Appendix E-15b
Laboratory SOPs

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS SAMPLES BY COLD VAPOR ATOMIC ABSORPTION, SW846 7470A AND EPA 245.1

(SUPERSEDES: KNOX-MT-0009, Rev. 9)

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Method 7470A and MCAWW Method 245.1.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery with both types of compounds.

1.3. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, wastes, wipes, and other leachates/extracts. It is also applicable to the analysis of air samples collected and prepared using Methods 29, D6784-02 and 0060. Certain solid and sludge type wastes may also be analyzed, however Methods 7471A and 7471B are usually the methods of choice (refer to KNOX-MT-0010, current revision). All matrices require sample preparation prior to analysis.

1.4. Method 245.1 is applicable to the determination of mercury in drinking, surface and saline waters, domestic and industrial wastes. All matrices require sample preparation prior to analysis.

1.5. The reporting limit for mercury in aqueous matrices is 0.2 ug/L.

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in sulfuric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate, and the mercury reduced to its elemental state with stannous chloride is aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. The sample is acidified after filtration.

3.2. Suspended Metals: Those elements which are retained by a 0.45 um membrane.

3.3. Total Metals: The concentration determined on an unfiltered sample following digestion.

3.4. Additional definitions can be found in the TestAmerica Knoxville Quality Assurance Manual (QAM), current revision.

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4. INTERFERENCES

4.1. Chemical and physical interferences may be encountered when analyzing samples using this method.

4.2. Potassium permanganate, which is used to break down organic mercury compounds, also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.3. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on the recovery of mercury from spiked samples.

4.4. Chlorides can cause a positive interference. Seawaters, brines and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

NOTE: Sufficient addition of permanganate is apparent when the purple color persists at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.5. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.6. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs, the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.7. The most common interference is laboratory contamination that may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

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5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2. Specific Safety Concerns or Requirements

5.2.1. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.2.2. When using the snap cap vials for Hg analysis, care should be taken not to close or invert the vials when the samples are still warm as they may quickly build pressure and become volatile. Samples should be handled in a fume hood with the sash closed as far as operations will permit, as necessary, and samples should be opened with the container pointing away from the analyst.

5.2.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and cleanup techniques before working with mercury. Since mercury vapor is toxic, precautions must be taken to avoid its inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as equal volumes of 0.1 M KMnO4 and 10% H2SO4 or 0.25% iodine in a 3% KI solution.

5.2.4. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.2.5. Cylinders of compressed gas must be handled with caution in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.2.6. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

5.3. Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

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Material (1)	**Hazards**	**Exposure Limit (2)**	**Signs and symptoms of exposure**
Mercury, 1,000 ppm stock std.	Oxidizer Corrosive Poison	0.1 mg/m^3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 mg/m^3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported **immediately** to a laboratory supervisor.

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6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath, capable of maintaining a temperature of 90-95 °C

6.2. Leeman Hydra AA (or equivalent) Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL)

6.2.3. Peristaltic pump that can deliver 1 L/min air

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min

6.2.5. Printer

6.2.6. Aeration Tubing: A straight glass frit having a course porosity and Tygon tubing is used for the transfer of mercury vapor from the sample bottle to the absorption cell and return.

6.2.7. Drying device (Leeman Hydra AA drying tube) to prevent condensation in cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that achieve the same purpose are also acceptable (e.g., Gore-Tex filter).

6.3. Polypropylene or equivalent digestion vessels with ribbed watch glasses, or equivalent

6.4. Nitrogen or argon gas supply, welding grade or equivalent

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes

6.6. Class A volumetric flasks

6.7. Thermometer (capable of accurate readings at 95 °C)

6.8. Disposable cups or tubes

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

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7.2. Stock mercury standards (1000 ppm in 10% HNO_3) are purchased as custom solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ppm): Take 1 mL of the 1000 ppm stock mercury standard (section 7.2) and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3 . The acid (2 mL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the 10 ppm intermediate mercury standard (section 7.3) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. The acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.5. The calibration and verification standards listed in Table I must be prepared fresh daily from the working standard (section 7.4) as described in section 11.1.

NOTE: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

7.6. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards. The calibration standard source is typically Spex, catalog number PLHG4-2Y. The verification standard source is typically Ultra Scientific, catalog number ICP-080.

7.7. Refer to Table I (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better

7.9. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better

7.10. Hydrochloric Acid (HCl), concentrated, trace metal grade or better

7.11. Stannous chloride solution: Add 50 grams of stannous chloride dihydrate to 500 mL reagent water containing 50 mL of concentrated hydrochloric acid. This solution should be made fresh daily.

7.12. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

NOTE: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

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7.13. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.14. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sampling is not performed for this method by TestAmerica Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, "Sample Receipt and Log In", current revision.

8.2. The sample holding time for mercury is 28 days from the date of collection to the date of analysis.

8.3. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. Refrigeration is not required. Preservation must be verified prior to processing.

9. QUALITY CONTROL

9.1. Table II provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.2. Linear Range Verification (LR) - The linear range is the concentration above which results cannot be reported without dilution of the sample.

9.2.1. For the initial determination of the upper limit of the linear dynamic range (LDR), determine the signal responses from a minimum of three to five different concentration standards across the estimated range. One standard is near the upper limit of the estimated range. The concentration measured at the LDR must be no more than 10% less than the expected level extrapolated from lower standards.

9.3. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a laboratory control sample (LCS) and a matrix spike/matrix spike duplicate (MS/MSD). In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.4. Sample Count - Laboratory generated QC samples (method blanks, LCS and MS/MSDs) are not included in the sample count for determining the size of a preparation batch.

9.5. Method Blank - One method blank must be processed with each preparation batch. The method blank consists of reagent water and all reagents specific to the method; it is carried through the entire analytical procedure, including preparation and analysis. The

method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank for aqueous samples should not contain mercury at or above one-half the reporting limit. Method blanks for air train, SEP, PM10, and low level waste samples should not contain mercury at or above the reporting limit.

- If the method blank does not meet the acceptance criteria, reanalyze the method blank. If the method blank meets the acceptance criteria after reanalysis, reanalyze all samples associated with the failed original method blank analysis. If the method blank is still outside acceptance limits, repreparation and reanalysis of all samples associated with the unacceptable method blank is required when reportable concentrations are determined in the samples (see exceptions noted below).
- If the method blank result is less then 10% of the sample concentration, the data may be reported. **Such action must be addressed in the project narrative**.
- If there is no mercury in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative**.
- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.6. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is a blank aqueous matrix (deionized water) to which a known concentration of mercury is added. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure.

- If the LCS does not meet the acceptance criteria, reanalyze the LCS. If the LCS meets the acceptance criteria after reanalysis, reanalyze all samples associated with the failed original LCS analysis. If the LCS is still outside established control limits, the system is out of control and corrective action must occur. Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable. A control limit of 90 - 110% recovery must be applied to aqueous samples. The LCS control limits for air train, PM10 and low level waste samples are 80-120% recovery, whereas, the LCS control limits for SEP samples are 75-125% recovery.
- In the instance where the LCS recovery is > 110% and the sample results are < RL, the data may be reported with qualifiers. **Such action must be addressed in the case narrative.**

9.7. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike is a field sample to which known

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concentrations of target analytes have been added. A matrix spike duplicate is a second aliquot of the same sample (spiked identically to the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSD analysis. Spiking levels are provided in Table I.

- If the recovery or RPD falls outside the acceptance range, the recovery must be in control for the LCS. Control limits of 85-115 % recovery and 20 RPD must be applied to the MS/MSD for aqueous samples. The MS/MSD control limits for air train and PM10 samples are 80-120% recovery and 20% RPD and the MS/MSD control limits for low level waste samples are 75-125% recovery and 20 RPD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results that fall outside the control limits must be addressed in the narrative.
- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level, the recovery data are reported as NC (i.e., not calculated) and MSB (i.e., the recovery and RPD were not calculated because the sample amount was greater than four times the spike amount).
- If the concentration in the original sample digestate exceeds the calibration range and is > 50 ppb (raw value), the original sample digestate will be diluted and reanalyzed. However, the MS/MSD digestates do not need reanalysis at a dilution because the native analyte exceeds the spike amount by a factor much greater than 4x. Report the MS/MSD with the NC, MSB qualifiers described above.
- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed.

9.8. Duplicate - One duplicate may be processed with the preparation batch instead of the matrix spike duplicate, at the request of the client. Samples identified as field blanks cannot be used for duplicate sample analysis.

9.9. If the sample results are greater than or equal to five times the RL, the control limit is ± 20 RPD for aqueous samples and ± 30 RPD for SEP samples.

- If either the sample or sample duplicate value is less than five times the RL, the control limit is ± the RL.
- If both the sample and sample duplicate results are below the MDL, the RPD is not calculated and no control criteria apply.

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9.10. Initial Calibration Verification and Blank (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% of the true value for 7470A and within 5% of the true value for 245.1. An initial calibration blank (ICB) is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall below the MDL for aqueous samples and below the RL for air train, SEP, PM10 and low level waste samples. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. (See Section 11.2.7 for required run sequence.) If the cause of the ICV or ICB failure was not directly instrument related, the corrective action would include repreparation of the associated samples.

9.10.1. The ICB is a digested method blank.

9.11. Continuing Calibration Verification and Blank (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 10% of the true value for method 245.1 and within 20% of the true value for method 7470A. A continuing calibration blank (CCB) is analyzed immediately following each CCV. (See Section 11.2.7 for required run sequence). The CCB result must fall below the MDL for aqueous samples and below the RL for air train, SEP, PM10 and low level waste samples. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, reanalyze the failing CCV/ CCB. If the CCV/CCB still fails, the analysis must be terminated, the problem corrected (e.g., re-pour standard digestates into clean autosampler cups), the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV or CCB failure was not directly instrument-related or due to cross-contamination during autosampler tube preparation, the corrective action will include repreparation of the associated samples.

9.11.1. The CCB is a digested method blank.

9.12. Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the sample prior to preparation. This technique compensates for a sample interferent that may enhance or depress the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences that cause a baseline shift. Refer to Appendix D for specific MSA requirements.

9.13. Reporting Limit Check Standard (CRA) - A CRA standard is run at the beginning of each sequence, after the ICV and ICB. The CRA standard contains mercury at 0.2 ug/L. The CRA result must fall within 30% of the true value. If the CRA does not meet the acceptance criteria, reanalyze the CRA. If it is still outside acceptance limits, the analysis is terminated, the problem corrected and the instrument recalibrated.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols, separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up . The instrument calibration date and time must be included in the raw data.

10.4. Set up the mercury analyzer using the operating parameters recommended by the manufacturer. For the Leeman Hydra AA system, the operating parameters are entered under the protocol 'Test' in the WinHg Database (DB) and are described below.

Gas flow rate:	0.40 LPM (Argon feed pressure of 75 psi, no entry for this in the protocol)
Pump rate:	5 mL/minute
Rinse time:	40 seconds
Uptake time:	18 seconds
Replicates:	1
Full Scale:	20
Integration:	15 seconds

Refer to the CVAA manual of the instrument in use for detailed setup and operation procedures. Whenever it is necessary to change the setup/operating parameters or to change instruments (e.g., acquiring a rental while one instrument is being serviced), new parameters/instruments should be validated by performing an IDL/MDL check or MDL study.

10.5. Calibrate the instrument using a minimum of five standards and a blank; typically, six standards are used. One standard must be at the reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

For the Leeman Hydra AA instrument, calibration standard and check standard concentrations and acceptable recovery ranges are entered under 'Line Info' in the WinHg database. The type of calibration curve, Linear, may be selected under 'Cal Curve' in the WinHg database. A calibration curve is generated by the 'Stnd Auto' method under 'Standard' in WinHg runner after selecting S1 through S6 (calibration standards), selecting 'Rep 1' (one replicate), selecting at least C1 through C3 (check standards CCB, ICV and CCV) along with their respective active cups, and selecting 'New Cal Reset' (resetting current calibration data).

10.6. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient.

For the Leeman Hydra AA, the correlation coefficient is automatically calculated by the instrument software and may be viewed along with the graph of relative absorbance vs. concentration under 'Cal Curve' in the WinHg Database. The curve should be accepted by hitting 'Accept', which will automatically result in the 'Calibrated'/'Accepted' boxes being checked. This data window should be printed and included with the completed run report.

10.7. Refer to Section 9 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Standard and Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure along with the field samples.

11.1.2. Transfer 50 mL of well mixed sample or reagent water to clean sample digestion vessels. Record the sample volume on the sample preparation worksheet (Appendix I).

NOTE: Reduced sample volumes can be used as long as a representative sample can be obtained and the reagent levels are adjusted to maintain the same sample to reagent ratio. All samples and standards must be processed similarly.

11.1.3. From the containers with reagent water, remove the following volumes, respectively: 0 mL, 50 uL, 100 uL, 250 uL, 500 uL, 2.5 mL, 5.0 mL (for the calibration standards) and 1.25 mL (ICV), 0 mL (ICB), 2.5 mL (CCV), 0 mL (CCB) and 100 uL (CRA). Volumes removed above will be replaced with the appropriate working standard solution (section 7.4) AFTER initial acid addition.

11.1.4. Add 2.5 mL of concentrated H_2SO_4, 1.25 mL of concentrated HNO_3, and 2.0 mL concentrated HCl (mixing after each addition).

11.1.5. Add the appropriate working standard solutions (section 7.4) to the calibration and calibration verification containers and spike sample QC, if applicable.

11.1.6. Add 7.5 mL of potassium permanganate solution. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. If after the addition of up to 12.5 mL additional permanganate the color does not persist, sample dilution prior to reanalysis may be required.

11.1.7. Add 4.0 mL of potassium persulfate solution and heat for two hours in a water bath or block digestor at 90 - 95 °C.

11.1.8. Cool samples briefly. Warm samples decolorize (section 11.1.9) more completely and at a faster rate than samples at room temperature.

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CAUTION: When using the snap cap vials for Hg analysis, care should be taken not to close or invert the vials when the samples are still warm as they may quickly build pressure and become volatile. Samples should be handled in a fume hood with the sash closed as far as operations will permit, as necessary, and samples should be opened with the container pointing away from the analyst.

11.1.9. Add 3.0 mL of sodium chloride-hydroxylamine hydrochloride solution to the samples to reduce the excess permanganate. (The permanganate has been reduced when no purple color remains.) Add this solution in 3.0 mL increments until the permanganate is completely reduced.

11.1.10. After decoloring samples, allow them to cool to room temperature. Bring all samples to a final volume of 70 mL using reagent water.

11.1.10.1. **NOTE**: If due to the addition of extra reagents, the final volume is greater than 70 mL, after the digestion is finished, adjust the final volume upward to a known final volume with reagent water. This is addressed through mathematical correction of the results to account for the resultant dilution effect. An example is provided in Section 12.

11.2. Analysis:

11.2.1. Detailed operating instructions are provided in Appendix H.

11.2.2. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.3. Automated determination: Follow instructions provided by instrument manufacturer, as described in section 10 for the Leeman Hydra AA.

11.2.4. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury. Refer to section 10.6 for the calibration criteria. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation based regression curve fitting techniques on concentration/response data is acceptable. Refer to section 10.5 for Leeman Hydra AA computer-automated calibration instructions.

11.2.5. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples that exceed the highest calibration standard.

11.2.6. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.7. The following run sequence is consistent with methods 7470A and 245.1.

Instrument Calibration

ICV
ICB
CRA
CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

NOTE: Samples include the method blank, LCS, MS, MSD, duplicate, PDS (if applicable) field samples and sample dilutions.

11.3. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and troubleshooting.

11.4. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure, except those specified by project specific instructions, shall be completely documented using a nonconformance memo and approved by a Technical Specialist, Project Manager and QA Manager. If contractually required, the client shall be notified.

11.5. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.6. Refer to TestAmerica Knoxville SOP KNOX-IT-0001, current revision for requirements for computer hardware and software.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{\text{Found(ICV)}}{\text{True(ICV)}}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{\text{Found(CCV)}}{\text{True(CCV)}}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

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Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration for an aqueous sample is calculated as follows:

Sample Concentration (µg/L) = C x D x E

Where:
C = Concentration (µg/L) from instrument readout
D = Instrument dilution factor, i.e., the dilution necessary to generate an instrument readout concentration within the calibration curve
E = Prep dilution factor: The prep dilution factor is used when the sample digestate must be brought to a final volume greater than the nominal final volume of 70 mL. (Refer to section 11.1.10.) Example: For a digestate with a final volume of 80 mL, the prep dilution factor = 80 mL/70 mL.

12.6. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.7. Sample results are reported with two significant figures for values <10 and three significant figures for values ≥ 10.

12.8. Refer to Appendix C for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

13. METHOD PERFORMANCE

13.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. Method Detection limits are determined and verified as specified in the current revision of SOP CA-Q-S-006 (and attachment) based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit.

13.2. Initial Demonstration of Capability – Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in TestAmerica Knoxville SOP KNOX-QA-0009, current revision.

13.3. Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

15.2. Acid waste consisting of sample and rinse solution will be collected and placed in the acidic waste stream 55 gallon HDPE drum. Never use metal containers for acidic waste.

16. REFERENCES

16.1. SW-846 Method 7470A, “Mercury in Liquid Waste (Manual Cold-Vapor Technique”, Revision 1, September 1994.

16.2. “Methods for the Chemical Analysis of Water and Wastes”, EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.1.

16.3. ASTM Method D6784-02, Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario Hydro Method).

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16.4. Method 29, "Determination of Metals Emissions from Stationary Sources".

16.5. SW-846 Method 0060, “Determination of Metals in Stack Emissions”, Revision 0, December 1996.

16.6. Policy “QA-003”, QC Program, current revision.

16.7. Leeman Hydra AA Operation Manual

16.8. TestAmerica Knoxville Quality Assurance Manual (QAM), current revision.

17. MISCELLANEOUS

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from both 7470A and 245.1.

17.1.1.1. The 200 series methods and Chapter 1 of SW-846 specify the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water.

17.1.1.2. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, “Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology.”

17.1.1.3. The alternate run sequence presented in Section 11.2.7 is consistent with method requirements. An additional QC analysis for the detection limit standard (CRA) was added.

17.1.2. Modifications from Method 7470A

17.1.2.1. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above ½ the reporting limit.

17.1.2.2. The addition of HCl to sample and standard preparation is necessary to achieve lower instrument detection limits as demonstrated by the mercury analyzer manufacturer’s quality assurance tests (Leeman Labs, Inc.).

17.1.3. Modifications from 245.1

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17.1.3.1. Method 245.1 Section 9.3 states concentrations should be reported as follows: Between 1 and 10 ug/L, one decimal; above 10 ug/L, to the nearest whole number. The laboratory reports all Hg results under this SOP to two significant figures for values <10 and to three significant figures for values ≥ 10.

17.1.3.2. The addition of HCl to sample and standard preparation is necessary to achieve lower instrument detection limits as demonstrated by the mercury analyzer manufacturer's quality assurance tests (Leeman Labs, Inc.).

17.2. List of Appendices

17.2.1. Appendix A, Figure 1: Flow Chart for Aqueous Sample Preparation for Mercury

17.2.2. Appendix A, Figure 2: Flow Chart for CVAA Mercury Analysis

17.2.3. Appendix B, Table I: Mercury Reporting Limits, Calibration Standard QC Standard and Spiking Levels

17.2.4. Appendix B, Table II: Summary of Quality Control Requirements

17.2.5. Appendix C: Example Hg Data Review Checklist

17.2.6. Appendix D: MSA Guidance

17.2.7. Appendix E: Troubleshooting Guide

17.2.8. Appendix F: Contamination Control Guidelines

17.2.9. Appendix G: Preventative Maintenance

17.2.10. Appendix H: Leeman HydraAA Operation Instructions

17.2.11. Appendix I: Example Sample Preparation Worksheet

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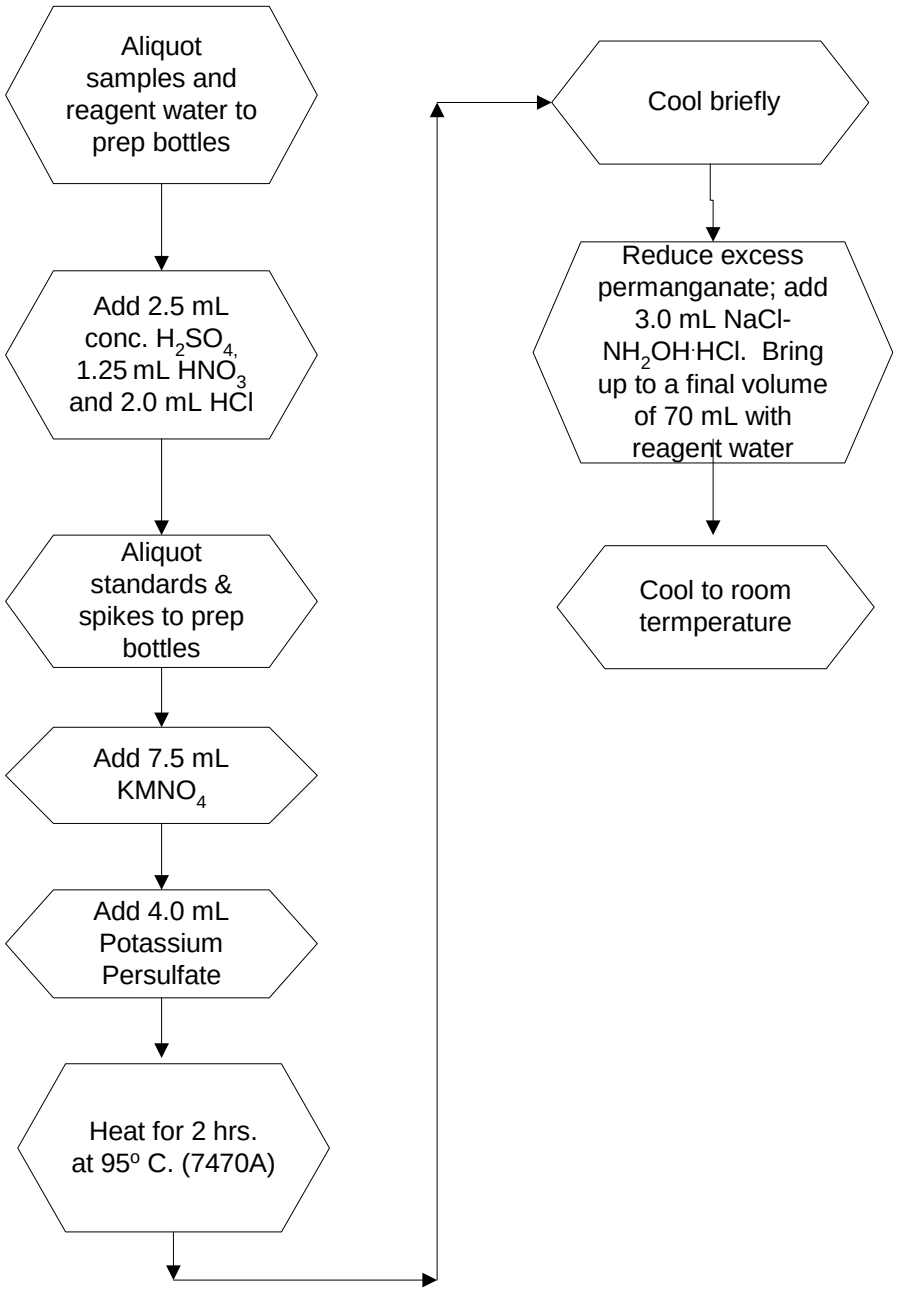
APPENDIX A, Figure 1. Aqueous Sample Preparation - Mercury



