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Guidelines for Mercury Measurements Using the Ontario Hydro Method

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PRODUCT DESCRIPTION

The Clean Air Mercury Rule (CAMR) requires measurement of mercury emissions from coal-fired power plants. The rule requires that all coal-fired power plants emitting >29 lb of mercury per year install continuous mercury measurement technology. Either a continuous mercury monitor (CMM) or sorbent traps meeting the requirements of 40 Code of Federal Regulations (CFR) Part 75, Appendix K, protocols must be used. To ensure the technologies are operating properly, CAMR also requires that a relative accuracy test audit (RATA) be completed initially for CMMs to certify the monitor and then annually thereafter. For the sorbent traps, an annual RATA is also required. Currently, the only reference methods allowed by the U.S. Environmental Protection Agency (EPA) are ASTM International (ASTM) D6784-02—the Ontario Hydro (OH) method—and EPA Method 29. Both wet-chemistry-based methods require a high level of quality assurance/quality control to obtain data that will meet CAMR requirements. This document provides guidance on using the OH method.

Results & Findings

An overview of the OH method is provided as well as detailed information on techniques used by leading researchers in this area to improve mercury emission data quality. Also included are checklists for the OH method that should improve the likelihood of obtaining the required number of valid data sets.

A project-planning section is provided to help in designing a measurement program with the appropriate test procedures, test durations, and quality control in place. Issues such as pretest preparations, field sampling protocols, and sample analysis, including selecting and managing analytical laboratories, are addressed.

Challenges & Objective(s)

Mercury emission measurement is one of the most difficult and challenging monitoring tasks faced by plant operators today. The concentration of mercury in flue gas is extremely low, and measurement problems are exacerbated by the multiple forms and reactivity of mercury. The objective of this report is to produce mercury measurement guidelines based on experience using the OH method in numerous mercury-sampling and control research programs.

Applications, Values & Use

Mercury monitoring techniques are not as well developed as those for SO_2 and NO_x. To meet the challenges of mercury monitoring as well as CAMR requirements, this report primarily addresses compliance-level measurements that would be used to prove a plant is meeting a mercury emission limit or to establish emission measurements for trading purposes. This information will also facilitate development of effective mercury-monitoring programs.

EPRI Perspective

The intent of this report is to help power plants as well as stack testers employ the OH method and minimize sampling and analytical issues and errors, thus improving the overall quality of mercury measurements and results. While the OH method is very detailed and prescriptive, there are a number of possible differences in both the sampling and analytical approach. There is also significant debate as to the level of quality assurance/quality control necessary to minimize issues in order to obtain “good” results. The guidance provided in this document represents the viewpoints of one organization that has been active in the development, evaluation, and implementation of the OH method. EPRI did seek to obtain feedback from a number of stack testing organizations, but with no success.

Approach

The authors of this report have a broad background in the field of mercury measurement. They have been instrumental in developing and evaluating mercury measurement techniques since the mid 1980s. This report represents the current state of knowledge on conducting accurate mercury measurements in the field using the OH method.

Keywords

Mercury Measurements
Mercury Analysis Techniques
Ontario Hydro Method

ABSTRACT

In March 2005, the U.S. Environmental Protection Agency (EPA) finalized the Clean Air Mercury Rule (CAMR) imposing mercury emission limits for coal-fired power plants. An important aspect of CAMR is measuring and reporting mercury emissions. By January 1, 2009, it will be required that utilities begin continuous monitoring of mercury emissions. Currently, the only reference methods for conducting the required relative accuracy test audits (RATAs) are the Ontario Hydro method (ASTM International D6784-02) and EPA Method 29. These methods are very complex and require a very high level of quality assurance/quality control. This document captures the "lore" of mercury measurement (sampling and analysis) learned and exercised by experts in this field and describes how to implement these techniques. It is designed to provide guidance for conducting the OH method so that it will be reasonably possible to obtain valid RATA data.

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INTRODUCTION AND BACKGROUND

The objective of this report is to provide an overview of ASTM International (ASTM) D6784-02, “Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources [Ontario Hydro (OH) Method]” and to provide specific recommendations for field and laboratory approaches that will improve the quality and reliability of the measurements. This report addresses the need for OH method mercury measurements to be performed in a high-quality fashion. It is not the intent of this document to simply restate what is written as to procedures as are outlined in ASTM D6784-02 but instead to detail QA/QC procedures that have been developed since the inception of the method and to provide guidance checklists for conducting a RATA. First and foremost, it is important to read the method and the sampling requirements under CAMR and fully understand the procedures.

Also included in this report are sampling and analytical procedural checklists that can be used to help obtain high-quality data (Appendix A).

Brief History of Mercury Measurement and the OH Method

Two general types of mercury measurement methods exist: manual methods and analyzer-based methods. Manual samples are captured in a batch mode (either wet-chemistry or dry sorbent sampling) from flue gases and then recovered in the field and submitted to a laboratory for analysis. Analyzer-based methods provide real- or semi-real-time data on-site. The full sampling and analytical system is located at the test unit, and results are available immediately or within minutes of sampling. Wet-chemistry manual methods have the longest history of measurement, while dry sampling methods have been in use since the early 1990s, and analyzer methods have been in development since the early 1990s, recently more rapidly with promulgation of CAMR.

Over the past decade, both manual and instrumental measurement methods have evolved, with data uses including estimation of anthropogenic mercury emissions, identification of atmospheric transport processes, deposition studies, assessing human health impacts and bioaccumulation, compliance demonstration, research and development on alternative measurement methods, and evaluation of mercury control technologies. The selection of a measurement method for a given application depends on the goals, timing, detection levels required, data type (speciated or total mercury), and flue gas matrix requirements. If power plant owners are making mercury control strategic decisions based on faulty data or if compliance is not met because mercury measurements are not made correctly, the consequences can be severe.

The basic wet-chemistry-based flue gas mercury methods that have long been utilized and accepted by the U.S. Environmental Protection Agency (EPA), Methods 29 and 101A, have been used for regulatory compliance when required by state or local agencies. The OH method, the focus of this guidance document, was developed and validated in the early 1990s to obtain accurate mercury speciation data from coal combustion flue gases in an isokinetic manner. In 2000, the method was accepted as ASTM D6784-02. The OH method was required by EPA for the Information Collection Request and, as such, was applied in 1999–2000 to 83 coal-fired units nationwide. This effort resulted in many more test companies and field and laboratory personnel becoming trained in the method, but did not always result in the highest-quality data. Issues of cleanliness, proper sampling and field procedures, sample recovery and storage, and laboratory analytical steps remain problematic when inexperienced personnel undertake the measurements. Even experienced personnel, when procedures are not well-established to prevent it, can cut corners and compromise the outcome of these measurements.

Overview of the OH Method

Unlike other wet-chemistry mercury measurement methods such as EPA Methods 29 and 101A, the OH method was designed to speciate mercury (elemental, oxidized, and particulate-bound mercury). It is, therefore, a complex method requiring an eight-bottle sample train and three different adsorbing solutions. To do the method successfully requires a high level of experience and quality control. A schematic of the OH sample train is shown in Figure 1-1.

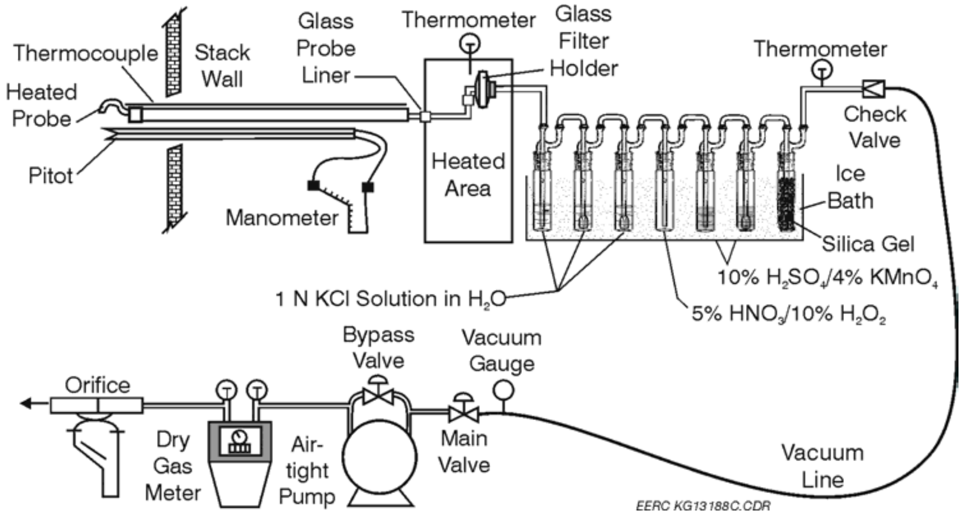

Figure 1-1
Schematic of the OH Mercury Speciation Method Sample Train

The OH method, using cold-vapor atomic absorption technology for analyzing the solution, has a stated lower limit of quantification of 0.5 µg/Nm^3. However, a study conducted by Ryan and Keeney *(1)* showed that measurements of <0.5 µg/Nm^3 can be achieved if low mercury calibration standards are used. At this low level, the method loses accuracy and precision. In addition, at very low mercury concentrations, achieving adequate blank samples may be difficult or impossible. The exact detection limit of the method has never been statistically determined.

