# GW – 001

# 2015 AGWMR

# PART 3 OF 5

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## 6.0 Analytical Procedures

All analytical methods used at HEAL incorporate necessary and sufficient Quality Assurance and Quality Control practices. A Standard Operating Procedure (SOP) is used to provide the necessary criteria to yield acceptable results. These procedures are reviewed at least annually and revised as necessary and are attached as a pdf file in the Laboratory Information Management System (LIMS) for easy access by each analyst. The sample is often consumed or altered during the analytical process. Therefore, it is important that each step in the analytical process be correctly followed in order to yield valid data.

When unforeseen problems arise, the analyst, technical director, and, when necessary, laboratory manager meet to discuss the factors involved. The analytical requirements are evaluated and a suitable corrective action or resolution is established. The client is notified in the case narrative with the final report or before, if the validity of their result is in question.

### List of Procedures Used

Typically, the procedures used by HEAL are EPA approved methodologies or 20th edition Standard Methods. However, proprietary methods for client specific samples are sometimes used. On occasion, multiple methods or multiple method revisions are used, in this event the SOP is written to include the requirements of all referenced methods. The following tables list EPA and Standard Methods Method numbers with their corresponding analytes and/or instrument classification.



**Methods Utilized at HEAL**

Drinking Water(DW) Non-Potable Water (NPW) Solids (S)

| Methodology | Matrix | Title of Method |
|---|---|---|
| 180.1 | DW<br>NPW | "Turbidity (Nephelometric)" |
| 200.2 | DW<br>NPW | "Sample Preparation Procedure For Spectrochemical Determination of Total Recoverable Elements" |
| 200.7 | DW<br>NPW | "Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry" |
| 200.8 | DW<br>NPW | "Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma-Mass Spectrometry." |
| 245.1 | DW<br>NPW | "Mercury (Manual Cold Vapor Technique)" |

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|---|---|---|
| 300.0 | DW<br>NPW<br>S | "Determination of Inorganic Anions by Ion Chromatography" |
| 413.2 | NPW<br>S | "Oil and Grease" |
| 418.1 | NPW<br>S | "Petroleum Hydrocarbons (Spectrophotometric, Infrared)" |
| 504.1 | DW | "EDB, DBCP and 123TCP in Water by Microextraction and Gas Chromatography" |
| 524.2 | DW | "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry" |
| 552.3 | DW | "Determination of Haloacetic Acids and Dalapon in Drinking Water by Ion-Exchange Liquid-Solid Extraction and Gas Chromatography with an Electron Capture Detector" |
| 624 | NPW | Appendix A to Part 136 Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater Method 624-Purgeables" |
| 1311 | S | "Toxicity Characteristic Leaching Procedure" |
| 1311ZHE | S | "Toxicity Characteristic Leaching Procedure" |
| 1664A | NPW | "N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material) by Extraction and Gravimetry" |
| 3005A | NPW | "Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy" |
| 3010A | NPW | "Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy" |
| 3050B | S | "Acid Digestion of Sediment, Sludge, and Soils" |
| 3510C | DW<br>NPW | "Separatory Funnel Liquid-Liquid Extraction" |
| 3540 | S | "Soxhlet Extraction" |
| 3545 | S | "Pressurized Fluid Extraction(PFE)" |
| 3665 | NPW<br>S | "Sulfuric Acid/Permanganate Cleanup" |
| 5030B | NPW | "Purge-and-Trap for Aqueous Samples" |
| 5035 | S | "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples" |
| 6010B | NPW<br>S | "Inductively Coupled Plasma-Atomic Emission Spectrometry" |

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|---|---|---|
| 7470A | NPW | "Mercury in Liquid Waste (Manual Cold-Vapor Technique)" |
| 7471A | S | "Mercury in Solid or Semisolid Waste (Manual Cold Vapor Technique)" |
| 8021B | NPW<br>S | "Aromatic and Halogenated Volatiles By Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors" |
| 8015D | NPW | "Nonhalogenated Volatile Organics by Gas Chromatography" |
| | S | (Gasoline Range and Diesel Range Organics) |
| 8081A | NPW<br>S | "Organochlorine Pesticides by Gas Chromatography" |
| 8082 | NPW<br>S | "Polychlorinated Biphenyls (PCBs) by Gas Chromatography" |
| 8260B | NPW<br>S | "Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)" |
| 8270C | NPW<br>S | "Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)" |
| 8310 | NPW<br>S | "Polynuclear Aromatic Hydrocarbons" |
| 9060 | NPW | "Total Organic Carbon" |
| 9067 | NPW<br>S | "Phenolics (Spectrophotometric, MBTH With Distillation)" |
| 9095A | S | "Paint Filter Liquids Test" |
| H-8167 | DW<br>NPW | "Method 8167 Chlorine, Total" |
| Walkley/Black | S | FOC/TOC WB |
| SM2320 B | DW<br>NPW | "Alkalinity" |
| SM2340B | NPW | "2340 Hardness" |
| SM2510B | DW<br>NPW | "2510 Conductivity" |
| SM2540 B | NPW | "Total Solids Dried at 103-105° C" |
| SM2540 C | DW<br>NPW | "Total Dissolved Solids Dried at 180° C" |
| SM2540 D | NPW | "Total Suspended Solids Dried at 103-105° C" |
| SM4500-H+B | DW<br>NPW | "pH Value" |
| SM4500-NH3 C | NPW<br>S | "4500-NH3" Ammonia |
| SM4500-Norg | NPW | "4500-Norg" Total Kjeldahl Nitrogen (TKN) |