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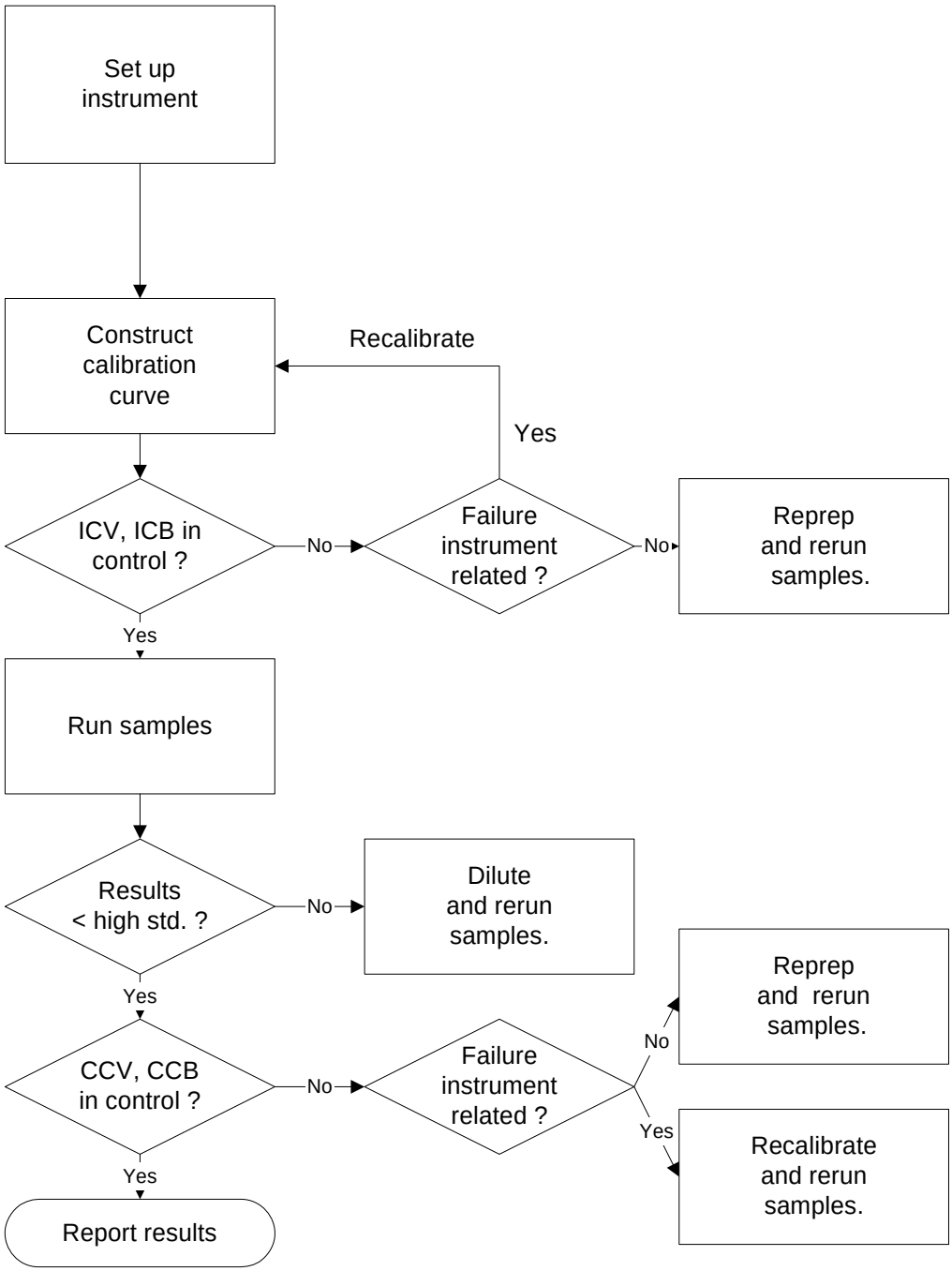
APPENDIX A, Figure 2. CVAA Mercury Analysis



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APPENDIX B, TABLE I: Mercury Reporting Limits, Calibration Standard[1], QC Standard and Spiking Levels

Standard	Concentration (ug/L)
Standard Aqueous RL	0.2
Std 0	0
Std 1[2]	0.1
Std 2	0.2
Std 3	0.5
Std 4	1.0
Std 5	5.0
Std 6	10.0
ICV	2.5[3]
LCS/CCV	5.0[3]
Aqueous MS	1.0
Aqueous PDS, if applicable	1.0
CRA	0.2

1 SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be approved by a facility Technical Specialist and Quality Assurance Manager prior to the preparation of client samples.

2 Only six points (including zero) are required for a standard curve. The 0.1 ug/L standard was introduced into the curve sequence in order to match the lowest RL criteria across all aqueous mercury SOPs at TestAmerica Knoxville.

3 Concentration level dependent on high calibration standard used. CCV must be 50% of the high standard concentration and ICV must be 20-25% of high standard concentration.

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APPENDIX B, Table II: Summary of Quality Control Requirements

Parameter/Method	QC Check	Frequency	Target Criteria	Corrective Action
Mercury by CVAA for water, soil and waste samples (Methods7470A & 245.1)	Initial Calibration Verification (ICV/ICB)	Beginning of analysis sequence	ICV • 95 - 105% recovery: Method 245.1 • 90 - 110% recovery: Method 7470A ICB • Concentration <MDL: Aqueous samples • Concentration < RL: Air train & SEP samples	1. Make necessary adjustments. 2. Repeat calibration.
	Continuing Calibration Verification (CCV/CCB)	After every 10 samples and at the end of the run	CCV • 90 - 110% recovery: Method 245.1 • 80 - 120 % recovery: Method 7470A CCB • Concentration <MDL: Aqueous samples • Concentration < RL: Air train & SEP samples	1. Repeat CCV/CCB. 2. If 1. fails, make adjustments and repeat calibration and reanalyze affected samples.
	Reporting Limit (RL) Check Standard (CRA)	One per analytical run	• 70 - 130% recovery	1. Repeat RL check standard. 2. If 1. fails, make adjustments and repeat calibration and reanalyze affected samples.
	Laboratory Method Blanks	Once per digestion batch (maximum 20 samples)	Target analyte concentrations • <½RL : Aqueous samples • < RL: Air train & SEP samples	1. Reanalyze method blank. 2. If 1. fails, reprepare and reanalyze samples associated with unacceptable blank. 3. Report results if sample results >10x blank result or sample results ND. See Section 9.4.
	Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)	Once per digestion batch (maximum 20 samples) LCSD not required if MS/MSD or MS/DUP performed	Accuracy • 90 - 110% recovery: aqueous samples • 80 - 120% recovery: air train & SEP samples Precision (if applicable) • ≤ 20% RPD	1. Reanalyze LCS/LCSD. 2. If 1. fails, reprepare and reanalyze samples associated with unacceptable LCS/LCSD. 3. Report results if LCS results > control limit and samples are ND. See Section 9.5.
	Matrix Spike/Matrix Spike Duplicate (MS/MSD)	Once per digestion batch (maximum 20 samples)	Accuracy • 85 - 115% recovery for aqueous samples • 80 - 120% recovery for air train & SEP samples Precision • ≤ 20% RPD	1. Flag the data; no flag required if the sample level is > 4x the spike added (see Section 9.6). 2. For TCLP see Section 11.2.8

APPENDIX C: EXAMPLE DATA REVIEW CHECKLISTS

TestAmerica Knoxville Mercury Data Review Checklist

Method: SW-846 7470A/7471A/0.2 RL

Analyst:	KND			**Instrument:**	Leeman Hydra AA Mercury Analyzer		
Run Date:	Sep-30-08	**Calibration Number:**	1	**Chart Name:**	m093008.prn	**Element:**	Hg

A. Calibration/Instrument Run QC	**N/A**	**Yes**	**No**	**Comments**
1. Instrument calibrated every 24 hours?		X		Calibration was 2 hours and 12 minutes long
2. Instrument calibrated using a minimum of a blank and 5 standards?		X		
3. Do standard absorbances increase as standard concentrations increase?		X		
4. Instrument calibrated with standards at the SOP levels?		X		
5. Correlation coefficient greater than or equal to 0.995?		X		Correlation coefficient was 0.9999
6. ICV analyzed directly after calibration?		X		
7. ICV within specified control limits?		X		
8. ICB analyzed immediately after ICV?		X		
9. ICB within acceptable range?		X		
10. CRA analyzed at the beginning of the run?		X		
11. CRA results within acceptable range?		X		
12. All CCV's within specified control limits?		X		
13. All CCB's within acceptable range?		X		
14. All CCB's analyzed immediately after CCV's?		X		
B. Client Sample and QC Sample Results				
1. Were all sample results within the linear range of the instrument ?		X		
2. Were there any samples with results more negative than Report Limit?			X	
3. Were samples analyzed within the holding time?				
C. Preparation/Matrix QC				
1. Was one method blank prepared for each batch?				
2. Were all method blanks less than the specified level?		X		
3. Was an LCS prepared for each batch?				
4. Were all LCS recoveries within QC limits?		X		
5. Were matrix spikes, sample duplicates and/or post-digestion spikes run at required frequency?				
6. Were all matrix spike recoveries within QC limits?			X	See Comments on Next Page
7. Were post-digestion spike recoveries within QC limits?				
8. Were duplicate RPDs within QC limits?		X		
D. Other				
1. Current IDL data on file?		X		
2. Current MDL data on file?				
3. Are all nonconformances documented appropriately?				
4. Were all project specific instructions followed?				NCM#:

Question Number:	Problem(s) Found:
C6	Matrix spike sample KW80KS at 9/30/2008 1:56:49 PM had 73.7% recovery.
C6	Matrix spike sample KW80KD at 9/30/2008 1:58:47 PM had 65.9% recovery.

Analyst: _____ **Date:** _____

Analyst Comments: _____

APPENDIX C: EXAMPLE DATA REVIEW CHECKLISTS, continued

TestAmerica Knoxville Mercury Data Review / Narrative Checklist
Methods 7470A/7471A, 7471B and 245.1/245.5 - KNOX-MT-0009, Rev 10 and KNOX-MT-0010, Rev 9 **Page 1 of 2**

Lot / SDG #:	

A. Review of QuantIMS / QDS Results	**NA**	**Yes**	**No**	***Why is data reportable?***
1. Were PM checklists, Lot Summary and any applicable QAS reviewed?				
2. Were all prep sheets, prep spreadsheets and any existing NCMs reviewed?				
3. Were manual calculations of results and RLs performed for each sample, blank, LCS, LCSD, MS, MSD and DUP? (Document 1 calculation per batch.)				
4. Were elements with negative results >RL reported as ND G?				
5. For each sample, blank, LCS, LCSD, MS, MSD and DUP, were flags, units, DFs, prep date, date/time of analysis verified to be correct?				
6. Were spike amounts verified for each LCS/MS? (Document 1 manual calculation.)				
7. Were method blank results ≤1/2 RL for water/solid samples or <RL for air train samples?				☐ **[mb3] No analyte >QC limit in associated samples.** ☐ **[mb5] Insufficient sample for reanalysis.*** ☐ **[mb7] Samples >10x blank**
8. LCS or LCS/LCSD within QC limits? (90-110%R)				☐ **[lcs2] Insufficient sample for reanalysis.** ☐ **[lcs3] LCS%R >QC limits & sample results < RL.***
9. MS/MSD or MS/DUP run at required frequency?				☐ [lcsd] Insufficient sample – lcs/lcsd analyzed.
10. MS %R or MS/MSD %R & RPD within QC limits?				☐ [ms1] ☐ [msd1] LCS acceptable - matrix effects. ☐ [ms2] ☐ [msd2] Native analyte > 4x spike level. ☐ [ms3] ☐ [msd3] Matrix effects & native >4x spike. ☐ [batch] Batch QC on client's sample outside limits.
11. DUP RPD within limits? (0-20 RPD for results ≥5xRL; +RL if result <5xRL)				☐ [rpd] LCS acceptable. Results indicate sample heterogeneity.
12. Were J flags added to the DUP as needed?				
13. Is DUP RPD=0 for two ND results and RPD=200 for one ND and a positive result?				
14. Are all results present for all samples?				
15. Were the samples analyzed within the holding time?				☐ [ht1] HT expired upon receipt ☐ *[ht2] Analysis requested after HT expired.* ☐ See comments section below.

Data Reviewer:	**Date:**
Calculation Checks / Comments:	

*Such action must be taken in consultation with client.
NOTE: Nonconformance memos are required for **bold** and *italicized* [autotext] statements: **Bold** = deficiency, *italicized* = anomoly.

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APPENDIX C: EXAMPLE DATA REVIEW CHECKLISTS, continued

TestAmerica Knoxville Mercury Data Review / Narrative Checklist
Methods 7470A/7471A, 7471B and 245.1/245.5 - KNOX-MT-0009, Rev 10 and KNOX-MT-0010, Rev 9 **Page 2 of 2**

Lot / SDG #:	

B. Review of QC Summary Forms ***Note:*** Y=Yes, N=No, NA=Not Applicable	**Chart #**	**Chart #**	**Chart #**	**Chart #**	***Why is data reportable?***
1. ICV within limits? (7470A/7471A/7471B=90-110%R; 245.1/245.5=95-105%R)					
2. CCV within limits? (7470A/7471A/7471B=80-120%R; 245.1/245.5=90-110%R)					If no, list details: _____
3. ICB/CCB within limits? (<MDL for water/solid samples; <RL for air train samples)					If no, list details: _____
4. CRA within limits? (The CRA standard contains mercury at 0.2 ug/L. The CRA result must fall within 30% of the true value.)					
5. PDS or PDS/PDSD run at required frequency?					
6. PDS/PDSD within limits? (75-125%R) **Reminder:** Place copy of PDS results in Sample Data Summary and QC Summary sections of report.					☐ [pds1] ☐ [pdsd1] LCS acceptable - matrix effects. ☐ [pds2] ☐ [pdsd2] Native analyte > 4x spike level. ☐ [pds3] ☐ [pdsd3] Matrix effects & native >4x spike.
7. Are the IDLs on summary forms current?					
8. Are the QC summary forms correct?					

Data Reviewer:	**Date:**
Comments:	

*Such action must be taken in consultation with client.
NOTE: Nonconformance memos are required for **bold** and *italicized* [autotext] statements: **Bold** = deficiency, *italicized* = anomoly.

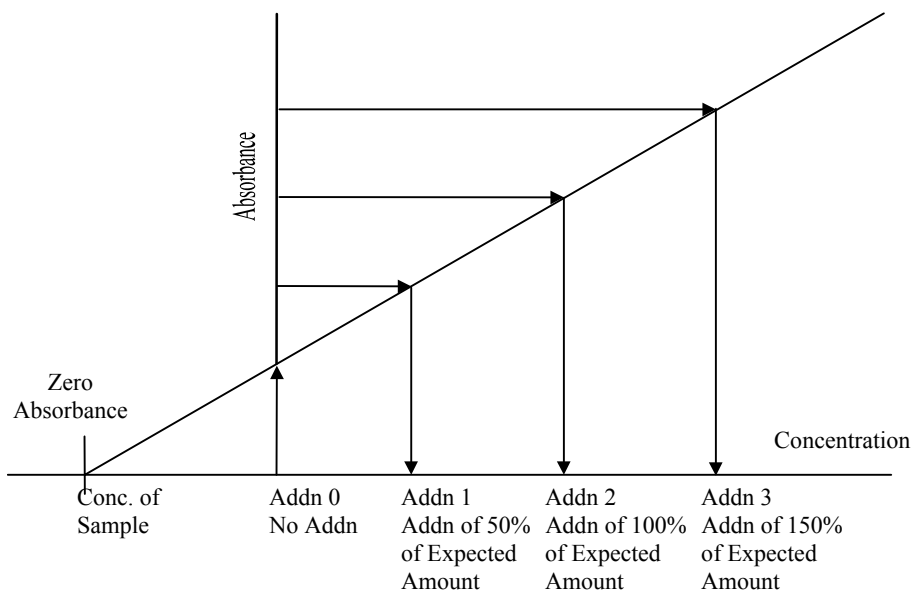
APPENDIX D: MSA GUIDANCE

Method of Standard Addition

Four equal volume aliquots of sample are measured and known amounts of standards are added to three aliquots. The fourth aliquot is the unknown and no standard is added to it. The concentration of standard added to the first aliquot should be 50% of the expected concentration. The concentration of standard added to the second aliquot should be 100% of the expected concentration and the concentration of standard added to the third aliquot should be 150% of the expected concentration. The volume of the unspiked and spiked aliquots should be the same (i.e., the volume of the spike added should be negligible in relation to the volume of sample).

To determine the concentration of analyte in the sample, the absorbance (or response) of each solution is determined and a linear regression performed. On the vertical axis the absorbance (or response) is plotted versus the concentrations of the standards on the horizontal axis using 0 as the concentration of the unspiked aliquot. An example plot is shown in Figure 1. When the resulting line is extrapolated back to zero absorbance, the point of interception of the horizontal axis is the concentration of the unknown. Calculate the correlation coefficient (r) and the x-intercept (where y=0) of the curve. The concentration in the digestate is equal to the negative x-intercept.

Figure 1



- For the method of standard additions to be correctly applied, the following limitations must be taken into consideration.
- The plot of the sample and standards must be linear over the concentration range of concern. For best results, the slope of the curve should be similar to that of a plot of the aqueous standard curve.
- The effect of the interference should not vary as the ratio of the standard added to the sample matrix changes.

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APPENDIX E: TROUBLESHOOTING GUIDE

Problem	**Possible Cause**
Poor or no absorbance or sensitivity check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Clogged reductant line Empty sample cup Incorrectly made standards Gas leak EDL power supply set on “Continuous”
Erratic readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware/digestion vessels Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL won’t light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell

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APPENDIX F: CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

All non-disposable labware that comes in contact with samples should be washed with detergent and tap water and rinsed with 1:3 nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Samples/standards in process should be covered whenever possible to reduce the contamination from laboratory dust particles.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Analyst should be careful not to touch samples poured into autosampler racks with gloves and inadvertently carry-over “contamination” to subsequent sample cups.

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APPENDIX G: PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date and instrument ID number, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Instrument Maintenance Schedule*

Cold Vapor Atomic Absorption (Leeman Hydra AA)

Daily Maintenance	As Needed Maintenance
Check tubing.	Adjust/change Hg lamp.
Check maintenance schedule flags.	Clean or replace optical cell.
	Lubricate pump and autosampler arm.
	Change the drying tube.

*Leeman has incorporated an automated maintenance schedule in its Hg software that flags the user when instrument maintenance is required. These flags or messages appear in the upper right hand corner of the main user window (refer to manual).

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APPENDIX H: LEEMAN HYDRAAA OPERATION INSTRUCTIONS

NOTE: Refer to the instrument manual for instructions re. detailed method setup, such as entering standard curve concentration values and check standard values, troubleshooting operations. Refer to the appropriate mercury prep SOP for instrument operating parameters and required run sequences.

- Turn off computer screensaver and log off the network, if applicable.
- Click 'WinHg' icon on desktop.
- Drop-down 'Protocol', beneath the toolbar, to select the appropriate method to analyze samples (e.g. '7ptcurve' refers to the method used to run a file with a seven-point calibration curve; 'ontariohydro' is used to analyze only Ontario Hydro samples; and 'test' is used to analyze samples with a six-point calibration curve).
- Click 'File' in the toolbar, then drop-down to 'new dataset'.
  - Enter file name (lower-case 'h' followed by month, day, year –hmmddyy-).
  - Another window will pop up requesting a batch name; hit 'cancel', since this refers to the automated prep system we don't use.
- Select the new file just created from the 'Dataset' list beneath 'Protocol' to ensure the new file name will print out with the raw data; otherwise the raw data will be labeled with the file name of the previous run.
- Place all tubing in the appropriate containers; secure pump tubing to pump (tension is released on the clips during shutdown from the previous run). 10% stannous chloride continuously runs through the instrument, but sample and stannous chloride are delivered simultaneously at a 1:5 rate of reductant to sample (e.g., as 3.4 mL of sample are delivered, only 0.650 uL reductant are delivered at the same time). They are mixed at the mixing tee prior to entering the liquid-gas separator where argon releases elemental mercury to the drying tube, prior to being measured at the optics.
- Click 'Control' tab, click 'On' under 'lamp', 'gas', and 'pump'.
- Click 'Standard' tab; depress buttons 'S1' through 'S6' if using a six-point standard curve or 'S1' through 'S7' if using a seven-point curve. These standards are placed in the first (back) row of a separate autosampler rack, in order from right to left.
  - Depress 'Rep 1' button if only one injection is desired per standard analysis (depress both 'Rep1' and 'Rep2' if standards analyzed in duplicate, etc.).
  - Depress 'New Cal Reset' button, which clears the previous calibration curve.
  - Depress buttons 'C1' through 'C3' under the 'check standards' section, representing the CCB, ICV, and CCV. These standards are placed in the second (front) row of the standard curve rack mentioned above, in order from right to left.
- Click the rack editor icon in the WinHg toolbar. The icon looks like the top view of an autosampler rack.
  - Drop-down 'File' in the rack editor window toolbar, then select the rack to be edited (e.g. 'rack1').
  - In the far-left column of the rack spreadsheet, enter the appropriate check standard ID's and work order ID's in the order that they should be injected. The first two entries of the first rack to be analyzed should include 'ICB' and 'CRA', respectively.
  - In the far-right column of the rack spreadsheets, the sequence 'C3 C1' should be entered in the same row as the 'CRA' entry (when applicable) and in the same row as every 10th work order ID. This sequence directs the instrument to inject a CCV (C3), then a CCB (C1) after the CRA and every 10th sample. The sequence 'C2 cp' should be entered in the same row as the ICB entry (when applicable), to direct the instrument to inject an ICV (C2) before (cp) it injects the ICB.
  - The following suffixes should be applied to a work order ID associated with batch QC or dilutions:
    - Blank: B (also type the batch number in the second column, 'extended ID', of the row containing a blank entry)
    - LCS: C
    - LCSD: L
    - MS: S
    - MSD: D
    - Duplicate: X
    - PDS: A
    - PDSD: AX
    - Dilution: Z, then dilution value: e.g. 1:10 dilution, Z10
    - Diluted MS/MSD (spike applied to diluted sample at prep): e.g. Z10S/Z10D

APPENDIX H: LEEMAN HYDRAAA OPERATION INSTRUCTIONS, continued

- Diluted MS/MSD (spike applied to undiluted sample at prep, diluted at analysis): e.g. SZ10/DZ10
- Diluted MS/MSD (mercury spike applied to undiluted ICP sample, ICP sample diluted at mercury prep): e.g. SZ10/DZ10
- Filtered batch QC/sample: F

- Click 'Sample' tab; this window allows the operator to enter the order in which multiple racks should be analyzed and which samples in each rack should be analyzed.
  - Drop-down the first 'rack' field and select the appropriate rack name; drop-down the first number of the sample cup to be injected within the rack selected, then drop-down and select the last sample cup# to be injected.
  - Follow the same instructions for the second rack to be analyzed. If a second rack is not required, make sure the fields are blank (drop-down and select the blank space).
  - If a third or fourth rack must be analyzed in the same dataset, these racks may not be entered until the instrument completes analysis of the first two racks. At that time, the instrument will be 'idle' and the operator may enter the next rack(s) as above.
  - If samples are to be analyzed in duplicate, click the database icon ('DB') in the Win Hg toolbar, then the 'Protocol' tab, then use the scroll arrows under 'Data Collection/Replicates' to change '1' to '2'.
- Pour up sample digestates, placing them in the appropriate sequence in racks loaded from right to left, back to front.
- When the operator is ready to begin collecting data, click 'Standard' tab, then 'Std Auto' button (referring to the automatic injection of the standard curve series). The WinHg window will indicate the instrument is 'busy'.
  - When the standard curve analysis is complete, click the 'DB' icon, then the 'Calibration Curve' tab. Depress the 'Accept' button if the linear regression coefficient (r) is greater than 0.995. Print the window (be sure all the raw data are included in the printout).
- With the calibration curve established and all racks loaded, click 'Sample' tab, then 'Run Auto' button. Monitor the collection of data to ensure all values are within SOP control limits. Re-run samples, if necessary, by stopping the instrument ('STOP' icon in WinHg toolbar), then re-starting ('Run Auto' under 'Sample' tab) when new samples are loaded and rack entries are adjusted.
- Report a dataset as follows:
  - Click 'Main' tab, depress the 'Form Feed' button under 'printer control' to print any remaining data stored in the file (If the number '0' is next to the button, this isn't necessary. The number represents the number of data points still stored in the printer's memory).
  - Click 'DB' icon, then 'Report' tab, then 'All' button. At this point, all data will be associated with a checked box. If a data point is not to be reported, remove the check from the box, then proceed.
  - Click 'Generate Report' button. A window will open. Select '.prn' for file type.* Enter the correct target drive/file name in which to store the report (e.g. C:/upload/h061402). Click 'Generate' button. Close window. Open 'My Computer' icon on desktop, then storage file, then select report file. Transfer the report file to data and upload drives on the network (this will require logging on), or to a floppy disk that can be transferred to another computer for this purpose.
    - *If 'printer' is selected for file type, the 'Generate' button will provide a post-run printout of raw data (as opposed to the real-time printout of data indicated in the method). The latter scenario may be used when the printer malfunctions during data collection.

