REMEDIATION AND REDEVELOPMENT DIVISION
STANDARD OPERATION PROCEDURE

Low Level Mercury Sample Collection
RRD SOP-36

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Distribution: All RRD Employees

PURPOSE

This Standard Operating Procedure (SOP) describes the department process for the collection of groundwater samples from monitoring wells for analysis using the United States Environmental Protection Agency (USEPA) Method 1631E, Mercury in Water by Oxidation, Purge-and-Trap, and Cold Vapor Atomic Fluorescence Spectrometry, USEPA, Office of Water, to evaluate mercury concentrations in groundwater venting to surface water and determine compliance with the groundwater surface water interface (GSI) criterion. The GSI criterion is based on "total" mercury, i.e., all forms of mercury existing in the groundwater. This includes both inorganic and organic types, dissolved, or attached to particulate present in the groundwater.

DEFINITIONS

Criteria or Criterion	Includes the cleanup criteria for Part 201 and the Risk-based Screening Levels as defined in Part 213 and R 299.5706a(4)
Facility	Includes "facility" as defined in Part 201 and "site" as defined in Part 213
Trace Metal Grade Reagents	Reagents that make no significant contribution of mercury to the sample
Dirty and Clean Hands	All operations involving contact with the sample bottle and transfer of the samples from the sample collection device to the sample bottle are handled by the individual designated as Clean Hands. The individual designated as Dirty Hands is responsible for the preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve direct contact with the sample.

STANDARD OPERATING PROCEDURE

This SOP is applicable to site investigations, response activities or corrective action conducted by department staff and their contractors where remediation of mercury to the water quality standard may be required in accordance with EGLE Policy on evaluating mercury in groundwater plumes (DEQ 09-014).The SOP is available as a technical reference that may be

informative and may be used as a reference for parties outside EGLE when conducting low level mercury sampling.

Please note that because the SOP was written for the department staff, it may contain references to specific equipment for field investigations that the department currently uses. Such references do not represent endorsements for particular vendors.

The Department's published list of Target Detection Limits and Designated Analytical Methods is authorized by Part 201 [Section 20101(1)(bbb) of the Natural Resources and Environmental Protection Act]. Where analysis is required under USEPA Method 1631E, collection of the sample is expected to be conducted using the USEPA Method 1669, Sampling Ambient Water for Trace Metals at USEPA Water Criteria Levels, July 1996, USEPA, Office of Water, Engineering and Analysis Division, Washington, DC. This method is designed for surface water samples but was used as a reference to develop guidance for the collection of groundwater samples from monitoring wells. The two-person team approach, as described in Method 1669, "Dirty Hands," and "Clean Hands" sampling was adopted, and quality assurance and control requirements of that method have been incorporated.

Modifications of this method, and other methods, may be proposed and used if found adequate by department management to produce reliable results for sampling groundwater for low level mercury. The presentations of information that validate the use of other methods or modifications of this method are the responsibility of the person proposing their use. This attachment is not intended to be used in place of Method 1669 when the use of that method is required.

Summary

Sampling equipment, materials, and containers are cleaned using high purity chemicals and double bagged for protection from contamination during storage and transportation. Highly purified reagent water is provided to the field personnel for the decontamination of the sample collection equipment between samples, and for the collection of field blanks.

A two-person team, as described in Method 1669, is used for sample collection. One member of the two-person sampling team is designated as "Dirty Hands," and the second member is designated as "Clean Hands." The individual designated as Clean Hands will handle all operations involving contact with the sample bottle and transfer of the samples from the sample collection device to the sample bottle. Dirty Hands is responsible for the preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve direct contact with the sample. Sampling teams wear clean non-talc gloves as well as clean, lint-free outer clothing to protect samples from contamination by lint and dust.

Special precautions are incorporated to minimize contamination. When possible, the facility history and results showing previous results of mercury levels at specific locations are used to design the collection process in order to minimize the chances of cross contamination. Sample collection is performed by a strict protocol designed to minimize contamination.

Because of the likelihood of positive blanks and the affect they have upon the results, staff should carefully evaluate blank levels before making regulatory decisions. Minimum quality control sampling requirements as recommended in Method 1631 are provided in Appendix 1.