Regulatory Environment

In March 2005, EPA finalized the Clean Air Mercury Rule (CAMR) imposing mercury emission limits for coal-fired power plants. In the CAMR, published in the Federal Register (40 CFR Part 60 and Part 75) in April 2005, EPA establishes standards limiting mercury emissions from new and existing utilities. This rule, under Section 111 of the Clean Air Act, created a market based "cap-and-trade" program that would reduce nationwide utility emissions of mercury in two distinct phases. In the first phase, due by 2010, total mercury emissions would be reduced from coal-fired boilers from 48 tons/yr to 38 tons/yr primarily by taking advantage of additional SO_2 and NO_x emission controls that will be required under a separate rule, the Clear Air Interstate Rule (CAIR). The second phase, to be in place by January 1, 2018, will require additional mercury reductions to limit emissions to 15 tons/yr. As part of CAMR, each state is to submit a plan to meet or exceed these requirements by November 17, 2006. A number of states have indicated that they will be requiring a higher level of control than that required by CAMR.

CAMR also provides specific requirements for measuring mercury emissions. This becomes critical as CAMR is a program jointly administered by participating states and EPA that would allocate to each state specified amounts of emission allowances for mercury, which essentially caps mercury emissions. The states would allocate those allowances to utilities. A utility must hold sufficient allowances to cover its emissions each year, so the limited number of allowances ensures that the required reductions are achieved. Utilities may sell or bank their excess emission allowances, providing an incentive to reduce mercury emissions.

In addition to requiring mercury reductions, CAMR requires every individual stack from coal-fired facilities >25 MW and generating >29 lb Hg/yr to monitor mercury on a continuous basis. This can be done in one of two ways. The first is to install a continuous mercury monitor (CMM); the second is to use sorbent traps as detailed in 40 CFR Part 75, Appendix K. Monitoring of mercury must begin by January 1, 2009. As part of the initial and ongoing certification of the CMMs and sorbent traps, relative accuracy test audits (RATAs) must be conducted. For CMMs a RATA must be performed initially as part of the certification process and then annually thereafter. If the sorbent traps are used, an initial RATA is not required, but annual RATAs must still be conducted. Although other methods including the use of sorbent traps are under review, currently, the only reference methods that can be used for the RATA are the OH method or EPA Method 29. Both methods are complex wet-chemistry methods and require a high degree of training and quality assurance/quality control (QA/QC). To successfully complete a RATA, it is required that nine valid paired OH or EPA Method 29 sample trains be obtained. A valid paired sample must have a relative difference of $\leq$ 10% if the mercury concentration is >1 $\mu g/m^3$ or 20% if the mercury concentration is $\leq$ 1 $\mu g/m^3$. Relative difference is calculated as the absolute difference between the paired samples divided by the sum of two samples. Because of the way CAMR is written, in most cases, 12 paired samples will be taken as part of the RATA (up to three data points can be discarded). RATA calculations are presented in Appendix B.

Definition of Measurement Purpose

It is assumed for purposes of this document that the OH method is being used as a reference method to conduct RATAs and potentially be used as a primary measurement method for low-mercury-emitting facilities (<29 lb/yr). It is critical that the sampling requirements for the RATA as detailed in CAMR be read and understood. If the method is being used for research purposes or to evaluate a mercury control technology, the overall sampling program and the QA/QC requirements could be somewhat different. However, the authors of this report believe that a high level of QA/QC is still required to obtain high quality data using the OH method. The checklists and the data quality objectives are still valid.

Sampling/Speciation Bias

As has been well-documented, gaseous mercury species in flue gases are capable of interacting with fly ash particles collected in the front half of the sampling train or on the particulate separation device (this is true of all mercury measurement methods). The fly ash can have two effects on the mercury being measured. The first is that the fly ash collected on the filter can adsorb mercury, resulting in high bias for particulate-bound mercury and subsequent low bias for the gas-phase mercury. The second effect is that the ash may catalyze the conversion of elemental mercury to oxidized mercury, resulting in a high bias for oxidized mercury. These biases can be identified by measuring the mercury on the ash collected by the electrostatic precipitator (ESP) or baghouse. Also, if measurements are made across the particulate control device, they become obvious.

In general, biases as a result of fly ash collecting on the filter are not a great concern when the OH method is being used as a reference method for conducting RATAs. First, CAMR only pertains to total vapor-phase mercury. Therefore, mercury speciation and particulate-bound mercury are not relevant to the measurement. Second, these measurements are made after the particulate control device; therefore, the actual amount of particulate matter collected, as well as the mercury collected, on the filter over the sampling period, typically 2 hours, is insignificant.

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PROJECT PLANNING

When mercury is being measured, it is important to evaluate the purpose, schedule, and methodology prior to testing and apply this to determine the extent of pretest documentation needed to obtain the desired results. This section addresses planning and management for a sampling campaign to measure mercury for compliance purposes. There are several areas that can improve a project's overall quality. For a comprehensive test program, having a quality assurance plan (QAP) that addresses sampling, analysis, coordination, and data-handling issues is invaluable.

Quality Assurance Plan

To obtain accurate data with a high degree of certainty and to assure that proper QA/QC is used, the first critical element is to develop a quality QAP prior to doing the tests. The basic parts of a QAP are as follows:

- Definition of what is to be measured and where
- Identification of test methodology
- Project organization
- Description of test coordination, conditions, and schedule
- Quality objectives, quality control requirements, and assessment of quality and planned corrective action
- Documentation

As stated previously, for purposes of this document, measurement methodology is the OH method and the purpose is to prove compliance with CAMR. Further detail is provided on project organization, selecting sampling contractors and analytical laboratories, coordination, testing, quality objectives, and documentation.

Project Organization

Project organization has the purpose of providing structure and a decision-making chain. It has two primary features. The first is the personnel structure, including the management and plant personnel involved. At a minimum the team members that need to be included in a project organizational chart are the project manager from each organization involved in the testing and the key personnel for the group(s) doing the sampling and managing the analyses, including the field leader or supervisor and, if applicable, a QA/QC manager. The most important QA/QC aspect of the project team is to have well-qualified personnel. Mercury sampling is complex, and given problems that can and do occur in the field, having highly trained personnel cannot be overemphasized.

The second aspect of the project organization is communication mechanisms. This includes the site visit (a site visit is crucial) by key participating personnel so that the project managers, samplers, and plant contact understand everyone's responsibilities in the project execution and ascertain that nothing is overlooked. It should be realized by the affected utility that a mercury RATA will be unlike other more routine RATA being performed at the plant. Therefore, at the site visit, a primary plant contact must be assigned to the project. This is a person, based at the plant, who can be contacted if there are problems with the sampling that may impact the plant and who will inform the field leader if there are problems at the plant that may affect the sampling. This person is critical to the success of the project.

A site visit is also conducted to inform all necessary people at the plant as to what the project will entail. Therefore, it is important that a representative be present from each operation of the plant that will be impacted by the project. For example, for a RATA, it is necessary that the plant load be maintained at a constant level near full load. Although not all-inclusive, a list of other issues that should be discussed at the site visit is outlined below:

- Unit access: As part of the site visit, a walk down of the plant needs to be conducted. All sample ports need to be located and the access to the ports determined. If any new ports are needed, arrangements must be made as to when that can be done. Measurements should be made to ensure that the proper length sample probes are available. It is advisable that pictures be taken of the sampling locations. Plant personnel should be asked to clean the ports prior the sampling team being on-site.
- Utilities: This includes space for sampling trailers, vehicle parking, and electrical requirements.
- Desired plant data: Plant load is essential, flue gas data, temperatures, flow rates, etc., are also desirable.
- Safety training/explanations: What, if any, training (videos, meetings, conferences, etc.) is required by the plant prior to beginning the project. All safety issues related to the sampling locations need to be discussed. Also the ultimate disposal of waste chemicals needs to be determined.
- Plant-supported sampling: Coordinate any balance-of-plant sampling such as coal, ash, or scrubber samples, including the timing and methodology for collection, storage, and analysis. For coal and ash samples, a schedule that includes composite sampling and which samples to analyze for which components is key.

Communication mechanisms that will occur during sampling, to check in and out of the site, to convey sampling delays or issues, to request and obtain special operating conditions or load blocks, and to track and manage samples for outside analysis need to be delineated. In addition a person must be designated who will make decisions on test conditions, start/stop times, repeating a test, and the appropriate action to take when an indication of a quality-related problem occurs.

A draft description or test plan should be completed prior to the site visit and sent to all relevant personnel. This document becomes the basis for the site visit discussions. Following the site visit and after receiving comments from all team participants, the test plan should be finalized. Although the sampling requirements for completing a RATA are detailed in CAMR, as anyone who has done field work knows, nothing ever goes exactly as planned; the test plan is the guiding document for the test. If changes need to be made and are agreed to by the project team, all changes should be noted, signed, and dated.

The test plan contains the following elements:

- Test objectives (as detailed as possible).
- Units to be tested and a general description of the units, containing information such as boiler type, boiler capacity, coal burned, and air pollution control devices present.
- Testing schedule and equipment including the dates sampling will be done, sampling locations, and equipment to be used.
- The role of plant personnel and what is expected from the plant as part of the test program (e.g., power supplied, coal or ash samples taken, unit operating data, and other support needed).
- The QA/QC test plan.
- Sample management from the point of collection to analysis and final data reduction.
- Timing of project reports and what they will include. As with the sampling objectives, the reporting requirements are provided in 40 Code of Federal Regulations (CFR) 60.51.

