ENERGY AND ENVIRONMENT CABINET
DEPARTMENT FOR ENVIRONMENTAL PROTECTION
DIVISION OF WATER

300 SOWER BOULEVARD
FRANKFORT, KENTUCKY 40601

KLCP Guidance for Laboratories Accepting Low Level Metals Samples for Analysis

Specifically sampling by EPA 1669 for analysis by EPA 1631E

EPA 1631E[1] and EPA 1669[2] are a critical pair of methods that must be followed in order to best avoid contamination in the sampling process. Both methods clearly state that it is easier to contaminate a sample than to not contaminate a sample. Because of this, The Kentucky Laboratory Certification Program (KLCP) is providing this document in order for the laboratory as well as the client/permittee to be confident of the handling of the sample in the field.

A few things to be aware of:

- The laboratory must provide clear and complete sampling instructions that accompany the sample bottle kit and laboratory-tested, mercury-free water for field sampling.
    - The sampling instructions should follow EPA 1669 and refer to the "clean hands - dirty hands" procedure as well as address PPE, equipment cleanliness, amalgam dental fillings
    - Samplers should be aware of the method hold times, appropriate preservation and sample temperature expectations upon receipt.
    - Samplers should familiarize themselves with the sample procedure prior to a trip to the field. This can take the form of SOP and sample instruction review, taking a practice sample while in laboratory, utilizing publically available guidance documents, or any other such preparation.
    - Refer to Attachment 1: KLCP Low Level Mercury Sampling Procedures document for more details.
- EPA 1669 Sec. 2.3 states "The laboratory or cleaning facility must prepare a large carboy or other appropriate clean container filled with reagent water for use with collection of **field blanks** during sampling activities. The reagent-water-filled container should be shipped to the field site and handled as all other sample containers and sampling equipment. At least one field blank should be processed per sampling site, or one per every ten samples, whichever is more frequent."
    - Because field blanks are a valuable indicator of contamination at the sample site, the laboratory must additionally provide clear but complete instructions on how to handle this reagent water in the field. Field blanks should be transferred from the laboratory-provided container into a sample bottle by going through the normal sampling procedure (including use of all sampling equipment.)
    - If the laboratory suspects a client of routine contamination, the laboratory must notify those clients and troubleshoot in order to avoid future contamination.
- Method Detection Limit (MDL) should be calculated using **method blanks** and spiked blanks.
    - "Method blanks are prepared and analyzed using sample containers, labware, reagents and analytical procedures"[1]
        - Three method blanks are required per analytical batch and all are used in the determination of the MDL_b as part of the study

ENERGY AND ENVIRONMENT CABINET
DEPARTMENT FOR ENVIRONMENTAL PROTECTION
DIVISION OF WATER

300 SOWER BOULEVARD
FRANKFORT, KENTUCKY 40601

- Spiked blanks should be prepared from a clean reagent water and spiked at a known concentration at or below the required reporting limit[4,5]
- KLCP has a MDL Study Workbook that is available for use.
- Based off EPA 1631E Sec 1.5, the calculated MDL should be ≤0.2 ng/L when no interferences are present.

- Method blanks and field blanks should be treated as indicators of a laboratory system that is susceptible to generating analytical results with high bias, due to contamination. Following your laboratory's SOP and EPA 1631E, report and qualify results that accompany high blanks appropriately.
  - At a minimum, blanks that are above the laboratory Minimum Reporting Limit (MRL) are not reportable (corrective action follows); blanks between the laboratory MRL and MDL are reportable, unless otherwise specified in a laboratory specific SOP, but a corrective action should take place to address the issues and data should be qualified

Note: This is not an extensive list of all quality control measures required by EPA 1631E or EPA 1669

[1] EPA 1631 Rev.E (2002) "Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry
[2] EPA 1669 (1996) "Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels"
[3]Guidance for Implementation and Use of EPA Method 1631 for the Determination of Low-Level Mercury; EPA 821-R-01-023
[4]Definition and Procedure for the Determination of the Method Detection Limit, Revision 2; EPA 821-R-16-006
[5]Kentucky Wastewater Laboratory Certification Manual, March 2018

ENERGY AND ENVIRONMENT CABINET
DEPARTMENT FOR ENVIRONMENTAL PROTECTION
DIVISION OF WATER

300 SOWER BOULEVARD
FRANKFORT, KENTUCKY 40601

Attachment 1: Low Level Mercury Sampling Procedures

Method	Range	Bottles to Use	Preservative*
EPA 245.7	5-100 ng/L	125-1000 mL Pluoropolymer or glass bottles with fluoropolymer or fluoropolymer-lined cap. Ensure bottles have been cleaned and double bagged according to EPA 1631E Sec 6.1.2 or EPA 245.7 Sec 6.1.1 Sampling equipment should also be thoroughly cleaned and double bagged for transport.	5 mL/L of pretested 12N HCl
EPA 1631E	0.5-100 ng/L		5 mL/L of pretested 12N HCl or BrCl

*Samples can be preserved in the field or shipped to the lab to be preserved there. They must be either preserved or analyzed within *48 hours* (preserved samples are stable for 90 days)

Sampling Instructions:

Because this method is so sensitive, much consideration should be given to every step of the collection process.

Collect as a *grab* sample, upwind if possible. Wear Talc-free gloves and a wind suits (or appropriate contamination-free clothing.)

Use *EPA 1669 as a complete guide* to proper sampling technique. The Clean Hands/ Dirty Hands is used as a division of responsibilities between a two person sampling team where one person, “Clean Hands”, handles all aspects that are directly related to the sample and sample bottle, while “Dirty Hands” handles sampling equipment and all other auxiliary aspects.

- Both Dirty Hands and Clean Hands put on clean gloves (Clean Hands also wears shoulder-length gloves) and wind suits (or suitable lint-free, contamination-free clothing)
- Dirty Hands sets up sampling equipment and opens outer plastic bags
- Clean Hands opens inner plastic bags, removes sample bottles, collects sample, returns sample bottle to inner bag, and closes inner bag.
- Dirty Hands closes outer bag and returns sample to cooler/ transport container

One *Field Blank* should be collected for every 10 samples per sample site. Some laboratories will send a carboy filled with suitable reagent water and some will send a couple sample bottles filled with water to be transferred into a pre-labeled “Field Blank” bottle, but in either case collect the Field Blank in the same manner used for sample collection, using reagent water that the lab has provided specific for these blanks. The Field Blank should be collected before the sample in order to demonstrate that samples have not been contaminated by the sample collection and transport activities.

References:

EPA 1669 (1996) “Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels”
EPA 1631 Rev.E (2002) “Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry
EPA 245.7 Rev 2.0 (2005) “Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry”
40 CFR 136