

MERCURY SAMPLING AND REPORTING GUIDANCE

For National Pollutant Discharge Elimination System (NPDES) Permit Compliance

I. EXECUTIVE SUMMARY

The Water Resources Division (WRD) has determined that some contract labs were reporting analytical results to their clients (permitted facilities) that did not meet the quality control (QC) acceptance criteria for EPA Method 1631 Revision E (1631E) and EPA Method 1669. In order to ensure and verify that the reported mercury monitoring data is valid and acceptable, permittees with mercury monitoring in their NPDES permit will be required to provide the mercury QC data when they report their effluent data to us on the daily sheets (also known as the Daily Discharge Monitoring Report [DMR]).

II. BACKGROUND

The WRD has identified a number of problems with how permittees and their contract labs collect, use, and report field duplicate, field blank, and trip blank data; much of which is inconsistent with the QC requirements of EPA Method 1631E and EPA Method 1669 as described in Title 40, Code of Federal Regulations, Part 136.

II. WHAT YOU NEED TO KNOW

1. EPA Method 1631E and EPA Method 1669 require that at least one field blank and at least one field duplicate be collected for each ten samples per sampling event at a given site.
 - a) A permittee collecting their **own** sample(s) needs to collect 1 field blank and 1 field duplicate (assuming they collect ten or less samples) **each date/time they collect a sample** regardless of the number of outfalls being collected at their facility/site.
 - b) A contract lab collecting mercury samples for multiple facilities/sites needs to collect one field blank and one field duplicate **at each facility/site** (assuming they collect ten or less samples at a single facility/site location).
2. A field duplicate is a second sample collected at the same time and place as the sample for QC purposes. The results of the field duplicate should be reported separately on the daily sheets and **NOT** averaged with the sample result for reporting purposes.
3. A field blank is reagent water that has been transported to the field and **treated as a sample in all respects**, including contact with the sampling devices and exposure to sampling site conditions, filtration, storage, preservation, and analytical procedures. The field blank is used to demonstrate that samples have not been contaminated by the sample collection and transport activities.
4. The Method 1631E acceptance criteria for field blanks is <0.5 ng/L or no greater than one-fifth (1/5) of the Hg in the associated sample(s), whichever is greater. If the field blank results exceed these criteria, the sample results cannot be reported for NPDES permit compliance purposes. We recommend that permittees take their mercury samples early in the month (or quarter if the permit only requires quarterly sampling) so they will have time to resample if the field blanks do not meet the Method 1631E acceptance criteria.

5. A method blank is reagent water that is placed in a sample bottle in the lab and analyzed using reagents and procedures that are identical to those used to prepare and analyze the corresponding sample. The method blank is used to demonstrate that the analytical system is free of contamination.
6. The Method 1631E acceptance criteria for method blanks is <0.5 ng/L. If the result for the method blank exceeds the acceptance criteria, the analytical system is out of control and the associated sample results cannot be reported. The laboratory must eliminate the contamination in the analytical system and reanalyze the samples. If the laboratory cannot reduce the contamination in the analytical system to acceptable levels before the DMR data must be submitted, the permittee should enter the code for analytical error on the DMR and contact their DEQ district office.
7. The results of the field blank, the field duplicate and method blank should be reported in the columns provided on the daily sheets (these columns will be available for the month of October, 2014, forward).
8. A trip blank is reagent water with preservative that is placed in a bottle in the lab with a custody seal over the cap. The trip blank is transported to and from the sampling site with the sample and field blank bottles but is never opened or removed from its double zipper bags.
9. There is nothing in Method 1631E or Method 1669 that prohibits the use of trip blanks or any other type of blanks as additional QC measures, but they are **NOT** acceptable substitutes for field blanks and cannot be used for blank correction of sample results.
10. **Only** field blanks or method blanks may be used report something lower than the actual sample analytical results (a blank correction). **Only one blank** (field or method) can be used for blank correction of a given sample result, and only if they meet the acceptance criteria (see *Quality Control Guidance Information for the sampling and analysis of Low Level Mercury in Water following EPA Method 1631 Revision E August 2002*).

III. BLANK CORRECTION EXAMPLES

1. A permittee obtained the following analytical results: 12 ng/L in the sample and 10 ng/L in the corresponding field blank.

As stated above, acceptance criteria for field blanks is <0.5 ng/L or no greater than one-fifth (1/5) of the Hg in the associated sample(s), whichever is greater. In this example 1/5 of the sample value $1/5 \times 12 \text{ ng/L}$ is 2.4 ng/L. Since 2.4 ng/L (1/5 of the sample value) is greater than 0.5 ng/L, the acceptance criteria for this sample is 1/5 of the sample value (2.4 ng/L). Because the field blank (10 ng/L) is greater than 1/5 of the Hg in the associated sample, the sample is invalid and may not be reported or otherwise used for regulatory compliance purposes. The permittee should resample to comply with NPDES permit monitoring requirements. The field blank result should be reported on the daily sheets, even though the sample result was invalid.

The permittee and/or lab should find the source of the field blank contamination and reduce it to acceptable levels before the next sampling event. The Method 1669 and Method 1631E guidance documents provide suggestions for reducing blank contamination. If the contamination cannot be reduced to this level, the permittee should retain a sampling team and/or lab capable of meeting acceptable QC requirements.

2. A permittee obtained the following analytical results: 5.6 ng/L in the sample, and 0.7 ng/L in the field blank.

Applying the same approach as above, first determine $1/5$ of the Hg in the sample. $1/5 \times 5.6 \text{ ng/L} = 1.12 \text{ ng/L}$ which is greater than 0.5 ng/L. Since the blank is $\leq 1/5$ of the sample result, the sample result may be blank corrected and the result reported as 4.9 ng/L. The sample and field blank results should be reported on the daily sheets. Only the corrected sample result is reported on the DMR.

3. A permittee obtained the following analytical results: 1.5 ng/L in the sample and 0.4 ng/L in the field blank.

First determine $1/5$ of the Hg in the sample. $1/5 \times 1.5 \text{ ng/L} = 0.3 \text{ ng/L}$. This is less than 0.5 ng/L. Since the blank is less than 0.5 ng/L the sample results may be blank corrected and reported as 1.1 ng/L. The sample and field blank results should be reported on the daily sheet. The corrected sample result is reported on the DMR.

4. A permittee got the following analytical results: 1.5 ng/L in the sample, 0.2 ng/L in the field blank and 0.4 ng/L in the method blank.

First determine $1/5$ of the Hg in the sample. $1/5 \times 1.5 \text{ ng/L} = 0.3 \text{ ng/L}$. This is less than 0.5 ng/L. Since the blanks are less than 0.5 ng/L the sample results may be blank corrected using either the field blank result **or** the method blank result. It is expected that most people would choose the larger correction and report the result as 1.1 ng/L. Both the sample and method blank results should be reported on the daily sheet. The corrected sample result is reported on the DMR.