    When a report has been generated, transfer the stannous chloride line to water and allow the instrument to flush while data is being validated/uploaded. The instrument will automatically stop pumping after one hour.

Leeman HydraAA Instrument Shutdown:

- After rinsing the system with water, remove all tubing and sample tip from liquid containers and pump to dryness. The sample tip is removed to air by clicking the 'Sample' tab, then the 'To Air' button on the right-hand side of the resulting window.
- When tubing is dry, click 'Control' tab; then click 'Off' under 'lamp', 'pump', and 'gas'.
- Under the 'Sample' tab, return the sample tip 'To Rinse'.
- Release tension clips on the pump tubing.
- Close all windows on desktop.
- Turn off monitor. The computer may also be shutdown at this point if desired, esp. if the instrument will not be used for an extended time.

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APPENDIX I: EXAMPLE SAMPLE PREPARATION WORKSHEET

TestAmerica Knoxville
Mercury Aqueous Sample Preparation Worksheet
SOP KNOX-MT-0009

Page 1 of 2

Batch Number:
Prep Date:
Comp Date:

Mercury Prep Analyst: _____ Prep Date: _____
2nd Level Review by: _____ Review Date: _____

Lot Number	Lot Sample Number	Suffix	Method Code	Client ID	WO #	Initial Sample Volume (mL)	Final Sample Volume (mL)	Hg Bench Dilution Factor	QuantIMS Upload Dilution Factor	QuantIMS Upload Multiplier

Digestion Vial ID: _____

Comments: _____

QuantIMS Upload Dilution Factor and Multiplier = Final Digestate Volume (mL)/Initial Sample Volume (mL) x 50 mL/50 mL x Hg Bench Dilution Factor

Mercury Aqueous Prep Rev 2a1 Mercury Aqueous Prep Rev 2a.xlt Printed 2/18/2011 10:35 AM

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APPENDIX I: EXAMPLE SAMPLE PREPARATION WORKSHEET, continued

TestAmerica Knoxville
Mercury Aqueous Sample Preparation Worksheet
SOP KNOX-MT-0009

Page 2 of 2

Batch Number: _____ Time In: _____ Bath A Temp: _____ °C
Analyst: _____ Time Out: _____ Bath B Temp: _____ °C
Prep Date: _____ LCS Pipet ID: _____ Thermometer ID: MT-2
MS Pipet ID: _____ (Acceptance range 90° – 95°C)

Standard Type	Standard ID	Working Standard		Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
		Source	Conc.(ug/L)			
Calibration Std 1	N/A	N/A	N/A	N/A	50	Blank
Calibration Std 2	I-CAL-	SPEX	100	0.05	50	0.1
Calibration Std 3	I-CAL-	SPEX	100	0.1	50	0.2
Calibration Std 4	I-CAL-	SPEX	100	0.25	50	0.5
Calibration Std 5	I-CAL-	SPEX	100	0.5	50	1
Calibration Std 6	I-CAL-	SPEX	100	2.5	50	5
Calibration Std 7	I-CAL-	SPEX	100	5	50	10

Standard Type	Standard ID	Working Standard		Volume Used (mL)	Final Volume/ Weight	Final Concentration
		Source	Conc.(ug/L)			
ICV	I-VER-	ULTRA	100	1.25	50 mL	2.5 ug/L
CCV	I-CAL-	SPEX	100	2.5	50 mL	5.0 ug/L
CRA	I-CAL-	SPEX	100	0.1	50 mL	0.2 ug/L
Aqueous LCS	I-CAL-	SPEX	100	2.5	50 mL	5.0 ug/L
Aqueous MS	I-CAL-	SPEX	100	0.5	50 mL	1.0 ug/L
Soil LCS	I-CAL-	SPEX	100	2.5	0.3 g	0.83 mg/kg
Soil MS	I-CAL-	SPEX	100	0.5	0.3 g	0.17 mg/kg
TCLP MS	I-CAL-	SPEX	100	2.5	50 mL	5.0 ug/L

REAGENTS			
Conc. H_2SO_4 Lot #:		5% $KMnO_4$ ID #:	
Conc. HNO_3 Lot #:		5% $K_2S_2O_8$ ID #:	
Conc. HCL Lot #:		$SnCl_2$ Solution ID #:	
12% NaCl NH_2OH HCL ID #:		Aqua Regia ID #:	

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN SOLID SAMPLES BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY, SW846 7471A, 7471B AND EPA METHOD 245.5

(SUPERSEDES: KNOX-MT-0010, Rev. 8)

Prepared By: _____

Reviewed By: _____ 2/25/11
Technical Specialist

Approved By: _____ 02/25/11
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Approved By: _____ 2-25-11
Environmental, Health and Safety Coordinator

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1. SCOPE AND APPLICATION

1.1. This procedure describes the preparation and analysis of mercury (Hg, CAS # 7439-97-6) by Cold Vapor Atomic Absorption Spectroscopy (CVAA) using SW-846 Methods 7471A, 7471B and EPA Method 245.5.

1.2. CVAA analysis provides for the determination of total mercury (organic and inorganic). The combination of the oxidants, potassium permanganate and potassium persulfate, has been found to give 100% recovery for both types of compounds.

1.3. Methods 7471A, 7471B and 245.5 are applicable to the preparation and analysis of mercury in soils, sediments, bottom deposits and sludge-type materials. All matrices require sample preparation prior to analysis.

1.4. The reporting limit for mercury in solid matrices is 0.033 mg/kg based on a 0.3 g sample aliquot (wet weight).

2. SUMMARY OF METHOD

2.1. This SOP describes a technique for the determination of mercury in solution. The procedure is a physical method based on the absorption of radiation at 253.7 nm by mercury vapor. A representative portion of the sample is digested in hydrochloric and nitric acids. Organic mercury compounds are oxidized with potassium permanganate and potassium persulfate, and the mercury is reduced to its elemental state with 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 spectrophotometer. Absorbance is measured as a function of mercury concentration. Concentration of the analyte in the sample is determined by comparison of the sample absorbance to the calibration curve (absorbance vs. concentration).

3. DEFINITIONS

3.1. Definitions can be found in the TestAmerica Knoxville Quality Assurance Manual (QAM).

4. INTERFERENCES

4.1. Chemical and physical interferences may be encountered when analyzing samples using this method.

4.2. Potassium permanganate that is used to break down organic mercury compounds also eliminates possible interferences from sulfide. Concentrations as high as 20 mg/Kg of sulfide as sodium sulfide do not interfere with the recovery of inorganic mercury from reagent water.

4.3. Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on the recovery of mercury from spiked samples.

4.4. Chlorides can cause a positive interference. Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are

converted to free chlorine, which also absorbs radiation at 253.7 nm. Care must be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This is accomplished by adding excess hydroxylamine reagent (25 mL) and purging the sample headspace before stannous chloride is added. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater using this technique.

NOTE: Sufficient addition of permanganate is apparent when the purple color persists for at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.5. Interference from certain volatile organic materials that absorb at this wavelength may also occur. If suspected, a preliminary run without stannous chloride can determine if this type of interference is present. While the possibility of absorption from certain organic substances present in the sample does exist, this problem is not routinely encountered. This is mentioned only to caution the analyst of the possibility. If this condition is found to exist, the mercury concentration in the sample can be determined by subtracting the result of the sample run without the reducing reagent (stannous chloride) from that obtained with the reducing reagent.

4.6. Samples containing high concentrations of oxidizable organic materials, as evidenced by high COD levels, may not be completely oxidized by this procedure. When this occurs, the recovery of mercury will be low. The problem can be eliminated by reducing the volume of original sample used.

4.7. The most common interference is laboratory contamination that may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Safety Manual and this document.

5.2. Specific Safety Concerns or Requirements

5.2.1. Samples that contain high concentrations of carbonates or organic material or samples that are at elevated pH can react violently when acids are added.

5.2.2. When using the snap cap vials for Hg analysis, care should be taken not to close or invert the vials when the samples are still warm as they may quickly build pressure and become volatile. Samples should be handled in a fume hood with the sash closed as far as operations will permit, as necessary, and samples should be opened with the container pointing away from the analyst.

5.2.3. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and cleanup techniques before working with mercury. Since mercury vapor is toxic, precautions must be taken to avoid

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inhalation, ingestion or absorption through skin. All lines should be checked for leakage and the mercury vapor must be vented into a hood or passed through a mercury absorbing media such as equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4 or 0.25% iodine in a 3% KI solution.

5.2.4. Do not look directly into the beam of the Hg lamp. The UV light that these lamps radiate is harmful to the eyes.

5.2.5. Cylinders of compressed gas must be handled with caution in accordance with local regulations. It is recommended that, wherever possible, cylinders be located outside the laboratory and the gas led to the instrument through approved lines.

5.2.6. The CVAA apparatus must be properly vented to remove potentially harmful fumes generated during sample analysis.

5.3. Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE**: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	**Hazards**	**Exposure Limit (2)**	**Signs and symptoms of exposure**
Mercury, 1,000 ppm stock std.	Oxidizer Corrosive Poison	0.1 mg/m^3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. May affect the central nervous system. Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1 mg/m^3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2 ppm-TWA 4 ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Hydrochloric	Corrosive	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of

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Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acid	Poison		the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Permanganate	Oxidizer	5 mg/m^3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, burns, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4. All work must be stopped in the event of a known or potential compromise to the health and safety of an associate. The situation must be reported **immediately** to a laboratory supervisor.

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining temperature of 90 - 95 °C).

6.2. Leeman Hydra AA (or equivalent) Atomic Absorption Spectrophotometer equipped with:

6.2.1. Absorption Cell with quartz end windows perpendicular to the longitudinal axis. Dimensions of the cell must result in sufficient sensitivity to meet the SOP defined reporting limit. The quartz windows must be maintained to provide accurate measurements. Any scratches or fingerprints can alter the absorption of UV radiation.

6.2.2. Mercury specific hollow cathode lamp (HCL) or electrodeless discharge lamp (EDL)

6.2.3. Peristaltic pump that can deliver 1 L/min air

6.2.4. Flowmeter capable of measuring an airflow of 1 L/min

6.2.5. Printer

6.2.6. Aeration Tubing: A straight glass frit having a coarse porosity and Tygon tubing is used for the transfer of mercury vapor from the sample container to the absorption cell and return.

6.2.7. Drying device (Leeman Hydra AA drying tube, or equivalent) to prevent condensation in the cell. The lamp is positioned to shine on the absorption cell, maintaining the air temperature in the cell about 10 °C above room temperature. Other drying devices that achieve the same purpose are also acceptable (e.g., Gore-Tex filter).

6.3. Polypropylene or equivalent digestion vessels with ribbed watch glasses, or equivalent

6.4. Nitrogen or argon gas supply, welding grade or equivalent

6.5. Calibrated automatic pipettes or Class A glass volumetric pipettes

6.6. Class A volumetric flasks

6.7. Top-loading balance, capable of reading up to two decimal places

6.8. Thermometer (capable of accurate readings at 95 °C)

6.9. Disposable cups or tubes

6.10. PTFE boiling chips

7. REAGENTS AND STANDARDS

7.1. Reagent water must be produced by a Millipore DI system or equivalent. Reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

7.2. Stock mercury standards (1000 ppm in 10% HNO_3) are purchased as custom solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Stock standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the stock solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem.

7.3. Intermediate mercury standard (10 ppm): Take 1 mL of the 1000 ppm stock mercury standard and dilute to 100 mL with reagent water. The intermediate standard must be made monthly and must be prepared in a matrix of 2% HNO_3 . The acid (2 mL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.4. Working mercury standard (0.1 ppm): Take 1 mL of the 10 ppm intermediate mercury standard (section 7.2) and dilute to 100 mL with reagent water. The working mercury standard must be made daily and must be prepared in a matrix of 0.15% HNO_3. The acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot.

7.5. The calibration and verification standards listed in Table I must be prepared fresh daily from the working standard (section 7.4) as described in Section 11.1.

NOTE: Alternate approaches to standard preparation may be taken and alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

7.6. The initial calibration verification standard must be made from a different stock solution than that of the calibration standards. The calibration standard source is typically Spex, catalog #PLHG4-24. The verification standard source is typically Ultra Scientific, catalog #ICP-080.

7.7. Refer to Table I for details regarding the working standard concentrations for calibration, calibration verification and spiking solutions. All standards must be processed through the entire analytical procedure including sample preparation.

7.8. Nitric acid (HNO_3), concentrated, trace metal grade or better

7.9. Sulfuric acid (H_2SO_4), concentrated, trace metal grade or better

7.10. Hydrochloric acid (HCl), concentrated, trace metal grade or better

7.11. Aqua Regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.12. Stannous chloride solution: Add 50 g of stannous chloride dihydrate to 500 mL reagent water containing 50 mL of concentrated hydrochloric acid. This solution should be made fresh daily.

7.13. Sodium chloride-hydroxylamine hydrochloride solution: Add 12 g of sodium chloride and 12 g of hydroxylamine hydrochloride to every 100 mL of reagent water.

NOTE: Hydroxylamine sulfate may be used in place of hydroxylamine hydrochloride.

7.14. Potassium permanganate, 5% solution (w/v): Dissolve 5 g of potassium permanganate for every 100 mL of reagent water.

7.15. Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate for every 100 mL of reagent water.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Sampling is not performed for this method by TestAmerica Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, “Sample Receipt and Log In”, current revision.

8.2. The sample holding time for mercury is 28 days from the date of collection to the completion of sample analysis.

8.3. Soil samples do not require preservation but must be stored at $\leq$6° C until processing begins.

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9. QUALITY CONTROL

9.1. Table II provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.2. Preparation Batch - A group of up to 20 samples that are of the same matrix and are processed together using the same procedures and reagents. The preparation batch must contain a method blank, a laboratory control sample (LCS) and a matrix spike/matrix spike duplicate (MS/MSD). In some cases, at client request, it may be appropriate to process a matrix spike and sample duplicate in place of the MS/MSD. If clients specify samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.3. Sample Count - Laboratory generated QC samples (method blanks, LCS and MS/MSDs) are not included in the sample count for determining the size of a preparation batch.

9.4. Method Blank - One method blank must be processed with each preparation batch. The method blank consists of 0.3 g of PTFE boiling chips and all reagents specific to the method; it is carried through the entire analytical procedure, including preparation and analysis. The method blank is used to identify any system and process interferences or contamination of the analytical system that may lead to the reporting of elevated analyte concentrations or false positive data. The method blank should not contain any mercury at or above one-half the reporting limit.

- If the method blank does not meet the acceptance criteria, reanalyze the method blank. If the method blank meets the acceptance criteria after reanalysis, reanalyze all samples associated with the failed original method blank analysis. If the method blank is still outside acceptance limits, repreparation and reanalysis of all samples associated with the unacceptable method blank is required when reportable concentrations are determined in the samples (see exceptions noted below).
- If the method blank result is less than 10% of the sample concentration, the data may be reported. **Such action must be addressed in the project narrative.**
- If there is no mercury in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**
- If the above criteria are not met and reanalysis is not possible, then the sample data must be qualified. **This anomaly must be addressed in the project narrative and the client must be notified.**

9.5. Laboratory Control Sample (LCS) - One solid LCS must be processed with each preparation batch. The LCS is a blank solid matrix (0.3 g PTFE boiling chips) to which a known concentration of mercury is added. The LCS is used to monitor the accuracy of the analytical process. Ongoing monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines. The LCS must be carried through the entire analytical procedure.

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- If the LCS does not meet the acceptance criteria, reanalyze the LCS. If the LCS meets the acceptance criteria after reanalysis, reanalyze all samples associated with the failed original LCS analysis. If the LCS is still outside established control limits, the system is out of control and corrective action must occur. Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable. A control limit of 90 - 110% recovery must be applied.
- In the instance where the LCS recovery is > 110% and the sample results are < RL, the data may be reported with qualifiers. **Such action must be addressed in the project narrative.**
- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate is a second aliquot of the same sample (spiked identically to the MS) prepared and analyzed along with the sample and matrix spike. Some client specific data quality objectives (DQO's) may require the use of sample duplicates in place of or in addition to MSDs. The MS/MSD results are used to determine the effect of a matrix on the precision and accuracy of the analytical process. Due to the potential variability of the matrix of each sample, these results may have immediate bearing only on the specific sample spiked. Samples identified as field blanks cannot be used for MS/MSDs. Spiking levels are provided in Table I.

- If the recovery or RPD falls outside the acceptance range, the recovery must be in control for the LCS. Control limits of 85-115% recovery and 20% RPD must be applied to the MS/MSD. If the LCS recovery is within limits, then the laboratory operation is in control and the results may be accepted. If the recovery of the LCS is outside limits, corrective action must be taken. Corrective action will include repreparation and reanalysis of the batch. MS/MSD results which fall outside the control limits must be addressed in the narrative.
- If the native analyte concentration in the sample exceeds 4x the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated) and MSB (i.e., the recovery and RPD were not calculated because the sample amount was greater than four times the spike amount).
- If the concentration in the original sample digestate exceeds the calibration range and is > 50 ppb (raw value), the original sample digestate will be diluted and reanalyzed. However, the MS/MSD digestates in this case will not need reanalysis at a dilution because the native analyte exceeds the spike amount by a factor much greater than 4x. Report the MS/MSD with the NC, MSB qualifiers described above.
- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed.

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9.7. Initial Calibration Verification and Blank (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% of the true value. An initial calibration blank (ICB) is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall below the MDL. If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. See Section 11.2.6 for the required run sequence. If the cause of the ICV or ICB failure was not directly instrument related, the corrective action would include repreparation of the associated samples.

9.7.1. The ICB is a digested method blank.

9.8. Continuing Calibration Verification and Blank (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV must be a mid-range standard at a concentration and from a source other than that of the ICV. The CCV result must fall within 10% of the true value for method 245.5 and within 20% of the true value for methods 7471A and 7471B. A continuing calibration blank (CCB) is analyzed immediately following each CCV. (See Section 11.2.6 for required run sequence.) The CCB result must fall below the MDL for soil samples. Each CCV and CCB analyzed must reflect the conditions of analysis of all associated samples. Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, reanalyze the failing CCV/CCB pair and associated samples. If the CCV or CCB still fails, the analysis must be terminated, the problem corrected (e.g., re-pour standard digestates into clean autosampler cups), the instrument recalibrated, the calibration verified and the affected samples reanalyzed. If the cause of the CCV or CCB failure was not directly instrument-related or due to cross-contamination during autosampler tube preparation, the corrective action will include repreparation of the associated samples.

9.9. In the case of CCV/CCB failure due to digestates containing excessive amounts of mercury, the instrument should be flushed with 10% HCl rinse (and possibly replace the pump tubing) before attempting reanalysis. The Leeman Hydra AA has an automatic response to such samples which prevents further uptake of digestate and initiates “fast pump” mode to flush the tubing.

9.10. Reporting Limit Check Standard (CRA) - A CRA standard is run at the beginning of each sequence, after the ICV and ICB. The CRA standard contains mercury at 0.2 ug/L. The CRA result must fall within 30% of the true value. If the CRA does not meet the acceptance criteria, reanalyze the CRA. If it is still outside acceptance limits, the analysis is terminated, the problem corrected and the instrument recalibrated.

10. CALIBRATION AND STANDARDIZATION

10.1. Calibration standards must be processed through the preparation procedure as described in Section 11.1.

10.2. Due to the differences in preparation protocols, separate calibration and calibration verification standards must be prepared for aqueous and solid matrices.

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10.3. Calibration must be performed daily (every 24 hours) and each time the instrument is set up. The instrument calibration date and time must be included in the raw data.

10.4. Set up the mercury analyzer using the operating parameters recommended by the manufacturer. For the Leeman Hydra AA system, the operating parameters are entered under a known protocol (e.g., 7pointcurve) in the WinHg Database (DB) and are described below.

Gas flow rate:	0.40 LPM (Argon feed pressure of 75 psi, no entry for this in the protocol)
Pump rate:	5 mL/minute
Rinse time:	40 seconds
Uptake time:	18 seconds
Replicates:	1
Full Scale:	20
Integration:	15 seconds

10.4.1. Refer to the CVAA manual of the instrument in use for detailed setup and operation procedures. Whenever it is necessary to change the setup/operating parameters or to change instruments (e.g., acquiring a rental while one instrument is being serviced), new parameters/instruments should be validated by performing an IDL/MDL check or MDL study.

10.5. Calibrate the instrument using a minimum of five standards and a blank. Typically, six standards are used. One standard must be at the reporting limit. Analyze standards in ascending order beginning with the blank. Refer to Section 7.5 and Table I for additional information on preparing calibration standards and calibration levels.

10.5.1. For the Leeman Hydra AA instrument, calibration standard and check standard concentrations and acceptable recovery ranges are entered under ‘Line Info’ in the WinHg database. The type of calibration curve, Linear, may be selected under ‘Cal Curve’ in the WinHg database. A calibration curve is generated by the ‘Stnd Auto’ method under ‘Standard’ in WinHg Runner after selecting S1 through S6 (calibration standards; S7, S8, etc., are selected when using more than a six-point curve), selecting ‘Rep 1’ (one replicate), selecting at least C1 through C3 (check standards CCB, ICV and CCV) along with their respective active cups, and selecting ‘New Cal Reset’ (resetting current calibration data).

10.6. The calibration curve must have a correlation coefficient of ≥0.995 or the instrument shall be stopped and recalibrated prior to running samples. Sample results cannot be reported from a curve with an unacceptable correlation coefficient.