Guidance for Selection of a Sampling Contractor

There are a number of factors that should be considered when evaluating a sampling contractor. These are:

- Experience and training
- Frequency of equipment calibration
- Chain-of-custody procedures
- Collection and handling of reagent and field blanks
- Do they routinely do field spikes?
- Procedures for handling glassware

Experience

By far the most important factor in selecting a sampling contractor is experience. The OH method is complex and requires attention to detail to perform properly. The following questions need to be asked:

- What is the overall experience of the sampling organization in doing OH sampling?
- What is the experience level of the personnel who will be on-site?
- What training practices does the organization have for new employees?
- Have they successfully completed an OH RATA? Unfortunately, at this time, the number of sampling contractors who have successfully completed an OH RATA is very limited.
- Does the sampling contractor have any type of certification (i.e., SES QSTI).

In all cases, references should be requested from the contractor and followed up as well contacting other sources.

Frequency of Equipment Calibration

All sampling equipment needs to be precleaned and calibrated according to the requirements of the reference method prior to transport to the job site. All gas-sampling equipment is to be calibrated at a minimum according to the Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III Stationary Source Specific Methods. Also, as explained in more detail in Data Quality Objectives, calibration requirements need to be tighter for doing an OH RATA.

Chain-of-Custody and Sampling/Handling Procedures

It is expected that the collected samples will be handled in the field by a number of individuals. To ensure there is no mix-up of samples, it is critical that chain-of-custody forms and sample labels be made up prior to each test. The mercury data sheets need to provide a detailed record of custody during sampling (including all labeling information), with the initials noted of the individuals who load and recover impingers and filters and perform probe rinses.

Procedures for Handling Glassware

A critical aspect of the OH method is the handling of glassware. The OH method is extremely glassware-intensive, and proper cleaning of the glassware is essential. For proper cleaning of glassware, the method suggests that all bottles, impingers, and connectors be 1) washed thoroughly with soap and water, 2) rinsed with tap water, 3) triple rinsed with distilled water, 4) soaked for 4 hours in a 10% nitric acid bath, and finally 5) rinsed with distilled water and set out to dry. The glassware-cleaning procedure is detailed in Section 8.1.1 of EPA Method 29. (Note: there is an error in ASTM D6784-02, as it references Section 5.1.1 of EPA Method 29). Based on experience, it is no longer suggested that the glassware be cleaned in this manner but should be considered a requirement. It is recognized that this is a complex procedure, but unless the glassware is cleaned in this manner, there is no way to ensure good field blanks.

Field Spikes

Although field spikes were not specifically required in the method as written in ASTM D6784-02, these samples are essential to proving sampling accuracy. Therefore, the authors strongly urge utilities when hiring a sample contractor to insist they be done. Field spikes are similar to field blanks in that they are sample trains that are set up and torn down just as if they had been used to sample flue gas. The only difference is that instead of a blank, a known quantity of mercury is added to each solution. These samples are then labeled and sent to the analytical lab as if they were actual samples. More detail on field spikes is presented in the Quality Objectives section of this report.

Guidance for Commercial Analytical Laboratory Selection

The management and analysis of samples at one or more laboratories is an area that requires good management in order to maintain quality control. Although most commercial labs are well equipped to measure mercury in various matrices, appreciable lab-to-lab variation can be encountered with respect to analytical and quality control procedures utilized. It is therefore, important to ensure that a selected lab will utilize proper chain of custodies and procedures. Good dialogue with the chosen laboratory will enable the project manager to evaluate the quality of the data received. The project manager should carefully review the QA/QC results to verify that the laboratory followed the agreed-upon QA/QC procedures. Suspicious data should be discussed directly with the laboratory. Data that fall outside of the QA/QC criteria should be flagged in the final gas concentration results.

It is important to conduct an interview with potential commercial laboratories before selecting one as the analytical subcontractor. If the gas-sampling organization is responsible for selecting the commercial analytical laboratory, it is still imperative to conduct an interview with the laboratory. When selecting a commercial laboratory, it is very important to know what questions to ask. While many analytical laboratories may routinely analyze samples for mercury, not all are properly trained to analyze impinger samples from methods as complex as the OH method or even coal and ash samples. Suggested lab screening questions and explanations as to why they should be asked are listed below. The explanations below primarily mention issues associated with samples collected by the OH method; however, the same concerns apply to samples collected if EPA Method 29 is used as a reference method.

To complete a successful RATA using the OH method, it is important that results for each paired sample train be obtained in a timely manner. The decision as to how many paired trains are needed to obtain nine valid sets must be made while the team is in the field. Therefore, the analysis of these OH samples must either be done in the field or through an arrangement with a commercial lab so that a 24-hour turn around can be achieved. In either case, care must be taken to select a laboratory experienced in analyzing OH samples.

What Method is used to Prepare and Analyze the Samples?

All samples that are analyzed for mercury must undergo some type of preparation procedure. Laboratories must be experienced with EPA Method 7470, since it is used to prepare many of the OH samples. Method 7470 outlines a preparatory digestion followed with analysis by either cold-vapor atomic adsorption spectroscopy (CVAAS) or cold-vapor atomic fluorescence spectroscopy (CVAFS). Some labs may routinely use inductively coupled plasma–mass spectroscopy (ICP–MS). This instrument is adequate for most trace metals; however, ICP–MS is not the best or even accepted way to analyze for mercury.

While a lab may be familiar with Method 7470, it may not have previous experience applying this method to the preparation of OH samples. The method was developed for the analyses of water samples and requires some minor modifications when applied to OH gas samples. OH samples require additional care and preparatory steps, which are discussed in the OH method procedure (ASTM D6784-02). If the selected lab is not familiar with the analysis of OH samples, it is important to have the laboratory obtain a copy of the OH method which lists information specific to the analysis of the solution matrices generated by the OH sampling which are not discussed in Method 7470.

Does the Lab Have Experience with the Analysis of Samples Collected by the Gas- Sampling Method of Choice (E.G., OH or EPA Method 29)?

In general, commercial laboratories will fall into one of two categories. One type is a high-volume, certified commercial lab. Such labs are generally less expensive because they are proficient at handling and analyzing large volumes of samples on a daily basis. The other lab type is a certified lab that specializes in the analytical procedures associated with specific gas-sampling methods such as the OH method and/or EPA Method 29. While the high-volume commercial laboratories are trained to use EPA Method 7470 and are generally more cost effective, their primary experience is typically analyzing water and soil samples. The labs that specialize in the analytical procedures associated with the gas-sampling methods are typically more expensive, but generally have a better chance of producing quality data because of their familiarity with the applicable sampling method. As stated in the first question above, the OH method contains instructions specific to the analysis of the solution matrices produced.

What QC Criteria does the Lab Follow?

It is important to attain an understanding of the QC procedures used by a given laboratory. The primary QC criteria used to evaluate data quality are precision and accuracy, which are defined under Data Quality Objectives. Laboratories check precision by running a duplicate analysis of a sample and comparing the results of the two duplicate samples. Duplicate analyses are useful because they provide a check on the ability of the laboratory to reproduce a result from a sample composed of a complicated matrix.

It is important to note that the OH method calls for duplicate analysis of all collected samples and a triplicate analysis of every tenth sample. The frequency with which a lab duplicates a sample analysis will vary from lab to lab. A common practice for many commercial laboratories is to duplicate a sample analysis once every 10 or even 20 samples prepared. Furthermore, if samples from multiple clients are batched together, it is often likely that samples from some of the clients will not undergo a duplicate analysis. Therefore, it is very important to clarify with the laboratory that precision checks will be conducted as called for in the OH sample analysis. Despite the fact that the method calls for such rigorous QC, a special request to the laboratory may be required to ensure that the proper sample replication is performed. Such requests will likely lead to extra costs.

Although QC procedures are typically part of every analytical lab’s standard operation, many of the QC procedures outlined in the OH method require more stringent acceptance criteria than most laboratories employ. It is important to convey the acceptance limits for spike recoveries and frequency required for blanks, replicates, and spikes. There can also be appreciable lab-to-lab variability encountered with regard to how the lab deals with failed QC results. Some labs will simply report the failed QC and leave it up to the end user to determine how to treat the data. Therefore, it is important to clarify upfront with the laboratory what corrective actions should be taken when the measured precision and accuracy do not meet the required criteria. Such corrective actions are described in ASTM D6784-02, Section 13.

Once the QC criteria and procedures have been clarified, it is important to request that the QC results for each analysis set be included in the final data report issued by the lab. Report formats can vary dramatically from lab to lab so it could be helpful to obtain an example of a data report from the lab prior to sending the samples.

What Are the Method Detection Limits?

It is important to obtain detection limit information for mercury analysis from the laboratory to verify that the lab will be able to provide accurate results at the expected mercury levels. Method detection limits (MDL) are very different from instrument detection limits (IDL) but are often used interchangeably by many laboratories. The IDL is the mercury concentration that produces a signal greater that five times the signal/noise ratio of the instrument. The MDL is the mercury concentration, when processed through the complete method, produces a signal with a 99% probability that it is different from the blank. The MDL is larger than the IDL and will vary with sample type. Laboratories usually do not report either the IDL or the MDL, but a limit of quantitation (LOQ), which is the concentration that produces a signal sufficiently greater than the blank that can be detected within specified limits by good laboratories during routine operating conditions. Typically the LOQ is 10 times the IDL. (3) A reasonable LOQ for mercury in the OH samples is ≤1 μg/L, which means that the IDL and MDL are considerably less than this. It is important to clarify these definitions with prospective laboratories in advance.