Contamination and Interferences

1. The need to avoid contamination when collecting samples for extremely low-level measurements cannot be overemphasized. Field collection personnel should be familiar with the potential sources of mercury contamination and implement those steps necessary for adequate control. Field and equipment blanks are used to discover contamination problems during the collection steps.
2. Potential Sources of Mercury Contamination: These include metallic and metal-containing equipment, containers, lab ware, reagents, de-ionized water, improperly cleaned and stored equipment, atmospheric sources such as dirt and dust, automobile exhaust, laboratory workers, and cigarette smoke. Well construction materials, e.g., the gravel pack and well screen may also be a source of contamination.
3. Potential Contamination from Well Construction Materials: Levels of mercury in groundwater samples can be a result of natural background, well construction material, or environmental contamination. To reliably distinguish the mercury contribution of both natural background and well construction materials from environmental contamination, measurements from upgradient background wells, constructed in the same manner as downgradient wells, are necessary.
4. Use of Peristaltic Pumps: Peristaltic pumps have distinct advantages in controlling contamination and should be used when possible. Most other pumps have metal parts that may come in contact with the sample; hence, pumps must be decontaminated. For peristaltic pumps, only the tubing is in contact with the sample; consequently, clean tubing is all that is necessary to minimize contamination.
5. Control: The best way to control contamination is to minimize exposure of the sample and sampling equipment to possible sources of contamination. When possible, prior knowledge of mercury levels at sampling locations is used for planning collection activities to minimize chances of contamination from high sources, cross contamination resulting from sequentially sampling locations of high and low levels, and cross contamination during storage and transportation. Appropriate equipment and field blanks are used to discover contamination.
6. Filtering: If filtering is necessary, it is recommended that sample filtration be performed at the laboratory due to the potential for contamination. If samples cannot be sent to the laboratory within 24 hours of collection, they should be filtered in the field in a clean area.
7. Preservation: Samples must be either preserved or analyzed within 48 hours of collection. Samples may be preserved with bromine monochloride (BrCL) or hydrochloric acid (HCl). If samples are oxidized in the sample bottles with BrCL, preservation may be extended to 28 days. It is recommended that samples be preserved at the laboratory due to the potential for contamination and the hazards of BrCl. Preserved samples are stable for up to 90 days from the date of collection.

Apparatus and Materials

1. Disposable Materials: Disposable materials such as gloves, storage bags, and plastic wrap may be used new without additional cleaning unless the equipment blank results identify any of these materials as a source of contamination. If new disposable materials are found to be a source of contamination, then a different supplier must be obtained, or the materials must be cleaned.
2. Sample Bottles: Fluoropolymer (FEP, PTFE) or borosilicate glass, 125 ml to 1 L, depending upon laboratory specifications with fluoropolymer or fluoropolymer lined caps, cleaned according to Method 1669/1631 procedures, with airtight cap. Containers are received empty or filled with reagent water, tightly capped, double bagged in new polyethylene zip-type bags until needed, and stored in cardboard boxes until use.

3. Tubing for Use With Low Flow Sampling Pump: Use fluoropolymer tubing in lengths as required to reach the sampling point. Tubing is cleaned by soaking in a 5-10% HCl solution for 8-24 hours, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with mercury-free air or nitrogen. Tubing must be double bagged in clear polyethylene bags, serialized with a unique number to identify it in case of contamination problems, and stored until use.
4. Peristaltic Pump: 115V A.C., 12V D.C. internal battery, variable speed, single head, Cole-Palmer or equivalent, portable, "Masterflex L/S," Catalog No. H-07570-10 drive with Quick Load Pump Head, Catalog No. H-07021-24, or equivalent.
    a. Tubing for use with peristaltic pump. Styrene/ethylene/butylene/silicone (SEBS) resin, approximately 3/8 in. internal diameter (i.d.) by approximately 3 ft., Cole-Palmer size 18, Catalog No. G-06464-18, or approximately ¼ in. i.d., Cole-Palmer size 17, Catalog No. G06464-17, or equivalent. Tubing is cleaned and stored as provided above.
    b. Tubing for connection to peristaltic pump as provided above. Fluoropolymer, 3/8 or ¼ in. outside diameter (o.d.), in lengths required to reach the point of sampling. Tubing is cleaned and stored as provided above. If necessary, more aggressive cleaning (e.g., concentrated nitric acid) may be used.
5. Bladder Pump: QED[1] Model MP-SP-4P.
    a. Water Level Meter: Provided as part of the QED bladder pump equipment, QED Part No. MP30-150.
    b. Controller: Provided as part of the QED bladder pump equipment, QED Part No. MP-15.
    c. Bladders: QED Bladder Kit, Part No. 38360. Unless it is known, the bladders do not contribute to contamination. The bladders must be cleaned and stored as provided above.
    d. Spare CO2 Tank: QED Part No. 38304.
6. Water Quality Instruments: Use instruments capable of measuring temperature, hydrogen ion activity (pH), specific conductance, redox, dissolved oxygen, and turbidity to determine when formation water is entering the pump. With the equipment provided to staff, a separate meter is necessary for turbidity measurements.
7. Gloves: Clean, non-talc polyethylene, latex, vinyl, or polyvinylchloride (PVC); various lengths.
8. Gloves: PVC-Fisher Scientific Part No. 11-394-100B, or equivalent.
9. Wind Suit: Suitable to protect samples from contamination from lint and dust. Unlined, long sleeve wind suit consisting of pants and jacket constructed of nylon or synthetic fiber are suitable. Tyvek® suits are used in this procedure.
10. Storage Bags: Clean, zip-type, non-vented, colorless polyethylene (various sizes). Large size bags are needed for storage of the pump during transportation between sampling locations.
11. Plastic Wrap: Clean, colorless polyethylene.
12. Cooler: Clean, nonmetallic, with white interior for shipping samples.
13. Carboys: Dedicate one specific carboy for "Reagent Water."
14. Plastic Decontamination Tubs: Containers of various sizes to immerse the submersible pump, sampling tubing, and the wetted parts of the water level meter and multi-parameter monitor. Four tubs are needed; one for a soap solution, one for tap water rinse solution, one for reagent water rinse, and one to hold the reagent water for obtaining field blanks.
15. Pipette: Automatic pipette, capable of dispensing 10.0 ml and automatic tip ejector.
16. Pipette Tips: Colorless, 10 ml, for use with automatic pipette. Pipette tips must be cleaned and stored as described under tubing as described in item 3.