10.6.1. For the Leeman Hydra AA, the correlation coefficient is automatically calculated by the instrument software and may be viewed along with the graph of relative absorbance vs. concentration under ‘Cal Curve’ in the WinHg Database. The curve should be accepted by hitting ‘Accept’, which will automatically result in the ‘Calibrated’/‘Accepted’ boxes being checked. This data window should be printed and included with the completed run report.

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10.7. Refer to Section 9 for calibration verification procedures, acceptance criteria and corrective actions.

11. PROCEDURE

11.1. Standard and Sample Preparation:

11.1.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB) are processed through the digestion procedure along with the field samples.

11.1.2. Add 5 mL reagent water to all of the calibration standard containers (except the high calibration standard) and the calibration verification standard containers. Then remove the following volumes of reagent water from the containers: 0 mL, 50 uL, 100 uL, 250 uL, 500 uL, 2.5 mL (for the first 6 calibration standards) and 1.25 mL (ICV), 0 mL (ICB), 2.5 mL (CCV), 0 mL (CCB) and 100 uL (CRA). Volumes removed above will be replaced with the appropriate working standard solution (section 7.4). The high calibration standard is prepared by adding 5 mL of the working standard solution to an empty container. After initial acid addition, continue preparation as described in section 11.1.4.

11.1.3. Weigh a 0.3 ± 0.05 gram portion of a solid sample by transferring triplicate (approximately) 0.1 g portions of a well mixed sample into a clean sample digestion container. Record the sample weight on the sample preparation worksheet (Appendix H). Add 2.5 mL reagent water to each sample container (do not add to the standard containers) and continue the preparation as described below in section 11.1.4.

NOTE: For method 7471B, triplicate 0.1g aliquots are not required.

11.1.4. Add 2.5 mL aqua regia to all containers.

11.1.5. Add appropriate volumes of working stock solutions to the standard containers and spike sample QC containers, if applicable. Loosely cap with a watch glass to prevent cross contamination of samples.

11.1.6. Heat for 2 minutes in a water bath at 90 - 95 ° C.

11.1.7. Cool.

11.1.8. Add 25 mL of reagent water.

11.1.9. Add 7.5 mL of potassium permanganate solution. For samples high in organic materials or chlorides, additional permanganate may be added. Shake and add additional portions of permanganate solution until a purple color persists for at least 15 minutes. If after the addition of up to 12.5 mL additional permanganate the color does not persist, sample dilution prior to reanalysis may be required.

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CAUTION: When using the snap cap vials for Hg analysis, care should be taken not to close or invert the vials when the samples are still warm as they may quickly build pressure and become volatile. Samples should be handled in a fume hood with the sash closed as far as operations will permit, as necessary, and samples should be opened with the container pointing away from the analyst.

11.1.10. Add 4 mL of potassium persulfate solution; mix thoroughly. Loosely cap with a watch glass to prevent cross contamination of samples.

11.1.11. Heat for 30 minutes in the water bath at 90 - 95 °C.

11.1.12. Cool briefly. Warm samples will decolorize (section 11.1.13) more completely at a faster rate than samples at room temperature.

11.1.13. Add 3.0 mL of sodium chloride-hydroxylamine hydrochloride solution to reduce the excess permanganate.

11.1.14. Allow samples and standards to cool to room temperature. Add enough reagent water (~25 mL) to bring to a final volume of 70 mL.

11.2. Analysis: Detailed operating instructions are provided in Appendix G.

11.2.1. Automated determination: Follow the instructions provided by the instrument manufacturer, as described in Section 10 for the Leeman Hydra AA.

11.2.2. The samples must be allowed to cool to room temperature prior to analysis or a decrease in the response signal can occur.

11.2.3. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. ug/L of mercury. Refer to section 10.6 for the calibration criteria. Determine the mercury concentration in the samples from the linear regression fit of the calibration curve. Calibration using computer or calculation-based regression curve fitting techniques on concentration/response data is acceptable. Refer to Section 10.5 for the Leeman Hydra AA computer-automated calibration instructions.

11.2.4. All measurements must fall within the defined calibration range to be valid. Dilute and reanalyze all samples that exceed the highest calibration standard.

11.2.5. If the sample results are negative and the absolute value of the negative result is greater than the reporting limit, the sample must be diluted and reanalyzed.

11.2.6. The following run sequence is consistent with methods 7471A, 7471B and 245.5. This run sequence is used to accommodate multiple method requirements in one analytical run:

Instrument Calibration
ICV
ICB
CRA

CCV
CCB
10 samples
CCV
CCB
Repeat sequence of 10 samples between CCV/CCB pairs as required to complete run.
CCV
CCB

NOTE: Samples include the method blank, LCS, MS, MSD, duplicate, PDS (if applicable), field samples and sample dilutions.

11.3. Guidelines are provided in Appendices D, E and F on procedures to minimize contamination of samples and standards, troubleshooting and preventive maintenance.

11.4. One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure, except those specified by project specific instructions, shall be completely documented using a nonconformance memo and approved by a Technical Specialist, Project Manager and QA Manager. If contractually required, the client shall be notified.

11.5. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.6. Refer to TestAmerica Knoxville SOP KNOX-IT-0001, current revision for requirements for computer hardware and software.

12. DATA ANALYSIS AND CALCULATIONS

12.1. ICV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{\text{Found(ICV)}}{\text{True(ICV)}}\right)$$

12.2. CCV percent recoveries are calculated according to the equation:

$$\%R = 100\left(\frac{\text{Found(CCV)}}{\text{True(CCV)}}\right)$$

12.3. Matrix spike recoveries are calculated according to the following equation:

$$\%R = 100\left(\frac{SSR - SR}{SA}\right)$$

Where:
SSR = Spike Sample Result
SR = Sample Result
SA = Spike Added

12.4. The relative percent difference (RPD) of matrix spike/matrix spike duplicates or sample duplicates are calculated according to the following equations:

$$RPD = 100\left[\frac{|MSD - MS|}{\left(\frac{MSD + MS}{2}\right)}\right]$$

Where:
MS = determined spiked sample concentration
MSD = determined matrix spike duplicate concentration

$$RPD = 100\left[\frac{|DU1 - DU2|}{\left(\frac{DU1 + DU2}{2}\right)}\right]$$

Where:
DU1 = Sample result
DU2 = Sample duplicate result

12.5. The final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

Sample Concentration (mg/kg, dry weight) = (C x V x D)/ (W x S)

Where:
C = Concentration (ug/L) from instrument readout
V = Nominal Final Sample Volume (L), i.e., 0.050 L *
D = Instrument dilution factor
W = Weight in g of wet sample digested
S = Percent solids/100

* The Nominal Final Volume (0.050 L) is the nominal volume of reagent water used for sample calculations. This volume does not include the volume of reagents added during the digestion process.

NOTE: A percent solids determination is performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on a wet weight basis, the “S” factor is omitted from the above equation.

12.6. The LCS percent recovery is calculated according to the following equation:

$$\%R = 100\left(\frac{Found(LCS)}{True(LCS)}\right)$$

12.7. Sample results are reported with two significant figures for values < 10 and with three significant figures for values $\geq$ 10.

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12.8. Refer to Appendix C for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data

13. METHOD PERFORMANCE

13.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP CA-Q-S-006, current revision based on 40 CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit.

13.2. Initial Demonstration of Capability – Each analyst must perform an initial demonstration of capability (IDOC) prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in TestAmerica Knoxville SOP KNOX-QA-0009, current revision.

13.3. Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

14.1. This method allows for the proportional reduction of sample and reagent volumes to decrease waste generation.

15. WASTE MANAGEMENT

15.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the policies in section 13 of the Corporate Safety Manual for “Waste Management and Pollution Prevention.”

15.2. Waste Streams Produced by this Method: Acid waste consisting of sample and rinse solution will be collected and placed in the acidic waste stream 55 gallon HDPE drum. Never use metal containers for acidic waste.

16. REFERENCES

16.1. SW-846 Method 7471A, “Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique”, Revision 1, September 1994.

16.2. SW-846 Method 7471B, “Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique”, Revision 2, February 2007.

16.3. “Methods for the Chemical Analysis of Water and Wastes”, EPA-600/4-79-020, U.S.EPA, August 1983, Method 245.5.

16.4. TestAmerica Policy QA-003, “Quality Control”.

16.5. Leeman Hydra AA Operation Manual.

16.6. TestAmerica Knoxville Quality Assurance Manual (QAM), current revision.

17. MISCELLANEOUS (TABLES, APPENDICES, ETC.)

17.1. Modifications/Interpretations from reference method.

17.1.1. Modifications from 7471A, 7471B and 245.5.

17.1.1.1. A potassium persulfate oxidation step has been included to facilitate the breakdown of organic mercurials which are not completely oxidized by potassium permanganate. Use of potassium persulfate in combination with the permanganate improves the recovery of mercury from organo-mercury compounds. The use of persulfate has been incorporated in several recent EPA mercury protocols.

17.1.1.2. The run sequence presented in Section 11.2.7 is consistent with method requirements. An additional QC analysis (CRA) was added to accommodate the CLP protocol requirements.

17.1.2. Modifications from Methods 7471A/7471B

17.1.2.1. Chapter 1 of SW-846 specifies the use of reagent water with a purity equivalent to ASTM Type II water. This SOP specifies the use of a Millipore DI system or equivalent to produce reagent water.

17.1.2.2. Chapter 1 of SW-846 states that the method blank should not contain any analyte of interest at or above the MDL. This SOP states that the method blank must not contain any analyte of interest at or above ½ the reporting limit.

17.1.2.3. This SOP allows for the use of reduced sample volumes to decrease waste generation. Reagent levels are adjusted to maintain the same ratios as stated in the source methods. According to a letter from Robert Booth of EPA EMSL-Cinn to David Payne of EPA Region V, “Reduction in sample size and appropriate corresponding reduction in sample volume is not considered a significant change in the methodology.”

17.1.2.4. Method 7471B states that the heating source must be maintained at a temperature of 95 $\pm$ 3^{0}C. The guidelines in method 7471A are followed and the water bath is maintained at 90-95^{0}C.

17.1.3. Modifications from 245.5

17.1.3.1. Method 245.5 Section 9.3 states concentrations should be reported as follows: Between 0.1 and 1 ug/g, to the nearest 0.01

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ug; between 1 and 10 ug/g, to the nearest 0.1ug; above 10 ug/g, to the nearest ug. The laboratory reports Hg results under this SOP to two significant figures for values < 10 and to three significant figures for values ≥ 10.

17.2. List of Appendices

17.2.1. Appendix A, Figure 1: Flow Chart for Solid Sample Preparation for Mercury

17.2.2. Appendix A, Figure 2: Flow Chart for CVAA Mercury Analysis

17.2.3. Appendix B, Table I: Mercury Reporting Limits, Calibration Standard, QC Standard and Spiking Levels

17.2.4. Appendix B, Table II: Summary Of Quality Control Requirements

17.2.5. Appendix C: Example Hg Data Review Checklist

17.2.6. Appendix D: Troubleshooting Guide

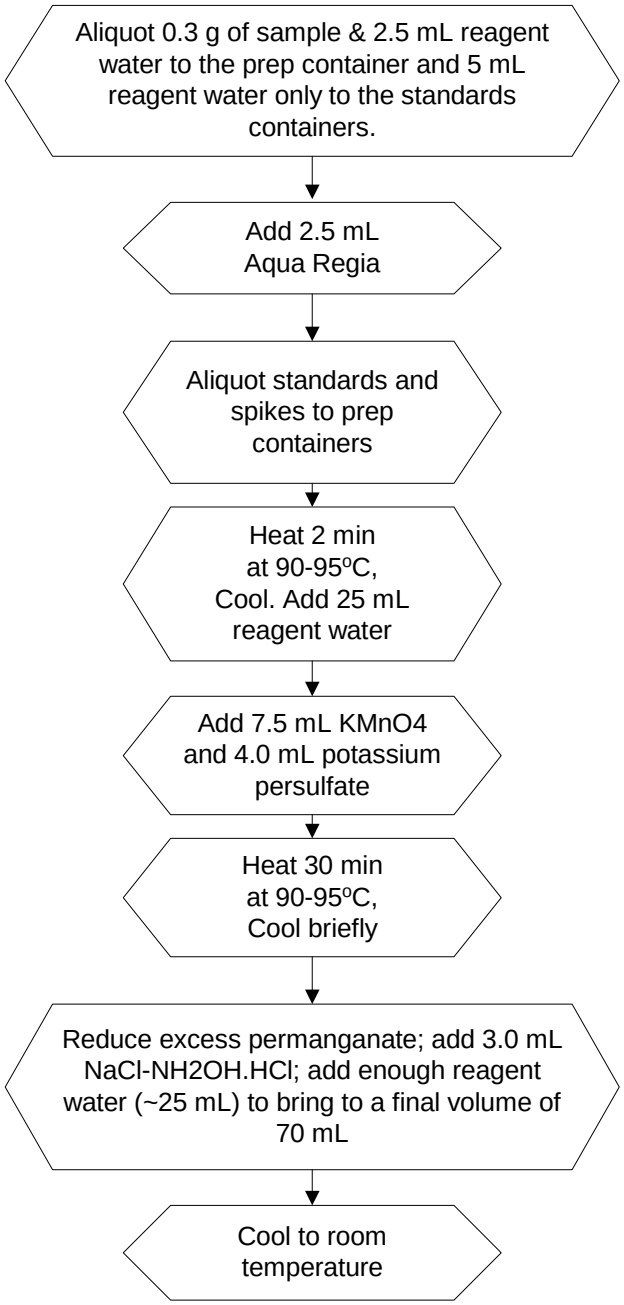
17.2.7. Appendix E: Contamination Control Guidelines

17.2.8. Appendix F: Preventive Maintenance

17.2.9. Appendix G: Leeman HydraAA Operating Instructions

17.2.10. Appendix H: Example Sample Preparation Worksheet

APPENDIX A, Figure 1: Solid Sample Preparation for Mercury - Water Bath Procedure



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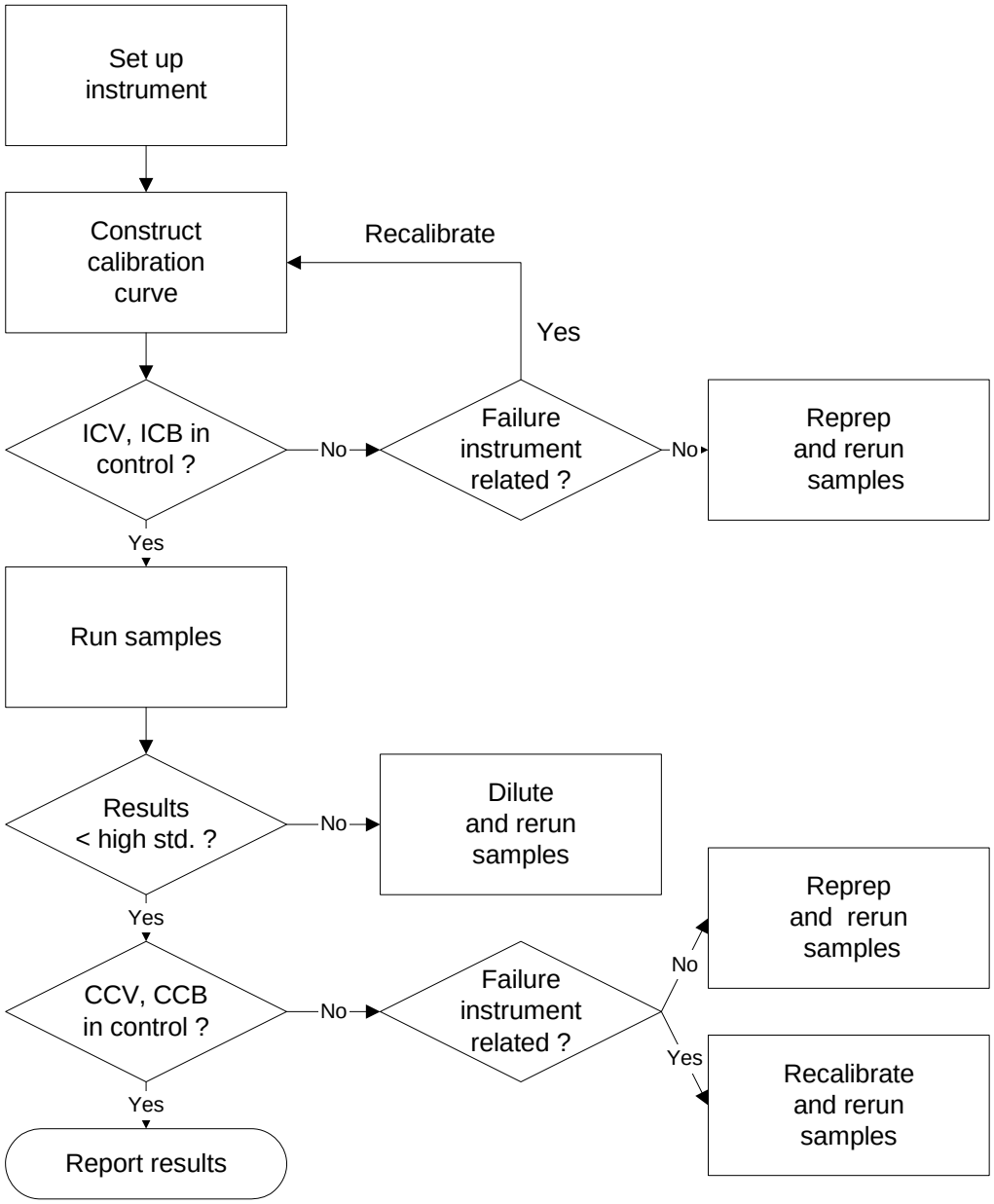
APPENDIX A, Figure 2: CVAA Mercury Analysis



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APPENDIX B, TABLE I: Mercury Reporting Limits, Calibration Standard[1], QC Standard and Spiking Levels

Standard	Concentration
Soil RL	0.033 mg/kg
Std 0	0 ug/L
Std 1[2]	0.1 ug/L
Std 2	0.2 ug/L
Std 3	0.5 ug/L
Std 4	1.0 ug/L
Std 5	5.0 ug/L
Std 6	10.0 ug/L
ICV	2.5 ug/L[3]
CCV/LCS	5.0 ug/L[3]
MS	1.0 ug/L/0.17 mg/kg
PDS, if applicable	1.0 ug/L
CRA	0.2 ug/L

[1] SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be approved by a facility Technical Specialist and Quality Assurance Manager prior to the preparation of client samples.

[2] Optional standard which is used when analyzing samples from projects requiring a 0.1 ppb reporting limit. Instrument configuration allows the use of 10 standards when appropriate cup holder racks are purchased.

[3] Concentration level dependent on high calibration standard used. CCV must be 50% of the high standard concentration and the ICV must be 20-25% of the high standard concentration.

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APPENDIX B, Table II: Summary Of Quality Control Requirements

QC Check	Frequency	Target Criteria	Corrective Action
Initial Calibration Verification (ICV/ICB)	Beginning of analysis sequence	ICV • 95 - 105% recovery: Method 245.5 • 90 - 110% recovery: Method 7471A ICB • Concentration <MDL	1. Make necessary adjustments. 2. Repeat calibration.
Continuing Calibration Verification (CCV/CCB)	After every 10 samples and at the end of the run	CCV • 90 - 110% recovery: Method 245.5 • 80 - 120 % recovery: Method 7471A CCB • Concentration <MDL	1. Repeat CCV/CCB. 2. If 1. fails, make adjustments and repeat calibration and reanalyze affected samples.
Reporting Limit (RL) Check Standard (CRA)	One per analytical run	• 70 - 130% recovery	1. Repeat RL check standard. 2. If 1. fails, make adjustments and repeat calibration and reanalyze affected samples.
Laboratory Method Blanks	Once per digestion batch (maximum 20 samples)	Target analyte concentrations • <½RL	1. Reanalyze method blank. 2. If 1. fails, reprepare and reanalyze samples associated with unacceptable blank. 3. Report results if sample results >10x blank result or sample results ND. See Section 9.4.
Laboratory Control Sample/Laboratory Control Sample Duplicate (LCS/LCSD)	Once per digestion batch (maximum 20 samples) LCSD not required if MS/MSD or MS/DUP performed	Accuracy • 90 - 110% recovery	1. Reanalyze LCS/LCSD. 2. If 1. fails, reprepare and reanalyze samples associated with unacceptable LCS/LCSD. 3. Report results if LCS results > control limit and samples are ND. See Section 9.5.
Matrix Spike/Matrix Spike Duplicate (MS/MSD)	Once per digestion batch (maximum 20 samples)	Accuracy • 85 - 115% recovery Precision • ≤ 20% RPD	1. Flag the data; no flag required if the sample level is > 4x the spike added (see Section 9.6). 2. For TCLP see Section 11.2.8

APPENDIX C: EXAMPLE DATA REVIEW CHECKLISTS

TestAmerica Knoxville Mercury Data Review Checklist

Method: SW-846 7470A/7471A/0.2 RL

Analyst:	KND			**Instrument:**	Leeman Hydra AA Mercury Analyzer		
Run Date:	Sep-30-08	**Calibration Number:**	1	**Chart Name:**	m093008.prn	**Element:**	Hg

A. Calibration/Instrument Run QC	**N/A**	**Yes**	**No**	**Comments**
1. Instrument calibrated every 24 hours?		X		Calibration was 2 hours and 12 minutes long
2. Instrument calibrated using a minimum of a blank and 5 standards?		X		
3. Do standard absorbances increase as standard concentrations increase?		X		
4. Instrument calibrated with standards at the SOP levels?		X		
5. Correlation coefficient greater than or equal to 0.995?		X		Correlation coefficient was 0.9999
6. ICV analyzed directly after calibration?		X		
7. ICV within specified control limits?		X		
8. ICB analyzed immediately after ICV?		X		
9. ICB within acceptable range?		X		
10. CRA analyzed at the beginning of the run?		X		
11. CRA results within acceptable range?		X		
12. All CCV's within specified control limits?		X		
13. All CCB's within acceptable range?		X		
14. All CCB's analyzed immediately after CCV's?		X		
B. Client Sample and QC Sample Results				
1. Were all sample results within the linear range of the instrument ?		X		
2. Were there any samples with results more negative than Report Limit?			X	
3. Were samples analyzed within the holding time?				
C. Preparation/Matrix QC				
1. Was one method blank prepared for each batch?				
2. Were all method blanks less than the specified level?		X		
3. Was an LCS prepared for each batch?				
4. Were all LCS recoveries within QC limits?		X		
5. Were matrix spikes, sample duplicates and/or post-digestion spikes run at required frequency?				
6. Were all matrix spike recoveries within QC limits?			X	See Comments on Next Page
7. Were post-digestion spike recoveries within QC limits?				
8. Were duplicate RPDs within QC limits?		X		
D. Other				
1. Current IDL data on file?		X		
2. Current MDL data on file?				
3. Are all nonconformances documented appropriately?				
4. Were all project specific instructions followed?				NCM#:

Question Number:	Problem(s) Found:
C6	Matrix spike sample KW80KS at 9/30/2008 1:56:49 PM had 73.7% recovery.
C6	Matrix spike sample KW80KD at 9/30/2008 1:58:47 PM had 65.9% recovery.