| C | S | |
|---|---|---|
| SM5210 B | NPW | "5210 B. 5-day BOD Test" |
| SM5310 B | DW | "5310" Total Organic Carbon (TOC) |
| SM9223B | NPW<br>DW | "9223 Enzyme Substrate Coliform Test" |
| 8000B | NPW<br>S | "Determinative Chromatographic Separations" |
| 8000C | NPW<br>S | "Determinative Chromatographic Separations" |

**Criteria for Standard Operating Procedures**

HEAL has Standard Operating Procedures (SOPs) for each of the test methods listed above. These SOPs are based upon the listed methods and detail the specific procedure and equipment utilized as well as the quality requirements necessary to prove the integrity of the data. SOPs are reviewed or revised every twelve months or sooner if necessary. The review/revision is documented in the Master SOP Logbook filed in the QA/QC Office. All SOPs are available in the LIMS under the Documents and SOPs menu.
Hand written corrections or alterations to SOPs are not permitted. In the event that a correction is needed and a revision is not immediately possible, a corrective action report will be generated documenting the correction or alteration, signed by the section Technical Director and the QA/QC Officer and will be scanned into the current SOP and will document the change until a new revision is possible.

Controlled documents such as calibration summary forms, analysis bench sheets, etc. are tracked as appendices in SOPs, through the Controlled Document Logbook with copies available through the LIMS or through the MOAL as bound logbooks.

Each HEAL test method SOP shall include or reference the following topics where applicable:

Identification of the test method;
Applicable matrix or matrices;
Limits of detection and quantitation;
Scope and application, including parameters to be analyzed;
Summary of the test method;
Definitions;
Interferences;
Safety;
Equipment and supplies;
Reagents and standards;

Sample collection, preservation, shipment and storage;
Quality control parameters;
Calibration and standardization;
Procedure;
Data analysis and calculations;
Method performance;
Pollution prevention;
Data assessment and acceptance criteria for quality control measures;
Corrective actions for out-of-control data;
Contingencies for handling out-of-control or unacceptable data;
Waste management;
References; and
Any tables, diagrams, flowcharts and validation data.

## 7.0 Calibration

All equipment and instrumentation used at HEAL are operated, maintained and calibrated according to manufacturers' guidelines, as well as criteria set forth in applicable analytical methodology. Personnel who have been properly trained in their procedures perform the operation and calibration. Brief descriptions of the calibration processes for our major laboratory equipment and instruments are found below.

### Thermometers

The thermometers in the laboratory are used to measure the temperatures of the refrigerators, freezers, ovens, water baths, incubators, hot blocks, ambient laboratory conditions, TCLP Extractions, digestion blocks, and samples at the time of log-in. All NIST traceable thermometers are either removed from use upon their documented expiration date or they are checked annually with a NIST-certified thermometer and a correction factor is noted on each thermometer log. See the most current Login SOP for detailed procedures on this calibration procedure.

Data Loggers are used to record refrigerator temperatures. These data loggers are calibrated quarterly with NIST-certified thermometers.

The NIST thermometer should be recalibrated at least every five years or whenever the thermometer has been exposed to temperature extremes.



### Refrigerators/Freezers

Each laboratory refrigerator or freezer contains a thermometer capable of measuring to a minimum precision of 0.1°C. The thermometers are kept with the bulb immersed in liquid. Each day of use, the temperatures of the refrigerators are recorded to insure that the refrigerators are within the required designated range. Samples are stored separately from the standards to reduce the risk of contamination.

See the current Catastrophic Failure SOP for the procedure regarding how to handle failed refrigerators or freezers.

### Ovens

The ovens contain thermometers graduated by 1° C. The ovens are calibrated quarterly against NIST thermometers and checked each day of use as required and in whatever way is dictated by or appropriate for the method in use.