[1] QED, P.O. Box 3726, Ann Arbor, Michigan 48160.

Reagents

1. Reagent Water: Ultra-pure de-ionized water, starting from a pre-purified (distilled, reverse osmosis, etc.) source, 18 Megaohms minimum, provided in a carboy suitable to prevent mercury contamination. The water should be tested at the laboratory for suitability for sampling. The quantity needed depends on the amount of water needed for each decontamination cycle and the number of wells sampled. The laboratory should provide this water.
2. Soap: Alconox[2] CITRANOX®, suitable for cleaning instruments for low level mercury sampling. Prepare a 2% solution as per the manufacturer's instructions.

Site Sampling Plans and Sample Delivery Strategies to Minimize Contamination

1. Sample Collection Strategy: Sample collection activities should be designed that will minimize the potential for cross contamination.
   a. If possible, use previous facility data showing mercury levels at the locations to be sampled. If mercury data is not available, use other information to make a judgment whether the mercury level is suspected to be high or low. For example, if data is available for other metal levels, the relative levels of these metals may be a good indicator of whether high or low mercury levels are suspected.
   b. Arrange the sampling sequence in order of their known or expected levels of mercury. Collect samples starting from locations known to have the lowest and approximate same levels of mercury and proceed to those of higher levels. In this manner, if decontamination procedures fail to remove all residual mercury, the effect on samples will be minimized.
   c. Group samples so that samples of high and low levels are separately grouped in storage and transportation. For purposes of separating samples based on expected concentration levels, samples believed to have concentrations more than 200 ng/L of mercury should be identified as high-level samples, and low-level samples less than or equal to 200 ng/L.
2. Sample Information Provided to the Laboratory: Laboratory areas and instrumentation used for low level analysis of mercury are extremely clean and designed to prevent mercury contamination from outside sources. Processing a sample with an extremely high level of mercury in these areas can result in contamination of the area and instrumentation, resulting in delays and additional expense. Using the evaluation described above, provide information to the laboratory regarding the known or expected levels of mercury for each location sampled. Information useful to the laboratory and recommended to be provided is as follows:

Mercury (Hg) Level	**Provide to Laboratory**
Hg levels not known and high levels expected	Expected > 200 ng/L
Hg levels not known and low levels expected	Expected < 200 ng/L
Hg levels previously found	Provide Data
Hg levels and expectations not known	Not Known

[2]Alconox, Inc., 30 Glenn Street, Suite 309, White Plains, New York 10603.