Analyst: _____ **Date:** _____

Analyst Comments: _____

APPENDIX C: EXAMPLE DATA REVIEW CHECKLISTS, continued

TestAmerica Knoxville Mercury Data Review / Narrative Checklist
Methods 7470A/7471A, 7471B and 245.1/245.5 - KNOX-MT-0009, Rev 10 and KNOX-MT-0010, Rev 9 **Page 1 of 2**

Lot / SDG #:		

A. Review of QuantIMS / QDS Results	**NA**	**Yes**	**No**	***Why is data reportable?***
1. Were PM checklists, Lot Summary and any applicable QAS reviewed?				
2. Were all prep sheets, prep spreadsheets and any existing NCMs reviewed?				
3. Were manual calculations of results and RLs performed for each sample, blank, LCS, LCSD, MS, MSD and DUP? (Document 1 calculation per batch.)				
4. Were elements with negative results >RL reported as ND G?				
5. For each sample, blank, LCS, LCSD, MS, MSD and DUP, were flags, units, DFs, prep date, date/time of analysis verified to be correct?				
6. Were spike amounts verified for each LCS/MS? (Document 1 manual calculation.)				
7. Were method blank results ≤1/2 RL for water/solid samples or <RL for air train samples?				☐ **[mb3] No analyte >QC limit in associated samples.** ☐ **[mb5] Insufficient sample for reanalysis.*** ☐ **[mb7] Samples >10x blank**
8. LCS or LCS/LCSD within QC limits? (90-110%R)				☐ **[lcs2] Insufficient sample for reanalysis.** ☐ **[lcs3] LCS%R >QC limits & sample results < RL.***
9. MS/MSD or MS/DUP run at required frequency?				☐ [lcsd] Insufficient sample – lcs/lcsd analyzed.
10. MS %R or MS/MSD %R & RPD within QC limits?				☐ [ms1] ☐ [msd1] LCS acceptable - matrix effects. ☐ [ms2] ☐ [msd2] Native analyte > 4x spike level. ☐ [ms3] ☐ [msd3] Matrix effects & native >4x spike. ☐ [batch] Batch QC on client's sample outside limits.
11. DUP RPD within limits? (0-20 RPD for results ≥5xRL; +RL if result <5xRL)				☐ [rpd] LCS acceptable. Results indicate sample heterogeneity.
12. Were J flags added to the DUP as needed?				
13. Is DUP RPD=0 for two ND results and RPD=200 for one ND and a positive result?				
14. Are all results present for all samples?				
15. Were the samples analyzed within the holding time?				☐ [ht1] HT expired upon receipt ☐ *[ht2] Analysis requested after HT expired.* ☐ See comments section below.

Data Reviewer:	**Date:**
Calculation Checks / Comments:	

*Such action must be taken in consultation with client.
NOTE: Nonconformance memos are required for **bold** and *italicized* [autotext] statements: **Bold** = deficiency, *italicized* = anomoly.

APPENDIX C: EXAMPLE DATA REVIEW CHECKLISTS, continued

TestAmerica Knoxville Mercury Data Review / Narrative Checklist
Methods 7470A/7471A, 7471B and 245.1/245.5 - KNOX-MT-0009, Rev 10 and KNOX-MT-0010, Rev 9 **Page 2 of 2**

Lot / SDG #:	

B. Review of QC Summary Forms *Note:* Y=Yes, N=No, NA=Not Applicable	**Chart #**	**Chart #**	**Chart #**	**Chart #**	***Why is data reportable?***
1. ICV within limits? (7470A/7471A/7471B=90-110%R; 245.1/245.5=95-105%R)					
2. CCV within limits? (7470A/7471A/7471B=80-120%R; 245.1/245.5=90-110%R)					If no, list details: _____
3. ICB/CCB within limits? (<MDL for water/solid samples; <RL for air train samples)					If no, list details: _____
4. CRA within limits? (The CRA standard contains mercury at 0.2 ug/L. The CRA result must fall within 30% of the true value.)					
5. PDS or PDS/PDSD run at required frequency?					
6. PDS/PDSD within limits? (75-125%R) **Reminder:** Place copy of PDS results in Sample Data Summary and QC Summary sections of report.					☐ [pds1] ☐ [pdsd1] LCS acceptable - matrix effects. ☐ [pds2] ☐ [pdsd2] Native analyte > 4x spike level. ☐ [pds3] ☐ [pdsd3] Matrix effects & native >4x spike.
7. Are the IDLs on summary forms current?					
8. Are the QC summary forms correct?					

Data Reviewer:	**Date:**
Comments:	

*Such action must be taken in consultation with client.
NOTE: Nonconformance memos are required for **bold** and *italicized* [autotext] statements: **Bold** = deficiency, *italicized* = anomoly.

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APPENDIX D: TROUBLESHOOTING GUIDE

Problem	**Possible Cause**
Poor or no absorbance or sensitivity check failed	Incorrect wavelength Dirty windows Window loose Etched or dirty optics Wrong lamp Bad lamp Not enough or no sample introduced Clogged reductant line Empty sample cup Incorrectly made standards Gas leak EDL power supply set on “Continuous”
Erratic readings	Source lamp not aligned properly Lamp not prewarmed Injection tip partially clogged Contaminated reagents Contaminated glassware Drying tube saturated Bad lamp Injection tip hitting outside of tube Injection tip coated or not set properly Leak in sample tubing Power fluctuations Air bubbles in tubing
EDL won’t light	Lamp cable not plugged in Lamp power set at 0 Lamp is dead Power supply fuse is blown Short in cord
Standards reading twice or half normal absorbance or concentration	Incorrect standard used Incorrect dilution performed Dirty cell

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APPENDIX E: CONTAMINATION CONTROL GUIDELINES

The following procedures are strongly recommended to prevent contamination:

All work areas used to prepare standards and spikes should be cleaned before and after each use.

Sample related labware should be washed with detergent and tap water and rinsed with 25% nitric acid followed by deionized water.

Proper laboratory housekeeping is essential in the reduction of contamination in the metals laboratory. All work areas must be kept scrupulously clean.

Powdered or Latex Gloves must not be used in the metals laboratory since the powder contains silica and zinc, as well as other metallic analytes. Only vinyl or nitrile gloves should be used in the metals laboratory.

Samples/standards in process should be covered whenever possible to reduce the contamination from laboratory dust particles.

The following are helpful hints in the identification of the source of contaminants:

Reagents or standards can contain contaminants or be contaminated with the improper use of a pipette.

Analyst should be careful not to touch samples poured into autosampler racks with gloves and inadvertently carry over “contamination” to subsequent sample cups.

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APPENDIX F: PREVENTIVE MAINTENANCE

A maintenance log is used to record when maintenance is performed on instruments. When an instrument problem occurs indicate the date, then identify the problem and corrective action in the maintenance log.

The following procedures are required to ensure that that the instrument is fully operational.

Instrument Maintenance Schedule*

Cold Vapor Atomic Absorption (Leeman Hydra AA)

Daily Maintenance	As Needed Maintenance
Check tubing.	Adjust/change Hg lamp.
Check maintenance schedule flags.	Clean or replace optical cell.
	Lubricate pump and autosampler arm.
	Change the drying tube.

*Leeman has incorporated an automated maintenance schedule in its Hg software that flags the user when instrument maintenance is required. These flags or messages appear in the upper right hand corner of the main user window (refer to manual).

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APPENDIX G: LEEMAN HYDRAAA OPERATION INSTRUCTIONS

NOTE: Refer to the instrument manual for instructions re. detailed method setup, such as entering standard curve concentration values and check standard values, troubleshooting operations. Refer to the appropriate mercury prep SOP for instrument operating parameters and required run sequences.

- Turn off computer screensaver and log off the network, if applicable.
- Click 'WinHg' icon on desktop.
- Drop-down 'Protocol', beneath the toolbar, to select the appropriate method to analyze samples (e.g. '7ptcurve' refers to the method used to run a file with a seven-point calibration curve; 'ontariohydro' is used to analyze only Ontario Hydro samples; and 'test' is used to analyze samples with a six-point calibration curve).
- Click 'File' in the toolbar, then drop-down to 'new dataset'.
  - Enter file name (lower-case 'h' followed by month, day, year –hmmddyy-).
  - Another window will pop up requesting a batch name; hit 'cancel', since this refers to the automated prep system we don't use.
- Select the new file just created from the 'Dataset' list beneath 'Protocol' to ensure the new file name will print out with the raw data; otherwise the raw data will be labeled with the file name of the previous run.
- Place all tubing in the appropriate containers; secure pump tubing to pump (tension is released on the clips during shutdown from the previous run). 10% stannous chloride continuously runs through the instrument, but sample and stannous chloride are delivered simultaneously at a 1:5 rate of reductant to sample (e.g., as 3.4 mL of sample are delivered, only 0.650 uL reductant are delivered at the same time). They are mixed at the mixing tee prior to entering the liquid-gas separator where argon releases elemental mercury to the drying tube, prior to being measured at the optics.
- Click 'Control' tab, click 'On' under 'lamp', 'gas', and 'pump'.
- Click 'Standard' tab; depress buttons 'S1' through 'S6' if using a six-point standard curve or 'S1' through 'S7' if using a seven-point curve. These standards are placed in the first (back) row of a separate autosampler rack, in order from right to left.
  - Depress 'Rep 1' button if only one injection is desired per standard analysis (depress both 'Rep1' and 'Rep2' if standards analyzed in duplicate, etc.).
  - Depress 'New Cal Reset' button, which clears the previous calibration curve.
  - Depress buttons 'C1' through 'C3' under the 'check standards' section, representing the CCB, ICV, and CCV. These standards are placed in the second (front) row of the standard curve rack mentioned above, in order from right to left.
- Click the rack editor icon in the WinHg toolbar. The icon looks like the top view of an autosampler rack.
  - Drop-down 'File' in the rack editor window toolbar, then select the rack to be edited (e.g. 'rack1').
  - In the far-left column of the rack spreadsheet, enter the appropriate check standard ID's and work order ID's in the order that they should be injected. The first two entries of the first rack to be analyzed should include 'ICB' and 'CRA', respectively.
  - In the far-right column of the rack spreadsheets, the sequence 'C3 C1' should be entered in the same row as the 'CRA' entry (when applicable) and in the same row as every 10th work order ID. This sequence directs the instrument to inject a CCV (C3), then a CCB (C1) after the CRA and every 10th sample. The sequence 'C2 cp' should be entered in the same row as the ICB entry (when applicable), to direct the instrument to inject an ICV (C2) before (cp) it injects the ICB.
  - The following suffixes should be applied to a work order ID associated with batch QC or dilutions:
    - Blank: B (also type the batch number in the second column, 'extended ID', of the row containing a blank entry)
    - LCS: C
    - LCSD: L
    - MS: S
    - MSD: D
    - Duplicate: X
    - PDS: A
    - PDSD: AX
    - Dilution: Z, then dilution value: e.g. 1:10 dilution, Z10
    - Diluted MS/MSD (spike applied to diluted sample at prep): e.g. Z10S/Z10D

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APPENDIX G: LEEMAN HYDRAAA OPERATION INSTRUCTIONS, continued

- Diluted MS/MSD (spike applied to undiluted sample at prep, diluted at analysis): e.g. SZ10/DZ10
- Diluted MS/MSD (mercury spike applied to undiluted ICP sample, ICP sample diluted at mercury prep): e.g. SZ10/DZ10
- Filtered batch QC/sample: F

- Click ‘Sample’ tab; this window allows the operator to enter the order in which multiple racks should be analyzed and which samples in each rack should be analyzed.
  - Drop-down the first ‘rack’ field and select the appropriate rack name; drop-down the first number of the sample cup to be injected within the rack selected, then drop-down and select the last sample cup# to be injected.
  - Follow the same instructions for the second rack to be analyzed. If a second rack is not required, make sure the fields are blank (drop-down and select the blank space).
  - If a third or fourth rack must be analyzed in the same dataset, these racks may not be entered until the instrument completes analysis of the first two racks. At that time, the instrument will be ‘idle’ and the operator may enter the next rack(s) as above.
  - If samples are to be analyzed in duplicate, click the database icon (‘DB’) in the Win Hg toolbar, then the ‘Protocol’ tab, then use the scroll arrows under ‘Data Collection/Replicates’ to change ‘1’ to ‘2’.
- Pour up sample digestates, placing them in the appropriate sequence in racks loaded from right to left, back to front.
- When the operator is ready to begin collecting data, click ‘Standard’ tab, then ‘Std Auto’ button (referring to the automatic injection of the standard curve series). The WinHg window will indicate the instrument is ‘busy’.
  - When the standard curve analysis is complete, click the ‘DB’ icon, then the ‘Calibration Curve’ tab. Depress the ‘Accept’ button if the linear regression coefficient (r) is greater than 0.995. Print the window (be sure all the raw data are included in the printout).
- With the calibration curve established and all racks loaded, click ‘Sample’ tab, then ‘Run Auto’ button. Monitor the collection of data to ensure all values are within SOP control limits. Re-run samples, if necessary, by stopping the instrument (‘STOP’ icon in WinHg toolbar), then re-starting (‘Run Auto’ under ‘Sample’ tab) when new samples are loaded and rack entries are adjusted.
- Report a dataset as follows:
  - Click ‘Main’ tab, depress the ‘Form Feed’ button under ‘printer control’ to print any remaining data stored in the file (If the number ‘0’ is next to the button, this isn’t necessary. The number represents the number of data points still stored in the printer’s memory).
  - Click ‘DB’ icon, then ‘Report’ tab, then ‘All’ button. At this point, all data will be associated with a checked box. If a data point is not to be reported, remove the check from the box, then proceed.
  - Click ‘Generate Report’ button. A window will open. Select ‘.prn’ for file type.* Enter the correct target drive/file name in which to store the report (e.g. C:/upload/h061402). Click ‘Generate’ button. Close window. Open ‘My Computer’ icon on desktop, then storage file, then select report file. Transfer the report file to data and upload drives on the network (this will require logging on), or to a floppy disk that can be transferred to another computer for this purpose.
    - *If ‘printer’ is selected for file type, the ‘Generate’ button will provide a post-run printout of raw data (as opposed to the real-time printout of data indicated in the method). The latter scenario may be used when the printer malfunctions during data collection.

    When a report has been generated, transfer the stannous chloride line to water and allow the instrument to flush while data is being validated/uploaded. The instrument will automatically stop pumping after one hour.

Leeman HydraAA Instrument Shutdown:

- After rinsing the system with water, remove all tubing and sample tip from liquid containers and pump to dryness. The sample tip is removed to air by clicking the ‘Sample’ tab, then the ‘To Air’ button on the right-hand side of the resulting window.
- When tubing is dry, click ‘Control’ tab; then click ‘Off’ under ‘lamp’, ‘pump’, and ‘gas’.
- Under the ‘Sample’ tab, return the sample tip ‘To Rinse’.
- Release tension clips on the pump tubing.
- Close all windows on desktop.
- Turn off monitor. The computer may also be shutdown at this point if desired, esp. if the instrument will not be used for an extended time.

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APPENDIX H: Example Sample Preparation Worksheet

TestAmerica Knoxville
Mercury Solid Sample Preparation Worksheet
SOP KNOX-MT-0010

Page 1 of 2

Batch Number:
Prep Date:
Comp Date:

Mercury Prep Analyst: _____ Prep Date: _____
2nd Level Review by: _____ Review Date: _____

Lot Number	Lot Sample Number	Suffix	Method Code	Client ID	WO #	Initial Sample Weight (g)	Final Sample Volume (L)	Hg Bench Dilution Factor	QuantIMS Upload Dilution Factor	QuantIMS Upload Multiplier

Digestion Vial ID: _____

Comments: _____

QuantIMS Upload Dilution Factor and Multiplier = Final Digestate Volume (L)/Initial Sample Weight (g) x 0.3g/0.050L x Hg Bench Dilution Factor

Mercury Solid Prep Rev 2a1 Mercury Solid Prep Rev 2a.xlt Printed 2/22/2011 2:30 PM

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APPENDIX H: Example Sample Preparation Worksheet (continued)

TestAmerica Knoxville
Mercury Solid Sample Preparation Worksheet
SOP KNOX-MT-0010

Page 2 of 2

Batch Number: _____ Time In: _____ Bath A Temp: _____ °C
Analyst: _____ Time Out: _____ Bath B Temp: _____ °C
Prep Date: _____ LCS Pipet ID: _____ Thermometer ID: MT-2
MS Pipet ID: _____ (Acceptance range 90°–95°C)

Standard Type	Standard ID	Working Standard		Volume Used (mL)	Final Volume (mL)	Final Concentration (ug/L)
		Source	Conc.(ug/L)			
Calibration Std 1	N/A	N/A	N/A	N/A	50	Blank
Calibration Std 2	I-CAL-	SPEX	100	0.05	50	0.1
Calibration Std 3	I-CAL-	SPEX	100	0.1	50	0.2
Calibration Std 4	I-CAL-	SPEX	100	0.25	50	0.5
Calibration Std 5	I-CAL-	SPEX	100	0.5	50	1
Calibration Std 6	I-CAL-	SPEX	100	2.5	50	5
Calibration Std 7	I-CAL-	SPEX	100	5	50	10

Standard Type	Standard ID	Working Standard		Volume Used (mL)	Final Volume/ Weight	Final Concentration
		Source	Conc.(ug/L)			
ICV	I-VER-	ULTRA	100	1.25	50 mL	2.5 ug/L
CCV	I-CAL-	SPEX	100	2.5	50 mL	5.0 ug/L
CRA	I-CAL-	SPEX	100	0.1	50 mL	0.2 ug/L
Aqueous LCS	I-CAL-	SPEX	100	2.5	50 mL	5.0 ug/L
Aqueous MS	I-CAL-	SPEX	100	0.5	50 mL	1.0 ug/L
Soil LCS	I-CAL-	SPEX	100	2.5	0.3 g	0.83 mg/kg
Soil MS	I-CAL-	SPEX	100	0.5	0.3 g	0.17 mg/kg
TCLP MS	I-CAL-	SPEX	100	2.5	50 mL	5.0 ug/L

REAGENTS			
Conc. H_2SO_4 Lot #:		5% $KMnO_4$ ID #:	
Conc. HNO_3 Lot #:		5% $K_2S_2O_8$ ID #:	
Conc. HCL Lot #:		$SnCl_2$ Solution ID #:	
12% NaCl NH_2OH HCL ID #:		Aqua Regia ID #:	

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SOP No.: KNOX-ID-0004
Revision No.: 10
Revision Date: 2/14/11

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Analysis of Polychlorinated Dioxins/Furans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) Based on Methods 8290, 8290A, 1613B, 23, 0023A, and TO-9A

(SUPERSEDES: KNOX-ID-0004, Rev. 9)

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1. Scope and Application

1.1 This procedure is used for the determination of tetra- through octa- chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in water, soils, solids, sediments, wipes, biological samples, fly ash, XAD resin, filters, still bottoms, waste oils, and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). This procedure is designed to meet analytical program requirements where US EPA Method 8290, 8290A, 1613B, 23, 0023A, or TO-9A is specified.

1.2 The seventeen 2,3,7,8-substituted and total Tetra-Hepta PCDDs/PCDFs listed in Table 1 can be determined by this procedure. Specifications are also provided for separate determination of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) and 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). In addition, total homologs (i.e., Total TCDD, Total TCDF, etc.) can be identified by this method.

1.3 The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (MLs) in Table 2 are the levels at which the PCDDs/PCDFs can be quantitated with no interferences present.

1.4 This procedure is designed for use by analysts who are experienced with residue analysis and skilled in HRGC/HRMS. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5 Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain PCDDs or PCDFs. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2. Summary of Method

2.1 This procedure uses high resolution capillary column gas chromatography/high resolution mass spectrometry (HRGC/HRMS) techniques.

2.2 Samples are spiked with a solution of known amounts of the isotopically labeled internal standards listed in Table 13 and Table 15. The samples are then extracted using matrix specific extraction procedures.

2.2.1 Water samples are extracted using separatory funnel techniques with methylene chloride as the extraction solvent.

2.2.2 Solid samples are extracted by Soxhlet extraction with the appropriate solvent.

2.2.3 Organic liquid waste samples are diluted in solvent.

2.3 After extraction, the sample is concentrated and solvent exchanged to hexane. The extract is then subjected to one or more optional cleanup steps to remove the sample of

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interferences. The final extract is prepared by adding a known amount of the labeled recovery standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD) and concentrating to the final volume.

2.4 The acid-base cleanup of the sample is used before column chromatography for samples that contain large amounts of basic and acidic coextractable compounds. If such interferences are not removed before column chromatography, they can cause a shift in the predicted elution pattern. Conditions which can indicate the need for this procedure are as follows: Samples which are highly colored, samples which contain lipids or other oxidizable compounds or samples which contain known large amounts of polar organics.

2.5 Dual Column Cleanup: Silica gel is effective in removing chlorophenoxy herbicide residues, while alumina partitions PCBs, 2,4,5-trichlorophenol and hexachlorophene.

2.6 When the above cleanup techniques do not completely remove interferences, an activated carbon cleanup is used to remove interferences.

2.7 An aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high resolution ($\geq$10,000 resolution) mass spectrometer (HRMS). Two exact m/z's are monitored for each analyte.

2.8 The identification of the target 2,3,7,8 substituted isomers is based on their retention time relative to the labeled internal standards as established during routine calibration and the simultaneous detection of the two most abundant ions in the molecular ion region. All other PCDD/PCDF congeners are identified by their retention times falling within retention time windows as established during routine calibration, and the simultaneous detection of the two most abundant ions in the molecular ion region. Confirmation of identification is based on comparing the calculated ion ratios with the theoretical ion abundances. The identification of 2,3,7,8-TCDF is confirmed on an isomer specific (DB-225) GC column.

2.9 Quantitation of the 2,3,7,8-substituted PCDD/PCDF isomers, total PCDDs, and total PCDFs is based on their relative response to the internal standards. A multipoint calibration is performed to establish mean response factors for the target analytes. The instrument performance is routinely checked by the analysis of continuing calibration standards. Method performance is demonstrated by the analysis of method blanks, initial precision and recovery samples, and ongoing precision and recovery samples.

3. Definitions

3.1 Analyte: A PCDD or PCDF tested for by this method. The analytes are listed in Table 1.

3.2 Calibration Standard: A solution prepared from a secondary standard and/or stock solution and used to calibrate the response of the instrument with respect to analyte concentration.

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3.3 Calibration Verification Standard (VER): The mid-point calibration standard (CS3) that is used to verify calibration. See Table 5 and Table 6.

3.4 Cleanup Standard: Solution containing $^{37}Cl_4$-2,3,7,8-TCDD that is added to the calibration solutions and to every 1613B and 8290A sample, blank, and quality control spike sample. It is added after extraction but prior to extract cleanup, and the analysis results are used to judge the efficiency of the cleanup procedures.

3.5 Column Performance Solution Mixture (CPSM): A mixture of TCDD or TCDF isomers (including the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer) known to elute close to the retention time of 2,3,7,8-TCDD or 2,3,7,8-TCDF on the analytical column being used. It is used to demonstrate acceptable resolution between the 2,3,7,8-TCDD or 2,3,7,8-TCDF isomer and all other TCDD or TCDF isomers on analytical column (percent valley ≤ 25).

3.6 Congener: Any member of a particular homologous series, for example, 1,2,3,7,8-pentachlorodibenzofuran.

3.7 CS1, CS2, CS3, CS4, CS5: See Calibration Standard and Table 5 and Table 6.

3.8 Estimated Detection Limit (EDL): The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level.

3.9 Estimated Maximum Possible Concentration (EMPC): The calculated concentration of a signal in the same retention time region as a target analyte but which does not meet the other qualitative identification criteria defined in the procedure.

3.10 GC: Gas chromatograph or gas chromatography

3.11 Homologous Series: A series of compounds in which each member differs from the next member by a constant amount. The members of the series are called homologs.