Many commercial labs prepare their samples using a 'standard' dilution, and in many cases this dilution is too high. If the resulting mercury concentration of the sample prepared by this high standard dilution falls below or on the low end of the calibration curve, the lab may only report a 'less than' value even though there may be detectable mercury in the sample. If the standard dilution used by the lab is not high enough and the resulting mercury concentration falls outside of the high end of the calibration curve the lab may simply flag it and move on to the next analysis set. The proper treatment of sample results that fall outside of the calibration curve should be discussed and agreed upon in advance. The agreement should mandate that the lab rerun samples at an alternate dilution if the first result falls outside of the calibration curve. Such an agreement may result in extra costs.

What is the Maximum Amount of Time Allowed to Elapse between the Completion of the Method 7470 Preparatory Digestion and the Beginning of the Instrumental Analysis of the Sample?

Another possible source of error with mercury samples digested using the Method 7470-type procedure can be the devolatilization of mercury from the digestate during the period following sample digestion and before sample analysis. The final product of Method 7470 is a sample solution fixed under a slightly reducing environment. This reducing environment subsequently causes mercury to reduce back to the elemental form. Elemental mercury is insoluble and volatile and will not remain in solution. Therefore, mercury can escape from the solution if it is allowed to sit too long prior to the analysis step, resulting in a low bias. It is, therefore, important to determine a candidate's standard laboratory procedures regarding digested sample hold times. Some labs utilize different personnel for performing digestion and analytical procedures, which can subsequently result in long delays between the two steps. If the lab normally allows digested samples to sit for more than 1 hour, a special request should be placed with the lab to shorten this time; it is recommended that the samples be analyzed immediately following digestion and no longer than 1 hour afterwards. As mentioned in the explanation to the first question, make sure the lab has a copy of ASTM D6784-02 which details analyzing the digested samples immediately.

Once the analytical laboratory has been screened and chosen, it is strongly recommended to submit a preprepared spiked sample of each matrix type to the laboratory along with the collected OH samples as a QC check. The laboratory can be advised of the spiked samples, but not the level at which they are spiked. The recommended final mercury concentrations of the spiked solutions should be comparable to levels expected in the field samples, however, greater than 1 ppb.

For field spikes, the spiking procedures need to be arranged with the gas-sampling group long before the sampling effort takes place. A spiking solution and a detailed written procedure will need to be prepared in advance and sent with the sampling team.

3
DATA QUALITY OBJECTIVES

The quality objectives are essentially the criteria that will be used to determine whether a data set is of high quality and reliable. Mercury is notoriously difficult to measure and can be quite variable. Therefore, to ensure that the data obtained are accurate, it is key that data quality objectives are met. There are five major aspects of sampling where quality objectives are critical to obtaining good data. Documentation in each of these areas is important to a successful measurement program. These are:

- Up-front preparations and setup in the field
- The actual sampling effort
- Sample recovery
- Sample handling and storage
- Sample preparation and analysis
- Data handling

Pretest Preparations and Setup

Equipment Calibrations

As stated earlier, all sampling equipment needs to be precleaned and calibrated according to the requirements of the reference method. Prior to transport to the job site, sample trains should be assembled, heated, and leak-checked to ensure proper operation of all sample train components. In addition, prior to the testing, all gas-sampling equipment is to be calibrated at a minimum according to the *Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III Stationary Source Specific Methods*.

According to EPA Methods 1–5 and 17 (Table 3-1), a three-point calibration must be performed on the gas meter using a wet test meter, and based on these results, a calibration coefficient is calculated, YD. Prior to testing, a single-point calibration is performed using a wet test meter or a critical orifice, and the coefficient must be ± 5% of the original value to be valid. However, to consistently obtain relative difference of <10% between the paired OH sample trains, this requirement should be reduced to ± 2%. It is also required that a pre- and post-leak check be completed. When 15 in Hg vacuum is applied, the leak rate must be <4% or 0.02 cfm, whichever is less. It is necessary that the leak rate be significantly less than 0.02 cfm to consistently meet the RATA requirements. If the sample boxes are properly maintained and, as is highly recommended, o-ring seal glassware are used, the leak rate should be essentially zero (<0.01 cfm). All calibration records are to be maintained and should be inspected by a QA/QC officer to ensure they are being correctly done and that they are accurate.

Table 3-1
Checklist and Limits for EPA Methods 5 and 17 Sampling

Quality Control Activity	Acceptance Criteria and Frequency/Corrective Action	Reference
Premobilization Checks		
Gas Meter/Orifice Check	Before test series, Y_D ±5% (of original Y_D)	Method 5, Section 5.3 for OH RATA should be ±2%
Probe Heating System	Continuity and resistance check on element	
Nozzles	Note number, size, material	
Glassware	Inspect for cleanliness, compatibility, o-ring seals	
Thermocouples	Same as Method 2	
Pretest Checks		
Nozzle	Measure inner diameter before first run	Method 5, Section 5.1
Probe Heater	Confirm ability to reach temperature	
Pitot Tube Leak Check	No leakage	Method 2, Section 3.1
Visible Inspection of Train	Confirm cleanliness, proper assembly	
Sample Train Leak Check	≤0.02 ft^3 at 15 in. Hg vacuum	Method 5, Section 4.1.4 for OH RATA should be ≤0.01 ft^3
During Testing		
Probe and Filter Temperature	Monitor and confirm proper operation	
Manometer	Check level and zero periodically	
Nozzle	Inspect for damage or contamination after each traverse	Method 5, Section 5.1
Probe/Nozzle Orientation	Confirm at each point	
Posttest Checks*		
Sample Train Leak Check	≤0.02 ft3 at highest vacuum achieved during test	Method 5, Section 4.1.4
Pitot Tube Leak Check	No leakage	Method 2, Section 3.1
Isokinetic Ratio	Calculate, must be 90%–100%	Method 5, Section 6
Dry Gas Meter Calibration Check	After test series, YD ±5%	Method 5, Section 5.3 for OH RATA should be ±2%
Thermocouples	Same as Method 2	
Barometer	Compare w/standard, ±0.1 in. Hg	

*If these criteria are not met, the data must be flagged and an explanation given regarding the deviation and its effect on the data.

Nozzle Selection

The selected nozzle size is determined by a number of factors. First, it is required that all OH sampling be done isokinetically. As such, the velocity of the flue gas through the nozzle must be the same as the velocity in the stack. It is also required by CAMR that the minimum sample time for each paired set of OH samples be 2 hr (not more than 3 hr). Finally, based on the method (ASTM D6784-02, p. 6), the total flue gas sampled should be about 1 to 2.5 Nm^3. As is shown in Table 3-1, for a valid sample, the percent isokinetic must be between 90% and 110%. If sampling from a source that has mid to high levels of SO_2 the nozzle size and sample flow rate should be set to target the lower end of the allowed sample volume. This will reduce the possibility of losing mercury as a result of depletion of the $KMnO_4$ solution.

Glassware

There are two ways to ensure clean glassware. The first is to bring enough glassware into the field that so that every train can be set up. The second is to clean the glassware in the field. This requires a large enough space in a trailer or laboratory to do the soak. In addition, depending on how much sampling will be done, it may require an extra person on-site.

The argument has been made that the rinses used to remove the mercury sample are designed to remove all the mercury and, therefore, it is not necessary to follow such a complex washing method. However, if a mistake is made and for some reason all the mercury is not removed, this will show up in the next sample as well give an erroneous result, the source of which will never be known. If the bottles are "clean" before the next sample is started, the mistake only affects the one sample. Simply put, to successfully provide nine valid paired OH tests on a regular basis, you MUST start with clean glassware each time.

Data Requirements

In addition to the mercury concentrations, other data that must be collected for each RATA run using the OH method are:

- O_2 and CO_2 in the stack gas on a dry basis, %
- Moisture content of the stack, %
- Average stack temperature, °F
- Plant load during testing, MW

The plant load and the O_2 and CO_2 concentrations in the flue gas at the stack may be part of the plant data package; however, it is important that this is determined beforehand do determine if a portable instrument is needed as part of the test. The moisture and stack temperature are recorded as part of the OH sampling procedure.

Field Sampling

Once equipment is set up for sampling, it is again inspected and tested to ensure everything is working properly. All testing personnel must be well trained in sampling procedures and proper maintenance of sampling equipment. Enough sampling equipment must be on-site so that common spare parts are available. Arrangements should be made so that, if necessary, spare parts can be shipped next-day to the site.

The actual sampling procedures and the QA/QC related to the sampling are fully described in the OH method and need to be followed, including the leak-check procedures and filter preparation and handling. Although the particulate-bound mercury is not considered when the calculations are made to determine the relative accuracy of the CMM or Appendix K traps when doing a RATA, the total mercury including the particulate-bound mercury must be reported. Therefore, as previously discussed, it is required that sampling be done isokinetically. In the event of an equipment failure or unit disturbance that could impact the validity of results, the single point of contact (a project manager) should be immediately notified by the sampling team member who notices the failure. The project manager makes a decision on whether to suspend or cancel sampling. Note that all team members are empowered to suspend sampling at any time for equipment problems. If the failure or disturbance is considered severe enough that the test objective cannot be met, the test should be canceled and repeated.

Isokinetic Traversing

The requirements for traversing for reference method testing with the OH method are defined in PS 2 of 40 CFR Part 60, Appendix B. The traversing is to be a three-point traverse along a single line. The standard traversing is 16.7%, 50.0%, and 83.3% of the measurement line. If the distance is greater than 2.4 meters and a wet scrubber is not present, then a distance of 0.4, 1.2, and 2.0 meters along the line from the stack wall can be used. In either case, it is likely that additional sampling ports will need to be installed. This should be an item of discussion during the initial site visit. Prior to moving the sample train probe, the sample pump should be shut off and the gas sample and time noted. If a wet scrubber is present and the stack has a diameter >2.4 m, then the OH sampling train will need to be moved to another sample port during traversing. If this is the case, caution should be taken in moving the equipment to ensure there is no breakage or loose connections that may cause a leak in the system.