Sample Collection and Handling Considerations
Sampling precautions should be taken as follows:

1. Use low flow rates (0.5 L/min.) during both purging and sampling to maintain minimal drawdown in the well.[3]
2. Place the sampling pump intake at the proper sampling point.
3. Minimize disturbance of the stagnant water column above the screened interval during water level measurement and sampling device insertion.
4. Make proper adjustments to stabilize the flow rate as soon as possible.
5. Monitor water quality indicators during purging.
6. Collect unfiltered samples to represent contaminant loading and transport potential in the subsurface system.
7. Filtering (if necessary): If it is not feasible to collect samples representative of the water flowing in the aquifer, and filtering is determined necessary, collect duplicate samples and identify one of these to be filtered and preserved upon receipt at the laboratory. Appropriate arrangements must be made with the laboratory to ensure the filtering and subsequent preservation is accomplished for identified samples immediately upon receipt. Arrangements with the laboratory to utilize appropriate filters should be made well in advance of sample collection so that immediate filtering and preservation at the laboratory can be accomplished upon receipt of samples.
8. Water samples should not be taken immediately following well development. Sufficient time should be allowed for the groundwater flow regime in the vicinity of the monitoring well to stabilize and to approach chemical equilibrium with the well construction materials. This lag time will depend on facility conditions and methods of installation but often exceeds one week.
9. Well purging is nearly always necessary to obtain samples of water flowing through the formation associated with the screened interval. The required purging procedure relies on the stabilization of several water quality parameters to determine when formation water is being pumped. The pH, specific conductance, redox, dissolved oxygen, and turbidity are monitored for this purpose. Temperature is also measured and recorded during this process but is not used as an indicator for formation water. Data on pumping rate drawdown, not to exceed 0.1 meter, and volume required for parameter stabilization can be used as a guide for conducting subsequent sampling activities.
10. Water Level Measurements and Monitoring: Well depth should be obtained from the well logs. Since measuring to the bottom of the well casing will cause re-suspension of the settled solids and require longer purging times for turbidity equilibration, measure well depth after sampling is completed. The water level measurement should be taken from a permanent reference point, which is surveyed relative to ground elevation.

Sample Collection Using Bladder Pumps
1. Upon arrival at the sample location, one member of the two-person sampling team is designated as Dirty Hands and the other as Clean Hands.
2. An area, expected or known to be free of high levels of mercury, is selected.
3. The team removes the bags containing the pump, monitoring instruments, tubing, carbon dioxide (CO2) cartridges, gloves, plastic wrap, and wind suits from the coolers or storage containers in which they are packed.
4. The team puts on wind suits and PVC gloves.

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[3]Puls, R. W. and Barcelona, M. J., 1996 Low Flow (Minimal Draw Down) Ground Water Sampling Procedures, EPA Ground Water Issues, U.S. EPA, Office of Research and Development, EPA/540/S-95/504.

5. The team generates the initial equipment blank, following the steps listed under the section Decontamination and Initial Equipment Blank.
6. The team proceeds to the sampling location.
7. The team opens the well.
8. The team changes gloves.
9. Keeping both bags together, Dirty Hands opens the outer bag containing the pump.
10. Clean Hands opens the inner bag and removes the pump.
11. Clean Hands lowers the submersible sampling pump into the monitoring well. Lower the pump slowly and carefully to the middle of the screened interval or slightly above the middle. This should minimize excessive mixing of the stagnant water above the screen with water in the screened interval and minimize suspension of solids from the bottom of the well.
12. Dirty Hands opens bag containing static water level meter. Clean Hands removes water level meter. Clean Hands sets up the water level meter.
13. Clean Hands connects the multi-meter flow through the cell to the pump outlet.
14. Dirty Hands turns on the submersible pump, sets the pump for the allowable water level drawdown (not to exceed 0.1 meters), and slowly pumps the water while monitoring the water level to assure that the pumping rate does not result in drawdown of the water level. With the QED bladder pump in this standard operating procedure (SOP), the pump will turn off automatically if this level is exceeded. As the well is pumped, water quality parameters are monitored to determine when formation water is flowing through the pump. Formation water is considered to be flowing if three consecutive measurements of the water quality parameters, conducted at 3–5-minute intervals, meet the following requirements:
    a. Turbidity, within ± 10%.
    b. pH, within ± 0.1 pH units.
    c. Specific conductance, within 3%.
    d. Redox, within ± 10 millivolts
    e. Dissolved oxygen, within ± 10%. If dissolved oxygen is used for comparison to criteria or a mixing zone calculation, the dissolved oxygen calibration must be corrected for local barometric pressure reading and elevation. The equipment in this procedure (YSI multi-parameter meter) automatically corrects the dissolved oxygen for these conditions.
15. After stabilization, Clean Hands disconnects the meter.
16. The team changes gloves.
17. Dirty Hands retrieves the sample containers required and unzips their outer bags. Retrieve two sample containers if filtering is required, for duplicate samples, or for field blanks. If split samples are to be generated, a larger size container is required, at least twice the size of normal samples.
18. Dirty Hands prepares the label(s).
19. Clean Hands opens the inner bag, removes the sample container, and reseals the inner bag.
20. Clean Hands removes the cap for the sample being collected, and while holding the cap upside down, discards the diluted acid into a waste carboy or empties the reagent water onto the ground.
21. If a field blank is being generated, proceed as follows:
    a. Clean Hands opens the inner bag and places the emptied sample bottle and its cap in its inner bag. This bottle is to be identified as the field blank.
    b. Clean Hands obtains another sample bottle from its inner bag, removes, and discards its cap.
    c. Clean Hands retrieves the field blank bottle and pours the contents of the sample bottle into the field blank bottle.
    d. Skip to Step 27.