## Analytical and Table Top Balances

The table top balances are capable of weighing to a minimum precision of 0.01 grams. The analytical balances are capable of weighing to a minimum precision of 0.0001 grams. Records are kept of daily calibration checks for the balances in use. Working weights are used in these checks. The balances are annually certified by an outside source and the certifications are on file with the QA/QCO.

Balances, unless otherwise indicated by method specific SOPs, will be checked each day of use with at least two weights that will bracket the working range of the balance for the day. Daily balance checks will be done using working weights that are calibrated annually against Class S weights. Class S weights are calibrated by an external provider as required. The Class S weights are used once a year, or more frequently if required, to assign values to the Working Weights. During the daily balance checks, the working weights are compared to their assigned values and must pass in order to validate the calibration of the balance. The assigned values, as well as the daily checks, for the working weights are recorded in the balance logbook for each balance.

## Instrument Calibration

An instrument calibration is the relationship between the known concentrations of a set of calibration standards introduced into an analytical instrument and the measured response they produce. Calibration curve standards are a prepared series of aliquots at various known concentration levels from a primary source reference standard. Specific mathematical types of calibration techniques are outlined in SW-846 8000B and/or 8000C. The entire initial calibration must be performed prior to sample analyses.

The lowest standard in the calibration curve must be at or below the required reporting limit.

Refer to the current SOP to determine the minimum requirement for calibration points.

Most compounds tend to be linear and a linear approach should be favored when linearity is suggested by the calibration data. Non-linear calibration should be considered only when a linear approach cannot be applied. It is not acceptable to use an alternate calibration procedure when a compound fails to perform in the usual manner. When this occurs, it is indicative of instrument issues or operator error.

If a non-linear calibration curve fit is employed, a minimum of six calibration levels must be used for second-order (quadratic) curves.

When more than 5 levels of standards are analyzed in anticipation of using second-order calibration curves, all calibration points MUST be used regardless of the calibration option employed. The highest or lowest calibration point may be excluded for the purpose of narrowing the calibration range and meeting the requirements for a specific calibration option. Otherwise, unjustified exclusion of calibration data is expressly forbidden.

Initial Calibration Verification (ICV) samples are from a source independent of the calibration standards and are analyzed after calibration to verify the calibration curve.

Analytical methods vary in QC acceptance criteria. HEAL follows the method specific guidelines for QC acceptance. The specific acceptance criteria are outlined in the analytical methods and their corresponding SOPs.

**pH Meter**

The pH meter measures to a precision of 0.01 pH units. The pH calibration logbook contains the calibration before each use, or each day of use, if used more than once per day. It is calibrated using a minimum of 3 certified buffers. Also available with the pH meter is a magnetic stirrer with a temperature sensor. See the current pH SOP (SM4500 H+ B) for specific details regarding calibration of the pH probe.

**Other Analytical Instrumentation and Equipment**

The conductivity probe is calibrated as needed and checked daily when in use.

Eppendorf (or equivalent brands) pipettes are checked gravimetrically prior to use.

**Standards**

All of the source reference standards used are ordered from a reliable commercial vendor. A Certificate of Analysis (CoA), which verifies the quality of the standard, accompanies the standards from the vendor. The Certificates of Analysis are dated and stored on file by the Technical Directors or their designee. These standards are traceable to the National Institute of Standards (NIST). When salts are purchased and used as standards the certificate of purity must be obtained from the vendor and filed with the CoAs.

All standard solutions, calibration curve preparations, and all other quality control solutions are labeled in a manner that can be traced back to the original source reference standard. All source reference standards are entered into the LIMS with an appropriate description of the standard. Dilutions of the source reference standard (or any mixes of the source standards) are fully tracked in the LIMS. Standards are labeled with the date opened for use and with an expiration date.

As part of the quality assurance procedures at HEAL, analysts strictly adhere to manufacturer recommendations for storage times/expiration dates and policies of analytical standards and quality control solutions.

**Reagents**

HEAL ensures that the reagents used are of acceptable quality for their intended purpose. This is accomplished by ordering high quality reagents and adhering to good laboratory practices so as to minimize contamination or chemical degradation. All reagents must meet any specifications noted in the analytical method. Refer to the current Purchase of Consumables SOP for details on how this is accomplished and documented.

Upon receipt, all reagents are assigned a separate ID number, and logged into the LIMS. All reagents shall be labeled with the date received into the laboratory and again with the date opened for use. Recommended shelf life, as defined by the manufacturer, shall be documented and controlled. Dilutions or solutions prepared shall be clearly labeled, dated, and initialed. These solutions are traceable back to their primary reagents and do not extend beyond the expiration date listed for the primary reagent.

