



REFERENCES

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