Based on experience, the less traversing done the better. If acceptable to the administrator, there is the potential that the traversing requirement may be relaxed for the reference method if there is proof that no stratification exists. This can be done by doing a complete traverse (12-point traverse) using an SO_2 or NO_x analyzer. If these gases do not show stratification in the stack, then it may be assumed that mercury will also not be stratified. In this way, a sampling location that is well-mixed and representative of the stack flow can be determined. This is a better procedure for the following reasons:

1. EPA Methods 5 and 17 traversing protocols were designed to provide a good representation of the dust loading in a stack or duct. Although the particulate-bound mercury must be reported for a RATA, only gas-phase mercury is being measured by a CMM or Appendix K traps. Also, the amount of dust captured at a stack location is so low that the particulate-bound mercury is almost always insignificant regardless of the concentration of mercury on the particles.
2. The OH sampling train is a very complex setup involving eight glass impingers and a glass-lined probe. Moving this train can easily result in breakage and leakage.

3. Early on in the validation testing of the method, it was determined that the KCl impingers had the potential to offgas mercury. Therefore, at the completion of the sampling procedure, the solutions are preserved using $KMnO_4$ solution. The potential for offgassing was related to the concentration of SO_2 in the flue gas and how much the solution was disturbed during sampling. During traversing, the solution is disturbed more than when sampling at a single point. Although low, the potential is greater for losing mercury when traversing.
4. The sorbent traps and CMMs used to meet the requirements for CAMR are single-point methods.

Wet Stacks and the Particulate Fraction

Generally, it is the recommendation that EPA Method 17 (in situ particulate sampling) procedures be used if possible. It is required by the method that the filter be maintained at the temperature of the flue gas, and by having the filter in the duct, this is ensured. In addition, Method 17 has the added advantage that only a small portion of the probe/nozzle (that prior to the filter) collects ash that needs to be brushed onto the filter. The exception, when EPA Method 5 procedures must be used, is when the temperature of the flue gas is below the water dew point (wet stack). In this case, EPA Method 5 must be used, and the filter is then maintained at 120°C. Sampling is done isokinetically, and the nozzle is pointed in the direction of flow. The nozzle and sample line are heated to above 180°C to ensure the water is vaporized; in this way, any mercury in the water droplets is also measured.

Sample Recovery

At the completion of the sampling activities the sample train must be recovered. The recovery process, as shown in Table 3-2, generates a substantial number of samples. As with all aspects of the OH method proper sample recovery requires a high degree of training. It is assumed for purposes of this document that the recovery procedures provided in ASTM D6784-02 are well understood. Based on experience once field sampling activities have been completed it is important that the sample train be taken immediately to the recovery location, and within a short period of time, <2 hrs the KCl impingers stabilized with $KMnO_4$ solution and all samples are recovered. Although it is important to use a minimum $KMnO_4$, the slight purple must remain. Also during recovery hydroxylamine hydrochloride is used to remove the brown from the bottles containing $KMnO_4$ solution. Be sure to use only a few drops as there is potential if too much is used to result in loss of mercury. If needed a small amount of 0.1N nitric acid can be added to increase the liquid contact with the bottle. To ensure the lowest possible detection limit is important that the total volume of each rinse solutions be limited to the greatest extent possible to ensure all the mercury is recovered. It is the authors recommendation that the KCl (sample container 2) and $KMnO_4$ (sample container 3) solutions plus rinses be no more than 500 ml and the H_2O_2/HNO_3 (sample container 4) solution plus rinses be 250 ml.

Sample Handling and Storage

It is expected that the collected samples will be handled in the field by a number of individuals. To maintain the identity of samples throughout the process, clear and descriptive labels must be associated with each sample. The sampling data sheets that accompany each set of samples must provide a detailed record of custody during sampling. All individuals who handle the samples in the field must initial their work. If sampling locations and the number of samples are well defined before a sampling event, it is recommended that sample labels and data sheets be prepared in advance. Once the samples have been collected and recovered, it is important that they are stored in either glass or Teflon bottles. Polypropylene or polyethylene bottles cannot be used. Ryan and Keeney [1] recommended that the samples be stored in glass amber bottles to prevent possible deterioration by ultraviolet (UV) light. This may or may not be necessary, but regardless, the samples need to be stored out of direct sunlight.

Ryan and Keeney [1] also recommend that the KCl samples not be refrigerated, but the H_2O_2/HNO_3 and $KMnO_4/H_2SO_4$ samples should be stored at 4°C. Although the authors agree that this is ideal, it is not always possible. When shipping, these samples are defined as hazardous solutions and need to be packaged accordingly, and this may not always be compatible with refrigeration. The authors have periodically analyzed nonrefrigerated samples that have been stored at room temperature for over 5 years, and the concentrations in these samples have changed less than 15%. Therefore, our recommendation is that these samples do not require refrigeration between sampling and analysis.

Table 3-2
Samples Recovered for the OH Method

Container	Description
Samples	
Container 1	Filter + particulate matter
Container 2	Probe rinse
Container 3	KCl impingers (combined)
Container 4	HNO_3–H_2O_2 impinger
Container 5	H_2SO_4–$KMnO_4$ impingers (combined)
Desiccant (not analyzed)	
Container 6	Silica gel
Blanks	
Container 7	0.1*N* HNO_3 reagent blank solution
Container 8	1*N* KCl reagent blank solution
Container 9	5% $^{v}/_{v}$ HNO_3–10% $^{v}/_{v}$ H_2O_2 reagent blank solution
Container 10	10% $^{v}/_{v}$ H_2SO_4–4% $^{w}/_{v}$ $KMnO_4$ reagent blank solution
Container 11	10% $^{w}/_{v}$ $(NH_2OH)_2 \cdot HCl$ reagent blank solution
Container 12	Filter blank

Sample Preparation and Analysis

As has been stated earlier, it is very important that all personnel who are doing the sample preparation and analysis be familiar with ASTM D6784-02. Although in most cases the method is similar to Method 7470, there are some subtle differences. A checklist is provided in Appendix A that should be helpful in following the method.

In addition to the QA/QC associated with the preparation and analysis steps of the OH method, there is a need to better define the quality objectives and criteria used for ensuring quality of the data. Also, as part of the overall QA/QC program, corrective actions must be clearly stated and implemented if the quality objectives are not met. Most of the terms and definitions used in this section have been taken from the Quality Control chapter of the SW-846 manual [2] and the QA/QC section of Standard Methods for the Examination of Water and Wastewater [3].

Accuracy

Accuracy is defined as how well the measured mercury concentration represents the true value. In the OH method, accuracy is assessed by means of reference samples and percent recovery of spiked samples. As the true mercury value in the flue gas is what is being measured, accuracy is determined by measuring a known concentration of mercury from another source, which is accomplished by preparing field spikes during a sampling event. Field spikes are prepared and analyzed to determine how well a known mercury concentration can be recovered from the sampling train and measured. Preparation of field spikes is discussed in further detail below. It is important to note that the process of preparing and analyzing field spikes can only address the accuracy of the recovery and analysis process of the OH method and does not include sampling accuracy. This can only be accomplished by adding a known amount of mercury in the flue gas. Although, this is impractical at a full-scale power plant, pilot-scale studies have shown good recovery of mercury from spiked flue gas [4].

Analytical method accuracy for determining particulate-bound mercury in the filter ash is assessed by means of recovery of mercury from a certified reference material. The acceptance criteria for spiked samples and reference materials are shown in Table 3-3.

Precision

Precision is the measure of how well multiple analyses of a given sample agree with each other. Analytical precision for OH samples is assessed by replicate analyses of the same solution. One set of triplicate analyses is performed on each of the absorbing solution types (KCl, H_2O_2/HNO_3, and $KMnO_4/H_2SO_4$) at a frequency of one per batch or 10%, whichever is greater. The analytical precision includes errors associated with the instrumental analysis and is calculated from the standard deviation of the three readings. The analytical precision criteria and frequency are shown in Table 3-3. In order to determine the precision of the overall method, replicate samples of the same flue gas must be taken simultaneously. This precision includes the random errors involved in sampling as well as the errors in sample preparation and analysis.

Spikes

Matrix spikes are used in the OH method to provide a measure of accuracy for different matrices. A spike is performed by adding a known amount of mercury to a given matrix prior to preparation and/or analysis. There are three types of spikes employed in the OH method: 1) field spike; 2) laboratory method spike; and 3) analytical instrument spike. A field spike is a prepared sampling train that has had a predetermined amount of mercury added to each of the three impinger solutions. This train is not used for sampling but is recovered and analyzed the same as actual field samples. If there is prior knowledge of the flue gas mercury concentration, the amount of mercury spiked into each impinger solution should be comparable to the levels expected in the actual samples. If not, it is recommended that the spike amounts are varied with each daily field spike to help ensure that the range of spiked values will bracket the amount of mercury found in the samples.

A laboratory method spike is performed by adding a known amount of mercury to a recovered OH sample prior to preparation or digestion in the laboratory. The predigestion spike should be added at a range of 50%–150% of the mercury expected in the sample. This serves as a check on mercury recovery during the laboratory preparation procedures.

Finally, the analytical instrument spike is prepared by adding a known amount of mercury to a sample after it has been digested and analyzed. Once a reading has been determined, the amount of mercury added to the sample should be approximately 50%–150% of what was found in the sample. This spike serves as a check on mercury recovery from a particular matrix after preparation or digestion. Acceptance criteria and frequency for all OH spiked samples are listed in Table 3-3.

