United States Environmental Protection Agency
Office of Water 4303
EPA 821-R-01-023 March 2001

# Guidance for Implementation and Use of EPA Method 1631 for the Determination of Low-Level Mercury (40 CFR part 136)

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## Acknowledgments

This guidance document was developed under the direction of William A. Telliard and Maria Gomez-Taylor of the Engineering and Analysis Division (EAD) within the U.S. Environmental Protection Agency's (EPA's) Office of Science and Technology (OST). EPA expresses appreciation to Roger Stewart of the Virginia Department of Environmental Quality (DEQ), Paul Boothe of Albion Environmental Laboratories, Beverly van Buuren and Nicolas Bloom of Frontier Geosciences, Mark Hoeke of the Association of Metropolitan Sewerage Agencies, and representatives of the Alliance of Automobile Manufacturers, the American Chemistry Council, the Utility Water Act Group, and the American Forest and Paper Association for providing technical assistance and review during document development.

## Disclaimer

This *Guidance for Implementation and Use of EPA Method 1631 for Determination of Low-Level Mercury* (the "Guidance") is provided to help implement national policy on the use of EPA Method 1631. The material presented is intended solely for guidance and does not alter any statutory requirements. This guidance does not substitute for Clean Water Act (CWA) requirements or EPA regulations, nor is it a regulation itself. Thus, it cannot impose legally binding requirements on EPA, States, Tribes, or the regulated community and may not apply to a particular situation based upon case-specific circumstances. EPA and State decision makers retain the discretion to adopt approaches on a case-by-case basis that differ from this guidance where appropriate. This guidance may be changed based on any future information made available to EPA.

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# Foreword

The latest recommended water quality criteria (WQC) published by the U.S. Environmental Protection Agency (EPA) are those listed in the National Toxics Rule (58 FR 60848) and the Stay of Federal Water Quality Criteria for Metals (60 FR 22228), and codified at 40 CFR 131.36. In addition to the WQC published at 131.36, EPA has established WQC for protection of aquatic life, human health, and wildlife in the Water Quality Guidance for the Great Lakes System at 40 CFR 132. The lowest WQC for mercury is a criterion for protection of wildlife of 1.3 ng/L. EPA developed Method 1631 to specifically address State needs for the reliable measurement of mercury at WQC levels.

Measurement of mercury by Method 1631 is accomplished by oxidation of mercury with bromine monochloride (BrCl), sequential reduction with ammonium hydroxide and stannous chloride to convert Hg(II) to volatile Hg(0), purge of Hg(0) from water onto a gold-coated sand trap, thermal desorption from the trap, and detection by cold-vapor atomic fluorescence spectrometry (CVAFS). Tests of the initial version of Method 1631 were directed at making measurements in ambient waters at WQC levels. In data gathering, EPA found that Method 1631 also could be applied to effluents and other matrices. These applications were supported by data from laboratories within the U.S. and overseas and by a comprehensive survey of waters in the State of Maine (Maine DEP, *Mercury in Wastewater: Discharges to the Waters of the State*). Method 1631 was validated initially in four single-laboratory studies, and the resulting performance specifications were validated in an interlaboratory validation involving twelve participant laboratories and one referee laboratory. The highest method detection limit (MDL) determined by all laboratories in reagent water was 1.8 ng/L. Results from these studies indicate that the Method is capable of producing reliable measurements of mercury in aqueous matrices at WQC levels.

In May 1998, EPA proposed Method 1631 at 40 CFR part 136 for use in determining mercury at ambient WQC levels in EPA's CWA programs, and subsequently published a Notice of Data Availability (64 FR 10596) that included additional data supporting application of the Method to effluent matrices. On June 8, 1999, EPA responded to numerous public comments on the proposed method and promulgated EPA Method 1631, Revision B: *Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry* at 40 CFR part 136 for use in EPA's CWA monitoring programs.

The purpose of this guidance is to assist regulatory agencies, control authorities, dischargers, generators, industrial users, and laboratories in the application of EPA Method 1631 to ambient water and wastewater, provide information on the use of "clean techniques" to preclude contamination, give details on how to overcome matrix interferences, and answer frequently asked questions (FAQs). We trust that this guidance will assist you in using Method 1631 to produce reliable measurements of mercury at the levels necessary to address EPA and State water quality criteria.

Following publication of this Guidance, EPA is planning to promulgate Method 1631, Revision C to clarify requirements for the reporting and use of field blank results. This Guidance addresses those requirements. In addition, EPA plans to sign a notice of proposed rulemaking by September 30, 2001 of specific requirements for clean techniques and quality control to be used in conjunction with Method 1631. The proposal should be published in the Federal Register by October 2001. The proposed requirements will be based on comments received from several stakeholders since promulgation of Method 1631, Revision B. After proposal and review and consideration of comments received during the public comment period, EPA would take final action during 2002 on the proposed revisions to Method 1631 addressing clean technique and quality control requirements. At that time, EPA may revise this Guidance in accordance with any new requirements.

# Chapter 1: Introduction

This guidance is intended to provide assistance to the analytical community in the application and use of Method 1631 and to include more detailed information on certain aspects of the Method. This guidance also explains the flexibility allowed within the scope of Method 1631 and answers frequently asked questions (FAQs) about the Method. To help in this process, this Guidance is divided into the following topics:

- **Chapter 1** discusses the purpose and contents of this document and provides background information concerning the development of Method 1631 and its application to ambient and effluent waters.
- **Chapter 2** discusses the use of "clean" techniques to prevent and control contamination.
- **Chapter 3** discusses known matrix interferences and provides suggestions as to how you can overcome these and other interferences.
- **Chapter 4** discusses flexibility in Method 1631.
- **Chapter 5** presents responses to frequently asked questions (FAQs) by the analytical community regarding use of Method 1631.
- **Chapter 6** provides a list of information sources pertaining the regulatory background and data gathering for Method 1631.
- **Chapter 7** provides sources of information and EPA contacts that may help you answer any remaining questions you may have regarding Method 1631.

## Subjects addressed in this guidance

*Use of "clean" and "ultra-clean" techniques*

The terms "clean" and "ultra-clean" have been applied to the techniques needed to reduce or eliminate contamination in trace metals determinations. However, these terms are not well defined, and their meaning varies widely among researchers and other users of the techniques. For example, the U.S. Geological Survey's (USGS's) Water Quality Laboratory has defined "clean" to mean measurements to a concentration of 0.1 $\mu$g/L and "ultra-clean" to mean measurements to a concentration of 0.01 $\mu$g/L. The method detection limit (MDL; 40 CFR 136, Appendix B) in Method 1631 is 0.0002 $\mu$g/L (0.2 ng/L), well below these levels. As a result, the terms "clean" and "ultra-clean" are not used in Method 1631. However, in response to requests from the analytical community, this guidance addresses "clean" and "ultra-clean" techniques. In this guidance, the term "clean" refers to the suite of techniques needed to reduce or eliminate contamination when Method 1631 is used. The term ultra-clean is not employed.

*Potential matrix interferences*

The proposed version of Method 1631 contained the statement that there were no observed interferences in determination of mercury by Method 1631. Commenters on the proposal pointed out that precious metals (primarily gold), were interferents, and that high concentrations of iodide and organic matter could be interferents. After consideration and confirmation of the comments, EPA revised the language in Method 1631 to state that gold and iodide were known interferents. This guidance provides suggestions for overcoming potential interferences, procedures for demonstrating that a matrix interference exists, and procedures for calculating matrix-specific MDL/MLs.

*Frequently asked questions*

This guidance also gives details concerning the flexibility inherent in Method 1631 and provides answers to frequently asked questions (FAQs). For ease of use, Chapters 2 through 5 are presented in question and answer format. In each question, the pronouns "I" and "we" refer to the questioner whereas the pronoun "you" refers to EPA. In the answers, the pronouns "we," "us," and "our" refer to EPA whereas the pronouns "you" and "your" refer to the questioner and to other users of Method 1631.

While this guidance attempts to address issues and situations pertinent to Method 1631, it also identifies and references other analytical methods and sampling techniques and provides a list of EPA and other authorities to contact for additional information and guidance.

# Chapter 2: Use of "Clean" Techniques to Preclude Contamination

This chapter discusses the techniques that may be used to preclude contamination, how to determine if contamination exists, and how to evaluate the effects of contamination on results. For information on the specific contamination control techniques required for use with Method 1631, refer to *Guidelines Establishing Test Procedures for the Analysis of Pollutants; Measurement of Mercury in Water (Method 1631, Revision B); Final Rule* at 40 CFR part 136, published in the *Federal Register* (64 FR 30417; June 8, 1999). For additional information on the techniques that may be helpful in precluding contamination when Method 1631 is used, refer to the *Sampling Guidance* (*EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*, EPA-821-R-96-011) and video (*Sampling Ambient and Effluent Waters for Trace Metals*, EPA 821-V-97-001).

## What is the contamination control philosophy behind Method 1631 ?

The philosophy behind contamination control is to reduce or eliminate contamination in order to produce a reliable result. The basis of this philosophy is given in the *Sampling Guidance* (EPA Method 1669): "The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is nonmetallic and free from any material that may contain metals of concern." This means that mercury in the sample bottle, reagents, laboratory, and labware is eliminated or reduced to a level that will not compromise the measurement. It also means that mercury is eliminated or reduced from air in the laboratory and must be prevented from entering the sample at the sampling site.

Laboratories that have been conducting measurements with Method 1631 for years, such as those that participated in EPA's validation studies (see *Interlaboratory Validation Study Report* in the Water Docket for proposal of Method 1631), have addressed the laboratory aspects of contamination control. These laboratories demonstrated in the method validation study, that they were capable of controlling contamination to levels that would not compromise reliable mercury determinations. For a laboratory that is just preparing to conduct measurements using Method 1631, we have made several documents available. These documents are Method 1631 itself, the *Sampling Guidance* (EPA Method 1669), *Guidance on Establishing Trace Metals Clean Rooms in Existing Facilities* (EPA 821-B-95-001; colloquially known as the "Clean Spaces Guidance"), and a document produced under contract to EPA by the Research Triangle Institute (RTI) titled "Trace Metal Cleanrooms" (RTI/6302/04-02 F). These documents, in combination, will impart the philosophy needed to allow your laboratory to make reliable mercury determinations at levels as low as can be measured by Method 1631.

## What are "clean" techniques and how are they used ?

As stated in Chapter 1 of this guidance, "clean" is not a specific set of steps or procedures, but rather a philosophy of field and laboratory techniques designed to preclude contamination. Specific techniques may vary among laboratories or sites, but when appropriately applied, clean techniques result in contaminant-free measurements. Some specific requirements for controlling contamination are given in Method 1631 and further suggestions are provided in the *Sampling Guidance* (EPA Method 1669).

The greatest risk from contamination in sampling and analysis for mercury occurs during sample collection because the sample container is opened and filled in an uncontrolled environment.
The *Sampling Guidance* identifies the precautions that can be taken to avoid sample contamination, and includes a detailed description of the "clean hands/dirty hands" technique commonly used by researchers when collecting water samples that will be analyzed for mercury. This technique is demonstrated in the

Trace Metals Sampling video (EPA-821-V-97-001). In this technique, a person designated as "clean hands" handles all operations involving direct contact with the sample bottle. "Dirty hands" is responsible for all activities that do not involve direct contact with the sample bottle. (See Section 8.2.3 of the *Sampling Guidance*.) This division of responsibility precludes contamination by controlling how the sample is handled during collection and preparation for shipment to the laboratory.

It is also possible for sample contamination to occur from the sampling equipment used or in the laboratory. The sample collection team must use collection bottles and equipment that have been demonstrated to be clean (Section 9.4.4). The laboratory should demonstrate that the laboratory equipment is free of contamination and also must demonstrate that the reagents used are free of contamination (Section 9.4.2) The laboratory environment can be controlled and made free from mercury by using steps described in Method 1631 and in the *Clean Spaces and Trace Metal Cleanroom* guidance documents cited previously and referenced in Chapter 6 of this Guidance.

## What level of contamination control is required ?

The terms "shall" and "must" in Method 1631, Revision B define procedures that are required for producing reliable data. The terms "should" and "may" indicate optional steps that may be modified or omitted if the laboratory can demonstrate that the modified method produces equivalent or superior results. The following clean techniques are requirements of Method 1631, Revision B:

- Sampling personnel must wear clean, non-talc latex gloves during all operations involving handling of the Apparatus, samples, and blanks (Section 4.3.6). Non-talc vinyl or polyethylene gloves may be substituted to avoid allergic reactions to latex and to sample for metals other than mercury, provided that the gloves would not compromise measurement of mercury at the levels required.
- All apparatus used for determination of mercury at ambient water quality criteria levels must be nonmetallic, or free of material that may contain metals, or both (Section 4.3.7).
- All materials that will directly or indirectly contact the sample must be cleaned using the procedures in Method 1631 and must be known to be clean and mercury-free before proceeding (Sections 4.3.7.1 and 6.0).
- Sampling must not proceed if it is possible that the Apparatus is contaminated (Section 4.3.7.3).
- Use clean fluoropolymer or glass sample bottles (Section 4.3.7.1).
- Reagent blanks must be analyzed for contamination prior to use. If reagent blanks are contaminated, a new batch of reagents must be prepared (Section 4.3.8.5)
- Each laboratory must perform and meet the minimum requirements of Method 1631 Quality Control (Section 9.0). For details on these requirements, see the answer to the FAQ "What quality control (QC) tests are required by Method 1631 and what performance criteria must be met?"