All gases used with an instrument shall meet specifications of the manufacturer. All safety requirements that relate to maximum and/or minimum allowed pressure, fitting types, and leak test frequency, shall be followed. When a new tank of gas is placed in use, it shall be checked for leaks and the date put in use will be written in the instrument maintenance logbook.

HEAL continuously monitors the quality of the reagent water and provides the necessary indicators for maintenance of the purification systems in order to assure that the quality of laboratory reagent water meets established criteria for all analytical methods. The majority of HEAL methods utilize medium quality deionized reagent water maintained at a resistivity greater than 1MΩ in accordance with SM1080.

Reagent blank samples are also analyzed to ensure that no contamination is present at detectable levels. The frequency of reagent blank analysis is typically the same as calibration verification samples. Refrigerator storage blanks are stored in the volatiles refrigerator for a period of one week and analyzed and replaced once a week.

## 8.0 Maintenance

Maintenance logbooks are kept for each major instrument and all support equipment in order to document all repair and maintenance. In the front of the logbook, the following information is included:

Unique Name of the Item or Equipment
Manufacturer
Type of Instrument
Model Number
Serial Number
Date Received and Date Placed into Service
Location of Instrument
Condition of Instrument Upon Receipt

For routine maintenance, the following information shall be included in the log:

Maintenance Date
Maintenance Description
Maintenance Performed by Initials

A manufacturer service agreement (or equivalent) covers most major instrumentation to assure prompt and reliable response to maintenance needs beyond HEAL instrument operator capabilities.

Refer to the current Maintenance and Troubleshooting SOP for each section in the laboratory for further information.

## 9.0 Data Integrity

For HEAL's policy on ethics and data integrity, see section 3.0 of this document. Upon being hired, and annually thereafter, all employees at HEAL undergo documented data integrity training. All new employees sign an Ethics and Data Integrity Agreement, documenting their understanding of the high standards of integrity required at HEAL and outlining their responsibilities in regards to ethics and data integrity. See the current Document Control Logbook for a copy of this agreement.

In instances of ethical concern, analysts are required to report the known or suspected concern to their Technical Director, the Laboratory Manager, or the QA/QCO. This will be done in a confidential and receptive environment, allowing all employees to privately discuss ethical issues or report items of ethical concern.

Once reported and documented, the ethical concern will be immediately elevated to the Laboratory Manager and the need for an investigation, analyst remediation, or termination will be determined on a case-by-case basis.

All reported instances of ethical concern will be thoroughly documented and handled in a manner sufficient to rectify any breaches in data integrity with an emphasis on preventing similar incidences from happening in the future.

## 10.0 Quality Control

### Internal Quality Control Checks

HEAL utilizes various internal quality control checks, including duplicates, matrix spikes, matrix spike duplicates, method blanks, laboratory control spikes, laboratory control spike duplicates, surrogates, internal standards, calibration standards, quality control charts, proficiency tests and calculated measurement uncertainty.

Refer to the current method SOP to determine the frequency and requirements of all quality controls. In the event that the frequency of analysis is not indicated in the method specific SOP, duplicate samples, laboratory control spikes (LCS), Method Blanks (MB), and matrix spikes and matrix spike duplicates (MS/MSD) are analyzed for every batch of twenty samples.

When sample volume is limited on a test that requires an MS/MSD an LCSD shall be analyzed to demonstrate precision and accuracy and when possible a sample duplicate will be analyzed.

Duplicates are identical tests repeated for the same sample or matrix spike in order to determine the precision of the test method. A Relative Percent Difference (RPD) is calculated as a measure of this precision. Unless indicated in the SOP, the default acceptance limit is </= 20%.

Matrix Spikes and Matrix Spike Duplicates are spiked samples (MS/MSD) that are evaluated with a known added quantity of a target compound. This is to help determine the accuracy of the analyses and to determine the matrix effects on analyte recovery. A percent recovery is calculated to assess the quality of the accuracy. In the event that the acceptance criteria is not outlined in the SOP, a default limit of 70-130% will be utilized. When an MSD is employed an RPD is calculated and when not indicated in the SOP shall be acceptable at </= 20%.

> In an effort to evaluate all received matricies, MS/MSD samples are chosen randomly. Notable exceptions to this policy are when a client requests the MS/MSD be analyzed utilizing their sample or in the event the matrix requires such a significant dilution that utilizing it as an MS/MSD is impractical.

When appropriate for the method, a Method Blank should be analyzed with each batch of samples processed to assess contamination levels in the laboratory. MBs consist of all the reagents measured and treated as they are with samples, except without the samples. This enables the laboratory to ensure clean reagents and procedures. Guidelines should be in place for accepting or rejecting data based on the level of contamination in the blank. In the event that these guidelines are not dictated by the SOP or in client specific work plans, the MB should be less than the MDL reported for the analyte being reported.