3.12 HRGC: High resolution GC

3.13 HRMS: High resolution MS

3.14 ICV: Initial Calibration Verification Standard. A calibration standard from a second source, traceable to a national standard if possible. The ICV is analyzed after the initial calibration to verify the concentration of the Initial Calibration Standards.

3.15 Internal Standards: Isotopically labeled analogs of the target analytes that are added to every sample, blank, quality control spike sample, and calibration solution. They are added to the sample before extraction and are used to calculate the concentration of the target analytes or detection limits.

3.16 Initial Precision and Recovery (IPR): See Initial Demonstration of Capability in Sections 9.1 and 13.2.

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3.17 Isomer: Chemical compounds that contain the same number of atoms of the same elements, but differ in structural arrangement and properties. For example, 1,2,3,4-TCDD and 2,3,7,8-TCDD are structural isomers.

3.18 Laboratory Blank: See Method Blank.

3.19 Laboratory Control Sample (LCS): A laboratory blank spiked with known quantities of analytes. The LCS is analyzed exactly like a sample. Its purpose is to assure that the results produced by the laboratory remain within the limits specified in this method for precision and recovery..

3.20 Maximum Level (MaxL): The concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. Also referred to as the upper method calibration limit (UMCL). It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.21 Method Blank: An aliquot of reagent water, sand, sodium sulfate, or other representative matrix, free of the targets of interest and interferences, that is extracted and analyzed along with the samples to monitor for laboratory contamination.

3.22 Minimum Level (MinL): The level at which the entire analytical system must give a recognizable signal and acceptable calibration point for the analyte. Also referred to as the lower method calibration limit (LMCL). It is equivalent to the concentration of the lowest calibration standard assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.23 MS: Mass spectrometer or mass spectrometry.

3.24 Multiple Ion Detection (MID): A MS operational mode in which only selected ions are monitored rather than scanning the instrument to obtain a complete mass spectrum.

3.25 Ongoing precision and recovery standard (OPR): See Laboratory Control Sample.

3.26 PCDD: Polychlorinated dibenzo-p-dioxins.

3.27 PCDF: Polychlorinated dibenzofurans.

3.28 PFK: Perfluorokerosene; the mixture of compounds used to calibrate the exact m/z scale in the HRMS.

3.29 FC-43 (PFTBA): Perfluorotributylamine

3.30 Recovery Standard: Solution containing $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD that is added to every sample, blank, and quality control spike sample extract just prior to analysis. The results are used to measure the recovery of the internal standards and the cleanup standard.

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3.31 Percent Difference (%D): A measure of the difference between two values normalized to one of the values. It is used to determine the accuracy of the concentration measurements of second source verification standards.

3.32 Relative Response Factor (RRF): The ratio of the response of the mass spectrometer to a known amount of a compound relative to that of a known amount of a reference standard as measured in the initial and continuing calibrations. It is used to determine instrument performance and it is used to calculate the concentration of target analytes, internal standard recoveries, or detection limits in samples, blanks, and quality control samples.

3.33 Signal to Noise Ratio: The ratio of the mass spectrometer response of a GC peak to the background noise signal.

3.34 Split Ratio (S): The decimal expression of the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards.

3.35 Window Defining Mix: A solution which contains the first and last eluting isomers of each homologue group and is used to verify that the switching times between the MID descriptors have been appropriately set.

3.36 Additional definitions can be found in the Test America Knoxville QAM.

4. Interferences

4.1 Solvents, reagents, glassware and other sample processing hardware can yield discrete artifacts or elevated baselines that can cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by performing laboratory method blanks. Analysts must not use PVC gloves, powdered gloves, or gloves with levels of phthalates which cause interference.

4.2 The use of high purity reagents and solvents (pesticide grade) helps minimize interference problems. Where necessary, reagents are cleaned by extraction or solvent rinse.

4.3 Interferences coextracted from the samples can vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, and polychlorinated alkyldibenzofurans that can be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. While certain cleanup techniques are provided as part of this method, unique samples can require additional cleanup steps to achieve lower detection limits.

5. Safety

5.1 Employees must abide by the policies and procedures in the Corporate Safety Manual, Radiation Safety Manual and this document.

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5.2 Eye protection that satisfies ANSI Z87.1 (as per the Corporate Safety Manual), laboratory coat and appropriate gloves must be worn while samples, standards, solvents and reagents are being handled. Disposable gloves that have become contaminated must be removed and discarded, other gloves must be cleaned immediately.

5.2.1 Latex and vinyl gloves provide no protection against most of the organic solvents used in this method. For the operations described herein, Nitrile gloves are to be worn. For operations using solvents that may splash, SilverShield® gloves are recommended. SilverShield® gloves protect against breakthrough for most of the solvents used in this procedure.

5.3 The effluents of sample splitters for the gas chromatograph and roughing pumps on the mass spectrometer must be vented to the laboratory hood exhaust system or must pass through an activated charcoal filter.

5.4 The gas chromatograph and mass spectrometer contain zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them or use thermal protection when working on them while they are above room temperature.

5.5 The mass spectrometer is under high vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source. Alternatively, the source can be removed from the vacuum manifold through a vacuum interlock.

5.6 There are areas of high voltage in both the gas chromatograph and the mass spectrometer. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power. If the work involved requires measurement of voltage supplies, the instrument can be left on.

5.7 Primary Materials Used: The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	**Hazards**	**Exposure Limit (2)**	**Signs and symptoms of exposure**
Methylene chloride	Carcinogen, Irritant	25 ppm-TWA, 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. Can be absorbed through skin.

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Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hexane	Flammable, Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure can cause lightheadedness, nausea, headache, and blurred vision. Vapors can cause irritation to the skin and eyes.
Methanol	Flammable, Poison, Irritant	200 ppm-TWA	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure can include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and can cause skin to become dry and cracked. Skin absorption can occur; symptoms can parallel inhalation exposure. Irritant to the eyes.
Toluene	Flammable, Poison, Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation can cause irritation of the upper respiratory tract. Symptoms of overexposure can include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness can be produced. Causes severe eye and skin irritation with redness and pain. Can be absorbed through the skin.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Can cause coughing, dizziness, dullness, and headache.
Cyclohexane	Flammable, Irritant	300 ppm TWA	Inhalation of vapors causes irritation to the respiratory tract. Symptoms can include coughing, shortness of breath. High concentrations have a narcotic effect.
Tetradecane	Irritant	None established	Inhalation of vapors can cause difficulty breathing, headache, intoxication and central nervous system damage.
Benzene	Flammable, Toxic, Carcinogen	PEL: 1 ppm TWA ; 5 ppm, 15 min. STEL	Causes skin irritation. Toxic if absorbed through skin. Causes severe eye irritation. Toxic if inhaled. Vapor or mist causes irritation to mucous membranes and upper respiratory tract. Exposure can cause narcotic effect. Inhalation at high concentrations can have an initial stimulatory effect on the central nervous system characterized by exhilaration, nervous excitation and/or giddiness, depression, drowsiness or fatigue. Victim can experience tightness in the chest, breathlessness, and loss of consciousness.
Nonane	Flammable	None established	Harmful if inhaled/swallowed. Vapor/mist is irritating to eyes, mucous membranes and upper respiratory tract. Causes skin irritation.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.7.1 Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA regulations include benzene and methylene chloride, 2,3,7,8-TCDD and all other 2,3,7,8- substituted PCDD or PCDF isomers.

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NOTE: The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have toxicities comparable to that of 2,3,7,8-TCDD. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

5.8 Exposure to chemicals must be maintained as low as reasonably achievable; therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers must be kept closed unless transfers are being made.

5.9 All procedures that involve solvents such as acetone, toluene, methylene chloride, and hexane (e.g., glassware cleaning and the preparation of standards and reagents) must be conducted in a fume hood with the sash closed as far as the operations permit.

5.10 Personal Hygiene: Thorough washing of hands and forearms is recommended after each manipulation and before breaks (coffee, lunch, and shifts).

5.11 All work must be stopped in the event of a known or potential compromise to the health or safety of an associate. The situation must be reported immediately to a laboratory supervisor.

6. Equipment and Supplies

6.1 Sample Analysis Equipment.

6.1.1 Gas Chromatograph – Must have splitless or on-column injection port for capillary column, temperature program with isothermal hold, and must meet all of the performance specification in Section 10.

6.1.1.1 GC column for PCDDs/PCDFs and for isomer specificity for 2,3,7,8-TCDD – 60m x 0.32mm ID x 0.25µm film thickness DB-5 or RTX-5 fused silica capillary column (J&W No. 123-5062, Restek No.10227 or 10227-125 IntegraGuard) or equivalent is required.

6.1.1.2 GC column for isomer specificity for 2,3,7,8-TCDF – 30m x 0.32mm ID x 0.25µm film thickness DB-225 or RTX-225 fused silica capillary column (J&W No. 123-2232 or Restek No.14024) or equivalent is required.

6.1.2 Mass Spectrometer – Electron impact ionization with the filament electron volts (eV) optimized for best instrument sensitivity, stability and signal to noise ratio. Must be capable of repetitively selectively monitoring 12 exact m/z's minimum at high resolution (≥10,000) during a period of approximately 1 second and must meet all of the performance specifications in Section 10.

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6.1.3 GC/MS Interface – The mass spectrometer (MS) must be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beam.

6.1.4 Data System – Capable of collecting, recording, and storing MS data.

7. Reagents and Standards

7.1 Standards and Calibration Solutions: Certified Reference Standards purchased from Cambridge Isotope Laboratories (CIL, Andover Massachusetts), and Wellington Laboratories (Guelph, Ontario, Canada). If the chemical purity is 98% or greater, the weight can be used without correction to compute the concentration of the standard. When not being used, standards are stored in the dark at room temperature in screw-capped vials with PTFE-lined caps. Standards are used as received after being sonicated and transferred to 2.0 mL amber glass vials with PTFE lined caps.

7.1.1 Stability of Solutions: Standards have an expiration of ten (10) years from date of receipt unless otherwise specified by the manufacturer. Standard solutions used for quantitative purposes must be analyzed periodically, and must be assayed against reference standards before use.

7.2 Initial Calibration Standards:

7.2.1 1613B/8290/8290A: CS1-CS5. CIL Catalog No. EDF-9999. (See Table 5).

7.2.2 23/0023A/TO-9A: CS1-CS5. Wellington Catalog No. EPA-23 CS1-5. (See Table 6).

7.3 Initial Calibration Verification Standards:

7.3.1 1613B/8290/8290A: Wellington Catalog No. EPA-1613-CS3.

7.3.2 23/0023A/TO-9A: CS3. CIL Catalog No. EDF-4052-3.

7.4 Daily Calibration Verification Standards

7.4.1 1613B/8290/8290A: CS3. CIL Catalog No. EDF-9999-3. (See Table 7).

7.4.2 1613B/8290/8290A: CS3. CIL Catalog No. EDF-4141. (See Table 7).

NOTE: This standard can be used as both the Continuing Calibration Standard and the DB/Rtx-5 GC Window Defining Mix/Column Performance Check Solution.

7.4.3 23/0023A/TO-9A: CS3. Wellington Catalog No. EPA-23-CS3. (See Table 8).

7.5 Native Standards

7.5.1 Native Standard Stock Solution: CIL Catalog No. EDF-7999-10x, 400-4000 ng/mL in nonane, 1.2 mL.

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7.5.2 Native Standard Working Stock Solution: Dilute 0.300 mL of the native standard stock solution to 3.0 mL in a volumetric flask with nonane for a final concentration of 40-400 ng/mL.

7.5.3 Native LCS Spiking Solution: Dilute 500 µL of the native standard working stock solution to 100 mL in a 125 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 0.2-2.0 ng/mL. 1.0 mL of this solution is added to each LCS, LCSD or MS/MSD sample. See Table 11 for a complete list of compounds and their concentrations.

7.6 1613B/8290/8290A Internal Standards

7.6.1 1613B/8290/8290A Internal Standard Stock Solution: CIL Catalog No. EDF-8999, 100 ng/mL ($^{13}C_{12}$-OCDD 200 ng/mL) in nonane, 500 µL.

7.6.2 1613B/8290/8290A Internal Standard Spiking Solution: Dilute 2000 µL of the internal standard stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank and QC sample. See Table 12 for a complete list of compounds and their concentrations.

7.7 2,3,7,8-TCDD/2,3,7,8-TCDF Internal Standards

7.7.1 $^{13}C_{12}$-2,3,7,8-TCDD Internal Standard Stock Solution: CIL Catalog No. ED-900, 50 µg/mL in nonane, 1.2 mL

7.7.2 $^{13}C_{12}$-2,3,7,8-TCDF Internal Standard Stock Solution: CIL Catalog No. EF-904, 50 µg/mL in nonane, 1.2 mL

7.7.3 $^{13}C_{12}$-TCDD/$^{13}C_{12}$-TCDF Internal Standard Secondary Stock Solution: Dilute 0.100 mL of the stock solutions above to 5 mL in a volumetric flask with nonane to a final concentration of 1000 ng/mL.

7.7.4 $^{13}C_{12}$-TCDD/$^{13}C_{12}$-TCDF Internal Standard Spiking Solution: Dilute 200 µL of the internal standard secondary stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 1.0 ng/mL. 1.0 mL of this solution is added to each sample, method blank and QC sample extract that is extracted for TCDD and/or TCDF analysis only. See Table 2 for a complete list of compounds and their concentrations.

7.8 23/0023A/TO-9A Internal Standards

7.8.1 23/0023A/TO-9A Internal Standard Stock Solution: Wellington Catalog No. EPA-23ISS, 1000 ng/mL ($^{13}C_{12}$-OCDD 2000 ng/mL) in nonane/toluene (80:20 v:v), 1.2 mL.

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7.8.2 23/0023A/TO-9A Internal Standard Spiking Solution: Dilute 200 µL of the internal standard stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with iso-octane to a final concentration of 1.0 ng/mL ($^{13}C_{12}$-OCDD 2.0 ng/mL). 1.0 mL of this solution is added to each sample, method blank, and QC sample. See Table 15 for a complete list of compounds and their concentrations.

7.9 Recovery Standards

7.9.1 $^{13}C_{12}$-1,2,3,4-TCDD Recovery Standard Stock Solution: CIL Catalog No. ED-911, 50 µg/mL in nonane, 1.2 mL

7.9.2 $^{13}C_{12}$-1,2,3,7,8,9-HxCDD Recovery Standard Stock Solution: CIL Catalog No. ED-996, 50 µg/mL in nonane, 1.2 mL

7.9.3 Recovery Standard Secondary Stock Solution: Dilute 1.0 mL of the stock solutions above to 10 mL in a volumetric flask with nonane to a final concentration of 5.0 µg/mL.

7.9.4 Recovery Standard Spiking Solution: Add 10 mL of nonane to a 12 mL amber vial with a Class A glass pipette. With a syringe, remove 200 µL of nonane from the vial and add 200 µL of the recovery standard secondary stock solution to a final concentration of 0.1 µg/mL. 20 µL of this solution is added to each sample, method blank and QC sample extract. See Table 2 for a complete list of compounds and their concentrations.

7.10 1613B and 8290A Cleanup Standards

7.10.1 Cleanup Standard Stock Solution: CIL Catalog No. ED-907, 50 µg/mL in nonane, 1.2 mL

7.10.2 Cleanup Standard Secondary Stock Solution: Dilute 0.100 mL of the 50 µg/mL cleanup standard stock solution to 1.0 mL in a volumetric flask with nonane to a final concentration of 5.0 µg/mL.

7.10.3 Cleanup Standard Working Stock Solution: Dilute 0.120 mL of the 5.0 µg/mL cleanup standard secondary stock solution to 3.0 mL in a volumetric flask with nonane to a final concentration of 200 ng/mL.

7.10.4 Cleanup Standard Spiking Solution: Dilute 200 µL of the 200 ng/mL working stock solution to 200 mL in a 250 mL amber bottle with a PTFE lined cap with hexane to a final concentration of 0.20 ng/mL. 1.0 mL of this solution is added to each 1613B or 8290A sample, method blank and QC sample extract prior to cleanup. See Table 17 for a complete list of compounds and their concentrations.

7.11 23/0023A/TO-9A Surrogate Standards

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7.11.1 23/0023A/TO-9A Surrogate Standard Stock Solution: Wellington Catalog No. EPA-23SSS, 1000 ng/mL in nonane/toluene (95:5 v:v), 1.2 mL.

7.11.2 23/0023A/TO-9A Surrogate Standard Spiking Solution: Dilute 500 µL of the surrogate standard stock solution to 25 mL in a graduated cylinder with nonane to a final concentration of 20 ng/mL. 100 µL of this solution is added to each sample train components before sampling. See Table 16 for a complete list of compounds and their concentrations.

7.12 PCDD/PCDF Window Defining and Isomer Specificity Standard

7.12.1 PCDD/PCDF Window Defining and Isomer Specificity Mixture: CIL Catalog No. EDF-4141. This standard contains the daily standard, window defining mix and the isomer specificity mix.

7.13 Perfluorokerosene (PFK) is used in neat form to tune and calibrate the mass spectrometer. Fluka (Catalog No. - 77275) has been found to be superior to other sources of PFK.

7.14 FC-43 (PFTBA) is used in neat form to tune and calibrate the mass spectrometer. (Scientific Instrument Services Catalog No. FC-43-35).

8. Sample Collection, Preservation and Storage

8.1 Sampling is not performed for this method by TestAmerica Knoxville. For information regarding sample shipping, refer to SOP KNOX-SC-0003, “Sample Receipt and Log In”, current revision. Sample container and preservation recommendations are listed in the table below.

Method:	**1613B**	**8290/8290A[1]**	**23**	**0023A[1]**	**TO-9A**
Holding Times	Samples – 1 year from collection to extraction Extracts – 1 year from extraction to analysis	Samples – 30 days from collection to extraction Extracts – 45 days from extraction to analysis Tissue Extracts –45 days from collection to analysis	Samples – 30 days from collection to extraction Extracts – 45 days from extraction to analysis	Samples – 30 days from collection to extraction Extracts – 45 days from extraction to analysis	Samples – 7 days from collection to extraction Extracts – 40 days from extraction to analysis
Containers	Amber Glass	Amber Glass	See KNOX-ID-0012	See KNOX-ID-0012	See KNOX-ID-0012

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Method:	**1613B**	**8290/8290A[1]**	**23**	**0023A[1]**	**TO-9A**
Preservation:					
Aqueous Samples	≤6 °C in the dark If residual chlorine is present, add 80 mg/L sodium thiosulfate. If pH > 9, adjust to pH 7-9 with sulfuric acid	≤6 °C in the dark If residual chlorine is present, add 80 mg/L sodium thiosulfate.	N/A	N/A	N/A
Solid Samples	<-10 °C in the dark	≤6 °C in the dark	N/A	N/A	N/A
Tissue Samples	<-10 °C in the dark	<-20 °C in the dark[2]	N/A	N/A	N/A
Air Samples	N/A	≤6 °C in the dark	≤6 °C in the dark	≤6 °C in the dark	≤6 °C in the dark

Notes:

1 For method 8290, 8290A and 0023A the holding times listed are recommendations. PCDDs and PCDFs are very stable in a variety of matrices, and holding times under the conditions listed can be as high as a year for certain matrices. The results of samples analyzed after the holding time expiration date must be considered to be minimum concentrations and must be identified as such in the final report. Sample extracts, however, must always be analyzed within 45 days of extraction. (For the State of South Carolina and the New Jersey DEP, the holdings times are as listed in the table and are not considered recommendations.)

2 If the freezer used to store samples is not capable of reaching a temperature of <-20 °C when the temperature control is set to its maximum limit, a storage higher temperature is acceptable as long as it is <-10 °C.

9. Quality Control

9.1 The Initial Demonstration of Capability (IDOC) studies described in Section 13 must be completed with acceptable results before analysis of samples can begin.

9.2 The Method Detection Limit (MDL) study described in Section 13 must be completed with acceptable results before analysis of samples can begin.

9.3 A laboratory method blank must be run along with each analytical batch of 20 (10, including field blank if provided, for TO-9A) or fewer samples. The method blank is normally analyzed immediately after the calibration standards. The method blank must meet the following acceptance criteria:

9.3.1 The concentration of target analytes in the method blank must be less than the minimum level (ML) and “B” qualifiers are added to all associated samples with analytes detected in the method blank above the estimated detection limit (EDL).

9.3.2 If the concentration of target analytes in the method blank is greater than minimum level (ML) but less than 5% of the concentration in the associated samples, corrective action is required but the associated data can be reported. At a minimum, corrective action must include the addition of "B" qualifiers to all associated samples with analytes detected in the method blank above the ML and documentation in the case narrative.

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9.3.3 If the method blank sample fails to meet the acceptance criteria, the Project Manager is notified and the entire sample batch is re-extracted. If there is insufficient sample volume remaining for re-extraction, the client is contacted for information about the availability of additional sample volume. If there is no additional sample available, the original sample data is flagged and reported. A nonconformance memo is initiated describing the problem and corrective action. The problem and corrective action is documented in the project narrative.

9.3.4 If there is no target analyte greater than the minimum levels (ML) in the samples associated with an unacceptable method blank, the data can be reported with qualifiers. Such action must be done in consultation with the client.

9.3.5 The method blank internal standard recoveries must be within the established control limits. If internal standard recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination.

9.3.5.1 If internal standard recoveries are low in the method blank and there are analytes >ML in the associated samples re-extraction of the blank and affected samples is required if the method blank does not demonstrate that the analysis is free of contamination.

9.3.5.2 If the method blank internal standard recoveries are outside the QC limits and the decision is made to report the sample results, an NCM must be initiated and the reason for accepting the sample results clearly documented. Consultation with the client before acceptance must take place.

9.3.6 Refer to the QC Program document (QA-003) for further details of the corrective actions.

9.4 Instrument Blank

9.4.1 Instruments must be evaluated for contamination during each 12 hour analytical sequence. This is accomplished by analysis of a method blank if available. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of solvent with the internal standards and recovery standards added. It is evaluated in the same way as the method blank.

9.5 Laboratory Control Sample

An LCS is analyzed along with each analytical batch of 20 (10, including field blank if provided, for TO-9A) or fewer samples. The LCS consists of reagent water for aqueous samples, and a clean solid matrix (sodium sulfate) for solid samples. The LCS extract must be subject to the same clean up procedures as the associated sample extracts. LCS spike components, concentrations, and control limits are given in Table 11.

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9.5.1 If any analyte in the LCS is outside the control limits, corrective action must occur. Corrective action includes:

9.5.1.1 If the LCS fails to meet the acceptance criteria, the Project Manager is notified and the entire sample batch is re-extracted. If there is insufficient sample volume remaining for re-extraction, the client is contacted for information about the availability of additional sample volume. If there is no additional sample available, the original sample data is flagged and reported. A nonconformance memo is initiated describing the problem and corrective action. The problem and corrective action is documented in the project narrative.

9.5.1.2 If the batch is not re-extracted and reanalyzed, an NCM must be initiated and the reasons for accepting the batch must be clearly presented in the project records and the report. (An example of an acceptable reason for not reanalyzing might be that the matrix spike and matrix spike duplicate recoveries are within control limits, the method blank and sample internal standard recoveries are within limits, and the data clearly demonstrates that the problem was confined to the LCS).

9.5.1.3 For method TO-9A calculate the precision (%D) from the LCS/LCSD. The precision must be within ± 30%.

9.5.2 Ongoing monitoring of the LCS provides evidence that the laboratory is performing the method within accepted QC guidelines for accuracy and precision.