22. Clean Hands rinses the sample bottle and cap three times with the formation water flowing from the pump and collects the sample from the flowing tube.
23. Clean Hands caps the sample, opens the inner bag, and places the sample in its inner bag.
24. If filtering is required or a duplicate sample is to be taken, Steps 18 through 23 are repeated to immediately take another sample.
25. Clean Hands caps the sample(s), opens the inner bag(s) for the sample(s), places the sample bottle(s) into the inner bag(s), and seals the inner bag(s).
26. Dirty Hands seals the outer bag(s), writes sample identification information in permanent ink on the outside of the plastic bag(s), places the sample(s) in the cooler (on ice), and closes the cooler.
27. Dirty Hands measures and records the depth to the bottom of the well.
28. Dirty Hands records the sample number(s) in the sampling log, water quality parameters, and notes any unusual observations.
29. Clean Hands removes the equipment from the well, removes the water level meter, and places them into bags for transportation.
30. Both Dirty and Clean Hands move to the decontamination area with the equipment.
31. The section Decontamination Between Sampling Locations steps are used to decontaminate the equipment.
32. If other samples are to be taken at the facility, the team proceeds to the next sampling location and collects another sample beginning with Step 6.
33. If samples are to be split, proceed as follows:
    a. The team selects a suitable place for splitting samples.
    b. The team changes gloves.
    c. Dirty Hands opens the cooler, removes the bag containing the sample to be split. The volume of this sample must be at least twice the volume of normal samples.
    d. Dirty Hands removes two bags with sample containers and unzips their outer bags. These containers will hold the split samples.
    e. Dirty Hands prepares the label(s).
    f. Clean Hands opens the inner bags holding all containers, removes the containers, removes the caps of all containers, and places them in their respective inner bags.
    g. Clean Hands discards the diluted acid from the two sample containers into a waste carboy or empties the reagent water onto the ground.
    h. Clean Hands pours from the container holding the sample to be split into each of the sample containers.
    i. Clean Hands discards the container that held the sample to be split.
    j. Clean Hands retrieves the caps, seals the samples with their respective caps, places the samples into their inner bags, and seals the inner bags.
    k. Dirty Hands seals the outer bag(s), writes sample identification information in permanent ink on the outside of the plastic bag(s), places the sample(s) in the cooler (on ice), and closes the cooler.
    l. Repeat steps for each additional split sample.
    m. Information specific for splitting samples must be documented. If others request split samples, use the EGLE laboratory's chain of custody sheet. If EGLE is requesting the split sample and a chain of custody is not forthcoming from the sampler, use the EGLE chain of custody, fill out information, sign it, and request this be signed by the provider of the samples.

Sample Collection Using Peristaltic Pumps

1. Upon arrival at the sample location, one member of the two-person sampling team is designated as Dirty Hands and the other as Clean Hands.