The following additional techniques may further aid in identifying or precluding contamination:

- Sampling personnel should be trained in techniques for sampling mercury at low levels.
- Collect samples using"Clean Hands/Dirty Hands" sampling techniques described in Method 1669.
- The frequency of blank samples can be increased beyond that required by Method 1631 (e.g., field blanks may be collected at each site immediately before and after sample collection, reagent blanks can be analyzed daily).
- Establish and maintain a laboratory QA program with control limits to monitor laboratory air, reagent water, acid vats, and work surfaces.

The extent of contamination control that may be necessary varies. For example, while observing sampling for mercury and other metals in San Francisco Bay, EPA noted that researchers were able to use pre-cleaned and double-bagged equipment and non-talc latex gloves as their only form of contamination control. In contrast, we also evaluated techniques in which sampling technicians led by Dr. Carl Watras wore precleaned wind suits, hats, shoulder-length gloves, and latex gloves to collect samples from Trout Lake Station, Wisconsin. Each group of researchers used contamination control techniques that had been demonstrated (through repeated collection of clean field blanks) to be appropriate for the environment being sampled. Later, we retained Dr. Watras for a 1994 study that required sampling several publicly-owned treatment works (POTWs) in the Great Lakes Basin. In this study, sampling crews wore precleaned suits, hats, and shoulder-length, non-talc latex gloves. The only sample that demonstrated contamination was collected during a rainstorm. In a later study conducted during 1996 and 1997, we collected samples from two POTWs in the Great Lakes Basin to evaluate several types of clean sampling techniques. This evaluation included a comparison of samples collected when wearing only latex gloves vs. the use of gloves and precleaned wind suits. In general, we found that latex gloves were necessary and that the wind suits did make some difference. (Recognizing that some people can be sensitive to latex, use of clean, non-talc gloves made from other materials; e.g., vinyl or polyethylene, may also be acceptable.) Results from the 1994 study and the 1996/1997 study are presented in separate reports referenced at the end of this guidance (*An Analytical Survey of Nine POTWs from the Great Lakes Basin*, 12/15/94 and *Evaluating Field Techniques for Collecting Effluent Samples for Trace Metals Analysis*, EPA 821-R-98-008).

## What level of contamination control and clean techniques should be required for compliance monitoring under National Pollutant Discharge Elimination System ("NPDES") permits ?

EPA believes that the use of clean techniques is necessary when analyzing samples at low water quality criteria levels such as those established in the Great Lakes Guidance. For this reason, we recommend that state and federal agencies measuring ambient water quality for compliance with water quality standards at very low concentrations should require, as a matter of internal agency protocol, that their personnel use clean techniques. However, we have avoided specifying an exact suite of protocols that must be employed in every NPDES compliance monitoring situation because some of these protocols may vary according to the experience of the sampling teams and analytical laboratory, the environment from which the sample is collected, and the permit limit (some water quality-based permit limits are higher than others).

EPA suggests that NPDES permits specify the use of clean techniques, on a permit-by-permit basis, depending on the measurement level of concern, upon request by the permit applicant. For discharger or facilities required to meet the ambient criterion of 12 ng/L in the National Toxics Rule (58 FR 60848; 40 CFR 131.36) or lower, a prudent course would be to institute all of the clean techniques recommended in Method 1631 and in this Guidance.

EPA is planning to propose additional requirements for clean techniques by October 2001. Following review of public comments, EPA will take final action to establish any additional requirements by October 2002. At that time, EPA may revise this Guidance in accordance with the new requirements.

## How will I know if my sample is contaminated ?

In general, if the performance criteria specified in Method 1631 are met, samples can be considered uncontaminated and collection and analytical clean techniques can be considered sufficient. The best way to determine if contamination has occurred during sampling is to collect a sufficient number of field blanks and equipment blanks. Section 9.4.3.1 of Method 1631 requires collection of at least one field blank for each set of samples (samples collected from the same site at the same time, to a maximum of ten samples). The Method also requires analysis of sampling equipment blanks (Section 9.4.4). Field blanks are produced by transferring reagent water that is carried to the site into a sample bottle at the same time (within minutes) that the sample is collected and using the same techniques that were used to collect the sample. Equipment blanks are produced by rinsing the sampling equipment with reagent water prior to use and collecting the rinse water.

If mercury is present in the field or equipment blanks at levels that would compromise reliable measurement of mercury in the sample, you should assume that the sample was contaminated during collection or transit. If the level in the associated blank(s) is equal to or greater than the ML or greater than 1/5 the level in the associated sample, whichever is higher (see Section 9.4.3 of Method 1631), assume that the sample is contaminated. If the sample is contaminated during collection or transit, you should eliminate any source of contamination that has been identified and re-sample the site. Additional guidance concerning the interpretation of blank data is provided in *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring*, which is referenced in Chapter 6 of this document.

Samples also may be contaminated during laboratory processing activities. You can determine if your sample was contaminated in the laboratory by examining results from the field, reagent, and bubbler blanks. Field blanks, reagent blanks and bubbler blanks are required by Method 1631 at Section 9.4. Please refer to the question "How can I determine if the laboratory and my analytical system are sufficiently clean?" below for more information on this subject.

## What "clean" techniques are necessary in the laboratory ?

The contamination control philosophy described above applies in the laboratory as well as in the field. Controlling contamination in the laboratory starts with the facility. It is best to use a facility that is not constructed of metal or to build an isolated, non-metallic facility within the metallic facility. Method 1631 states that the ideal environment for processing samples is a class-100 clean room. If such a room is not available, samples should be prepared in a class-100 clean bench or a nonmetal glove box fed by mercury- and particle-free air or nitrogen. EPA cautions that sample digestion with BrCl and mineral acids in a clean bench can pose a significant health risk if the bench blows air outward, toward the analyst. Sample digestion should be done in an exhaust hood that is monitored for atmospheric mercury.

Existing facilities can be made acceptable for use by following the suggestions in the Clean Spaces Guidance (EPA 821-B-95-001). One suggestion is to paint the walls with metal-free paint (epoxy- or latex- based) to which has been added a small amount of sulfur powder to react with mercury that could diffuse out of the underlying surfaces. To the extent practicable, all metal fixtures and appliances should be replaced with non-metal counterparts. For new laboratories or laboratories being renovated, non-metal cabinetry is now available. If any former use of the facility involved handling mercury, the mercury has likely adsorbed or been amalgamated into all parts of the facility. In this situation, it may be impossible to reduce the contamination to levels low enough to allow measurements at the method detection limit (MDL) and minimum level of quantitation (ML) in Method 1631 (0.2 ng/L and 0.5 ng/L, respectively).

The clean techniques that are currently required or necessary in the laboratory are described above and include equipment cleaning, use of non-metallic areas and apparatus, and analysis of quality control samples. The following additional laboratory clean techniques are further recommended, but currently not required, for use with Method 1631:

- Perform operations in a clean room or clean bench (Section 4.3.3 and Section 8.5.3).
- Minimize exposure of the apparatus to potential sources of mercury (Section 4.3.4).
- Clean all work surfaces in which samples will be processed with a lint-free cloth or wipe soaked with reagent water (Section 4.3.5).
- When an unusually concentrated sample is encountered, immediately analyze a bubbler and blank the traps to check for carryover (Section 4.3.8.1 and Section 11.2.4).
- Samples known or suspected to contain the lowest concentration of mercury should be analyzed first followed by samples containing higher levels (Section 4.3.8.1).
- Monitor reagent water for Hg (Section 7.1).
- Samples known to contain high levels of mercury (greater than 100 ng/L) should be diluted prior to bringing them into the clean room or area (Section 4.3.8.2).
- Process samples as far as possible from sources of airborne contamination (Section 4.3.8.4).
- Bring outside air, which is very low in mercury, directly into the clean room air intake (Section 7.2).
- Avoid condensation of water in gold traps by predrying the traps and discarding traps that absorb large quantities of water vapor (Section 4.4.3).
- Pass the effluent from the CVAFS through either a column of activated charcoal or a trap containing gold or sulfur to amalgamate or react mercury vapors (Section 5.3.6).
- Store sample bottles in clean (new) polyethylene bags until sample analysis (Section 8.6).

In summary, the best way to control contamination is to completely avoid exposure of the samples and the sample processing and analysis equipment to contamination in the first place.

## How can I determine if the laboratory and my analytical system are sufficiently "clean" ?

Determining that the laboratory, including the equipment, is sufficiently clean involves running bubbler blanks, reagent blanks, and equipment blanks as necessary, depending on the suspected mercury source. If a blank is found to contain mercury at a level that could compromise measurements, the source of mercury contaminating that blank should be pursued and eliminated or reduced until the mercury emanating from that source is sufficiently controlled. Section 9.4 of Method 1631 requires analysis of at least three bubbler blanks per analytical batch and one reagent blank per batch of reagents with verification in triplicate each month and provides levels of mercury contamination that could compromise reliable measurements. EPA's *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring* provides detailed recommendations concerning the use and interpretation of laboratory blank results.

## Can I use off-the-shelf bottles from a bottle supplier and still comply with Method 1631, Section 4.3.7.1 ?

Clean sample bottles play a critical role on the credibility of analytical results. You may use bottles "off the shelf" from a bottle supplier provided the supplier cleans the bottles using the procedures in Section 6.1.2.1 or by another procedure that will result in bottles that will not contaminate samples (i.e., result in Hg levels less than the ML or less than or equal to one-fifth the Hg level of the associated samples). You or the bottle supplier must run bottle blanks to demonstrate that the bottles are clean (Section 9.4.4). A representative, randomly selected subset of a lot should be tested to show that the bottles in the lot are contamination free. We recommend you test a minimum of one bottle per cleaned batch or lot of up to 20 bottles.

## How can I prevent contamination of my laboratory from samples containing high concentrations of mercury ?

It would be prudent to pre-screen each sample known or suspected to contain a high concentration of Hg or in which the Hg concentration is unknown. Screening could be either by cold vapor atomic absorption spectrometry (CVAAS) or by dilution of the sample by a large factor (e.g., 100 to 10,000) and analysis by EPA Method 1631.

## What other documents address contamination control issues ?

This guidance is not intended to be comprehensive in covering the subject of contamination control. For greater detail, see the suggestions in Method 1631, Method 1669, the Clean Spaces Guidance, “Trace Metal Cleanrooms,” and the additional references listed in Chapter 6 of this guidance. The National Aeronautics and Space Administration, the U.S. Department of Energy, the U.S. Geological Survey, and other Government and private sector organizations also have addressed the issue in great detail over the years and have established systems based on the contamination to be controlled. The philosophy and details of those systems are incorporated in documents that are referenced in Methods 1669 and 1631, and have been used by the authors of some of the documents referenced in this Guidance.

# Chapter 3: Matrix Interferences

In the context of EPA Method 1631, matrix interferences are non-mercury substances in a sample that can interfere with or compromise reliable measurement of mercury. Because EPA Method 1631 is performance based, the laboratory is permitted to modify the Method to overcome interferences provided performance criteria are met. This chapter discusses how matrix interferences can be identified and reduced or eliminated.

## What are the known matrix interferences in the determination of mercury using Method 1631 ?

Section 4.4.1 of Method 1631 states "At the time of promulgation of this method, gold and iodide were known interferences." EPA has also received comments suggesting that high concentrations of organic matter may compromise measurements at low levels (<1 ng/L) of mercury.

## How can I determine that a matrix interference exists ?

The best way to determine that a matrix interference exists is to analyze the matrix spike/ matrix spike duplicate (MS/MSD) as described in Section 9.3 of the Method. A recovery outside of the MS/MSD QC acceptance criteria limits suggests the presence of an interference. If results of the MS/MSD are similar but fail the QC acceptance criteria for recovery, and if results for the initial precision and recovery (IPR) and ongoing precision and recovery (OPR) tests are within their respective QC acceptance criteria, suggestions in the Method for reducing or eliminating interferences should be applied.

Another means to determine if a matrix interference exists, particularly at low levels approaching the ML in Method 1631, is to analyze the sample in duplicate. If the relative percent difference (RPD) does not meet the QC acceptance criteria in Method 1631, a matrix interference may be present.

If a sample is expected to contain an interference, you may wish to screen the sample prior to analysis for mercury. For gold, we estimate that a concentration roughly equivalent to the concentration of Hg being determined could interfere. Gold can be determined at the mg/L level by sample concentration and ICP/MS; iodide can be determined by EPA Method 345.1 (titrimetry); and the organic content can be determined by TOC measurement using EPA Method 415.1.

## Can dilution be used to overcome matrix interferences ?

EPA recognizes dilution as a means to overcome matrix interferences (see EPA's *Guidance on Evaluation, Resolution and Documentation of Analytical Problems Associated with Compliance Monitoring*; EPA 821-B-93-001) and EPA Method 1631 does not preclude sample dilution to overcome matrix interferences. Dilution is, in fact, necessary for samples in which the concentration of mercury exceeds the range of the analytical system. For example, if a sample is known or suspected to contain a concentration of Hg greater than 100 ng/L, the sample can be diluted to bring the concentration into the analytical range and to avoid carryover of Hg into a subsequent sample.

Dilution would be inappropriate, however, if the sample is diluted to a mercury concentration below the minimum level of quantitation (ML) or the level needed to determine regulatory compliance, whichever is higher. To overcome a matrix interference, a good rule of thumb is to dilute the sample by the minimum amount necessary. If further dilution is necessary to overcome a matrix interference, do not dilute below

the ML. Samples can be screened for dilution levels by analyzing aliquot volumes and dilution levels along with MS/MSD analyses until the MS/MSD results are satisfactory.