9.6 Internal Standards

Internal standards are spiked into all samples, blanks, and laboratory control samples to assess method performance on the sample matrix. The recovery of each labeled internal standard must be within the limits in Table 13 for methods 1613B, 8290 and 8290A or in Table 15 for methods 23, 0023A, and TO-9A.

9.6.1 If the recovery is outside these limits the following corrective action must be taken:

9.6.1.1 Check all calculations for error.

9.6.1.2 Ensure that instrument performance is acceptable.

9.6.1.3 Recalculate the data and/or reanalyze if either of the above checks reveal a problem.

9.6.1.4 If the recovery of any internal standard is less than the lower control limit, calculate the S/N ratio of the internal standard. If the S/N is > 10 and the estimated detection limits (EDLs) are less than the

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minimum levels (MLs), report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the estimated detection limits (EDLs) are greater than the minimum levels (MLs), re-extract and re-analyze the sample. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample can be re-extracted or additional clean-ups can be employed. The decision to reanalyze or flag the data is made in consultation with the client.

9.7 Matrix Spike/Matrix Spike Duplicate (MS/MSD) – Method 8290 only.

When method 8290 is performed a matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every 20 samples of a given matrix. **Note that a MS/MSD is not required for Method 8290A**. The MS/MSD is spiked with the same subset of analytes as the LCS (See Table 12). Compare the percent recovery and relative percent difference (RPD) to that in the laboratory specific historically generated limits.

9.7.1 If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action is to check the recovery of that analyte in the Laboratory Control Sample (LCS). Generally, if the recovery of the analyte in the LCS is within limits, then the laboratory operation is in control and analysis can proceed. The reasons for accepting the batch must be documented in the report narrative.

9.7.2 If the recovery for any component is outside QC limits for both the MS/MSD and the LCS, the analysis is out of control and corrective action must be taken. Corrective action normally includes repreparation and reanalysis of the batch.

9.7.3 If a MS/MSD is not possible due to limited sample, then a LCSD must be analyzed. The LCSD is evaluated using the same acceptance criteria as the LCS. The RPD of the LCS and LCSD are compared to the acceptance limits in Table 12.

9.7.4 The MS/MSD must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds are diluted out.

9.8 Surrogate Standards – Methods 23, 0023A, TO-9A

Field surrogate standards are added to the collection media prior to sample collection when performing methods 23, 0023A, or TO-9A. The surrogate recoveries are calculated relative to the internal standards and are a measure of sampling efficiency. The recovery of the surrogate standards must be within the limits specified in Table 16. Poor recoveries of the surrogate standards can indicate breakthrough in the sampling train.

9.8.1 If the recovery is outside these limits the following corrective action must be taken:

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9.8.1.1 Check all calculations for error.

9.8.1.2 Ensure that instrument performance is acceptable.

9.8.1.3 Recalculate the data and/or reanalyze if either of the above checks reveal a problem.

9.8.1.4 Flag the results that are outside control limits and notify the Project Manager. The client must be notified and consulted for additional corrective action.

10. Calibration and Standardization

10.1 Two types of calibration procedures are required. One type, initial calibration, is required before any samples are analyzed and is required intermittently throughout sample analyses as dictated by the results of continuing calibration procedures described below. The other type, continuing calibration, consists of analyzing the column performance check solution and a calibration solution (CS3). No samples are to be analyzed until acceptable calibration as described in sections 10.2 and 10.2.9.1 is demonstrated and documented. A 2uL injection volume is specified for all extracts, blanks, calibration solutions and performance check samples. A 1uL injection volume can be used; however, the laboratory must keep the injection volume the same throughout calibration and analysis.

10.2 Initial Calibration

10.2.1 Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 5 for methods 1613B and 8290/8290A or in Table 6 for methods 23, 0023A, or TO-9A. Store calibration standards at room temperature in the dark. Calibration standard solutions have an expiration date of ten (10) years from date of receipt unless otherwise specified by the manufacturer/supplier.

10.2.2 Establish operating parameters for the GC/MS system (suggested operating conditions are displayed in Figure 1 and Figure 2). For method 1613B adjust the GC conditions to meet the relative retention times for the PCDDs/PCDFs listed in Table 3. The cycle time for MID descriptors must be ≤ 1 sec.

10.2.3 By using a PFK or FC-43 molecular leak, tune the instrument to meet the minimum resolving power of 10,000 (10 percent valley) at m/z 304.9824 (PFK) or 313.9838 (FC-43) or any other reference signal close to the m/z 303.9016 (from TCDF).

10.2.4 By using peak matching conditions and the aforementioned either PFK or FC-43 reference peak, verify that the exact mass of m/z 380.9760 (PFK) or m/z 363.9807 (FC-43) is within 5 ppm of the required value. Document that the resolving power at reduced accelerating voltage of m/z 380.9760 (PFK) or m/z 363.9807 (FC-43) is greater than 10,000 (10 percent valley).

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10.2.5 Analyze 2µL of the Window Defining Mixture and set the switchpoints for the MID descriptors. The switchpoints must be set to encompass the retention time window of each congener group.

10.2.6 If the initial calibration is being performed on the DB-5 or RTX-5 column, analyze 2µL of the Column Performance solution. The chromatographic peak separation between 2,3,7,8-TCDD and the closest eluting non-2,3,7,8-TCDD isomer must be resolved with a % Valley of ≤ 25, where

$$\%\ \text{Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8-TCDD}} \times 100$$

If the initial calibration is being performed on the DB-225 or RTX-225 column, analyze 2µL of the TCDF Column Performance solution. The chromatographic peak separation between 2,3,7,8-TCDF and the closest eluting non-2,3,7,8-TCDF isomer must be resolved with a % Valley of ≤ 25, where

$$\%\ \text{Valley} = \frac{\text{baseline to valley height of closest eluting isomer}}{\text{peak height of 2,3,7,8-TCDF}} \times 100$$

10.2.7 Analyze 2µL of each of the five calibration standards and calculate the RRF of each analyte vs. the appropriate internal standard listed in Table 3 for methods 1613B, 8290/8290A or in Table 4 for methods 23, 0023A, and TO-9A using the following equation;

$$\text{RRF} = \frac{\text{As} \times \text{Cis}}{\text{Ais} \times \text{Cs}}$$

where:

As = sum of the areas of the quantitation ions of the compound of interest
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Cis = concentration of the appropriate internal standard
Cs = concentration of the compound of interest

10.2.7.1 Calculate the mean relative response factor (mean RRF) and the percent relative standard deviation (RSD) of the relative response factors for each compound of interest in the five calibration standard solutions using the following equations;

$$\overline{\text{RRF}}_{n=5} = \frac{1}{n} \times \sum_{i=1}^{n} \text{RF}_i$$

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$$RSD_{n=5} = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_i - \overline{RF}\right)^2}{n-1}} \times \frac{100}{\overline{RRF}}$$

10.2.8 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met for each initial calibration standard before sample analyses are performed. If acceptable initial calibration is not achieved, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to problems with an individual analysis within the calibration series, follow the procedure in Test America Policy CA-T-P-002 Selection of Calibration Points, current revision (see reference section 16.10).

10.2.8.1 The percent relative standard deviation (RSD) for the mean relative response factors must be within the acceptance criteria listed in Table 5 for methods 1613B, 8290/8290A or in Table 6 for methods 23, 0023A, and TO-9A.

10.2.8.2 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standards must have signal-to-noise ratios (S/N) ≥ 10.

10.2.8.3 The ion abundance ratios must be within the specified control limits in Table 22.

10.2.8.4 For method 1613B the absolute retention time of $^{13}C_{12}$-1234-TCDD must exceed 25.0 minutes on the DB/Rtx-5 column and 15.0 minutes on the DB/Rtx-225 column.

10.2.8.5 Corrective action can include replacing the injector port liner, replacing the injector port septum, removal of a small portion of the front of the analytical column, replacing the autosampler syringes and rinse solvent, adjusting the instrument tuning, cleaning the ion volume or ion source, installing a new analytical column and replacing the calibration standard solutions.

10.2.9 Analyze 2µL of the Initial Calibration Verification (ICV) Standard in section 7.3 after the completion of the initial calibration prior to sample analysis. Calculate the concentration of the ICV using the RRFs from the CS3 standard analyzed in section 10.2.7 and the formula in section 12.3.4. Calculate the percent difference (%D) between the expected and the calculated ICV concentration using the following formula.

$$\%D = \frac{\left(C_{Exp} - C_{Calc}\right)}{C_{Exp}} \times 100$$

Where:
C_{Exp} = The expected concentration of the Standard.

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C_{Calc} = The calculated concentration of the Standard.

10.2.9.1 The general criteria for percent difference acceptance limits is ±25% for all native compounds. The warning limits for percent difference is ±25% to ±35%.

10.2.9.2 All data associated with compounds with percent differences in the warning limits must be reviewed before acceptance.

10.2.9.3 All data associated with compounds with percent differences outside the warning limits must be documented as an NCM. Corrective action must be taken and can include the following:

- Reanalyze the ICV Standard
- Replace and reanalyze the ICV Standard
- Evaluate the instrument performance
- Evaluate the Initial Calibration Standards

10.3 Continuing Calibration

10.3.1 Continuing calibration is performed at the beginning of a 12 hour period after successful mass resolution and GC resolution performance checks. A calibration check is also required at the end of a 12 hour period when performing method 8290/8290A or 0023A.

10.3.2 Document the mass resolution performance as specified in sections 10.2.3 and 10.2.4. The mass resolution checks must be performed at the beginning and at the end of each 12-hour shift.

10.3.3 Analyze 2µL of the Window Defining Mixture and/or Column Performance Solution Mixture under the same instrument conditions used to perform the initial calibration. Determine and document acceptable column performance as described in section 10.2.5 and 10.2.6.

10.3.4 Analyze 2µL of the Daily Calibration Standard Solution (CS3). Calculate the concentrations and percent difference of the standard using the formulas in sections 12.3.4 and 10.2.9.

NOTE: The combined Continuing Calibration Standard/Window Defining Mix/Column Performance Solution specified in section 7.4.2 can be used in section 10.3.2, 10.3.4, and 10.3.6.

10.3.5 Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met at the beginning of each 12 hour period that samples are analyzed. If acceptable beginning continuing calibration criteria is not met, identify the root cause, perform corrective action and repeat the continuing calibration. If the second consecutive beginning continuing calibration does not

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meet acceptance criteria, additional corrective action must be performed. Acceptable performance must be demonstrated after two consecutive failing beginning continuing calibrations by the analysis of two consecutive acceptable beginning continuing calibrations or by analysis of a new initial calibration.

10.3.5.1 The measured concentration or percent difference for each compound must be within the acceptance criteria limits in Table 7 for methods 1613B, 8290/8290A or in Table 8 for methods 23, 0023A and TO-9A.

10.3.5.2 For method 1613B the relative retention times of PCDDs/PCDFs and labeled compounds in the standard must be within the limits in Table 3.

10.3.5.3 The peaks representing the PCDDs/PCDFs and labeled compounds in the calibration standard must have signal-to-noise ratios (S/N) ≥ 10.

10.3.5.4 The ion abundance ratios must be within the specified control limits in Table 22.

10.3.5.5 Corrective action can include all of the items specified in section 10.2.8.5.

10.3.5.6 When performing method 8290/8290A or 0023A, if the continuing calibration fails at the beginning of a 12-hour shift, the instructions in section 10.3.5 must be followed. If the continuing calibration check performed at the end of a 12 hour period fails by no more than ±25 %D for unlabeled native analytes and ±35 %D for labeled standards, the closing standard must not be used as a beginning calibration standard for the next 12-hour shift and the requirements in section 10.3.5 must be met before analysis can continue. Use the mean RRF from the two daily continuing calibration runs to compute the analyte concentrations instead of the RRFs obtained from the initial calibration. If the continuing calibration check performed at the end of a 12 hour period fails by more than ±25 %D for unlabeled native analytes and ±35 %RPD for labeled standards initiate corrective action and reanalyze all sample extracts analyzed during the 12 hour period encompassing the failed end of shift calibration check.

It is realized that it might not always be possible to achieve all RF criteria. For example, the RF criteria for $^{13}C_{12}$-HpCDD and $^{13}C_{12}$-OCDD were not met, however the RF values for the corresponding unlabeled compounds were within the criteria established in this procedure. The data quality for the unlabeled HpCDD and OCDD values were not compromised as a result of the calibration event. In these situations, the analyst must consult with the group manager and

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the project manager to assess the impact on the data quality objectives on the affected samples. Corrective action must be taken and any decision to report sample data in this situation must be made in conjunction with the client. An NCM must be initiated if the data is to be reported.

10.3.6 Daily calibration must be performed every 12 hours of instrument operation. The 12 hour shift begins with the documentation of the mass resolution followed by the injection of the Window Defining Mixture or Column Performance Solution Mixture and the Daily Calibration Standard.

10.3.6.1 For methods 1613B, 23, TO-9A- The mass resolution documentation must also be performed at the end of the 12 hour shift. If the lab is operating consecutive 12 hour shifts, the mass resolution check from the end of the previous period can be used for the beginning of the next period.

10.3.6.2 For method 8290/8290A or 0023A - The Continuing Calibration Standard check and mass resolution documentation must also be performed at the end of the 12 hour shift. If the lab is operating consecutive 12-hour shifts, the Window Defining Mixture and/or Column Performance Solution Mixture must be analyzed at the beginning of each 12-hour period. The mass resolution and continuing calibration checks from the previous period can be used for the beginning of the next period.

11. Procedure

11.1 One time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variations in sample matrix, radioactivity, chemistry, sample size or other parameters. Any variations in the procedure, except those specified by project specific instructions, must be completely documented using a Nonconformance Memo and approved by a Technical Specialist, Project Manager and QA Manager. If contractually required the client must be notified.

11.2 Any unauthorized deviations from this procedure must also be documented as a nonconformance with a cause and corrective action described.

11.3 Sample Extract Analysis

11.3.1 Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 2 µL into the GC/MS and acquire data until OCDF has eluted from the column.

11.3.2 Record analysis information in the instrument logbook. The following information is required:

Date of analysis

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Time of analysis
Instrument data system filename
Analyst
Lab sample identification
Additional information can be recorded in the logbook if necessary.

11.3.3 Generate ion chromatograms for the masses listed in Table 21 that encompass the expected retention windows of the PCDD and PCDF homologous series.

11.4 Refer to the TestAmerica Knoxville Quality Assurance Manual, current revision for the GC/MS instrument equipment maintenance table.

11.5 Refer to TestAmerica Knoxville SOP KNOX-IT-0001, current revision for requirements for computer hardware and software.

12. Data Analysis and Calculations

12.1 Refer to Figure 3 for an example data review checklists used to perform and document the review of the data. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data.

12.2 Qualitative identification criteria for PCDDs and PCDFs. For a gas chromatographic peak to be identified as a PCDD or PCDF, it must meet all of the following criteria:

12.2.1 The ion current response for both ions used for quantitative purposes must reach maximum simultaneously (± 2 seconds).

12.2.2 The signal-to-noise ratio (S/N) for each GC peak at each exact m/z must be ≥ 2.5 for positive identification of a PCDD/PCDF compound.

12.2.3 The ratio of the integrated areas of the two exact m/z's specified in Table 21 must be within the limits specified in Table 22, or alternatively when performing method 1613B, within ±10 percent of the ratio in the midpoint (CS3) calibration or the calibration verification (VER), whichever is most recent.

12.2.4 Method 1613B only - The relative retention time of the peak for a 2,3,7,8-substituted PCDD or PCDF must be within the limits in Table 3.

12.2.5 Method 8290, 8290A and 0023A only - For 2,3,7,8-substituted isomers, which have an isotopically labeled internal standard or recovery standard present in the sample extract, the retention time of the two ions used for quantitation purposes must be within -1 to +3 seconds of the isotopically labeled standard.

12.2.6 Method 23 and TO-9A only - For 2,3,7,8-substituted isomers, which have an isotopically labeled internal standard or recovery standard present in the sample extract, the retention time of the two ions used for quantitation purposes must be within ±3 seconds of the isotopically labeled standard.

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12.2.7 Method 8290, 8290A, 23, 0023A, and TO-9A only - For 2,3,7,8-substituted isomers, which do not have an isotopically labeled internal standard present in the sample extract, the retention time must fall within 0.005 retention time units of the relative retention times measured in the routine calibration.

12.2.8 The retention time of peaks representing non-2,3,7,8-substituted PCDDs/PCDFs must be within the retention time windows established in section 10.2.5.

12.2.9 No peaks detected in the polychlorinated diphenyl-ether (PCDPE) mass channel in the same retention time region (± 2 sec for method 8290, 8290A & 0023A) as a PCDF peak.

12.3 Quantitation for PCDDs and PCDFs.

12.3.1 Calculate the Internal Standard and Cleanup Standard Recoveries (Ris) relative to the Recovery Standard according to the following equation:

$$\mathrm{Ris} = \frac{\mathrm{Ais} \times \mathrm{Qrs}}{\mathrm{Ars} \times \mathrm{RRFis} \times \mathrm{Qis}} \times 100\%$$

Where:
Ais = sum of the areas of the quantitation ions of the appropriate internal standard (cleanup standard is single ion)
Ars = sum of the areas of the quantitation ions of the recovery standard
Qrs = ng of recovery standard added to extract
Qis = ng of internal standard or cleanup standard added to sample
RRFis = mean relative response factor of internal standard obtained during initial calibration

NOTE: In some situations, such as high-volume water sampling or air train samples, the extract is split for multiple analyses. In this case, Qrs must be correctly calculated to account for the splitting of extracts before the recovery standard was added.

$$\mathrm{Q}rs = \frac{Crs \times Vrs}{\mathrm{S}}$$

Where:
Qrs = ng of recovery standard added to extract
Crs = concentration of recovery standard added to the split portion of the extract
Vrs = volume of recovery standard added to the split portion of the extract
S = split ratio of the extract (decimal fraction of the extract used)

12.3.2 The split ratio represents the proportion of extract used from splits taken after the addition of internal standards and before the addition of recovery standards.

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The split ratio is calculated as the product of all split ratios generated between these steps:

$$S = Spis \times Spcs \times Spfc$$

Where:

Spis = the decimal fraction of extract used from split taken once the internal standard has been added and the extraction is performed.

Spcs = the decimal fraction of extract used from split taken once the cleanup standard (if used) has been added.

Spfc = the decimal fraction of extract used from split taken once the cleanup fractionation column has been run.

12.3.3 When properly applied, isotope dilution techniques produce results that are independent of recovery. The recovery of each internal standard must be within the limits specified in Table 13 for method 1613B, 8290 or 8290A or in Table 15 for method 23, 0023A, or TO-9A. If the recovery of any internal standard is not within the specified limits, calculate the S/N ratio of the internal standard. If the S/N is ≥ 10 and the method minimum levels are met, report the data as is with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the minimum levels are not achieved, re-extract and re-analyze the sample. If the poor internal standard recovery is judged to be a result of sample matrix, a reduced portion of the sample can be re-extracted or additional clean-ups can be employed.

12.3.4 Calculate the concentration of the 2,3,7,8 isomers according to the following equation:

$$C_{2,3,7,8\,\text{isomers}} = \frac{\text{Ata} \times \text{Qis}}{\text{Ais} \times \text{RRF} \times \text{Ws}}$$

Where:
C = Concentration of 2,3,7,8 isomers
Ata = sum of the areas of the quantitation ions of the target analyte
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor from initial calibration.
Ws = amount of sample spiked and extracted (grams or liters)

12.3.5 The concentrations of non-2,3,7,8-isomers are calculated using the RRF for the corresponding 2,3,7,8-isomer. If more than one 2,3,7,8-isomer exist for a

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particular level of chlorination, the average of the individual 2,3,7,8-isomer RRFs is used in the calculation.

$$C_{non\ 2,3,7,8\ isomer} = \frac{Ata \times Qis}{Ais \times RRF \times Ws}$$

Where:
Ata = sum of the areas of the quantitation ions of the non-2,3,7,8 isomer
Ais = sum of the areas of the quantitation ions of the appropriate internal standard
Qis = ng of internal standard added to sample
RRF = mean relative response factor from initial calibration for the corresponding 2,3,7,8 isomer.
Ws = amount of sample spiked and extracted (grams or liters)

12.3.6 Calculate the total concentration of all isomers within each homologous series of PCDDs and PCDFs by summing the concentrations of the individual PCDD or PCDF 2,3,7,8 and non-2,3,7,8 isomers.

$$C_{Total} = \sum C_{2,3,7,8\ isomers} + \sum C_{non\ 2,3,7,8\ isomers}$$

12.3.7 If solid samples are to be reported on a dry weight basis, the laboratory LIMS system performs the following calculation:

$$\text{Concentration (Dry Weight)} = \frac{C}{\%Solids \div 100}$$

Where:
C = Concentration of the target analyte
%Solids = The sample percent solids determined by moisture analysis

12.3.8 If no peaks are present in the region of the ion chromatogram where the compounds of interest are expected to elute, calculate the estimated detection limit (EDL) for that compound according to the following equation:

$$EDL = \frac{N \times 2.5 \times Qis}{His \times RRFs \times Ws \times Ssl}$$

Where:
N = average peak to peak noise of quantitation ion signals in the region of the ion chromatogram where the compound of interest is expected to elute
His = peak height of quantitation ions for appropriate internal standard
Qis = ng of internal standard added to sample
RRFs = mean relative response factor of compound from initial calibration
W = amount of sample spiked and extracted (grams or liters)
Ssl = decimal expression of percent solids (optional, if results are requested to be reported on dry weight basis)

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NOTE: The percent solids calculation is performed by the laboratory LIMS system prior to final reporting.

12.3.9 If peaks are present in the region of the ion chromatogram which do not meet the qualitative criteria listed in section 12.2, calculate an Estimated Maximum Possible Concentration (EMPC). Two different calculation formulas can be used depending upon specific client requirements.

12.3.9.1 When performing methods 8290, 8290A for EPA regulated analyses where the currently promulgated method is required by law (e.g. Trial Burns) and for all other analyses unless the client has specified otherwise, use the equation in section 12.3.4, except that Ata represents the sum of the area under the one peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The peak selected to calculate the theoretical area is the one which gives the lower of the two possible results (i.e. the EMPC is lower than the result calculated from the uncorrected areas).

12.3.9.2 When the client has specifically requested, use the equation in section 12.3.4 without correcting the areas. This method gives an EMPC which is always higher than the method above and would be considered the worst case.

12.3.10 If peaks are present in the diphenyl ether mass channel at the same retention time as a PCDF peak, the peak cannot be identified as a PCDF. Calculate the concentration of the peak using the equation in section 12.3.4 but report the concentration as an Estimated Maximum Possible Concentration.

12.3.11 If the concentration in the final extract of any 2,3,7,8-substituted PCDD/PCDF isomer (except OCDD or OCDF) exceeds the upper method calibration limits, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. For OCDD and OCDF, report the measured concentration and indicate that the value exceeds the calibration limit by flagging the results with “E”. Dilutions of up to 1/10 can be performed on the extract. If the compounds that exceed the calibration range cannot be brought within the calibration range by a 1/10 dilution, extraction of a smaller aliquot of sample can be performed or the sample can be analyzed by a more appropriate analytical technique such as HRGC/LRMS. Consultation with the client must occur before any re-extraction is performed.

12.3.12 Evaluate the ion chromatograms of the PFK or FC-43 lock mass and calibration mass for each MID group. The PFK or FC-43 mass intensity must be consistent throughout the retention time of the target compounds. Negative excursions or variations in the PFK or FC-43 mass intensity indicate the elution of interferences from the GC column that are causing suppression in the ion source of the mass spectrometer. This ion suppression can reduce the instrument

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sensitivity and quantitative result of any peaks that elute at the same retention time. Either additional extract cleanup or dilutions can reduce ion suppression. The quantitative results must be carefully evaluated when there is evidence of ion suppression present in the PFK or FC-43 mass traces.

