

WI DNR Laboratory Accreditation Program PFAS Update - July 1, 2024

EPA Method 1633 – Use of EPA 1633 vs. Wisconsin Expectations

On January 31, 2024, the EPA published their final version of EPA method 1633 (dated January 2024).

The WI DNR Laboratory Accreditation Program (Lab Cert) will require that laboratories use this final version of EPA 1633 by February 1, 2025, for non-drinking water matrices. After February 1, 2025, the WI DNR will no longer accept data generated using the Wisconsin Expectations document. If the EPA requires use of EPA 1633 prior to February 1, 2025, WI DNR would follow the EPA timing and guidance. If a permit is issued or administrative code is published that requires the use of EPA 1633 then that could also trigger the use of this method prior to February 1, 2025.

Between now and February 1, 2025, it is WI DNR's recommendation and preference that EPA 1633 be used when possible.

Since Lab Cert does not accredit by method for non-drinking water matrices, PFAS accredited laboratories may start using EPA 1633 if the laboratory follows the procedure and meets all the QC requirements in the January 2024 version. WI DNR believes it would be in the laboratory's best interest to provide Lab Cert with the laboratory's SOP for review so Lab Cert can help the laboratory bring this method online and resolve any interpretation or modification allowance questions – sooner rather than later. *To be clear though, this is a recommendation, not a requirement.* In addition, Lab Cert does get questions from consultants as to whether our program has reviewed the laboratory's EPA 1633 method. If Lab Cert did not review the lab's SOP and provide the laboratory with feedback, we would not be able to answer yes, unlike how we could for other laboratories that have had their SOP(s) reviewed. The SOPs may be sent to me by email at:

tom.trainor@wi.gov.

The scope of accreditations will not require an update since they will still indicate accreditation for the ##PFAS (group).

All 33 PFAS in the Wisconsin Expectations document are included in the 40 PFAS reportable by EPA 1633. Wisconsin is expecting laboratories to report all 40 PFAS compounds once EPA 1633 is used.

EPA Method 1633 – Information Update and Clarifications to Method Requirements

The laboratory IDC must use the currently approved procedure, precision and accuracy limits specified in EPA 1633 (January 2024) – versus an earlier version of 1633.

Regardless of the approach used to assess aqueous samples for solid content, the laboratory must maintain documentation of assessment of the solids content. EPA 1633 (11.1.1.7)

To prevent esterification, standards must be stored under basic conditions. EPA 1633 (7.3)

If aqueous sample containing solids are centrifuged, the original container must be rinsed and included in the extraction. EPA 1633 (11.1.15)

If the entire aqueous sample received is not used (subsampling occurs), the data must be clearly qualified as such. EPA 1633 (11.0 Note)

The TDCA standard must be analyzed and assessed with each analytical batch, regardless of the matrix being analyzed. EPA 1633 (10.2.2.5)

EPA Methods 537.1 and 533 – Information Update and Clarifications to Method Requirements

These methods have the following requirements:

- The same batch of preservative must be used for the FRBs as for the field samples. EPA 537.1 (8.3.2)
- The same lot of preservative must be used for the FRBs as for the field samples. EPA 533 (8.4)

Lab Cert has recently been told by the EPA that an option to satisfy this requirement is to document that all lots of preservatives will be monitored in advance of field sample and field reagent blank use to verify the absence of any PFAS background contamination. In essence, the laboratory is confirming that there are no quality differences between the different lots being used and that each are demonstrated as PFAS free. If this protocol is used, then the FRB preservative does not have to be the same as the preservative used in the samples if each lot is certified PFAS free. This modification must be explicitly stated as a deviation within the SOP with the justification provided here.

These methods have the following requirements:

- Concentrate the extract to dryness under a gentle stream of nitrogen in a heated water bath (60-65 °C) to remove all the water/methanol mix. EPA 537.1 (11.5)
- Concentrate the extract to dryness under a gentle stream of nitrogen in a heated water bath (55-60 °C.) EPA 533 (11.4.6)

Lab Cert has just recently been told by the EPA that temperatures below the lower limit are acceptable provided that all method QC criteria are met and that the extract is still taken to dryness. This flexibility would not extend to increasing the water bath temperature above the higher limit. This modification must be explicitly stated as a deviation within the SOP with the justification provided here.

These methods have the following requirements:

- Before extraction, verify that the sample pH is 6.5-7.5. EPA 537.1 (11.3.1)
- Verify that the sample containing 1 g/L ammonium acetate has a pH between 6.0 and 8.0. The sample pH must be checked, and the results documented. EPA 533 (11.3.2)

These methods both require use of a preservative that removes free chlorine. The laboratory must check for the presence of free chlorine (<0.1 mg/L) and document the results. This is required per the SDWA Manual section 6.4. When the laboratory is not responsible for sample collection and transport, it must verify that the paperwork, preservatives, containers and holding times are correct as required by the methods or reject the sample. This requirement has been confirmed with the EPA. Per the EPA, while the methods do not give explicit instructions on performing a residual chlorine check, it is required that the samples must be preserved. Ultimately, the purpose of this is to confirm that preservatives are present (to prevent loss of target analyte) and that they were not washed out of the sample bottles during sample collection.

- EPA 533 indicates that the 0.1 M phosphate buffer is to be verified that the solution pH is approximately 7.0. Per the EPA, “approximately” equates to a pH between 6.5 and 7.5. This is required for proper SPE conditioning. EPA 533 (7.8)
- EPA 533 indicates to prevent esterification, standards must be stored under basic conditions. Standards need to have approximately 4 molar equivalents of sodium hydroxide. Diluting won't change the molar equivalency but adding other standards that do not contain base (such as sulfonate PFAS) can cause a change in that molar ratio. The appropriate molar ratio needs to stay constant in the standards. M533 mixes may be purchased that have the NaOH already added, or the lab will need to ensure that NaOH is added at the correct ratio in the “in-house” prepared standards. Verification would be indicated by the CoAs of the standards (indicating if they contain base or not) or through the lab standard preparation sheets. EPA 533 (7.13.1)
- Nitrogen gas must be used to concentrate the samples. An alternative gas and its effects on the target analytes have not been studied. EPA 533 (6.9), EPA 537.1 (6.10)
- When available (many new ones are now available), quantitative and qualitative branched isomers must be used, as well as second source standards. EPA 533 (7.17.1), EPA 537.1 (7.2.3)

Let me know if you have any questions. Tom Trainor