EPA believes that if dilution is performed carefully, the mercury concentration can remain within the analytical range (above the ML) while the effects of the matrix interference are minimized. For example, if mercury needs to be measured at the ambient water quality criterion (WQC) of 12 ng/L in the National Toxics Rule, dilution of a sample by a factor of 10 would allow reliable measurement at this level. This is because the ML in Method 1631 is 0.5 ng/L and dilution of the sample by a factor of 10 would raise the ML to 5 ng/L (10 x 0.5 ng/L). This ML is still well below the 12 ng/L required.

In recognition that matrix characteristics can change, EPA cautions that the need for sample dilution should not only be matrix-specific, but also should be determined each time a sample from a particular site is analyzed. It is also possible that the matrix characteristics, including matrix interferences, may remain constant with time. If two consecutive samples from a given discharge require the same amount of dilution to meet the QC acceptance criteria, subsequent samples should be diluted to that level, unless there is an indication that the matrix characteristics have changed and dilution would not be sufficient or needed to overcome a matrix interference.

For those instances in which dilution is inappropriate, specific procedures given in EPA Method 1631 and presented below for overcoming interferences should be applied.

## How can I overcome a matrix interference ?

Because every situation is different, we can not specify a single detailed or rigorous protocol for overcoming every matrix interference. The following general suggestions are offered to guide the laboratory in attempting to overcome the interference:

The first step should be to evaluate the effect of dilution on the level that needs to be measured. For example, if the regulatory compliance level is 5 ng/L, the sample can be diluted by as much as a factor of 10 and reliable measurements can still be made because the ML will be raised to 5 ng/L. To make the most reliable measurement, the minimum amount of dilution should be used. Continuing with the example, if dilution by a factor of 2 would eliminate the interference (as determined by MS/MSD recoveries within the QC acceptance criteria in EPA Method 1631), this minimum amount of dilution should be used. We suggest dilution in successive factors of 2 until the QC acceptance criteria for the MS/MSD are met, followed by dilution by an additional factor of 2 (as additional assurance), provided that the concentration remains above the ML.

Another means for overcoming matrix interferences is the method of standard additions (MSA). MSA is described in *Methods for Chemical Analysis of Water and Waste* (EPA-600/4-79-020, Revised March 1983; NTIS PB84-123677) and in *Standard Methods for the Examination of Water and Wastewater*. For MSA, a minimum of 5 separate concentrations within the linear range of the analytical system, including one unspiked sample, is recommended.

If dilution or MSA are unsuccessful, there should be an attempt to determine the cause of the interference. If the interference is caused by iodide, gold, or biota, these can be overcome using the procedures recommended in Method 1631 and presented in response to the questions below. In this Guidance, we have attempted to provide the latest techniques successfully being used to overcome the few interferences that are known regarding the use of Method 1631. If the interference cannot be identified and overcome, the technical literature and experts in the field of trace mercury determinations using EPA Method 1631 can be

consulted. As technology develops, the literature and these experts would have the latest information for overcoming matrix interferences. In general these experts reside in the laboratories that participated in EPA's inter-laboratory validation study of EPA Method 1631 ("Results of the EPA Method 1631 Validation Study," February, 1998, available from the EPA Sample Control Center, 6101 Stevenson Ave, Alexandria, VA, 22304; 703-461-2100; SCC@dyncorp.com). We also suggest performance of an inter-comparison study with one of these laboratories to confirm the presence of the matrix effect.

If the matrix interference remains intractable, regulatory relief may be appropriate. For a discussion of regulatory relief, please see the response to the question "How can I demonstrate that my inability to meet the QC acceptance criteria for the MS/MSD is attributable to a matrix interference rather than a laboratory performance deficiency?"

## What is the nature of the iodide interference and how can it be overcome ?

Section 4.4.1 of Method 1631 states: "At a mercury concentration of 2.5 ng/L and at increasing iodide concentrations from 30 to 100 mg/L, test data have shown that mercury recovery will be reduced from 100 to 0 percent. At iodide concentrations greater than 3 mg/L, the sample should be pre-reduced with $SnCl_2$ (to clarify the brown color), and additional $SnCl_2$ should be added to the bubbler. If samples containing iodide concentrations greater than 30 mg/L are analyzed, it may be necessary to clean the analytical system with 4 N HCl after the analysis."

Another means for overcoming an iodide interference was given in an attachment to a comment on proposal of Method 1631. In this case, a discharger's laboratory observed that mercury was being complexed by high (30 - 40 mg/L) concentrations of iodide in the wastewater when using EPA Method 245.1. The laboratory added a small amount of sodium tetrahydroborate to aid in the reduction of mercury so that the mercury could be purged from solution and determined.

## Is it possible to overcome an interference from gold in the sample ?

No. Free mercury in the wastewater will amalgamate with gold and cannot be separated by the techniques in Method 1631. This interference can occur in precious metals mining operations. Permitting authorities should work with permittees on a case-by-case basis to determine appropriate actions and regulatory controls when gold interferences are present.

Because the atomic weights of gold and mercury are nearly identical, a concentration of gold in a sample equal to the mercury concentration could, potentially, amalgamate all of the Hg and prevent the mercury from being released and purged in EPA Method 1631. If the concentration of a sample is not being checked against a limit, the spike level for the MS/MSD is 5 ng/L (Method 1631, Section 9.3.1). Therefore, potentially, 5 ng/L of gold could prevent the QC acceptance criteria for the MS/MSD from being met. If an interference from gold is suspected, the method of standard additions may aid in determining that gold is amalgamating mercury and causing reduced recovery of the MS/MSD.

The laboratory is responsible for controlling gold interference that may be the result of laboratory contamination. EPA Method 1631 recommends that care be taken to prevent gold contamination of samples by protecting gold traps from free halogens or overheating, and replacing the traps or gold air filters if they are degrading.

## What if high concentrations of organic matter are present ?

A symptom of an interference caused by a sample containing a high concentration of organic matter is that the sample may foam when purged. If this indication of an organic interference is encountered, purge a fresh charge of reagent water in the bubbler for at least 10 minutes and discard the water.

One technique for overcoming an organic interference is by diluting a smaller sample aliquot with reagent water. If necessary to measure at a compliance level, a large volume of this diluted aliquot can be used. Sections 11.1.1.1 and 11.1.1.2 of Method 1631 also recommend that samples containing high concentrations of organic matter, such as biota, be oxidized with additional BrCl in order to release mercury that may be bound to, or complexed with, the organic materials.

Method 1631, Sections 3.1 and 11.1 suggests that recovery of mercury bound within microbial cells may require increased BrCl, elevated temperatures, or the additional step of photo-oxidation with ultra-violet (UV) light. Specific procedures for using the techniques are provided in response to the question below. An attachment to a comment on the proposal of Method 1631 gave an example in which a laboratory determined that an increased amount of BrCl and heat could be used successfully to oxidize organic matter present in a particular effluent.

As of the date of this Guidance, EPA is not aware of matrices for which Method 1631 procedures or these additional oxidation techniques have not been sufficient for overcoming organic interferences, and for this reason, EPA does not have data which indicate levels of organic matter that may exceed the capability of Method 1631. It is important to remember that if additional reagents, heat, or photo-oxidation are used for complete oxidation of samples, the corresponding quality control samples and the initial demonstration of capability (IPR and MDL) tests also should include the additional amounts of reagents, heat, or photo-oxidation.

## What are the specific procedures for use of additional BrCl or UV photo-oxidation ?

Section 11.1.1.1 of Method 1631 states that the amount of BrCl added to a clear or filtered 100-mL sample is 0.5 mL (see Section 7.6 of Method 1631 for details of the BrCl solution) and the amount added to a brown or turbid sample is 1.0 mL. Section 11.1.1.2 of Method 1631 suggests addition of up to 5 mL of BrCl solution for highly organic samples. This additional solution is added to a 100-mL sample in the sample bottle (see Method 11.1.1 of Method 1631). If necessary, more BrCl can be added. A commenter on this Guidance warns that a high concentration of BrCl in the bubbler can ruin the soda lime and gold traps and show up as a matrix interference itself. For this reason, it is important to make sure that all BrCl is reduced prior to purging (if possible). If this is not possible, then an analytical spike should be performed to show that the system is free from interference (see Section 11.2 of Method 1631). Because the sample is thoroughly purged during the purge-and-trap step, the additional volume associated with the BrCl should have no effect on purge efficiency.

During photo-oxidation, samples are placed in quartz or thin-walled fluoropolymer bottles and then placed in a UV-oxidation chamber for 6 to 8 hours. Following oxidation, the samples are allowed to cool to room temperature prior to analysis. Samples containing significant particulate matter may be periodically shaken, or the chamber placed on an orbital shaker, to keep the particles in the photon flux. Alternatively, samples in quartz bottles containing a fluoropolymer stirring bar are placed adjacent to a high-intensity (>100 $\mu$watt/cm$^2$) UV lamp and oxidized for a minimum of 2 hours until oxidation is complete. Oxidation is considered complete for samples in which a yellow color remains following photo-oxidation, but disappears with the addition of the hydroxylamine hydrolchloride ($NH_2OH{\cdot}HCl$). If however, the yellow

color disappears during photo-oxidation, additional BrCl should be added, and the sample returned to the UV-oxidation chamber. Complete oxidation can also be assessed using starch iodide indicating paper to test for residual free oxidizer (Method 1631, Section 11.1.2).

Again, if additional reagents or UV photo-oxidation are used for complete oxidation of samples, the corresponding quality control samples and the IPR and MDL tests also should include the additional amounts of reagents or UV photo-oxidation steps.

## Can the non-homogeneity of a sample containing high solids result in failure of the MS/MSD ?

If the MS/MSD RPD for a high-solids matrix does not meet the RPD performance criterion, there may be a problem with sample preparation or homogenization. Section 11.1.1 of Method 1631 requires thorough shaking to homogenize the sample. As of the date of this Guidance, we have not had reports that high solids have presented a problem in meeting the MS/MSD precision and recovery.

## How can I demonstrate that my inability to meet the QC acceptance criteria for the MS/MSD is attributable to a matrix interference rather than a laboratory performance deficiency ?

The initial precision and recovery (IPR), ongoing precision and recovery (OPR), blank, matrix spike and matrix spike duplicate (MS/MSD), and quality control sample (QCS) tests in Section 9 of Method 1631 allow separation of these variables. In general, if the blank and IPR/OPR tests are failed, there is a laboratory performance deficiency, and the laboratory is responsible for identifying and correcting the deficiency and repeating the blank and IPR/OPR tests (Method 1631, Section 9.2). If results for the blank and IPR/OPR tests are within the QC acceptance criteria, and the relative percent difference (RPD) QC acceptance criterion for the MS/MSD test is failed, the problem is likely attributable to a sample that is insufficiently homogenized or to imprecise aliquotting or spiking of the MS/MSD. In this case, the laboratory should evaluate the cause, correct the problem, and re-spike the MS/MSD. If the RPD for the MS/MSD remains above the QC acceptance criterion, the laboratory should run a duplicate OPR to assure that precision is being controlled. If the RPD for the duplicate OPR is within the QC acceptance criterion for the MS/MSD, the laboratory should dilute the sample in successive factors of 2 to determine if a matrix interference is causing the imprecision.

If the blank, IPR, OPR, and MS/MSD precision are within their respective QC acceptance criteria and the MS and MSD recoveries are not, a matrix interference is present, and the matrix interference needs to be overcome. If the matrix interference cannot be overcome, results of associated samples may not be reported or used for permitting or regulatory compliance purposes (Section 9.3.4.1).

If all suggestions given in EPA Method 1631 and this Guidance are unsuccessful in overcoming the interference, the discharger/permittee should submit the following information to the regulatory/control authority to demonstrate that regulatory relief may be appropriate:

- MDL, IPR, and blank data demonstrating that the laboratory can perform Method 1631
- Field, equipment, and reagent blank data demonstrating that the sampling and analysis systems are free from contamination at the levels required for reliable determination of mercury. Such blank data should be associated with the sample under evaluation.

- MS/MSD data demonstrating that a potential matrix interference exists because the recoveries and precision are not within the QC acceptance criteria of the Method
- Confirmation of the out-of-specification MS/MSD recovery by a second laboratory
- Steps taken to attempt to mitigate the interference (e.g., dilution; addition of a greater amount of BrCl; addition of $NH_2OH{\cdot}HCl$; use of UV photo-oxidation; etc.)

Once these data are received by the regulatory/control authority, the authority may make a determination that Method 1631 indeed does not produce reliable results for the measurement of mercury in that test sample matrix and that regulatory relief may be appropriate. An example of possible relief that is used in other EPA methods, is to dilute the sample with reagent water until the QC acceptance criteria are met. In cases where dilution results in an increased MDL/ML level, compliance would be evaluated at the least dilute level at which the QC acceptance criteria could be met. EPA would provide assistance to the regulatory/control authority, upon request, to assist in this determination in the event that the regulatory/control authority does not have the technical expertise to make the determination.

## Shouldn't EPA allow regulatory relief when a matrix interference is demonstrated ?

Method 1631 is performance-based. This means the laboratory is permitted to modify the Method to overcome interferences or lower the cost of measurement provided that all performance criteria are met. EPA supports solutions for overcoming matrix interference problems so that mercury can be measured at levels that could have an adverse effect on human health and the environment.

EPA believes that an automatic allowance for matrix effects is inappropriate and would provide a disincentive for addressing interferences that may be overcome easily using the procedures recommended in Method 1631. EPA has also provided suggestions in *Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring* (EPA 821-B-93-001) and in this Guidance to aid dischargers and laboratories in overcoming matrix interference problems. We also believe that a given discharger is most familiar with its wastewater and can find solutions to matrix interference problems. Some examples for overcoming interferences were submitted to EPA in attachments to comments on Method 1631 proposal and were discussed earlier as techniques for overcoming iodide and organic interferences.