2. The team opens the well to be sampled.
3. An area, expected or known to be free of high levels of mercury, is selected. Sampling should proceed from lowest to highest expected level of contamination.
4. The team removes the bags containing the pump, batteries, monitoring instruments, SEBS resin tubing, gloves, plastic wrap, and wind suits from the coolers or storage containers in which they are packed.
5. The team puts on wind suits and PVC gloves.
6. Dirty Hands removes the pump from its storage bag and opens the bag containing SEBS resin tubing.
7. Clean Hands installs the tubing in the well. Lower the tubing slowly and carefully to the middle of the screened interval or slightly above the middle. This should minimize excessive mixing of the stagnant water above the screen with water in the screened interval and to minimize re-suspension of solids from the bottom of the well.
8. Clean Hands installs tubing on the pump.
9. Dirty Hands opens bag with water level meter.
10. Clean Hands removes water level meter and lowers it into the well.
11. Clean Hands connects the multi-parameter meter flow through the cell to the pump outlet.
12. Dirty Hands turns on the peristaltic pump and slowly pumps the water while monitoring the water level to assure that the pumping rate does not result in excessive drawdown of the water level (not to exceed 0.1 meters). As the well is pumped, water quality parameters are monitored to determine when formation water is flowing through the pump. Formation water is considered to be flowing if three consecutive measurements of the water quality parameters, conducted at 3–5-minute intervals, meet the following requirements:
    a. Turbidity, within ± 10%.
    b. pH, within ± 0.1 pH units.
    c. Specific conductance, within 3%.
    d. Redox, within ± 10 millivolts.
    e. Dissolved oxygen, within ± 10%. If dissolved oxygen is used for comparison to criteria or a mixing zone calculation, the dissolved oxygen calibration must be corrected for local barometric pressure reading and elevation. The equipment in this procedure (YSI multi-parameter meter) automatically corrects the dissolved oxygen for these conditions.
13. After stabilization, Clean Hands disconnects the meter.
14. The team changes gloves.
15. Dirty Hands opens the cooler containing the sample bottle and unzips the outer bag containing the sample container. If the sample is to be split, a larger size container is required at least twice the size of normal samples. If filtering is necessary, a field blank is being generated or a duplicate sample is to be taken, Dirty Hands unzips the outer bag of another sample container.
16. Dirty Hands prepares the sample label(s).
17. Clean Hands opens the inner bag, removes the sample container, and reseals the inner bag.
18. Clean Hands unscrews the cap, and while holding the cap upside down, discards the diluted acid into a waste carboy or empties the reagent water onto the ground.
19. If a field blank is being generated, proceed as follows:
    a. Clean Hands places the sample bottle and its cap in its bag. This is to be identified as the field blank.
    b. Clean Hands obtains another sample bottle from its bag, unscrews, and discards the cap.

   c. Clean Hands retrieves the field blank bottle and pours the contents of the other bottle into the field blank bottle, discards this other bottle, retrieves the cap of the field blank, and caps the field blank.
   d. Skip to Step 22 below.
20. Clean Hands rinses the sample bottle and cap three times with the formation water and collects the sample from the flowing tube.
21. Clean Hands caps the sample.
22. Clean Hands places a label on the sample container and places it in its inner bag.
23. If filtering is required or a duplicate sample is to be taken, Steps 17 through 22 are repeated to immediately take another sample.
24. Clean Hands caps the sample(s), opens the inner bag(s) for the sample(s), places the sample bottle(s) into the inner bag(s), and seals the inner bag(s).
25. Dirty Hands seals the outer bag(s), writes sample identification information on the outer bag(s), places the sample(s) in the cooler (on ice), and closes the cooler.
26. Dirty Hands measures and records the depth to the bottom of the well.
27. Dirty Hands records the sample number(s) in the sampling log, water quality parameters, and notes any unusual observations.
28. Clean Hands removes the equipment from the well, removes the water level meter, and places them into bags for transportation.
29. Both Dirty and Clean Hands move to the decontamination area with the equipment.
30. In the section Decontamination Between Sampling Locations, steps are used to decontaminate the water level meter and multi-parameter meter. The SEBS resin tubing is replaced prior to sampling each new monitoring well.
31. If other samples are to be collected, the team proceeds to the next sampling location and collects another sample beginning with Step 1.
32. If samples are to be split, follow the steps in section Sample Collection Using Bladder Pumps, starting with Step 36.

Decontamination Between Sampling Locations

1. The team changes gloves.
2. Dirty Hands prepares the decontamination solutions.
3. Dirty Hands lowers pump into tub 1 containing the 2% Alconox/tap water solution.
4. Dirty Hands turns on controller and pumps three volumes of Alconox solution through the pump.
5. Clean Hands moves the pump to tub 2 containing tap water (fresh tap water should be used between each sampling location).
6. Dirty Hands turns on controller to pump three volumes of tap water through the pump.
7. Clean Hands moves the pump to tub 3 and pumps three volumes of reagent water (fresh reagent water should be used between each sampling location).
8. Clean Hands changes gloves.
9. Dirty Hands opens outer bag containing tubing and pump bladder.
10. Dirty Hands changes gloves.
11. Dirty Hands removes the pump from tub 3.
12. With Dirty Hands holding the pump, Clean Hands removes the bladder from the inner bag and places the bladder on the pump. Clean Hands removes tubing from the inner bag and installs tubing on pump and controller.
13. Clean hands places pump in reagent water in tub 4.
14. The team changes gloves.
15. Clean Hands places the pump in the storage bag or proceeds to place pump in monitoring well.

16. Clean Hands removes the water level meter from its storage bag, decontaminates the water level meter by successively cleaning with solutions from tub 1, 2, and 3, and places the meter back into a clean storage bag or into the monitoring well.
17. Clean Hands changes gloves.