Blanks

The success of a mercury measurement program depends on high-quality reagents with ultra low levels of background mercury. In most cases, inconsistent data have been linked to high blank measurements. To assess possible mercury contamination resulting from preparation and processing of the OH samples, two types of blanks are required: 1) reagent blanks and 2) field blanks.

Reagent Blank

Reagent blanks represent the “mercury-free” solutions that are used for preparing the OH trains. To help ensure mercury-free solutions, all reagents that are purchased need to be analytical grade. When the absorbing solutions (KCl, H_2O_2/HNO_3, and $KMnO_4/H_2SO_4$), rinse solutions, and other recovery solutions are being prepared prior to sampling, an aliquot of each type should be sampled and analyzed for mercury. Reagent blanks are required to be analyzed each time a new batch of reagents are prepared. If mercury is found in these solutions, corrective action must be taken immediately, before actual field samples are taken. Although the acceptance criterion for any reagent blank is a mercury concentration of <0.1 µg/L or 10 times the instrument detection limit, whichever is lower, in fact the reagent blanks should be at or near zero.

Field Blank

The second type of blank that is required is a field blank. A field blank is a sample train prepared and recovered in the same manner as those used for the actual sampling. Field blanks should be taken to the sampling location and remain at the location during the sampling period. These blanks are then recovered, stored, prepared, and analyzed exactly as the actual samples. The field blank serves as a check for possible contamination from the environment and handling of the samples at the field site. At a minimum, one field blank should be associated with each unit being tested per day of sampling. Although the OH method states that the amount of mercury in the field blank should not exceed 30% of the measured value at the location, this limit should be better defined. This would be reasonable if the measured concentrations were at or near the method lower limit of quantification of 0.5 μg/Nm^3; however, for higher flue gas concentrations, this limit is too high. If high-quality reagents are used and the sampling team is experienced with the method, it is feasible to obtain field blanks of <0.2 μg total mercury.

Table 3-3
Data Quality Objectives for Preparation and Analysis of Flue Gas Mercury Samples by the OH Method

Measure	Sample Type	Objective	Approach
Accuracy	Field spike	80%–120% of known value	Collect and analyze one field spike for each unit per day of testing (analysis must be done on each solution)
Accuracy	Laboratory method and instrument Spikes	85%–115% of known value	Frequency of one per batch per solution type or 10%, whichever is greater
Accuracy	Reference material	85%–115% of reference value	Frequency of one per test program
Precision	Replicate analyses	±10% of the previous analysis	Frequency of one per batch per solution type or 10%, whichever is greater
Contamination	Reagent blank	<0.1 μg/L or 10x the instrument detection limit, whichever is greater	Analyze one blank per batch of each reagent
Contamination	Field blank	<30% of sampled mercury concentration or <0.2 μg* in the complete train, whichever is lower	Collect and analyze one field blank for each unit per day of testing (analysis must be done on each solution)

*Based on a target flue gas volume of 1m^3.

Corrective Action

After reviewing the criteria listed in Table 3-3, the question becomes, “What course of action should be taken if data quality objectives for sample preparation and analysis are not met?” All corrective actions should be well documented and at a minimum include the following elements: identification of the problem; the person who discovered the problem; steps taken to determine the cause of the problem; and corrective action taken to eliminate the problem.

To minimize problems associated with overall data quality, the ideal circumstance would be that the analysis of OH samples be completed in the field. If the quality objectives are not met, problems can be addressed immediately, and the sample analysis can be repeated while the sampling team is still on-site. The next best arrangement would be to have samples shipped to a laboratory on a daily basis and have the results sent to the field manager prior to leaving the site. Again, if the quality objectives are not met, the sample analysis can be repeated with minimal expense. When it is known in advance that the sample analysis will not be completed until after the sampling team has left the site, and it would be cost prohibitive to return to the site and redo the testing, it is essential that 1) the required QA/QC criteria be discussed prior to the test, 2) any data that do not meet the listed criteria (Table 3-3) be flagged, 3) the results be discussed in light of the flagged data and a decision made on the validity of the data, and 4) a prearranged agreement is in place regarding decisions for repeating tests.

Summary of Sample Preparation and Analysis

The sample preparation steps are fully laid out in the method and need to be understood and followed. It should be noted that the following procedures are those used and recommended by the authors, and some groups may use minor variations. These alternative procedures are acceptable as long as they provide the same level of QA/QC.

When samples are received in the laboratory, it is imperative that all samples are inspected and checked against the chain-of-custody forms. Any damaged samples or discrepancies should be noted immediately. The sample weights of the filters (Container 1) should have been recorded by the sampling personnel that recovered them; however, if there is doubt about the weight, the filters should be weighed in the laboratory and the weights recorded. For most RATAs, the OH samples will be collected under low-dust conditions; therefore, the filter samples will likely contain very small amounts of ash (less than 0.5 g). Therefore, the entire sample (filter + ash) must be digested. The filter blank (Container 12) is also treated this way. In rare cases where the filter samples have ash amounts greater than 0.5 g, the ash is carefully removed from the filter and transferred to another container and mixed thoroughly. A portion of the mixed ash is prepared for analysis. Several suitable methods can be used for the determination of mercury in the filter ash. Some of the more commonly used methods include:

- EPA SW846 3052 (microwave-assisted digestion) followed by CVAAS.
- EPA SW846 7471A (mercury in solid waste followed by CVAAS)
- ASTM D6414 (acid extraction)
- ASTM D6722 (direct combustion)
- EPA 7473 (thermal decomposition)

A standard reference material should be prepared with each batch of ash samples as a method accuracy check.

Warning: Some of the digestion procedures referenced above call for the use of hydrofluoric acid (HF), which can readily penetrate the skin. Use extreme caution and always where gloves when handling HF and other acids.

The volumes for the remaining containers should be recorded by the sample recovery team. If not, the laboratory personnel should measure the volume of each container and record, or quantitatively transfer, the contents to a volumetric flask and dilute to volume with reagent water. This sample should be well mixed before taking an aliquot for digestion and analysis. With the exception of the H_2SO_4–$KMnO_4$ impinger samples *(Containers 5 and 10)*, the OH method requires that all samples be prepared using a modified version of EPA SW846 7470A. Ten-mL sample aliquots are recommended for the modified version to reduce chemical waste.

The prepared OH samples are analyzed for total mercury using either CVAAS or CVAFS; however, CVAAS is the more commonly used technique for OH samples. CVAAS is a based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state by means of a reducing agent, usually stannous chloride, and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrometer. Mercury concentration is proportional to the indicated absorbance. Most mercury analyzers require a preconditioning system to dry and clean the gas before it enters the absorption cell. Soda lime and magnesium perchlorate are commonly used.

Instrument calibration should include a blank and a minimum of four standards that fit the working range of the spectrometer. CVAAF is more sensitive than CVAAS and can be calibrated with standards as low as 5.0 ng/L. However, a typical working range for most CVAA spectrometers is 0.25 μg/L to 10 μg/L. This range usually covers the concentrations of mercury found in most OH samples. It is recommended that standards be prepared in a 10% ($^v/_v$) HCl solution, which is a highly stable matrix for mercury. Although the EPA SW846 7470A method states that calibration standards be matrix-matched and prepared in the same manner as the samples by including them in the persulfate digestion procedure, this is not necessary and increases the potential for analytical error associated with the calibration.

To verify the calibration of the instrument, a QC standard is analyzed immediately after the instrument is calibrated. This is also referred to as a calibration verification standard (CVS). This standard must be prepared from a different source than that used for the calibration standards and should have a value in the midpoint range of the calibration. The value should read 95%–105% of the true value. During sample analysis, the calibration is periodically check by analyzing one of the midpoint standards that was used for calibration. This is referred to as a check standard or continuing calibration standard (CCS). This calibration check should be run every ten samples, and the value should read 90%–110% of the known value. If the reading falls outside this range, the instrument is either resloped or recalibrated, checked against the initial QC, and analysis continued from the point of the last acceptable CCV.

It is important to monitor analytical performance over time by maintaining a control record of instrument response, calibration regression, QC standard values, check standards, spike recoveries, and replicate precision. Keeping a record of spike recoveries from OH samples will give the laboratory an indication of bias associated with the laboratory’s implementation of the method.

Field Data Management

The following steps should be taken to maintain data sheet custody and integrity:

- All field data sheets need to be initialed by the person completing the data sheet and reviewed for completeness and accuracy.
- The data sheets should be submitted to the project manager or field team leader, who reviews the data sheet for completeness and discusses any areas of concern or question with the person who completed the data sheet.
- Data sheets should be stored in a project notebook, which is kept in the custody of the project manager.
- All data recorded on computers, such as test spreadsheets, need to be backed up daily and stored separately from the computer.
- Only copies of original data sheets are used for reporting purposes, the originals should be stored for a minimum of 5 years.