A site-specific or facility-specific allowance may be warranted after all efforts to remove interferences have been exhausted, and should be handled on a case-by-case basis by the regulatory/control authority. See the response to the preceding question, the questions below, and the FAQs for further information on what may be appropriate regulatory relief when a matrix interference has been demonstrated and all attempts at overcoming this interference have been made.

## How can I expect Method 1631 to perform in the presence of matrix interferences ?

Statements of the performance of Method 1631 are estimates based on EPA's evaluation in various Method 1631 performance studies using reagent water, fresh water, marine water, and wastewater matrices. Section 1.5 of Method 1631 states: "The detection limit and minimum level of quantitation in this Method usually are dependent on the level of interferences rather than instrumental limitations." We believe most interferences can be overcome by procedures recommended in the Method and in this Guidance, however, it is possible that the Method may not achieve these performance characteristics in every sample matrix.

The Method 1631 MDL was determined to be 0.2 ng/L when no interferences are present. Therefore, the MDL and ML should be treated as "presumptive" performance characteristics, and may vary depending on

the presence of an interference and on the measurement concentration of interest. The 40 CFR 136, appendix B procedures for determining MDL state that a sample may be used for determining the MDL if the analyte level does not exceed 10 times the MDL of the analyte in reagent water. The variance of the analytical method changes as the analyte concentration increases from the MDL, hence the MDL determined under these circumstances may not truly reflect method variance.

## What permit relief is there if I cannot achieve the MDL and ML in my matrix ?

EPA suggests that the discharger/permittee attempt to achieve the MDL and ML stated in Section 1.5 of Method 1631, in the presence of matrix interferences, using the interference-reducing procedures in EPA's *Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring* (EPA 821-B-93-001) and contained in Method 1631 and this Guidance. These procedures include use of a higher BrCl level, dilution, heat, UV photo-oxidation, extra caution in sample handling, the method of standard additions, and the interference-reducing procedures given in Section 4.4 of the Method. Use of a larger sample volume may also be particularly useful when the MDL in Method 1631 cannot be achieved, because the concentration of Hg will be moved higher into the analytical range and away from the increased error that occurs in the region of the MDL. We are aware of laboratories that use sample volumes as large as 1000 mL, 10 times larger than the sample volume specified in Method 1631. If a larger volume is used, the instrument would need to be calibrated at this larger volume, all performance tests (IPR, Blank, OPR, MS/MSD) performed at this larger volume, and all QC acceptance criteria met. This approach also may be of use to dischargers and regulatory authorities as EPA and States develop policies for interim permitting and total maximum daily loads (TMDLs) for mercury in ambient waters and other applications of ambient WQC for mercury.

Use of a gold wire to remove mercury selectively and the use of oxidation also have been suggested for determining an MDL in the sample matrix with high mercury concentration. However, EPA cautions that mercury in environmental samples can be complexed with colloids and unavailable for amalgamation with gold. Releasing the mercury using BrCl oxidation followed by reduction with $SnCl_2$ would modify the matrix, thereby defeating the purpose of the gold wire.

When a discharger/permittee demonstrates that a different MDL/ML is appropriate for its effluent matrix based on the statement in Section 1.5 of Method 1631 and the MDL procedure in 40 CFR 136, appendix B, it is possible that a permit could specify a different detection or quantitation level. If the discharger/ permit applicant demonstrates that Method 1631 cannot achieve the presumptive detection and quantitation limits on an effluent-specific basis, the discharger/permittee and regulatory/control authority could work cooperatively to establish a higher reporting threshold using a procedure such as that given at 40 CFR 132, appendix F, Procedure 8 and to establish an alternative ML using the procedures for developing an interim ML as in EPA's draft *National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-based Effluent Limitations Set Below Analytical Detection/Quantitation Levels* (available from the EPA Sample Control Center). EPA recommends that such procedures be applied by dischargers/permittees and regulatory/control authorities when such interferences are demonstrated in the measurement of mercury generally.

The regulatory authority should take into account the procedures used to attempt to achieve the Method 1631 MDL in allowing establishment of a higher reporting threshold based on an inability to achieve the MDL and ML in Method 1631. In other words, EPA expects a discharger to make all reasonable attempts to reduce any interference problems before seeking approval of a higher MDL and ML.

# Chapter 4: Flexibility in EPA Method 1631

This chapter discusses the flexibility inherent in EPA Method 1631 and the process of demonstrating equivalent performance when the Method is modified. This discussion is summarized from Method 1631 and from *Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring* (EPA 821-B-93-001).

## Is there flexibility in Method 1631 ?

Yes. Method 1631 is "performance-based." This means you may modify the Method provided you demonstrate that your modification achieves performance equivalent or superior to the performance of Method 1631. See the FAQ "How can I demonstrate equivalent or superior performance for a method modification?" for details.

## What types of modifications may I make to Method 1631 ?

The typical changes that would make it easier for you to practice the Method without compromising performance or safety are allowed. For example, change of a beaker to an Erlenmeyer flask or change of a round purge vessel to a cylinder would be allowed, after a demonstration of equivalency, because they would not be expected to adversely affect method performance. Changes that would adversely affect performance or safety are not allowed. (Refer to Section 9.1.2 of Method 1631, excerpted below). Any modification to the Method beyond those expressly permitted, is considered a major modification and is subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

If the modification is to be permanent in the laboratory and the performance of the analytical system could be adversely affected by interferents (e.g., a change in the design of the gold traps or a change in the detector), the effect of interferents on the performance of the system should be evaluated.

As stated in Section 9.1.2 of Method 1631, the purpose of allowing changes to the Method is to improve Method performance or lower the cost of measurements. Section 9.1.2 states:

> In recognition of advances that are occurring in analytical technology, the laboratory is permitted certain options to improve results or lower the cost of measurements. These options include automation of the dual-amalgamation system, single-trap amalgamation (Reference 18), direct electronic data acquisition, calibration using gas-phase elemental Hg standards, changes in the bubbler design (including substitution of a flow-injection system), or changes in the detector (i.e., CVAAS) when less sensitivity is acceptable or desired. Changes in the principle of the determinative technique, such as the use of colorimetry, are not allowed. If an analytical technique other than the CVAFS technique specified in this Method is used, that technique must have a specificity for mercury equal to or better than the specificity of the technique in this Method.

You are also required to maintain records of modifications made to the Method, including the reason for the modification and results of quality control tests. Minimum requirements for these records are detailed in Method 1631, Section 9.1.2.2.

## How can I demonstrate equivalent or superior performance for a modification ?

You can demonstrate equivalent or superior performance by showing that results produced by your modification are equal or superior to results produced by the unmodified Method. The performance of a modified method is measured by precision and recovery (bias), and can be extended to include detection limit as well as other measures of method performance. You must perform the method detection limit (MDL) and initial precision and recovery (IPR) tests prior to practicing Method 1631. These tests are described in detail in Section 9 of the Method. If you modify the method, you must use those modifications when performing IPR studies, and you must repeat the MDL test using the modifications. Your modification is permitted if all QC acceptance criteria are met, including calibration, blank, MS/MSD, and QCS tests, as well as the IPR and MDL tests.

## May I eliminate one of the gold traps specified in Method 1631 ?

Yes, provided that you repeat the IPR, blank, and MS/MSD tests and meet the QC acceptance criteria in the Method. If the MDL will be affected by elimination of the trap, you must also achieve an MDL less than or equal to one-third the regulatory compliance level. See Section 9.1.2 and Section 9.1.2.1 in Method 1631 for details of the demonstration.

Although Method 1631 allows you to perform analyses without both of the gold traps, the reason for using both gold traps are (1) to preclude water from reaching the atomic fluorescence detector, and (2) to sharpen the mercury peak so that low levels of mercury can be measured reliably. EPA strongly cautions that elimination of one or both of these traps may not allow the Method precision, recovery, and detection limit to be achieved.

## Section 9.1.2 of the Method allows use of flow injection. We encountered a problem with flow injection when we analyzed an effluent containing high concentrations of organic materials. Can a flow injection system continue to be used for this effluent ?

The flow injection system can continue to be used provided that (1) you have performed the initial precision and recovery (IPR) test and met the QC acceptance criteria with the flow injection system as an integral part of the analytical system (Section 9.2 of Method 1631), (2) you have demonstrated that the MDL achieved with the flow injection system as an integral part of the analytical system is less than or equal to one-third the regulatory compliance level or less than or equal to the MDL of the Method, whichever is greater (Sections 9.1.2.2 and 9.2), (3) you have recalibrated the instrument if the change affected calibration (Section 9.1.2.2), and (4) you have assessed the performance of the Method on the sample matrix using the MS/MSD test in Section 9.3 of Method 1631 and have met the QC acceptance criteria for this test.

The MS/MSD test is most critical for this assessment. If the presence of organic or biological materials affects recovery or precision of the MS/MSD to the point at which the QC acceptance criteria cannot be met, the flow injection system cannot be used on that sample. If the QC acceptance criteria are met, use of the flow injection system is acceptable.

### Method 1631 states that a cold vapor atomic adsorption spectrometry (CVAAS) detector can be used. Can I achieve the Method detection and quantitation limits using CVAAS ?

No, the detection and quantitation limits specified in Method 1631 cannot be achieved using CVAAS. The allowance for use of CVAAS in Method 1631 (Section 9.1.2) was in response to requests from commenters on the proposal of the Method. Some commenters claimed that detection limits on the order of 1 - 3 ng/L could be achieved using CVAAS. If a CVAAS detector is used, Method 1631 states that you must demonstrate that an MDL less than or equal to one-third the regulatory compliance level or less than or equal to the Method MDL, whichever is greater, can be achieved (Method 1631, Section 9.1.2.1).

### Section 9.3.4.1 states that few interferences have been encountered with Method 1631. Would you expect this statement to be true when CVAAS is used ?

Although we would expect it to be true, we have not thoroughly investigated the issue. If matrix interference problems are encountered in the use of CVAAS that would not be encountered with use of cold-vapor atomic fluorescence spectrometry (CVAFS), CVAAS would not be considered equivalent to CVAFS and CVAFS would be required.

### What is the status of EPA Method 245.7 "Determination of Ultra-trace Level (ng Hg/L) Total Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry" and can it be used ?

We currently believe that EPA Method 245.7 is capable of reliably analyzing for mercury in water at levels as low as 1 - 3 ng/L and are evaluating EPA Method 245.7 for inclusion in the test methods at 40 CFR part 136. Until this evaluation is complete, EPA Method 245.7 is not approved for use in EPA's Clean Water Act programs. However, a discharger may seek approval for use of EPA Method 245.7 under the alternate test procedure (ATP) program at 40 CFR 136.4 and 136.5 or may negotiate its use in new permits if the permitting/control authority is willing to allow it.

# Chapter 5: Frequently Asked Questions (FAQs) Concerning EPA Method 1631

The questions below are those that we have been asked most frequently or those that have caused uncertainty in how the Method is to be used. Following proposal of Method 1631 and associated notices, commenters raised more than 100 questions and issues concerning the Method. We included written comments and our responses in the Water Docket to support the final rule. We urge dischargers/ generators/industrial users, regulatory/control authorities, laboratories, and others that have questions concerning Method 1631 to review the comments and responses in the administrative record at the Water Docket. Chapter 7, *Where to Get Additional Help*, provides contact information for the Water Docket.

## General Questions

### When should I use Method 1631 to measure mercury ?

If a method is not specified in your NPDES permit, you should use the Method when it is necessary to measure mercury concentrations in the range of 0.5 to 100 ng/L. Method 1631 can be used for measurements above this 100 ng/L range by dilution of the sample, but use of one of the other methods approved at 40 CFR part 136 may be more cost effective.

### Is use of Method 1631 required ?

If Method 1631 is specifically required by the NPDES permit, then it must be used for all compliance monitoring activities.

EPA regulations (Part 122 and Part 136) require use of Part 136 methods in the NPDES program, and in general, any of the methods approved for use at 40 CFR part 136 for determination of mercury concentrations may be used under EPA's Clean Water Act programs. Where there are two or more methods in Part 136 for a pollutant (as is the case for mercury), the regulations do not specify that the most sensitive method automatically be used. Instead, EPA expects that permitting authorities would use their best professional judgment to choose the most appropriate method for the situation. For example, if a permit writer needed to choose a method to monitor compliance with an effluent limit, the method should be adequate "to assure compliance with permit limitations" according to 40 CFR 122.44(i)(1). Accordingly, if permit limitations require a permittee to achieve very low concentrations of a pollutant, the permitting authority should require the specific sample collection techniques and analytical methods that would produce sufficiently precise results to assess compliance with that limit. When an effluent limitation is specified in a permit at higher levels, other less sensitive test methods could be incorporated and still assure that measurements are representative of that monitored activity and adequate to assess compliance.

The Agency developed EPA Method 1631 to enable reliable measurement of water samples at the levels established in water quality criteria. Consequently, EPA expects that when the measurement sensitivity of EPA Method 1631 is necessary to assess and implement effluent limitations that are at or near the water quality criteria values, Method 1631 will be used. If and when other methods for measuring mercury are promulgated in Part 136 or approved under the procedures at 136.3 that are also capable of measuring at these levels, the permitting authority would have the discretion to determine which method is most appropriate under the circumstances. (Please note that EPA recognizes that some States may need to

follow State procedures to adopt changes to Part 136 before they can require use of a newly promulgated method and allows States a reasonable time to accomplish this. See 40 CFR 123.62(e).

