Technical Advisory - Laboratory Analysis of Drinking Water Samples for Perfluorooctanoic Acid (PFOA) Using EPA Method 537 Rev. 1.1
Address questions concerning this document to:

Dan Hautman, Deputy Director Technical Support Center
Standards and Risk Management Division
U.S. EPA, Office of Ground Water and Drinking Water
26 W. Martin Luther King Dr.
Cincinnati, OH 45268
hautman.dan@epa.gov
Scope

EPA has recently learned that laboratories have identified different approaches for implementation of EPA Method 537 Rev 1.1 ("Method 537") for analysis of PFOA. Some laboratories have analyzed PFOA by quantitation of only the linear isomer while others have quantified both linear and branched-chain isomers to determine the concentration of PFOA. The linear isomer represents the predominant form of PFOA, but samples may also have some degree of branched-chain isomers. Method 537 specifically identifies PFOS, PFHxS, NetFOSAA and NMeFOSAA as containing branched isomers, and requires that quantitative standards be used to correctly identify and quantitate all chromatographic peaks for these chemicals. The method specifically addresses this for PFOS, PFHxS, NetFOSAA and NMeFOSAA because, at the time the method was written, a quantitative standard that contained mixed (linear and branched) isomers of these analytes was available (as it is today) and supported traditional quantitation of both isomer types.

EPA is recommending that laboratories analyzing samples for PFOA using EPA Method 537 quantify both linear and branched isomers in the future. Field sample measurement of PFOA may periodically show multiple chromatographic peaks (representing a mix of isomers) that should be included in the quantitation. EPA notes that the correct application of the method is to calibrate using a certified quantitative standard that includes both the linear and branched isomers of each analyte, if available. While, as of the release of this technical advisory, there is no certified quantitative mixed standard for PFOA, the available PFOA standards can be used to account for mixed isomers. EPA is providing the following Q&A to address the issue and provide clarifying information for laboratories, their customers, and others.

How should laboratories quantitate PFOA using EPA Method 537?

To account for linear and branched isomers of PFOA, EPA recommends that integration and quantitation of real-world drinking water samples include peaks that represent both linear and branched isomers. Since there is currently no certified quantitative PFOA standard that contains both linear and branched isomers that can be used to quantitate in the traditional manner, EPA recommends that until such standard is available, labs use the following approach:

- Calibrate instrumentation using a certified quantitative standard containing only the linear isomer.
- Identify the branched isomers by analyzing a “qualitative/semi-quantitative” PFOA mixed standard that includes both linear and branched isomers (Wellington Laboratories, cat#: T-PFOA or equivalent) and compare retention times and tandem mass spectrometry transitions.
- Quantitate PFOA by integrating the total response (i.e., accounting for peaks that are identified as linear and branched isomers) and relying on the initial calibration with the linear-isomer quantitative standard.
Will Method 537 require an addendum or revision?
EPA’s Office of Research and Development expects to publish a method revision in the near future to describe the recommended technique for addressing mixed isomers in the absence of a quantitative mixed standard. In the interim, EPA is posting this technical advisory to [EPA’s Drinking Water Analytical Methods web page](https://www.epa.gov) and [PFAS web page](https://www.epa.gov) and is advising laboratories currently running Method 537 to follow the approach described above when measuring PFOA.

How should laboratories that have analyzed UCMR 3 drinking water samples for PFOA using Method 537 address this advisory?
In considering this question EPA first undertook a reassessment of the PFOA results reported under the Unregulated Contaminant Monitoring Rule (UCMR 3). EPA applied conservative assumptions to estimate the potential contribution of branched isomers in samples, and has concluded that the impact on the UCMR 3 PFOA data is very limited. Whereas EPA had previously identified that 63 of 4909 public water systems (PWSs) (just under 1.3%) had one or more UCMR results with PFOA + PFOS above EPA’s Health Advisory value, the reassessment identified a total of 65 PWSs (just over 1.3%) that met the same criteria. The fact that the reassessment had such little impact on the conclusions is to be expected since less than 1% of the reported results for PFOA were at or above the minimum reporting level. Based on the findings of EPA’s re-assessment, the Agency has concluded that repeat UCMR sample collection and analysis for PFOA is not warranted. EPA Regions will continue to work with their states to reach out to any public water systems with reported or estimated PFOA + PFOS results above the Health Advisory value.

What action should I take if I contracted with a commercial laboratory to analyze my drinking water for PFOA?
If you contracted with a laboratory to analyze for PFOA in your drinking water and the combined concentration of PFOA and PFOS was between 50 and 70 ppt, you might consider contacting the laboratory to ensure that the analytical results reported by the laboratory are based on the more comprehensive technique for measuring PFOA.

Are results for PFOS impacted by this issue?
No, as long as the laboratory has followed Method 537 as written. Certified quantitative PFOS standards, containing both linear and branched isomers, are available today, as they were during UCMR 3 monitoring. Per Method 537, these mixed PFOS standards are to be used and quantitation is to include PFOS peaks that are identified as linear and branched isomers. EPA is not aware of situations where laboratories have been unable to procure the quantitative mixed PFOS standard for drinking water analyses by Method 537 or have otherwise deviated from the method requirements for PFOS.