4
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A
OPERATIONAL CHECKLISTS

OH Method Sampling Checklist

- ☐ Pretest meetings have been set up with sampling and plant personnel.
- ☐ Traverse requirements have been identified.
- ☐ Material safety data sheets (MSDSs) for chemicals are available.
- ☐ A plan for disposal of waste chemicals has been implemented.
- ☐ Chemicals are trace metal-grade.
- ☐ Chemicals have been analyzed for mercury.
- ☐ The test team is familiar with the method and understands it and its limitations.
- ☐ A procedure for collecting plant data is in place.
- ☐ Only clean glassware will be used (the reuse of rinsed glassware is not acceptable).
- ☐ Impingers are O-ring seal.
- ☐ Sample system components are Teflon, glass, or quartz.
- ☐ Mercury-containing devices have been eliminated from testing and staging areas, and areas are free from mercury contamination (i.e., manometers with mercury, broken fluorescent lamps, and thermometers).
- ☐ Equipment has been calibrated to U.S. Environmental Protection Agency (EPA) specifications; some calibration standards will need to be tighter than what EPA specifies (pre- and post-test calibrations of dry gas meters should be within 2% of last calibration value).
- ☐ If performing dual-train sampling, at least one operator for each train is required.
- ☐ A dedicated dual-sampling probe is recommended.
- ☐ The Method 17 sampling configuration is being used if the stack temperature is over 120°C.
- ☐ Nozzle sizes and flow rates are correct to provide adequate sample volume but not deplete the $KMnO_4$.
  - Too high of a flow rate will cause the KMnO4 to be depleted as it reacts with SO_2 in the final set of impingers; as the $KMnO_4$ is depleted, it will turn brown then clear and lose its ability to retain mercury.
  - Too much moisture picked up in the first set of impingers will dilute the sample and reduce detection limits; it is recommended that the KCl impingers be recovered into a 500-mL container.
- ☐ Heating equipment for probe and filter is operational and set at the correct temperatures.
- ☐ Pretest and posttest leak checks are performed, 0.01-cfm maximum (with o-ring seal glassware, this leak check should be 0).
- ☐ Plant operation is being monitored to ensure that it is operating within the parameters of the test plan.
- ☐ Chemicals are made fresh from prescreened reagents.
- ☐ Blank and spiked sample trains are being included as part of the test plan (at least one of each, each day).

- ☐ If an umbilical is used to connect the probe to the sample train it needs to be as short as possible.
  - If less than 0.5 m, unheated Teflon may be used.
  - If longer than 0.5 m, a heated (120°C) Teflon umbilical must be used.
- ☐ Ports must be sealed against air in-leakage.
- ☐ Test personnel are monitoring the color of the $KMnO_4$ impingers; if the impingers start to lose their purple color, the test may have to be terminated.
  - A purple going to uniform brown is okay.
  - Purple going to brown, going to clumps of brown with some small clear spaces, means the capacity of the $KMnO_4$ to capture SO_2 and mercury has been exceeded.
  - If the solution goes clear, the capacity of the $KMnO_4$ has been greatly exceeded.
- ☐ Sample recovery is performed by personnel with experience in recovering OH samples or is closely supervised by someone who is.
- ☐ Sample preparation and sample recovery personnel should have a diagram of sample preparation and sample recovery procedures for quick visual reference.
- ☐ Sample identification and chain-of-custody procedures need to be in place.
- ☐ A sturdy bottle holder should be available for building and recovering sample trains.
- ☐ Samples need to be recovered within 2 hours of test.
- ☐ All sample containers need to be glass or Teflon (polypropylene or polyethylene bottles are <u>not</u> acceptable).
- ☐ Sample volumes need to be kept to a minimum to improve detection limits.
  - Probe rinses should be no more than 250 mL (Container 2).
  - KCl samples should be no more than 500 mL (Container 3).
  - H_2O_2/HNO_3 samples should be no more than 250 mL (Container 4).
  - $KMnO_4$ samples should be no more than 500 mL (Container 5).
- ☐ The use of hydroxylamine hydrochloride should be kept to an **<u>absolute</u>** minimum when rinsing the $KMnO_4$ bottles to remove the brown stains (this chemical neutralizes the $KMnO_4$ that is helping retain the mercury in the sample).
- ☐ The KCl solutions (Container 3) require the addition of 10% nitric acid; enough acid should be added to ensure that the final nitric acid concentration in the sample is at least 1% or greater (this is necessary to prevent loss of mercury from the sample).
- ☐ Shipping procedures are put in place to ensure timely and safe transportation of these samples to the analytical lab.

Ontario Hydro Method Preparation and Analysis

This checklist provides a guide through the critical steps included in Sections 13.3 and 13.4 of the OH method (ASTM International D6784). For the purpose of these guidelines, preparation and analysis of the filter sample is limited to Case 2, where the filter is used for mercury determination only and not used to determine gravimetric particulate.

Sample Preparation (Section 13.3 of OH Method)

☐ Samples are inspected and inventoried upon receipt in the laboratory. Any discrepancies from chain-of-custody forms or damaged samples are noted.
☐ *Container 1:* The filter sample weights have been recorded by the sampling personnel. If not, the filter should be weighed in the laboratory and the weight recorded.
☐ For filter samples with small amounts of ash (less than 0.5 g) the entire sample (filter + ash) is digested and analyzed. The filter blank (*Container 12*) is also digested and analyzed.
☐ For filter samples with adequate amounts of ash (greater than 0.5 g), the ash is removed from the filter and prepared.
☐ A standard reference material is included in the digestion procedure as a method accuracy check.
☐ *Container 2:* The volume of the probe rinse has been recorded by the sample recovery team. If not, the volume is measured and recorded or quantitatively transferred to a volumetric flask and diluted to volume with reagent water.
☐ *Containers 3 and 8:* The KCl impinger solutions have retained a purple color. Small increments of hydroxylamine sulfate or hydroxylamine hydrochloride solid (not the solution) are added to clear the solution. The volume is measured and recorded or quantitatively transferred to a volumetric flask and diluted to volume with reagent water.
☐ *Containers 4 and 9:* The volumes of the HNO_3–H_2O_2 impinger samples have been measured and recorded. If not, the volume is measured and recorded or quantitatively transferred to a volumetric flask and diluted to volume with reagent water. These samples are prepared according to Section 13.3.4 of the OH method. ***Special Note***: It is recommended that <u>0.5 mL of HCl</u> be added to the sample rather than 0.25 mL as stated in the method. It is also recommended that the increments of saturated $KMnO_4$ be reduced to 0.25 mL or 0.5 mL.
☐ Samples in *Containers 2, 3, 4, 8, and 9* are prepared using modified EPA SW-846 7470A.
☐ Samples are spiked prior to 7470A preparation.
☐ *Containers 5 and 10:* The H_2SO_4–$KMnO_4$ samples solutions have retained a purple color. Small increments of hydroxylamine sulfate or hydroxylamine hydrochloride solid (not the solution) are added to clear the solution. The volume is measured and recorded or quantitatively transferred to a volumetric flask and diluted to volume with reagent water.
☐ *Containers 7 and 11*: The reagent blanks, 0.1*N* HNO_3 rinse solution and 10% $^{w}/_{v}$ $(NH_2OH)_2$•HCl solution, do not require further dilution or preparation prior to analysis.

Sample Analysis and Quality Control (Section 13.4 of OH Method)

☐ Prepared samples are analyzed by either cold-vapor atomic absorption spectroscopy (CVAAS) or cold-vapor atomic fluorescence spectroscopy (CVAFS) according to manufacturer instructions.

☐ *Standard Preparation*: Standards fit the working range of the spectrometer. CVAAF is more sensitive than CVAAS and can be calibrated with lower-level standards than CVAAS.

☐ There is fresh desiccant in the drying tube, and it is checked periodically throughout the analysis and replaced if necessary.

☐ Fresh rinse solution is maintained during the analysis. If the instrument does not have a rinse station that is continually flushed with fresh solution, the rinse container is replaced periodically with fresh solution.

☐ *Calibration*: The instrument is calibrated with a blank and a minimum of four standards. Regression (R^2) of the calibration curve is 0.999 or better. Regression is documented.

☐ *Quality Control (QC) Standard*: The calibration is verified with a QC standard prepared from a different source than that used for preparation of the calibration standards. Reading is within acceptable limits of 95%–105% and documented.

☐ *Calibration Check:* The calibration curve is checked every ten samples by reading one of the midpoint calibration standards. All values are within the acceptable range of 90%–110% and documented.

☐ *Spikes:* Each sample matrix is spiked at a frequency of one per batch or 10%, whichever is greater. Recoveries are within the acceptable range of 85%–115% and are documented.

☐ *Blanks:* All blanks (reagent blanks and field blanks) are below the acceptance criteria for mercury.

☐ All sample readings fall within the limits of the calibration curve. Samples with levels above the highest standard are diluted and reanalyzed.

☐ *Dilution Corrections*: All sample preparation and analytical dilutions are accounted for in the final reported results.

B
CALCULATIONS

Reporting Units and Conversions

$F_C = 321 \times 10^3 \times \%C/GCV$

where:

%C = Carbon in coal, % dry basis

GCV = gross calorific value, Btu/lb dry basis

F_c = scf CO_2/MMBtu

$E = lb_{Hg}/scf) \times F_C \times (100/\%CO_2) \times (10^6)(MBtu/TBtu)$

where:

$\%CO_2$ = percent CO_2 in the flue gas

TBtu = 10^6 MMBtu = 10^{12} Btu

E = emission rate, lb/TBtu

For example, for 2.5 µg/Nm^3 measured in the flue gas at 11.9% CO_2, with a coal C content of 77% dry and GCV of 13,100 Btu/lb:

$(2.5\ \mu g/Nm^3)*(\ Nm^3/(35.31*(293°K/273°K)ft^3))*(lb/454x10^6\ \mu g) =$

$1.45x10^{-10}$ lb Hg/scf

$F_c = 321{,}000*(77)/(13100) = 1{,}887$ scf CO_2/MMBtu

$E = (1.45x10^{-10}$ lb Hg/scf$)*(1887$ scf/MMBtu$)*(100/11.9)*10^6 = 2.3$ lb/TBtu

These calculations are the ones approved by EPA for reporting purposes and, thus, should be used when evaluating mercury emissions for comparison with proposed mercury standards in lb/TBtu. Some states have proposed standards in different units, including lb/GWh and mg/MWh.