### How rigorously must Method 1631 be followed ?

You must follow the Method rigorously. However, you are allowed to modify the Method under the performance-based allowances provided that you perform the equivalency demonstration and meet the QC acceptance criteria for the performance tests. See Chapter 4, Flexibility in EPA Method 1631, for guidance in making method modifications.

### Do you have analytical methods for determining elemental mercury ($Hg^0$) and methyl mercury ($CH_3Hg$) ?

We have drafted procedures for each of these forms of mercury but have not proposed these procedures for general use. For a copy of these draft procedures, please contact the EPA Sample Control Center at the address or phone number given in Chapter 6, Sources of Information.

### Is Method 1631 for total mercury or for dissolved and total recoverable mercury ?

Method 1631 is for determination of "total," "total recoverable," or "dissolved" mercury. Confusion continues over use of the terms “total” and “total recoverable.” For determinations of mercury using Method 1631, and for other EPA methods for determination of metals, the terms "total" and "total recoverable" are synonymous. For total/total recoverable measurements, the sample is not filtered prior sample processing. Therefore, if a "total" or "total recoverable" mercury concentration is reported, you should understand that the result represents the determined concentration of mercury in the combined dissolved and suspended fractions of the sample.

The “dissolved” measurement applies to total/total recoverable mercury that exists in the filtrate of a sample that has been passed through a 0.45 micron filter. (See EPA Method 1669 for a discussion of the details of a filter and for sampling for dissolved mercury.)

## Sampling Questions (also refer to Chapter 2, which discusses the use of clean techniques)

### Should samples in which dissolved mercury is to be determined be filtered in the field or in the laboratory ?

To preclude interchange of mercury between the dissolved and suspended forms, you should filter samples for dissolved mercury in the field at the time of collection (40 CFR 136.3, Table II, footnote 7). Because field filtration increases the risk of contamination, the field sampling team should be trained in the sampling techniques that will preclude contamination at the levels required to be measured. The use of inline filtration, described in Method 1669, can reduce contamination resulting from sample filtration and the associated increased sample handling. A reviewer of this Guidance suggests that it may be better to ship the sample to the laboratory and filter the sample before preservation and within 24 hours of collection under controlled conditions. Samples may be filtered in the laboratory prior to preservation if they are collected in fluoropolymer or glass bottles, filled to the top with no head space, capped tightly, and maintained at 0-4°C until preservation (Method 1631, Section 8.5). Filtered and unfiltered samples must be preserved within 48 hours after sample collection.

## Does Method 1631 allow use of continuous versus grab sampling ?

Section 8.3 of Method 1631 suggests use of the procedures found in EPA Method 1669 (the *Sampling Guidance*). EPA Method 1669 gives four procedures for sampling. Continuous (composite) sampling is not among these procedures. However, in tests performed at the Hampton Roads Sanitary District in Virginia, and in other locations, researchers have been able to construct continuous sampling systems that control contamination below levels that would compromise reliable measurement of mercury.

The NPDES program regulations at 40 CFR 122 require collection of a 24-hour composite sample, but also recognize that composite sampling may be waived for any outfall for which the applicant demonstrates that the use of an automatic sampler is infeasible and that the minimum of 4 grab samples will be a representative sample of the effluent being discharged (see 40 CFR 122.21(g)(7)). The Pretreatment regulations at 40 CFR part 403 contain similar requirements.

To date, we have not collected a sufficient amount of data to demonstrate that composite sampling systems can collect mercury samples that are free of contamination and that do not lose mercury via volatilization. For this reason, EPA strongly suggests that samples for mercury be collected using one of the four sampling procedures given in Section 8.2 of Method 1669. If a composite measurement is needed, four (or more) samples (as required by the regulations or in the permit) should be collected. These samples should be composited in the laboratory or, alternatively, the grab samples may be analyzed individually, and the results mathematically composited.

## Can plastic containers other than fluoropolymer be used for collection of samples for mercury ?

Not at present. Mercury has been shown to diffuse in and out of polyethylene and polypropylene containers. If another type of plastic container can be found that would not result in a loss or gain of mercury to the sample, EPA would consider allowing such a container under the ATP program.

## Is borosilicate glass (Section 6.1) really OK ? The sampling method does not allow glass for mercury; only fluoropolymer.

Sections 4.2.2.3.1 and 6.3 of the *Sampling Guidance* (EPA Method 1669) explicitly allow for use of glass for mercury. Only the earliest drafts (before April 1995) of the guidance would have precluded the use of glass. It has also been suggested that flint glass bottles may be acceptable, if properly cleaned. EPA currently has no data to support use of sample bottles other than fluoropolymer or borosilicate glass.

## Can I digest samples in polyethylene or polypropylene vessels ?

You must collect, preserve and store samples in a fluoropolymer or borosilicate glass bottle (Section 8.2). A polyethylene or polypropylene sample bottle must not be used because Hg may diffuse in or out of the bottle during transport or storage. However, you may use polyethylene or another material for sample digestion provided the digestion vessel is demonstrated to be free of contamination, and you repeat the initial demonstration of method performance in Section 9.2 and meet the QC acceptance criteria for the performance tests.

**The sampling procedures in the Method and in the *Sampling Guidance* are not explicit in stating the exact steps that are required for sample collection. Can you provide further guidance in this area ?**

As stated in Chapter 2 of this document, the *Sampling Guidance* (Method 1669) provides guidance for site-specific determination of what techniques are necessary to collect water samples for reliable measurement of mercury. The exact procedures required are dependent on the level of mercury expected in the sample and on the degree of potential contamination. However, to assist dischargers and others that need to make mercury measurements in the low- to sub-ppt range, Frontier Geosciences Inc. has developed a standard operating procedure (SOP) for sampling that it provides to its customers. This SOP has been modified to be consistent with the requirements in EPA Methods 1631 and 1669 and is presented in Appendix A to this guidance. This procedure should be viewed as containing the minimum steps necessary for reliable sampling, and some of the additional measures in the *Sampling Guidance* may be necessary to preclude contamination at some sampling sites.

The Virginia Department of Environmental Quality (VA-DEQ) has also developed an SOP for sampling water titled *Collection of Freshwater, Saltwaters, and Wastewaters for the Determination of Trace Elements* (Revision #: 20001105, December 7, 2000). This SOP is currently available from VA-DEQ, 629 E. Main Street, Richmond, VA 23219, attn: Roger Stewart, or call 804-698-4449.

In addition to the *Sampling Guidance* and these SOPs, we recommend that persons conducting sampling for mercury be trained in the "Clean Hands/Dirty Hands" sampling technique. We also recommend a demonstration of proficiency by sampling personnel prior to collection of a sample for regulatory compliance, consisting of collection of field and equipment blanks to show that samples will not be contaminated. Field audits also could be performed to ensure that proper sample collection procedures are being followed.

EPA has conducted trace metals workshops that have provided "hands-on" training for this purpose. In addition, EPA and State agencies are sponsoring training workshops titled *Mercury Collection and Analysis in Ambient and Effluent Waters Using EPA Method 1631*. The workshops will be held throughout the year 2001 in various EPA Region V states and at EPA's Annual Conference on the Analysis of Pollutants in the Environment on May 8-10, 2001 in Portsmouth, VA.

**Must I preserve samples in the field ?**

Samples may be shipped to the laboratory unpreserved if they are (1) collected in fluoropolymer or glass bottles, (2) filled to the top with no head space, (3) capped tightly, and (4) maintained at 0 - 4 °C from the time of collection until preservation. The samples must be acid-preserved within 48 hours after sampling. Otherwise, samples must be preserved in the field. (See Section 8.5 of Method 1631.) Samples for dissolved mercury must be filtered upon collection and prior to preservation. The acid used for preservation must be demonstrated to be free of mercury at levels that would compromise reliable measurement of mercury.

**Early versions of Method 1631 allowed a holding time of 6 months. Why was it changed ?**

The holding time was changed because the holding time table (Table II) at 40 CFR 136.3(e) specified a holding time of 28 days for mercury. Commenters on the proposal of Method 1631 pointed out the conflict between the holding time in the Method and in Table II. We searched for holding time data that would support

6 months and could not find data that would support the longer holding time. Therefore, the holding time of 28 days in Table II was required in Revision B of Method 1631, which was promulgated on June 8, 1999.

### Why is it necessary to test the pH of samples to ensure that they have been properly preserved, as stated in Section 8.2 of the Method ? Oxidation with BrCl is more important than preservation, and ensures that the samples will be at pH <2.

The purpose of determining the pH is to verify that samples were preserved in the field, thereby confirming the 48-hour holding time prior to preservation has not been exceeded.

### Is placing a serial number on each sample bottle a good idea ?

Yes, placing a serial number on each sample bottle and on each piece of apparatus used in the analysis is a good idea. That way, if a sample containing a high concentration of mercury is encountered, the sample bottle and other pieces of apparatus that the sample touched can be readily identified and decontaminated without contaminating the remainder of the apparatus or laboratory. In addition, serial numbers can be used to identify samples that are associated with any equipment that has been determined to be contaminated. The best means for serializing sample bottles and each piece of apparatus is engraving prior to cleaning. EPA cautions that indelible inks may contain mercury and contaminate the sample.

### Why is a sample preservation temperature of 0 °C specified ? This temperature may cause an aqueous sample to freeze and a glass sample bottle to break.

The preservation temperature specified is 0 - 4 °C. Water can exist in both liquid and solid phases at 0 °C. The purpose of allowing 0 °C is to allow samples to be partially frozen so that the heat capacity of ice can be used to extend the shipping time, if desired. See the SOP in Appendix A for additional details

### Is there really a need to refrigerate samples ?

The original draft of Method 1631 contained the requirement to cool samples to 1-4°C from the time of collection until preservation. Recognizing that it would be near impossible to maintain a sample temperature in this range during shipment, EPA wrote the requirement as 0-4°C. Until data demonstrate that refrigeration is not necessary, unpreserved samples must be maintained at 0-4°C.

Please note that this requirement is from the time of collection until preservation. If samples are collected and preserved in the field, refrigeration is not required for shipment or subsequent storage at the laboratory.

### Can you offer any other helpful tips on sampling ?

- Do not use sample containers that have not been demonstrated to be clean (See Section 4.3.7 of Method 1631 and Section 4.2.2.3 of EPA Method 1669).
- Either do not sample when it's raining or prevent rainwater from falling into the sampling container.
- Face upstream and upwind (See Section 8.2.2 of EPA Method 1669).
- Avoid all sources of potential contamination including improperly cleaned equipment, atmospheric inputs, and human contact.
- Do not breathe into the sample bottle if you have mercury amalgam fillings in your teeth (See Section 4.2 of Method 1631 and Section 4.1.2 of EPA Method 1669).

- Do not sample under or near a bridge or other metal structure. Metals particles can slough off of the structure and contaminate the sample (See Section 4.1.2 of EPA Method 1669).
- Do not sample when the wind could blow metal, debris, or dust particles into the sample bottle (See Section 4.3.8.4 of Method 1631 and Section 4.2.2.4.4 of EPA Method 1669).
- In general, the more blank samples that are collected and analyzed, the better the assessment of whether or not contamination has occurred. Method 1631 includes the minimum requirements for field and equipment blanks when collecting samples for mercury analysis at water quality criteria concentration levels.
- Train the sampling team in the use of the sampling techniques in EPA Methods 1631 and 1669.
- Put on more than one pair of gloves and strip off or change gloves frequently.

Blanks Questions (also refer to Chapter 2, which discusses the use of clean techniques)

**Is the bubbler blank the same as a laboratory (method) blank (i.e., does it cover the entire system) ? Also, what about field blanks and equipment blanks ?**

The bubbler blank is not the same as a method blank in that it does not include a fresh aliquot of the reagents. Method 1631, Section 9.4.1 states that bubbler blanks are analyzed to demonstrate freedom from system contamination. Bubbler blanks are analyzed immediately after analyzing a sample by placing a clean gold trap on the bubbler and purging the water in the bubbler a second time.

Field and equipment blanks are used to demonstrate freedom from contamination in the sampling equipment and sample collection techniques. Use of field and equipment blanks is addressed in Sections 9.4.3 and 9.4.4 of Method 1631, in Sections 9.3 and 9.4 of the *Sampling Guidance* (EPA Method 1669), and in Chapter 2 of this guidance.

Definitions for various blanks are as follows:

Bubbler Blank - A Bubbler Blank (see Section 9.4.1 of Method 1631) is used to demonstrate freedom from system contamination. At least three bubbler blanks must be run per analytical batch by placing a clean gold trap on the bubbler immediately following analysis of a sample, and analyzing the sample a second time.

Field Blank - A Field Blank (see Section 9.4 of EPA Sampling Method 1669) is generated by filling a large carboy or other appropriate container with reagent water in the laboratory, transporting the filled container to the sampling site, processing the reagent water through each of the sample processing steps and equipment (e.g., tubing, sampling devices, filters, etc.) that will be used for sample collection, collecting the reagent water in a sample bottle, and shipping the sample bottle to the laboratory for analysis in accordance with Method 1631. Field blanks are used to identify contamination from the sampling equipment, from sampling, and from transporting the sample to the laboratory.

Equipment Blank - A Bottle Blank or Sampler Check Blank (see Section 9.4.4 of Method 1631). Equipment blanks are used to identify contamination from sample bottles and the sampling equipment.

> Bottle Blank (see Section 9.4.4.1 of Method 1631) - A Bottle Blank is generated by filling a sample bottle with reagent water acidified to pH <2, capping the bottle, allowing the bottle to stand for a minimum of 24 hours, and the analyzing the water.

Sampler Check Blank (see Section 9.4.4.2 of Method 1631) - A Sampler Check Blank is generated at the laboratory or equipment cleaning facility by filling a large carboy or other container with reagent water, processing the reagent water through the sampling equipment using the same procedures that will be used in the field, and collecting and analyzing the water.