Sample Preservation and Holding Time

1. Preservation: Samples should be preserved at the laboratory using BrCl or HCl within 48 hours of collection. If samples are oxidized in sample bottles, preservation may be extended up to 28 days.
2. Laboratory Processing of Filtered Samples: If filtering is to be performed at the laboratory, make arrangements with the laboratory for receipt of samples well in advance since filtering should be done within 24 hours of collection. If special filters are necessary, these must be provided to the laboratory prior to sample collection activities or arrangements made with the laboratory to ensure they are available upon sample receipt. It is not advisable to plan sampling immediately preceding non-working days for the laboratory. Upon shipment of samples to a laboratory, it is good practice to immediately contact the laboratory. If the laboratory is not advised of these arrangements, extra effort and expense must be incurred to ensure necessary filtering and preservation. If it is not possible to submit to the laboratory within 24 hours, the sample must be filtered in a designated clean area in the field.
3. Sample analysis must be performed within 90 days of preserved samples.

Quality Assurance/Quality Control

Field Blanks: Field blanks are used to demonstrate that samples have not been contaminated by the sample collection and transportation activities. Field blanks should be collected in the same manner as samples using the same equipment. (See sections Sample Collection Using Bladder Pumps Step 21 and Sample Collection Using Peristaltic Pumps Step 19.) Field blanks should be collected first.

1. Frequency of Collection: One per facility, per day, or 10% per sampling event, whichever is greater.
2. Evaluation: If the mercury concentration in the field blank is greater or equal to 0.5 ng/L, or greater than one-fifth of the sample concentration, whichever is greater, the associated sample result is an estimate and may be unusable for regulatory application.

Field Duplicates: The purpose of field duplicates is to assess the precision for the field sampling and analytical process. A field duplicate is collected by filling a second sample container, in rapid succession after the first sample, from the outlet of the sampling stream.

1. Frequency of Collection: Collect duplicates minimally for every 10 samples collected or at the frequency specified in the project objectives. If possible, select a location with detectable amounts of mercury.

Split Samples: Split samples are used to independently confirm results of the laboratory performing the analysis. Typically, a laboratory known to produce valid, unbiased results is selected as the laboratory to which the split samples are sent.

1. Collection: Split samples are created by dividing one sample collected in the field into two aliquots. This requires the collection of at least twice the volume of sample normally collected, properly preserved if field preservation is performed. Because of the influence that equipment blanks may have upon the use of the data, an equipment blank associated with the sample should be provided along with the split sample. This will require the generation of two equipment blanks prior to the collection of the sample to be split.

LINKS TO ADDITIONAL INFORMATION

Evaluating Mercury in Groundwater Plumes Relative to the Groundwater/Surface Water Interface (GSI) Pursuant to Part 201 EGLE 09-014

APPENDICES

Appendix 1 - Minimum Quality Control Sampling Requirements Per Sampling Event

APPROVING AUTHORITY

DIVISION DIRECTOR APPROVAL:

Mike Neller, Director
Remediation and Redevelopment Division

HISTORY

Policy No.	Action	Date	Title
RRD-36	Original	10/22/2004	Standard Operating Procedure for Low Level Mercury Sample Collection
RRD-36	Revised	3/10/2016	Standard Operating Procedure for Low Level Mercury Sample Collection
RRD SOP-36	Reviewed	05/19/2022	Low Level Mercury Sample Collection

CONTACT/UPDATE RESPONSIBILITY

Any questions or concerns regarding this standard operating procedure should be directed to EGLE-RRD@Michigan.gov.

APPENDIX 1

Quality Control Guidance Information for the sampling and analysis of Low-Level Mercury in Water following USEPA Method 1631, Revision E August 2002

The following tables summarize **some** of the minimum quality control requirements for the routine sampling and analysis of Low Level Mercury in water following *USEPA Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry.* Additional quality control requirements can be found in USEPA Method 1631, Revision E. See USEPA 821-R-01-023 Guidance for Implementation and Use of USEPA Method 1631 for the Determination of Low-Level Mercury (40 CFR part 136), March 2001, Section 5-18 for further details.