Data Calculations

Calculation of Relative Difference (RD) Between Paired OH Sample Trains

$$RD = 100 \times \frac{\left|(C_a - C_b)\right|}{(C_a + C_b)}$$

where:

C_a and C_b are concentration values determined from each of the two samples, respectively.

To be a valid paired set:

If the measured mercury concentration is > 1 $\mu g/m^3$ then RD $\leq$ 10%

If the measured mercury concentration is $\leq$ 1 $\mu g/m^3$ then RD $\leq$ 20%

Calculation of Relative Accuracy (RA) of A Continuous Mercury Monitor (CMM) Using the OH Method as the Reference Method

$$RA = \frac{\left|\bar{d}\right| + \left|cc\right|}{RM} \times 100$$

where:

RM = Arithmetic mean of the OH values

d = The sum of the difference between the OH values and the corresponding CMM values or

$$\bar{d} = \sum_{i=1}^{n} d_i$$

where:

n = Number of data points

di = The difference between a reference method value and the corresponding CMM's value

(RM_i-CMM_i) at a given point in time, i

cc = The value of the confidence coefficient or

$$cc = t_{0.025} \frac{S_d}{\sqrt{n}}$$

where:

$t_{0.025}$ = Student t value (use statistical tables)

Sd = Standard deviation or

$$S_d = \sqrt{\frac{\sum_{i=1}^{n} d_i^{\,2} - \frac{\left(\sum_{i=1}^{n} d_i\right)^2}{n}}{n-1}}$$

n = Number of data points

The RATA is passed:

If the measured mercury concentration of the CMM is >1 μg/m^3, the RA is ≤ 20%.

If the measured mercury concentration of the CMM is ≤ 1 μg/m^3, the absolute difference between the RM and CMM must be ≤ 1 μg/m^3.

Calculation of Bias

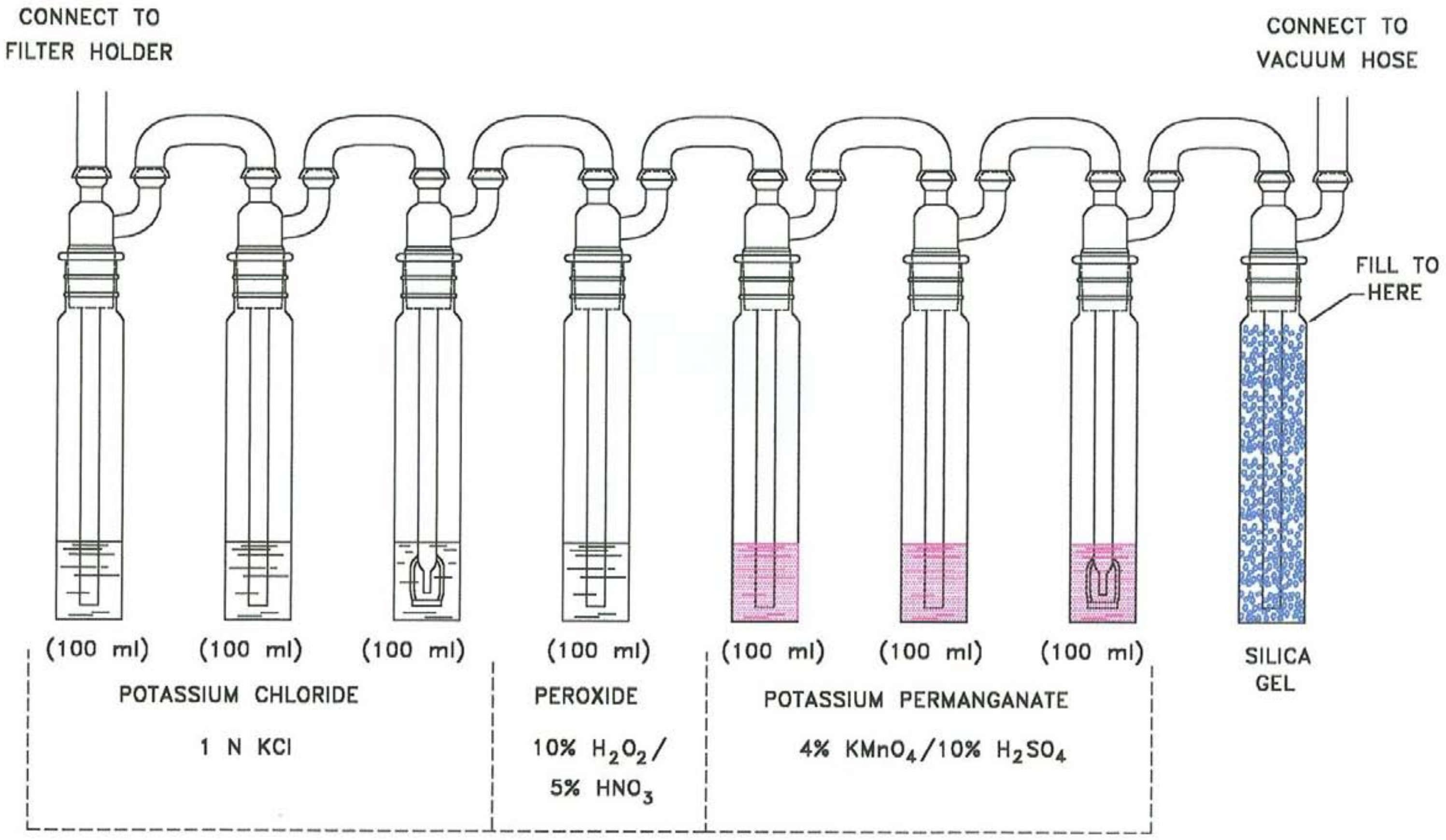
The bias test is passed if:

$$\bar{d} \leq |cc|$$

C

DIAGRAMS OF OH BUILD AND RECOVERY

ONTARIO–HYDRO METHOD TRAIN ASSEMBLY

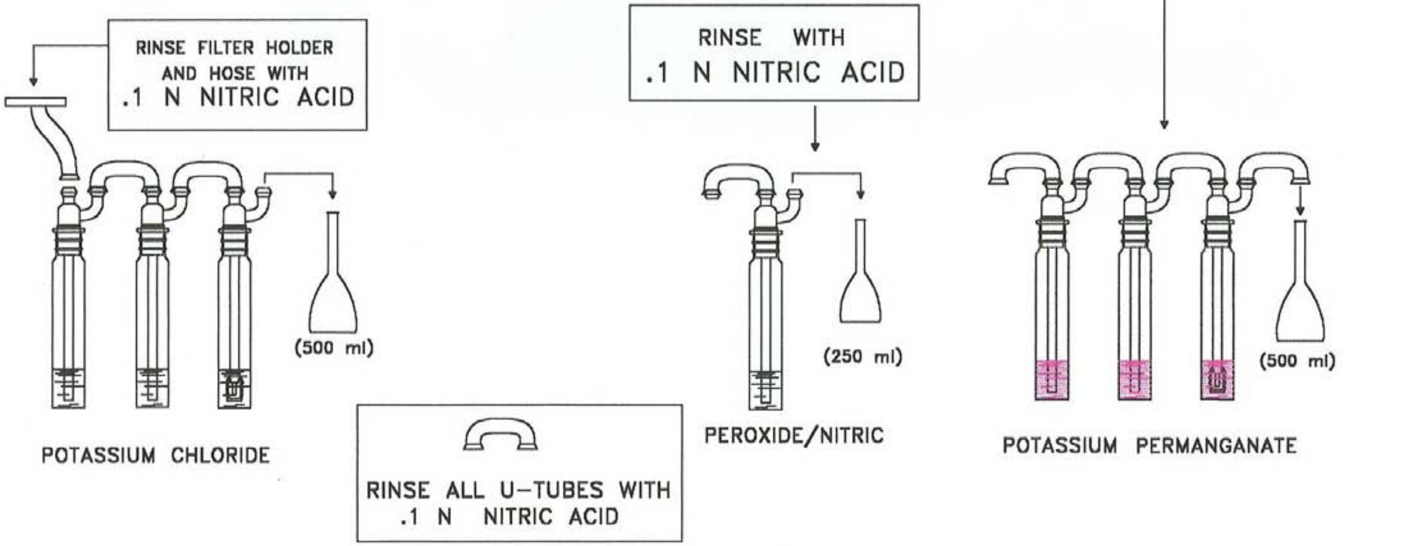


ONTARIO–HYDRO METHOD SAMPLE RECOVERY

1. ADD 5% $KMnO_4$ TO EACH KCl IMPINGER BOTTLE UNTIL PURPLE COLOR REMAINS.
2. RINSE WITH 10% NITRIC ACID.
3. IF BROWNISH STAINS REMAIN, ADD A FEW DROPS OF HYDROXYLAMINE CHLORIDE TO FINAL NITRIC RINSE.

RINSE BOTTLES SPARINGLY WITH:

— .1 N NITRIC ACID
— HYDROXYLAMINE CHLORIDE (few drops)
— .1 N NITRIC ACID



RINSE FILTER HOLDER AND HOSE WITH .1 N NITRIC ACID

RINSE WITH .1 N NITRIC ACID

RINSE ALL U–TUBES WITH .1 N NITRIC ACID

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