Reagent Blank - A Reagent Blank (see Section 9.4.2 of Method 1631) is generated by adding aliquots of BrCl, $NH_2OH$, and $SnCl_2$ to previously purged reagent water in the bubbler and analyzing the reagent water. Reagent blanks are used to identify contamination from the reagents.

Method Blank (Laboratory Blank) - An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, and reagents that are used with samples. The laboratory blank is used to determine if analytes or interferences are present in the laboratory environment, the reagents, or the apparatus. Method blanks are not required in EPA Method 1631; however, we strongly suggest that the laboratory run at least one method blank with each batch of samples.

## What is the required frequency for field blanks ?

Method 1631 requires that a minimum of 1 field blank accompany each set of samples collected at a given site (i.e., sampling point) at the same time, to a maximum of 10 samples. If one sample is collected at a given site at a given time, a minimum of one field blank must be collected for that sample; if one sample is collected at a given site at two different times, a minimum of one field blank must be collected for each of the two samples; if a sample is collected at two different sites at the same time, a minimum of one field blank must be collected for each of the two samples.

## How are field blanks collected if the sample is collected from a closed plumbing system ?

Collection of the field blank should simulate, as closely as possible, collection of the sample. For example, if a sample from a closed plumbing system is collected by opening a valve in the system, the field blank should be collected by pouring the reagent water carried to the field into a sample bottle adjacent to the sampling valve. In this way, any mercury in the atmosphere at the valve that could contaminate a sample would contaminate the field blank.

## Is it necessary to run a sampler check blank (Section 9.4.4.2) on each piece of sampling equipment that will be used in the field ?

All sampling equipment (bottles, tubing, dipper, transfer vessel, etc.) that will contact the sample in the field must be checked for contamination. Each piece may be tested individually or in combination as a whole sampling apparatus. You may test a representative number of the bottles and tubing as described in Section 9.4.4.3 of Method 1631. If a representative number of bottles and tubing are shown to be clean, the lot of bottles cleaned at the same time using the same procedure are assumed to be clean.

## Can I subtract field or equipment blank results from results for samples ?

If blank correction is requested or required, you may subtract the results from field or equipment blanks (but not both) provided that the results for the blanks meet the requirements in Section 9.4 of Method 1631. If the result from a field or equipment blank is subtracted, you may not additionally subtract the reagent blank result because the reagents also are used for the determination of mercury in the field and/or equipment blanks; i.e., subtraction of one blank only, among the reagent blank, field blank, or equipment

blank is allowed. The laboratory must also report results for the sample and the reagent, field, and equipment blanks separately so that the data user can judge the appropriateness of blank subtraction, if blank subtraction was performed. Again, results for all blanks must meet the specifications in Section 9.4 of Method 1631 before blank subtraction may be performed. If results for all blanks meet the respective specifications, the choice of which blank to subtract is at the discretion of the discharger/permittee and its laboratory.

### Can we use field blank correction ? (Section 12.4.2 of Method 1631 does not specifically state that it is allowed.)

Even though Method 1631, Revision B specifically addresses correction of test sample results for reagent blanks, silence on field blanks does not mean that field blank correction is precluded. The preamble to the final rule promulgating Method 1631B states: "There is no prohibition against reporting blank-subtracted results, provided, of course that results for blanks and samples are reported separately" (64 FR 30427).

EPA is planning to promulgate Method 1631, Revision C during June 2001 to clarify that field blank results must be reported separately and that field blank correction must be performed if requested or required by a regulatory authority or in a permit.

### Can I apply blank correction when multiple blanks are collected for a particular type of blank, as detailed in Section 9.4.3.3 of Method 1631 ?

Section 9.4.3.3 allows subtraction of the average concentration of multiple field blanks (a minimum of three). This subtraction may be performed for either the reagent, the field, or the equipment blank samples, provided that results for the blanks and samples also are reported separately and all the blanks being averaged are of the same type.

### How should we interpret results from the analyses of field blanks ?

Section 9.4.3.2 of Method 1631 states that if Hg or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML, or greater than one-fifth the level in the associated sample, whichever is greater, results for associated samples may be the result of contamination and may not be reported or otherwise used for regulatory compliance purposes.

The criteria for field blanks in Method 1631, Section 9.3.4.2 and the table provided in this Guidance in response to “What quality control tests are required by Method 1631 and what performance criteria must be met?,” can be interpreted to mean that a blank containing Hg just below the ML of 0.5 ng/L is acceptable for a sample result in the range of 1-5 times the ML (0.5-2.5 ng/L). This interpretation is not intended. Section 12.4.1 of EPA Method 1631 requires reporting of results for Hg in field blanks to the level of the MDL (0.2 ng/L). If a sample result is in the range of 1-2.5 ng/L and the field blank is less than the MDL, the concentration is likely not the result of contamination because the level in the blank is less than one-fifth the level in the sample. If the sample result is in the range of 0.5 ng/L, it would be prudent to analyze a larger sample volume (200-1000 mL) or to make measurements to a lower MDL to demonstrate that the concentration of Hg in the blank is less than one-fifth the concentration in the sample.

**Are field sample results void when field and equipment blanks do not meet the requirements in Section 9.4, in the same way that they are void when results for reagent blanks do not meet these requirements ?**

Generally speaking, yes. Sample results must not be allowed to be compromised by contaminated blanks. Samples that are associated with field or equipment blanks not meeting the requirements in Section 9.4 may not be reported or otherwise used for permitting or regulatory compliance purposes. However, field sample results that are associated with contaminated blanks, but also are still below the regulatory compliance threshold, may be used to demonstrate permit compliance. Please refer to EPA's *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring*, referenced in Chapter 6 of this Guidance.

**We have found that a minimum of triplicate reagent blanks are needed daily for reliable low-level mercury measurements. Can multiple blanks be used ?**

Nothing in Method 1631 precludes a laboratory from exceeding the QC requirements in the Method, and EPA applauds such actions. Therefore, a greater number of blanks, replicates, and spikes than required by the Method may be used. However, Method 1631 also requires that results of all blanks and samples be reported separately, unless otherwise requested or required by a regulatory authority or a permit.

Quality Control Questions

## What quality control (QC) tests are required by Method 1631 and what performance criteria must be met ?

Method 1631 requires the following QC tests and performance criteria:

| Test | Spike Amount | Minimum Frequency | Criteria |
|---|---|---|---|
| Method Detection Limit (MDL) | Follow 40 CFR 136, Appendix B | Initial demonstration | 0.2 ng/L or one-third the regulatory compliance limit, whichever is greater |
| Initial Precision and Recovery (IPR) | 5 ng/L | Initial demonstration 4 replicates | Average percent recovery = 79 - 121<br>Relative standard deviation 21% |
| Matrix Spike/Matrix Spike Duplicate (MS/MSD) | Compliance limit or 1-5x background, whichever is greater | 10% from a given sampling site or discharge | Percent recovery = 71 - 125<br>Relative Percent Difference 24 |
| Bubbler Blanks | NA | 1 after each OPR<br>At least 3 per batch | Each bubbler blank 50 pg<br>Mean of 3 bubbler blanks < 25 pg<br>Standard deviation of 3 < 10 pg |
| Reagent Blanks | NA | Each new batch of reagents, and in triplicate each month | 25 pg |
| Field Blanks | NA | 10% from same site at same time | < 0.5 ng/L or one-fifth Hg in associated sample(s), whichever is greater |
| Bottle Blanks | NA | 1 per cleaning batch | < 0.5 ng/L or one-fifth Hg in associated sample(s), whichever is greater |
| Sampler Check Blank | NA | 1 following each cleaning | < 0.5 ng/L or one-fifth Hg in associated sample(s), whichever is greater |
| Ongoing Precision and Recovery (OPR) | 5 ng/L | Prior to and after analysis of each analytical batch | Percent recovery = 77 - 123 |
| Quality Control Sample (QCS) | Within calibration range | 1 per batch | No specification; follow specification provided by supplier |

The type, frequency and criteria of the QC samples presented in the above table are the minimum required by Method 1631. Laboratories may wish to increase the level of QC to ensure reliable measurements of mercury. An increase in QC may be desirable, for instance, for commercial laboratories conducting a large number of low level analyses. For example, such laboratories may want to analyze one or more reagent blanks each day that low level mercury analyses are conducted rather than perform the minimum requirement of verification in triplicate each month.

## Can the QC be adjusted for measurements at high levels ?

The IPR, OPR, and blank levels are fixed in Method 1631 to allow measurement of mercury at low- and sub- ng/L levels. When Method 1631 was developed, we did not consider that laboratories would desire to make measurements in the 10 to 100 ng/L range only. Therefore, we specified IPR and OPR spiking levels at 5.0 ng/L, and did not allow higher levels of mercury in blanks, that would be consistent with higher levels of Hg in samples. Currently, the levels specified in the Method must be used and the QC criteria met to address these levels.

We want to caution that mixing use of Method 1631 at low and high levels establishes a system that can be confusing to analysts and would be more susceptible to mistakes than a system dedicated to low-level measurements because allowing blank contamination to a level of 0.2 ng/L is vastly different than allowing contamination to 10 ng/L.

## How do QC requirements differ as applied to an analytical batch and to a specific discharge ?

Requirements for batch- and discharge-specific QC are different, but overlap.

### *Batch-specific QC*

Batch-specific QC is required to demonstrate the analytical process is in control during the 12-hour shift in which samples, blanks, and standards will be analyzed. An “analytical batch” is defined in the Glossary at the end of Method 1631 as: “... up to 20 samples that are oxidized with the same batch of reagents and analyzed during the same 12-hour shift. Each analytical batch must also include at least three bubbler blanks, an OPR, and a QCS. If only 1 sample is analyzed, the batch size is 1; if 20 samples are analyzed, the batch size is 20. In addition, MS/MSD samples must be prepared at a frequency of 10% per analytical batch (one MS/MSD for every 10 samples).”

### *Discharge-specific QC*

Discharge-specific QC is required to assure the method is continuously applicable to a specific discharge. Method 1631, Section 9.3 states “...the laboratory must spike, in duplicate, a minimum of 10% from a given sampling site or, if for compliance monitoring, form a given discharge.” The definition of “discharge” is synonymous with "matrix type," or wastewater stream in a given industrial subcategory. (Industrial subcategories are defined in the wastewater regulations at 40 CFR parts 400-699.) "Matrix type" or “discharge” means a sample medium with common characteristics across a given industrial subcategory. Examples include: C-stage effluents from chlorine bleach mills in the Pulp, Paper, and Paperboard industrial category; effluents from the continuous casting subcategory of the Iron and Steel industrial category; publicly owned treatment work (POTW) sludges; and effluents being discharged to POTWs from plants in the Atlantic and Gulf Coast Hand-shucked Oyster Processing subcategory.

Discharge-specific QC is applicable on the basis of matrix type and is intended for routine monitoring of the same discharge. For example, if a commercial laboratory were analyzing C-stage effluents from several chlorine bleach mills in the Pulp, Paper, and Paperboard industrial category, it would be necessary to analyze an MS/MSD from any one of the C-stage effluents only. The reason that a single MS/MSD pair can be used to represent a particular wastewater stream is that a given wastewater stream from the same process can be expected to have the same characteristics. Analysis of a discharge must have an MS/MSD

performed on the 1st, 11th, 21st, etc. sample (or more frequently) to demonstrate that the nature of the discharge has not changed.

For application of discharge-specific QC, consider the following example: A laboratory receives two samples of different matrices, each from one of two clients. Client A's regulatory compliance limit is 12 ng/L and Client B's is 5 ng/L. Both samples have a background concentration of 2 ng/L of mercury.. Which sample must be spiked at what level ? If neither matrix has had an MS/MSD performed before, the MS/MSD must be performed on both. If either matrix has not had an MS/MSD performed within the last 10 samples, the MS/MSD must be performed for this matrix. Method 1631 Sections 9.3.1.1 and 9.3.1.2 require that the concentration be at the regulatory compliance limit, at 1-5 times the background concentration of mercury in the sample, or at 1-5 times the ML in Method 1631 (i.e, 0.5 - 2.5 ng/L), whichever is greater. (See also the response to the question "What spiking levels are required for the MS/MSD in a given batch?") For this example, the MS/MSD spike for Client A would be 12 ng/L, the regulatory compliance limit. For Client B, the spike would be in the range of 5 ng/L (regulatory compliance limit) -10 ng/L (5 times the background concentration).

We recognize that the discharge-specific QC can be troublesome for commercial laboratories that may not know that the sample is from a particular discharge, the regulatory compliance limit for the industrial subcategory, or the last time that an MS/MSD was performed. Therefore, it would be prudent for laboratories to obtain extra sample for the MS/MSD to meet the frequency requirement of 10 percent (1 in 10 samples). However, it is the discharger's responsibility to make sure that the requirements in EPA Method 1631 are followed, that all QC is performed, and that all QC acceptance criteria are met. It is advisable for a discharger to inform the laboratory of the particular matrix and the discharge-specific QC requirements so that the QC requirements in Method 1631 can be met.

## How do we combine batch-specific and matrix-specific QC requirements ?

EPA recognizes the possibility that requiring MS/MSD pairs to represent an analytical batch *and* a matrix type may force laboratories to analyze more than one MS/MSD pair per ten samples. Although it may not be possible to avoid this situation, EPA suggests the following tips to help mitigate the occurrence:

- Where possible, consider holding (and properly storing) samples to increase the analytical batch size relative to the QC frequency. This approach can be implemented only to the extent that sampling holding times and reporting thresholds are not compromised.
- Maintain control charts that track the frequency of MS/MSD pairs by batch and by matrix type. Because EPA allows any of the samples in an analytical batch to be used for MS/MSD purposes, laboratories that routinely analyze multiple matrix types can stagger MS/MSD analyses so that an MS/MSD pair for each matrix type is analyzed in different analytical batches. In determining which matrix should be spiked for a particular batch, the laboratory can consult the control chart and determine which matrix type needs to be spiked in order to stay within the 10% frequency.