- All data are the responsibility of the submitter if the data are to be used for regulatory compliance purposes.
- It is the responsibility of the submitter to ensure that all minimum quality control (QC) sampling requirements for USEPA Method 1631, Revision E are met.
  (see Table 1 below and USEPA Method 1631, Revision E)
- It is the laboratory's responsibility to make sure that all analytical QC acceptance criteria for USEPA Method 1631, Revision E are met
  (see Table 2 below and USEPA Method 1631, Revision E).
- Data not meeting the QC requirements of Method 1631, Revision E may not be used for compliance purposes.
- **Blank correction is not allowed except as specified in Tables 1 and 2 below and Method 1631, Revision E.**

Table 1: Minimum Quality Control Sampling Requirements per Sampling Event

Test	Definition per Method 1631E	Spike Amount	Minimum Frequency	Acceptance Criteria	Blank Correction Criteria
Bottle Blanks	To determine that the bottle is free from contamination prior to use. Reagent water is added to the bottle, acidified to pH<2 with BrCl, and allowed to stand for a minimum of 24 hours. After standing the water is analyzed.	NA	At least 5 % from a given lot should be tested prior to collection of samples	<0.5ng/l	Blank correction of Bottle Blanks is not allowed as the bottles must be demonstrated to be free from contamination prior to use.
Equipment Blanks	Reagent water that has been processed through the sampling device at a laboratory or other equipment cleaning facility prior to shipment of the sampling equipment to the sampling site. The equipment blank is used to demonstrate that the sampling equipment is free from contamination prior to use.	NA	1 following each cleaning	<0.5ng/l	Blank correction of Equipment Blanks is not allowed as the equipment must be demonstrated to be free of Hg and interferences before equipment may be used in the field.

APPENDIX 1

Field Blanks	Reagent water that has been transported to the sampling site and exposed to the same equipment and operations as a sample at the sampling site. The field blank is used to demonstrate that the sample has not been contaminated by the sampling and sample transport systems.	NA	10% from same site and same time	<0.5ng/l or no greater than one-fifth Hg in associated sample(s) whichever is greater	Must meet acceptance criteria prior to blank correction of laboratory data. Must be reported separately with associated sample(s). Only Field Blanks or Method Blanks must be sued for blank correction but not both.

APPENDIX 1

Table 2: Minimum Quality Control Requirements per Laboratory Analytical Batch NA= Not Applicable

Test	Definition per Method 1631E	Spike Amount	Minimum Frequency	Acceptance Criteria	Blank Correction Criteria
Bubbler Blanks	The bubbler blank is specific to the bubbler system and is used to determine that the analytical system is free from contamination. A minimum of three bubbler blanks is required for system calibration	NA	Three during calibration if using the Bubbler System	Each bubbler blank must be <0.5 ng/L; Mean of 3 bubbler blanks must be <0.25ng/L with a standard deviation	If the mean of 3 Bubbler Blanks is <0.25ng/L, the average peak height or area is subtracted from all raw data before results are calculated
System Blanks	The system blank is specific to the flow-injection system and is used to determine contamination in the analytical system and in the reagents used to prepare the calibration	NA	Three during calibration if using the Flow- Injection System	Each system blank must be <0.5 ng/L; Mean of 3 system blanks must be <0.5 ng/L with a standard	If the mean of 3 System Blanks is <0.5ng/L, the average peak height or area is subtracted from all raw data before results are calculated
Reagent Blanks	Reagent blanks are used to determine the concentration of mercury in the reagents that are used to prepare and analyze the samples. Reagent blanks	NA	Each new batch of reagents prepared for laboratory analysis	<0.2 ng/L	Blank correction of reagent blanks is not allowed
Method Blanks	Method blanks are used to determine the concentration of mercury in the analytical system during sample preparation and analysis and consist of a volume of reagent water that is carried through the entire sample preparation and analysis. Method blanks are prepared by placing reagent water in a sample bottle and analyzing	NA	3 per analytical batch	<0.5 ng/L	Must meet acceptance criteria prior to blank correction. Must be reported separately with associated sample(s). Only Method Blanks or Field Blanks may be used for blank correction but not both.
Quality Control Sample (QCS)	A sample containing mercury at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of	Within calibration range	1 per analytical batch	% Recovery - follow the specifications provided by the supplier of the	NA
Ongoing Precision and Recover (OPR)	To demonstrate that the analytical system is within the performance criteria of this Method and that acceptable precision and recovery is	5 ng/L	Prior to and after analysis of each analytical batch	% Recovery: 77-123%	NA

APPENDIX 1

Test	Definition per Method 1631E	Spike Amount	Minimum Frequency	Acceptance Criteria	Blank Correction Criteria
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	Aliquots of an environmental sample to which known quantities of the analyte(s) of interest is added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix	Compliance limit or 1-5x background level of the sample used for the MS/MSD	10% from a given sampling site or discharge	% Recovery: 71-125% Relative % Difference Maximum: 24%	NA