To illustrate, let's consider the case of a laboratory planning to analyze 8 samples during a 12-hour shift. Four of these samples are POTW effluents, two are effluents from the Pulp, Paper, and Paperboard Industry, one is an effluent from the Iron and Steel Industry's continuous casting subcategory, and the remaining sample is ambient water collected from Lake Michigan. The laboratory consults its control chart and determines that it has analyzed only three POTW effluent samples since the last POTW effluent MS/MSD pair. In this case, the laboratory can analyze the four POTW samples without needing another MS/MSD pair. Similarly, the laboratory has analyzed only six pulp and paper effluent samples since its last MS/MSD pair for that matrix, so the two pulp and paper effluent samples do not require another

MS/MSD pair. The laboratory determines that nine effluents from the continuous casting subcategory were analyzed following the last MS/MSD pair for that discharge type, so an MS/MSD pair for one of the two samples scheduled could meet the 10% frequency. Similarly, the laboratory has analyzed 10 ambient water samples from Lake Michigan since it last performed an MS/MSD pair for that matrix type. In this situation, the laboratory has two matrix types that require MS/MSD analysis but fewer than ten samples. The laboratory consults it's scheduling log and determines that it is due to receive several more Lake Michigan samples during the week. Therefore, this laboratory can choose to properly store the Lake Michigan sample, and run the remaining seven samples during the current shift using one of the iron and steel effluents to analyze an MS/MSD sample pair.

### We operate a commercial laboratory that receives samples from multiple clients. What spiking levels are required for the MS/MSD in a given batch ?

The required MS/MSD spiking level is defined in Section 9 of the Method as follows:

> 9.3.1.1 If, as in compliance monitoring, the concentration of Hg in the sample is being checked against a regulatory compliance limit, the spiking level shall be at that limit or at 1–5 times the background concentration of the sample, whichever is greater.
>
> 9.3.1.2 If the concentration of Hg in a sample is not being checked against a limit, the spike shall be at 1–5 times the background concentration or at 1-5 times the ML in Table 2, whichever is greater.

The "background concentration" is the concentration of mercury in the unspiked sample. This concentration is determined by analysis of an aliquot of unspiked sample using the procedure in Section 11 of EPA Method 1631 (see Sections 9.3.2 and 11 of EPA Method 1631). Once the background concentration is determined, the MS and MSD are spiked in the range of 1-5 times this concentration and analyzed. You may accompany analysis of the MS/MSD with analysis of another aliquot of unspiked sample, if desired, so that all analyses are conducted at the same time in order to produce the most accurate results. Spiking requirements are also provided in response to the question "How do QC requirements differ as applied to an analytical batch and to a specific discharge ?

To minimize error in spiking, the volume of the spike should be minimized so that the volume of the sample plus spike is not appreciably greater than the volume of the unspiked sample (nominally 100 mL in Method 1631), although the purge-and-trap system is relatively insensitive to volume changes. Also, the concentration and volume of the spike should be known and measurable to within, ideally, less than one percent, so that the error associated with spiking is minimized. If there is doubt about the concentration and volume of the spiking solution, test the solution using reagent water to make sure that the MS/MSD recovery and precision can be achieved using the concentration and volume selected.

## Must we use the regulatory compliance limit as the spike level for both influents and effluents ?

If there is a regulatory compliance limit for both an influent and an effluent (an unlikely occurrence), the spike level must be appropriate to each matrix type. For the influent, the spike level must be at the regulatory compliance limit for the influent, provided that the regulatory compliance limit for the influent is greater than 1-5 times the background concentration of mercury in the sample. Otherwise, the spike level must be at 1-5 times the background concentration of mercury in the influent sample. Similarly, for the effluent, the spike level must be at the regulatory compliance limit for the effluent, provided that the regulatory compliance limit for the effluent is greater than 1-5 times the background concentration of mercury in the sample. Otherwise, the spike level must be at 1-5 times the background concentration of mercury in the effluent sample.

The specific level in the 1-5 range is dependent on the level at which the sample will be spiked. If the sample will be spiked at 2 times the background concentration of mercury, the regulatory compliance limit would need to be greater than 2 times the background concentration in order for the sample to be spiked at the regulatory compliance limit rather than at 2 times the background concentration.

## If two analytical batches of 20 or fewer samples are run in the same day, must there be a total of 6 bubbler blanks, 2 OPRs, and 2 QCSs ?

No, there must be 3 bubbler blanks, 2 OPRs (one at the beginning and one at the end) and a QCS associated with each batch, as required by Section 9.1.7 of the Method.

## What frequency is required for the OPR ?

The OPR must be run at the beginning and end of each batch of 20 or fewer samples. If there is only one sample in the batch, an OPR must be run before and after the sample. See Section 9.5.1 of Method 1631. The purpose of requiring an OPR before and after the batch is to assure that the analytical system remains in calibration during the period that samples are run. The OPR at the end of one batch of samples can serve as the OPR at the beginning of the following batch of samples, so long as the 12-hour shift for the batch (Method 1613B, Section 9.1.7) is not exceeded.

## Laboratories are not always in contact with sampling teams. Why should we have to communicate that sampling precision is inadequate, as stated in Section 9.7 of the Method?

Section 9.7 of the method states that the laboratory may be required to analyze field duplicates if needed for specific program requirements. It also states that, when these are analyzed, the relative percent difference (RPD) between field duplicates should be <20% and that the laboratory should notify the sampling team if the RPD exceeds 20%. The words "should" in Section 9.7 convey that the action is recommended and is not required. The reason for the suggestion to communicate inadequate sampling precision to the sampling team was to alert the team that samples were not being collected precisely. This would allow the team to study its collection activities and attempt to determine why duplicate samples either were not collected correctly or resulted in different levels of mercury.

Miscellaneous Questions

### How much should I be concerned about contamination from the bromine monochloride (BrCl) and other reagents ?

Method 1631 requires analysis of at least one reagent blank (with monthly verification in triplicate) for each new batch of reagents. The degree of concern is based on the level of mercury to be measured and on the amount of reagent required for complete oxidation. The amount of reagent used depends on the matrix being analyzed (for example, samples that are high in organic material may require additional BrCl). The way in which you can make sure that any reagent used in the analysis will not contaminate a sample is to test that reagent using the reagent blank procedure in Section 9.4.2 of Method 1631. We suggest that laboratories test the reagents daily. If a method blank is run with each batch, the method blank can serve this purpose (see the subsection on the method blank under the question "Is the bubbler blank the same as a laboratory (method) blank?")

### How safe is bromine monochloride ? It seems dangerous to us.

BrCl is dangerous, as are the hot acid vat and the acids suggested for use in labware cleaning in Method 1631. Precautions for handling these materials are given in Section 5.0 and Section 7.0 and are further noted in various sections throughout the Method. Laboratory personnel should be trained in safe handling of these reagents and materials. See Section 5.0 (Safety) in Method 1631.

### How do I know when enough BrCl has been added to an opaque sample ?

Method 1631 requires the addition of 0.5 mL BrCl solution to clear samples and 1.0 mL BrCl solution to brown or turbid samples. There are matrices, particularly those with high organic content, that may require additional BrCl, elevated temperatures, or photo-oxidation. Method 1631 requires addition of BrCl (or complete oxidation) until a yellow color persists or until starch iodide paper indicates the presence of residual BrCl oxidizer (see Section 11.1.1 of Method 1631).

### Method 1631 uses calibration factors and the relative standard deviation of calibration factors for establishing calibration linearity. Nearly all other metals methods use linear regression. Why is Method 1631 different ?

The calibration factor approach is the simplest form of weighted regression that we have been able to devise. It assumes that a straight line through the origin is most representative for most instruments and analytical systems. We have studied various approaches to calibration over the past several years and have worked with statisticians to resolve the proper means of establishing calibration. Nearly all statisticians and knowledgeable analytical chemists now agree that, for nearly all analytical systems and instruments, a weighted regression is the proper form. Recently, the International Union of Pure and Applied Chemistry (IUPAC) came to the same conclusion (see *Pure and Applied Chemistry* **70**, 993-1014 (1998)).

For Method 1631, laboratories in our inter-laboratory method validation study had little difficulty using the calibration factor approach or in meeting the relative standard deviation (RSD) criterion of 15 percent in the calibration factor approach. Therefore, the 15 percent criterion was retained in Method 1631.

Regarding the regression used in nearly all metals methods, this regression is unweighted; i.e., it assumes that the standard deviation is the same at all concentrations. An unweighted regression is incorrect for

nearly all instruments and analytical systems. Weighting should be inversely proportional to concentration for nearly all analytical systems and instruments as we and IUPAC have learned (pH would be an exception). Therefore, we have required use of the simplest form of weighted regression in Method 1631.

### Can we use the slope, intercept, and correlation coefficient method of calibrating and calculating results, provided that we demonstrate equivalency ?

As stated above, we have found that a weighted regression is most appropriate for analytical chemistry measurements, and that the calibration factor approach is the simplest form of weighted regression. Therefore, only a weighted regression would be considered equivalent to the CF approach. The slope, intercept, and correlation coefficient method traditionally used for metals measurements, and that uses an unweighted regression, may not be used.

Recently, EPA allowed use of a "linear calibration" for automated calculations in metals methods. This "linear calibration" can be used for automated calculations provided that the linear calibration is weighted.

### Why doesn't EPA make every effort to communicate its expectations on linear regression to manufacturers of instruments ?

The calibration factor and weighted linear regression approach to calibration have been in existence for more than 25 years and have been used in automated GC/MS data systems since that time. Therefore, instrument manufacturers have known about this approach for some time. EPA proposed Method 1631 in May of 1998 and published the final rule in June of 1999. The calibration factor approach was included in the proposal, giving instrument manufacturers more than a year to implement the calibration factor/ weighted regression approach.

EPA reviewed a study performed by Tekran, Inc., one of the manufacturers of instruments for determination of mercury using EPA Method 1631, that used both the calibration factor/weighted regression (CF/WR) and unweighted regression approaches. The calibration included a data point at the Method 1631 MDL (0.2 ng/L). The RSD for the CF/WR approach was 7.8 percent. The coefficient of determination ($r^2$) for the unweighted approach was 1.000, indicating no error in calibration. The reason for the indication of zero error is that the low calibration points are, essentially, unweighted. Therefore, the unweighted regression is equivalent to a single-point calibration at the highest calibration point. We do not believe that this form of calibration is consistent with the best science.

### Why doesn't EPA require dilution when the concentration in a sample is greater than 90 percent of the linear dynamic range (LDR), as with some other EPA metals methods ?

The LDR for Method 1631 is to 100 ng/L. You may dilute the sample when 90 percent of the LDR is exceeded, if desired. The reason that we did not require dilution of the sample when this level is exceeded is that all of the laboratories in EPA's interlaboratory validation study of Method 1631 were able to demonstrate linearity to 100 ng/L.

### The highest ambient criterion for mercury is 12 ng/L. Why is calibration performed to 100 ng/L ?

The range of Method 1631 was established by the technology used. In initial tests it was found that the linear range extended to 100 ng/L. This range was verified in the interlaboratory validation study. If you chose to use a lesser range, you may dilute samples into the region of the ambient criterion. However, you must calibrate to 100 ng/L and demonstrate linearity to this level.

### Must our laboratory discard the secondary standard on the expiration date even if it is still within the control limits of Method 1631 ?

Yes. The secondary standard (typically 1.00 $\mu$g/mL Hg) must be discarded (Section 7.8 of the Method) . The reason is that there is error associated with testing the standard. If the results of testing show that the standard is barely within the high or low control limit, the results of sample analyses could be inaccurate. To preclude generation of waste containing mercury, the amount of the secondary standard prepared should be consistent with the amount that will be required during the life of the standard. Section 14.1 of Method 1631 states: "Standards should be prepared in volumes consistent with laboratory use to minimize the disposal of excess volumes of expired standards."

### Sections 7.9 and 7.10 state that the working standards "should" be replaced monthly. Does the word "should" imply that it is the laboratory's discretion ?

Yes. As defined in the Glossary at the end of Method 1631, "should" means that a given action, activity, or procedure is suggested, but not required. However, if it is later shown that a working standard held for more than one month was inaccurate, the intended objective of ensuring reliable measurements of mercury by Method 1631 would not have been met. It is the laboratory's responsibility to assure that measurements made are reliable.

### How expensive is it to set up Method 1631 ?

Depending on how many analyses are to be performed and whether new or used materials will be used for construction, costs can range from thousands to hundreds of thousands of dollars. The Clean Spaces Guidance can assist you in cost minimization. This document describes how costs to establish a trace metals laboratory at the University of California Santa Cruz were minimized to a few thousand dollars. For a complete, new, clean room for mercury analyses, we estimate the cost at approximately $150,000 and the costs for equipment and instrumentation at $50,000. If one or only a few samples are to be analyzed, the most cost-effective means is to contract through a laboratory routinely determining mercury at the levels required.

### What criteria should I use in selecting a laboratory ?

As with other analyses, selection should be based on the experience of the laboratory in making the particular measurement, the knowledge and skill of laboratory personnel with the particular technology, the quality assurance/quality control applied to the analysis, the documented history of performance of the laboratory in making the measurements, and to a lesser extent, the fee charge by the laboratory. For determination of mercury using Method 1631, particularly for making measurements at or near 1 ng/L, a documented history of freedom from contamination and recovery of OPRs and MS/MSDs within the QC acceptance criteria of Method 1631 provides an indication that the analyses are being performed reliably.

EPA believes that the laboratories that participated in the interlaboratory validation of Method 1631 are all capable of performing mercury determinations reliably. However, the user should review the performance of these and other laboratories in the context of the objectives of any study.

## What data can and cannot be reported for regulatory compliance purposes, and is it the laboratory or discharger's responsibility to make the determination ?

In general, only sample results that are associated with QC data that meet the QC requirements in Method 1631 may be reported or used for permitting or regulatory compliance purposes. See Sections 9.3.4.1, 9.3.4.2, 9.4.3.2, and 13.2 of Method 1631.

If the data are to be used for permitting or regulatory compliance under a permit, all data are the responsibility of the discharger/permittee. It is the laboratory's responsibility to make sure that all QC acceptance criteria are met. An exception would be if a matrix interference could not be overcome and precluded the MS/MSD recovery and precision criteria from being met. See the chapter on **Matrix Interferences** in this guidance for the action to be taken when a matrix interference is encountered.

In addition, a laboratory cannot be responsible for activities over which it has no control. If a discharger collects samples and a field blank, and the field blank is contaminated, it is the discharger's responsibility. If, however, a reagent or laboratory blank is contaminated and the associated field blank is contaminated, it is possible that the laboratory contaminated the field blank. In this case, the contaminated field blank would be the laboratory's responsibility. Regardless of whose responsibility it is, the result for a sample associated with a contaminated field blank generally may not be reported or otherwise used for permitting or regulatory compliance purposes (see Section 9.4.3.2 of Method 1631), unless the contamination has no negative effect on the objective of the monitoring program. For example, sample results that are associated with contaminated field blanks, but also are still below the regulatory compliance threshold, may be used to demonstrate permit compliance. Additional guidance concerning the possible use of data associated with certain types of QC failures is provided in *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring*, which is referenced in Chapter 6 of this document.

## Are reporting requirements in Section 12.4 of Method 1631 the laboratory's responsibility or the discharger's ?

For permitting or regulatory compliance purposes, the reporting requirements are the responsibility of the discharger/permittee. However, the discharger/permittee can only report results as reliable as those produced by the laboratory. In addition, the laboratory is closest to the analysis and, therefore, most familiar with the data being reported to the discharger/permittee. To the extent possible, the laboratory should provide data to the discharger/permittee that will satisfy the requirements in Section 12.4 and the permit.

## Can laboratories report results below the ML for field samples ?

Yes. There is nothing in Method 1631 that precludes laboratories from reporting results in ways different from those specified in Section 12.4, provided that the results are also reported as specified in Section 12.4. Section 12.4 requires that laboratories report results below the ML as <0.5 ng/L or as required by the regulatory authority or in the permit. However, if a regulatory/control authority or the permit requires reporting of results without censoring at the ML or MDL (i.e., at as low a level as possible), the result must be reported without censoring.

# Chapter 6: Sources of Information

This section provides sources of information related to the final guidelines establishing test procedures for measurement of mercury in water. Specifically, this section provides a listing of documents pertaining to the regulatory background and data gathering for EPA Method 1631.

## Regulatory Background

**Act**

Clean Water Act (CWA) - Public Law 92-500, et. seq.; 33 U.S.C. 1251 et. seq.

**Analytical methods under CWA Sections 301, 304, and 501**

History: see *Federal Register*, February 7, 1991 (56 FR 5090)
Support for effluent guidelines: see *Federal Register*, October 18, 1995 (60 FR 53988).
Proposal of Method 1631: See *Federal Register*, May 26, 1998 (64 FR 28867).
Promulgation of Method 1631, Revision B: See *Federal Register*, June 8, 1999 (64 FR 30417)

## Data Gathering for EPA Method 1631

**Proposal**

See *Federal Register*, May 26, 1998 (64 FR 28867)
See the administrative record in the Water Docket (Docket W-98-15) for reports supporting the proposal of Method 1631.

**Notice of data availability (NODA)**

See *Federal Register*, March 5, 1999 (64 FR 10596)

**Data received from commenters**

See the administrative record in the Water Docket (Docket W-98-15) for the final rule

**Final rule**

See *Federal Register*, June 8, 1999 (64 FR 30417)
See the administrative record in the Water Docket (Docket W-98-15) for reports supporting the promulgation of Method 1631, Revision B.

## Documents Supporting EPA Method 1631

- Bloom, Nicolas, Draft *Total Mercury in Aqueous Media*, Frontier Geosciences, Inc., September 7, 1994.
- Method 1669: *Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels*, EPA 821-R-96-011, July 1996
- *Sampling Ambient and Effluent Waters for Trace Metals*, EPA-821-V-97-001, 1997
- *Results of the EPA Method 1631 Interlaboratory Validation Study*, Available from the EPA Sample Control Center

- *Guidance on Establishing Trace Metal Clean Rooms in Existing Facilities* ("Clean Spaces Guidance"), EPA-821-B-96-001, April 1995
- Trace Metal Cleanroom, RTI/6302/04-02 F, Research Triangle Institute, October 1995.
- *An Analytical Survey of Nine POTWs from the Great Lakes Basin*, Draft Report, US EPA Office of Science and Technology, Analytical Methods Staff, December 15, 1994
- *Evaluating Field Techniques for Collecting Effluent Samples for Trace Metals Analysis*, EPA 821-R-98-008, June 1998
- *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for Clean Water Act Compliance Monitoring*, EPA 821B-96-004, July 1996

See also the references at the end of EPA Method 1631

## Documents on Compliance Monitoring and Methods

*Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring*, EPA-821-B-93-00, June 1993.

## Source for Documents

The documents listed in this guidance may be viewed at or obtained from the Water Docket (see the address below). Nearly all documents are also available from the EPA Sample Control Center:

EPA Sample Control Center
DynCorp I&ET
6101 Stevenson Avenue

Alexandria, VA 22304-3540
Tel: (703) 461-2100
Fax: (703) 461-8056
E-mail: SCC@DynCorp.com

EPA Water Docket
Waterside Mall
401 M Street,
Southwest
Washington, DC
Tel: (202) 260-3027

# Chapter 7: Where to Get Additional Help

This section lists reference locations and EPA contacts that may provide additional information related to the final guidelines establishing test procedures for measurement of mercury using EPA Method 1631.

## EPA contact for questions specifically related to Method 1631

Maria Gomez-Taylor
Engineering and Analysis Division (4303)
U.S. EPA
Ariel Rios Building
1200 Pennsylvania Avenue, N.W.
Washington, DC 20460
Tel: (202) 260-1639
Fax: (202) 260-7185
E-Mail: gomez-taylor.maria@epa.gov

## Water Docket

The administrative record (public comments, EPA responses, and all supporting documents for Method 1631, including those listed below) are available for review at the Water Docket. For access to docket materials, phone the Water Docket between 9:00 a.m. and 3:30 p.m. for an appointment. The address below is for the physical location of the Water Docket and is not a mailing address. For the EPA mailing address, see the address for the EPA contact above.

EPA Water Docket
Waterside Mall
401 M Street, Southwest
Washington, DC
Tel: (202) 260-3027

## Websites

EPA's home page on the World Wide Web: **http://www.epa.gov**

EPA's Office of Science and Technology's analytical methods and water documents pages on the World Wide Web:

**http://www.epa.gov/OST/Methods** (water methods)
**http://www.epa.gov/ost/guide** (water documents)

# APPENDIX A
# Standard Operating Procedure for Collection of Ambient Water and Wastewater Samples for Determination of Mercury Using EPA Method 1631 [1]

*Note*: This procedure should be viewed as containing the minimum steps necessary for reliable sampling. Some of the additional measures in the *Sampling Guidance* (EPA Method 1669) may be necessary to preclude contamination at some sampling sites. EPA Methods 1631 and 1669 are referenced throughout this SOP. Advice on training, equipment, and sampling technique is also available from laboratories analyzing samples using EPA Method 1631.

## 1.0 Scope and Application

**1.1** This standard operating procedure (SOP) gives details for collection of grab samples of ambient water and wastewater for the determination of low-level mercury. Adherence to this SOP can be expected to minimize contamination from the sample bottle and external sources.

**1.2** This SOP is for collection of a grab sample directly into the sample bottle (e.g., effluents, rapidly flowing streams/rivers) (Method 1669, Section 8.2.5). If transfer containers (e.g., dippers) or other equipment (sampling pumps, etc.) are required to obtain samples, including composite samples, refer to EPA Method 1669 for detailed guidance.

## 2.0 Sample bottle requirements

**2.1** Sample bottles may be either fluoropolymer that has been cleaned, tested, and double bagged in a Class-100 clean bench (Method 1631, Section 6.1.2.1 and Method 1669, Section 6.3), or borosilicate glass with fluoropolymer-lined lids obtained from a supplier that certifies cleanliness for metals sampling (e.g., I-Chem, Series 200 or equivalent). If sample bottles are from a bottle lot, a statistically relevant number of bottles in the lot should be tested to demonstrate freedom from contamination at levels that could compromise results (Method 1613B, Section 9.4.4.1). Untested sample bottles must not be used as they may be the source of possible contamination (Method 1613B, Section 9.4.4.1).

**2.2** Sample bottles may also be obtained in kit form from the laboratory. A kit would consist of double-bagged sample bottles, reagent water for the field blank(s), gloves, and ice. Blue Ice may be obtained from the laboratory or locally; wet ice should be obtained locally.

## 3.0 Sample collection

**3.1** Collection of samples is performed using the "clean hands-dirty hands" technique (Method 1669, Section 2.4). Bottles are sealed tightly and re-bagged using the opposite series of steps as were used to open them. Samples are either preserved immediately upon collection, or bottles are shipped to the analytical laboratory via overnight courier for preservation and analysis.

**3.2** Ideally, at least two persons each wearing fresh cleanroom gloves (Method 1631, Section 4.3.6 and Method 1669, Section 4.2.2.2) are required on a sampling crew. Cleanroom gloves should be worn at all times when handling samples or sampling equipment.

**3.3** One person (designated "dirty hands") removes a bagged bottle from the box or cooler, and opens the outer bag, avoiding touching the inside surface of that bag.

**3.4** The other person (designated "clean hands") reaches in, opens the inner bag, and removes the sample bottle. "Clean hands" should not touch anything but the outside surface of the sample bottle and cap, and the water being sampled. If anything other than the sample bottle, cap, or water is touched, "clean hands" must change gloves.

[1] This Standard Operating Procedure is based on a procedure provided by Frontier Geosciences, Inc.

**3.5** "Clean hands" opens the sample bottle and holds the bottle in one hand and the cap in the other. If it is necessary to set the cap down, it should be placed in the inner bag from which the sample bottle was removed.

*Note:* The person collecting the sample should be wary of disturbing the flow upstream of the sampling point. The insertion of the bottle into a flowing stream, or standing in the flow downstream of the sampling point, creates eddies (disturbances in the upstream flow) that can re-suspend solids near the sampling point. Entry of such re-suspended solids into the sample may produce a non-representative sample and could increase the mercury concentration.

**3.6** Rinse the sample bottle and inside surface of the cap three times with sample water, and fill the bottle to the top with sample (Method 1669, Section 8.2.5.5). Replace the cap and tighten securely.

*Note:* If the person collecting the sample cannot directly reach the water to be sampled, a pole-type sampler may be attached to the sample bottle to extend the reach for sample collection. The pole and bottle clamp should be made of plastic and/or stainless steel and the mouth of the bottle should be held facing upstream of the pole. The use of a transfer vessel should be avoided.

**3.7** Re-bag the bottle in the opposite order that it was removed.

**3.8** Cleanroom gloves should be changed between samples and whenever anything not known to be trace metal clean is touched.

**4.0 Collection of field blanks**

**4.1** EPA Method 1631 requires collection of a field blank with every 10 samples from a given site (Method 1631, Section 9.4.3.1). A sample bottle for the field blank should be requested from the laboratory when the sampling kit is requested (Section 2.2 of this SOP). A separate sample bottle as well as a bottle filled with reagent water are used to collect the field blank.

**4.2** To collect the field blank, open an empty sample bottle using the "clean hands-dirty hands" techniques described above. Also open the bottle containing the reagent water.

**4.3** Pour the reagent water into the empty sample bottle. This is now the field blank.

**4.4** Re-bag the field blank in the opposite order that it was removed.

**5.0 Preservation, packing, refrigeration, and shipment of samples**

**5.1** Following collection, samples must either be preserved (Method 1631, Section 8.5) or may be shipped unpreserved if they are (1) collected in glass or fluoropolymer bottles, (2) filled to the top with no head space, (3) capped tightly, and (4) maintained at 0–4°C from the time of collection until preservation. The samples must be acid-preserved within 48 h after sampling (Method 1631, Section 8.5.1).

**5.2** Pack sample bottles upright to prevent the area around the bottle cap from becoming wet. Wrap glass sample bottles with bubble-type packing to prevent breakage during shipment.

**5.3** Blue Ice or wet ice may be used to refrigerate sample bottles. The Blue Ice must be frozen prior to sampling. If the sample in a glass sample bottle is cooled to 0 °C prior to shipment and packed in frozen blue ice, the sample may freeze and rupture the bottle. Wet ice avoids this problem but increases the potential for mercury contamination because the sample bottle may become immersed in water from the melting ice. Packaging the wet ice in multiple plastic bags will preclude water from melted ice from reaching the sample bottle.