12.4 The DB-5 (RTX-5) column does not provide for isomer specificity of 2,3,7,8-TCDF using the operating condition required for this method. If a peak is determined to be present at the expected retention time of 2,3,7,8-TCDF and its calculated concentration is above the MinL, the sample extract must be analyzed on the DB-225 (RTX-225) column.

12.5 The Minimum Level (MinL) is defined as the level at which the instrument gives acceptable calibration assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. Deviation from the extraction amounts or final volumes listed Table 2 changes the MinL. The MinL is calculated as shown in the following equation:

$$\text{MinL} = \frac{C\min \times Vfe}{Ws}$$

Where:

Cmin = the concentration the analyte in the lowest calibration standard
Ws = amount of sample spiked and extracted (grams or liters)
Vfe = the final volume of the extract, corrected for all splits and dilutions

$$\text{V}fe = \frac{Vdel \times DFpr}{Spr \times S}$$

Where:

Vdel = the volume of extract delivered to the analysis
DFpr = the dilution factor for dilutions performed to the final extract
Spr = the split ratio for any post-recovery standard splits
S = the split ratio for any post-internal standard and post-cleanup standard splits

12.6 The Maximum Level (MaxL) is defined as the concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed. The MaxL is calculated as shown in the following equation:

$$\text{M}axL = \frac{C\max \times Vfe}{Ws}$$

Where:

Cmax = the concentration the analyte in the highest calibration standard Vfe and Ws are defined in Section 12.5.

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12.7 Flag all compound results in the sample that were detected in the method blank with a "B" qualifier.

12.8 Flag all compound results in the sample that are below the minimum level with a "J" qualifier.

12.9 Flag all compound results in the sample that are above the upper calibration limit with an "E" qualifier.

12.10 Flag all compound results in the sample that are "Estimated Maximum Possible Concentrations" with a "Q" qualifier.

12.11 Flag compound results in the sample that exhibit chromatographic evidence of co-eluting compounds with a "C" qualifier.

12.12 Flag compound results in the sample that are affected by ion suppression with a "S" qualifier.

12.13 Data Review

12.13.1 The analyst who performs the initial data calculations must initial and date the front chromatogram of the raw data package to document that they have performed the qualitative and quantitative analysis on the sample data.

12.13.2 A second analyst must verify all qualitative peak identifications. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.13.3 A second analyst must check all hand calculation and data entry into calculation programs, databases, or spreadsheets at a frequency of 100 percent. If discrepancies are found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.13.4 The reviewing analyst must initial and date the front chromatogram of the raw data package to document that they have performed the second level review on the sample data.

12.13.5 All items listed on the data review check list must be checked by both the analyst who performed the initial qualitative and quantitative analysis and the analyst who performed the second level review. Using the data review checklist, the analyst also creates a narrative which includes any qualifications of the sample data. An example data review check list is shown in Figure 3.

13. Method Performance

13.1 Method Detection Limit (MDL): An MDL must be determined for each analyte in each routine matrix prior to the analysis of any samples. The procedure for determination of the method detection limit is given in the SOP CA-Q-S-006, current revision, based on 40

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CFR Part 136 Appendix B. The result of the MDL determination must support the reporting limit.

13.2 Initial Demonstration of Capability: Each analyst must perform an initial demonstration of capability (IDOC) for each target analyte prior to performing the analysis independently. The IDOC is determined by analyzing four replicate spikes (e.g., LCSs) as detailed in Test America Knoxville SOP KNOX-QA-0009, current revision. Demonstration for both aqueous and solid matrices is required.

13.2.1 For aqueous samples, extract, concentrate, and analyze four 1-L aliquots of reagent water spiked with labeled internal standards and native analytes according to the procedures in section 11. For non-aqueous samples, extract, concentrate, and analyze four aliquots of sodium sulfate spiked with labeled internal standards and native analytes according to the procedures in section 11. It is recommended that a method blank be prepared with the IDOC samples. Extracts must be stored in the dark at room temperature in amber or clear glass vials prior to analysis.

13.2.2 Using the results of the set of four analyses, compute the average concentration (X) of the extracts in ng/mL and the standard deviation (S) of the concentration in ng/mL for each compound.

13.2.3 For each compound, compare S and X with the corresponding limits for initial precision and recovery in Table 9 for method 1613B and Table 10 for methods 8290, 8290A 23, 0023A, and TO-9A. If S and X for all compounds meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples can begin. If, however, any individual S exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that compound. Correct the problem and repeat the test.

13.3 Training Qualification: The group/team leader has the responsibility to ensure that this procedure is performed by an associate who has been properly trained in its use and has the required experience. Refer to SOP KNOX-QA-0009, current revision for further requirements for performing and documenting initial and on-going demonstrations of capability.

14. Pollution Prevention

14.1 All attempts will be made to minimize, as far as practical, the use of solvents and standard materials.

15. Waste Management

15.1 All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this method and the

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policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2 See the current revision of SOP KNOX-HS-0002 for specific waste handling guidelines.

15.3 The following waste streams are produced when this method is carried out.

15.3.1 Waste solvents must be placed in the flammable waste stream, contained in a steel satellite accumulation container or flammable solvent container.

15.3.2 Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials that may or may not be contaminated/hazardous must be placed in the incinerable laboratory waste stream, contained in a HDPE satellite accumulation container.

16. References

16.1 TestAmerica Knoxville Quality Assurance Manual (QAM), current revision.

16.2 EPA Method 1613: Tetra- Through Octa- Chlorinated Dioxins and Furans by Isotope Dilutions HRGC/HRMS, Revision B, October 1994.

16.3 SW-846 Method 8290, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Revision 0, September 1994.

16.4 SW-846 Method 8290A, Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), Revision 1, February 2007.

16.5 SW-846 Method 0023A, Sampling Method for Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofuran Emissions from Stationary Sources, Revision 1, December 1996.

16.6 USEPA Method 23 – Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors. 40 CFR Part 60 Appendix A.

16.7 Method TO-9A: Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Second Edition EPA/625/R-96/010b.

16.8 TestAmerica Knoxville SOP KNOX-ID-0012, "Method 0023A and Method 0010 Sampling Train Pre-Sampling Preparation and Sample Extraction Procedure (Includes TO-9A Sampling Components)", current revision.

16.9 TestAmerica Knoxville SOP KNOX-OP-0001, "Extraction of Polychlorinated Dioxins/Furans for Analysis by HRGC/HRMS Based on Methods 8290, 8290A and 1613B", current revision.

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16.10 TestAmerica Policy, CA-T-P-002, Selection of Calibration Points, current revision.

17. Miscellaneous

17.1 Deviations from Reference Methods.

17.1.1 Spiking levels have been reduced to minimize the amount of dioxin contaminated waste generated by this procedure. It has been demonstrated that the performance criteria specified in the method are not affected by this modification.

17.1.2 The absolute retention time requirements in Method 1613 section 15.4.1.1 is not required in this procedure. The routine maintenance required of GC columns when analyzing samples from hazardous waste sites makes this requirement virtually impossible to meet in a commercial laboratory environment. This requirement provides no additional quality assurance purpose beyond those already provided by the use of labeled internal standards and required relative retention time limits.

17.1.3 This procedure provides for additional calculation and reporting of sample specific detection limits and estimated maximum possible concentrations not required by Method 1613. These reporting conventions are similar to those required by EPA SW-846 Method 8290 and expected by data users familiar with EPA Office of Solid Waste program requirements.

17.1.4 Methods 8290/8290A do not require dilution and reanalysis of samples for which OCDD exceeds the calibration range. Although this allowance is not made by method 1613B, this procedure does not require dilution for OCDD on samples analyzed by that method.

17.1.5 The calibration standards specified in method 23 are used for method 0023A and TO-9A.

17.1.6 Extracts are stored at room temperature rather than at <10 °C as specified in method 1613B. Methods 8290 and 8290A allow for the storage of extracts at room temperature in the dark. All of the reference methods require that standards be stored at room temperature. Recovery studies performed by Cambridge Isotopes Laboratories (CIL) indicate freezing or refrigeration of standards causes problems with precipitation and irreversible adsorption to the inside surface of the vial. CIL recommends the storage of standards and extracts at room temperature as long as they are protected from exposure to UV and evaporative losses.

17.1.7 This procedure allows for the use of perfluorotributylamine (FC43) for mass calibration and resolution instead of the method recommended reference compound, Perfluorokerosene (PFK). FC43 is used on the newest HRMS instrument in the laboratory based on the manufacturer's recommendation. The

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use of another mass reference substance is noted in both reference methods 1613B and 8290A. FC43 provides for less noise and less ion source contamination than the method recommended PFK.

17.1.8 The percent valley column resolution criteria is ≤ 25% for this SOP. Among the reference methods both ≤ 25% and < 25% are represented.

17.2 List of tables and figures referenced in the body of the SOP.

17.2.1 Table 1 – Polychlorinated Dibenzodioxins and Furans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography /High Resolution Mass Spectrometry (HRGC/HRMS)

17.2.2 Table 2 – Methods – All, Minimum Levels by Matrix

17.2.3 Table 3 – Methods – 1613B and 8290/8290A, Retention Time References, Quantitation References, and Relative Retention Times

17.2.4 Table 4 – Methods – 23, 0023A, and TO-9A, Retention Time References and Quantitation References

17.2.5 Table 5 – Methods – 1613B and 8290/8290A, Initial Calibration Standard Concentrations and Acceptance Criteria

17.2.6 Table 6 – Methods – 23, 0023A, and TO-9A, Initial Calibration Standard Concentrations and Acceptance Criteria

17.2.7 Table 7 – Methods – 1613B and 8290/8290A, Daily Verification Standard (VER) Concentrations and Acceptance Criteria

17.2.8 Table 8 – Methods – 23, 0023A, and TO-9A, Daily Verification Standard (VER) Concentrations and Acceptance Criteria

17.2.9 Table 9 – Method – 1613B, Initial Demonstration of Capability (IDOC) Acceptance Criteria

17.2.10 Table 10 – Methods – 8290/8290A, 23, 0023A, and TO-9A, Initial Demonstration of Capability (IDOC) Acceptance Criteria

17.2.11 Table 11 – Laboratory Control Sample (LCS) Spiking Solution Component Concentrations and Acceptance Limits

17.2.12 Table 12 – Method – 8290/8290A. Matrix Spike and Matrix Spike Duplicate Sample (MS/MSD) Spiking Solution Component Concentrations and Acceptance Limits

17.2.13 Table 13 - Methods – 1613B and 8290/8290A, Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

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17.2.14 Table 14 – Method – 1613B, Cleanup Standard Spiking Solution Component Concentrations and Acceptance Limits

17.2.15 Table 15 – Methods – 23, 0023A, and TO-9A, Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

17.2.16 Table 16 – Methods – 23, 0023A, and TO-9A, Surrogate Standard Spiking Solution Component Concentrations and Acceptance Limits

17.2.17 Table 17 – Methods – All, Recovery Standard Spiking Solution Component Concentrations

17.2.18 Table 18 – Rtx-5/DB-5 Column Window Defining Standard Mixture Components. – Rtx-5 (DB-5) Column Performance Standard Mixture Components

17.2.19 Table 19 – Rtx-5/DB-5 Column Performance Standard Mixture Components

17.2.20 Table 20 – Rtx-225/DB-225 Column Performance Standard Mixture Components

17.2.21 Table 21 – DB-225 (Rtx-225) Column Performance Standard Mixture Components

17.2.22 Table 21 – Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

17.2.23 Table 22 – Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

17.2.24 Figure 1 – Recommended GC Operating Conditions

17.2.25 Figure 2 – Recommended MID Descriptors

17.2.26 Figure 3 – Example Data Review Checklist

17.2.27 Figure 4 – Analysis of PCDDs and PCDFs by HRGC/HRMS Flowchart

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Table 1

Polychlorinated Dibenzo-p-dioxins/Dibenzofurans Determined by Isotope Dilution and Internal Standard High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS)

PCDDs/PCDFs [1] Isomer/Congener	CAS Registry	Labeled Analog	CAS Registry
2,3,7,8-TCDD	1746-01-6	$^{13}C_{12}$-2,3,7,8-TCDD $^{37}Cl_4$-2,3,7,8-TCDD	76523-40-5 85508-50-5
Total TCDD	41903-57-5		
2,3,7,8-TCDF	51207-31-9	$^{13}C_{12}$-2,3,7,8-TCDF	89059-46-1
Total TCDF	55722-27-5		
1,2,3,7,8-PeCDD	40321-76-4	$^{13}C_{12}$-1,2,3,7,8-PeCDD	109719-79-1
Total PeCDD	36088-22-9		
1,2,3,7,8-PeCDF	57117-41-6	$^{13}C_{12}$-1,2,3,7,8-PeCDF	109719-77-9
2,3,4,7,8-PeCDF	57117-31-4	$^{13}C_{12}$-2,3,4,7,8-PeCDF	116843-02-8
Total PeCDF	30402-15-4		
1,2,3,4,7,8-HxCDD	39227-28-6	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	109719-80-4
1,2,3,6,7,8-HxCDD	57653-85-7	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	109719-81-5
1,2,3,7,8,9-HxCDD	19408-74-3	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	109719-82-6
Total HxCDD	34465-46-8		
1,2,3,4,7,8-HxCDF	70648-26-9	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	114423-98-2
1,2,3,6,7,8-HxCDF	57117-44-9	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	116843-03-9
2,3,4,6,7,8-HxCDF	60851-34-5	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	116843-05-1
1,2,3,7,8,9-HxCDF	72918-21-9	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	116843-04-0
Total HxCDF	55684-94-1		
1,2,3,4,6,7,8-HpCDD	35822-46-9	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	109719-83-7
Total HpCDD	37871-00-4		
1,2,3,4,6,7,8-HpCDF	67562-39-4	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	109719-84-8
1,2,3,4,7,8,9-HpCDF	55673-89-7	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	109719-94-0
Total HpCDF	38998-75-3		
OCDD	3268-87-9	$^{13}C_{12}$-OCDD	114423-97-1
OCDF	39001-02-0	none	

Notes:

1. Polychlorinated dioxins and furans

TCDD	= Tetrachlorodibenzo-p-dioxin	TCDF	= Tetrachlorodibenzofuran
PeCDD	= Pentachlorodibenzo-p-dioxin	PeCDF	= Pentachlorodibenzofuran
HxCDD	= Hexachlorodibenzo-p-dioxin	HxCDF	= Hexachlorodibenzofuran
HpCDD	= Heptachlorodibenzo-p-dioxin	HpCDF	= Heptachlorodibenzofuran
OCDD	= Octachlorodibenzo-p-dioxin	OCDF	= Octachlorodibenzofuran

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Table 2

Methods – All
Minimum Levels by Matrix

Analyte	Extract (ng/mL) [1]	Water (pg/L) [2]	Solids (pg/g) [3]	Biological Tissue (pg/g) [3]	Waste (pg/g) [4]	Air/Wipe (pg) [5]
2,3,7,8-TCDD	0.5	10	1	1	10	10
2,3,7,8-TCDF	0.5	10	1	1	10	10
1,2,3,7,8-PeCDD	2.5	50	5	5	50	50
1,2,3,7,8-PeCDF	2.5	50	5	5	50	50
2,3,4,7,8-PeCDF	2.5	50	5	5	50	50
1,2,3,4,7,8-HxCDD	2.5	50	5	5	50	50
1,2,3,6,7,8-HxCDD	2.5	50	5	5	50	50
1,2,3,7,8,9-HxCDD	2.5	50	5	5	50	50
1,2,3,4,7,8-HxCDF	2.5	50	5	5	50	50
1,2,3,6,7,8-HxCDF	2.5	50	5	5	50	50
2,3,4,6,7,8-HxCDF	2.5	50	5	5	50	50
1,2,3,7,8,9-HxCDF	2.5	50	5	5	50	50
1,2,3,4,6,7,8-HpCDD	2.5	50	5	5	50	50
1,2,3,4,6,7,8-HpCDF	2.5	50	5	5	50	50
1,2,3,4,7,8,9-HpCDF	2.5	50	5	5	50	50
OCDD	5.0	100	10	10	100	100
OCDF	5.0	100	10	10	100	100

Notes:
1 Concentration in the extract assuming a 20 µL volume.
2 Based on a sample volume of 1.0 L.
3 Based on a sample weight of 10.0 g.
4 Based on a sample weight of 1.0 g.
5 Based on extraction of the entire sample.

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Table 3

Methods – 1613B and 8290/8290A
Retention Time References, Quantitation References and Relative Retention Times

Analyte	Retention Time and Quantitation Reference	Relative Retention Time
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the recovery standard		
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0.999-1.002
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0.999-1.003
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0.999-1.002
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0.999-1.002
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0.999-1.002
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.976-1.043
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0.989-1.052
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0.923-1.103
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.567
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.000-1.425
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1.011-1.526
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the recovery standard		
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0.999-1.001
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0.998-1.004
1,2,3,7,8,9-HxCDD	--[1]	1.000-1.019
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0.999-1.001
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0.997-1.005
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	0.999-1.001
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0.999-1.001
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0.999-1.001
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0.999-1.001
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0.999-1.001
OCDD	$^{13}C_{12}$-OCDD	0.999-1.001
OCDF	$^{13}C_{12}$-OCDD	0.999-1.008
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.000
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.981-1.003
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.944-0.970
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.949-0.975
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.959-1.021
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.977-1.047
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.086-1.110
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.043-1.085
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.057-1.151
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1.032-1.311

Notes:

1 The retention time reference for 1,2,3,7,8,9-HxCDD is $^{13}C_{12}$-1,2,3,6,7,8-HxCDD. 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

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Table 4

Methods – 23, 0023A and TO-9A
Retention Time References and Quantitation References

Analyte	Retention Time and Quantitation Reference
Compounds using $^{13}C_{12}$-1,2,3,4-TCDD as the recovery standard	
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF
Compounds using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD as the recovery standard	
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
OCDD	$^{13}C_{12}$-OCDD
OCDF	$^{13}C_{12}$-OCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD

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Table 5

Methods – 1613B and 8290/8290A
Initial Calibration Standard Concentrations and Acceptance Criteria

	CS1	CS2	CS3	CS4	CS5	1613B	8290	8290A
Analyte	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**%RSD**	**%RSD**	**%RSD**
Native PCDD's and PCDF's								
2,3,7,8-TCDD	0.5	2.0	10	40	200	±20	±20	±20
2,3,7,8-TCDF	0.5	2.0	10	40	200	±20	±20	±20
1,2,3,7,8-PeCDD	2.5	10	50	200	1000	±20	±20	±20
1,2,3,7,8-PeCDF	2.5	10	50	200	1000	±20	±20	±20
2,3,4,7,8-PeCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000	±20	±20	±20
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000	±20	±20	±20
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000	±35	±20	±20
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000	±20	±20	±20
2,3,4,6,7,8-HxCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000	±20	±20	±20
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000	±20	±20	±20
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000	±20	±20	±20
OCDD	5.0	20	100	400	2000	±20	±20	±20
OCDF	5.0	20	100	400	2000	±35	±20	±20
Labeled Internal Standards								
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100	±35	±30	±20
$^{13}C_{12}$-OCDD	200	200	200	200	200	±35	±30	±20
Labeled Cleanup Standard								
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2.0	10	40	200	±35	-	-
Labeled Recovery Standard								
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	-	-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	-	-	-

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Table 6

Methods – 23, 0023A and TO-9A
Initial Calibration Standard Concentrations and Acceptance Criteria

	CS1	CS2	CS3	CS4	CS5	23 / TO-9A	0023A
Analyte	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**(ng/mL)**	**%RSD**	**%RSD**
Native PCDDs and PCDFs							
2,3,7,8-TCDD	0.5	1.0	5	50	100	±25	±20
2,3,7,8-TCDF	0.5	1.0	5	50	100	±25	±20
1,2,3,7,8-PeCDD	2.5	5	25	250	500	±25	±20
1,2,3,7,8-PeCDF	2.5	5	25	250	500	±25	±20
2,3,4,7,8-PeCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,6,7,8-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,7,8,9-HxCDD	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,6,7,8-HxCDF	2.5	5	25	250	500	±25	±20
2,3,4,6,7,8-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,7,8,9-HxCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,6,7,8-HpCDD	2.5	5	25	250	500	±25	±20
1,2,3,4,6,7,8-HpCDF	2.5	5	25	250	500	±25	±20
1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500	±25	±20
OCDD	5.0	10	50	500	1000	±25	±20
OCDF	5.0	10	50	500	1000	±30	±20
Labeled Internal Standards							
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100	±25	±30
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100	±25	±30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100	±30	±30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100	±30	±30
$^{13}C_{12}$-OCDD	200	200	200	200	200	±30	±30
Surrogate Standards							
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	1.0	5	50	100	±25	±30
$^{13}C_{12}$-2,3,4,7,8-PeCDF	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2.5	5	25	250	500	±25	±30
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500	±25	±30
Labeled Recovery Standard							
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100	-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100	-	-

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Table 7

Methods – 1613B and 8290/8290A
Daily Verification Standard (VER) Concentrations and Acceptance Criteria

Analyte	VER (ng/mL)	1613B All Isomers (ng/mL)	1613B Tetra only (ng/mL)		8290/8290A Shift Open %D	8290/8290A Shift Close[1] %D
Native PCDDs and PCDFs						
2,3,7,8-TCDD	10	7.8-12.9	8.2-12.3		±20	±25
2,3,7,8-TCDF	10	8.4-12.0	8.6-11.6		±20	±25
1,2,3,7,8-PeCDD	50	39-65	-		±20	±25
1,2,3,7,8-PeCDF	50	41-60	-		±20	±25
2,3,4,7,8-PeCDF	50	41-61	-		±20	±25
1,2,3,4,7,8-HxCDD	50	39-64	-		±20	±25
1,2,3,6,7,8-HxCDD	50	39-64	-		±20	±25
1,2,3,7,8,9-HxCDD	50	41-61	-		±20	±25
1,2,3,4,7,8-HxCDF	50	45-56	-		±20	±25
1,2,3,6,7,8-HxCDF	50	44-57	-		±20	±25
2,3,4,6,7,8-HxCDF	50	44-57	-		±20	±25
1,2,3,7,8,9-HxCDF	50	45-56	-		±20	±25
1,2,3,4,6,7,8-HpCDD	50	43-58	-		±20	±25
1,2,3,4,6,7,8-HpCDF	50	45-55	-		±20	±25
1,2,3,4,7,8,9-HpCDF	50	43-58	-		±20	±25
OCDD	100	79-126	-		±20	±25
OCDF	100	63-159	-		±20	±25
Labeled Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD	100	82-121	85-117		±30	±35
$^{13}C_{12}$-2,3,7,8-TCDF	100	71-140	76-131		±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	62-160	-		±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	76-130	-		±30	±35
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	77-130	-		±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	85-117	-		±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	85-118	-		±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	76-131	-		±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	70-143	-		±30	±35
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	73-137	-		±30	±35
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	74-135	-		±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	72-138	-		±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	78-129	-		±30	±35
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	77-129	-		±30	±35
$^{13}C_{12}$-OCDD	200	96-415	-		±30	±35
Labeled Cleanup Standard						
$^{37}Cl_4$-2,3,7,8-TCDD	10	7.9-12.7	8.3-12.1		-	-
Labeled Recovery Standard						
$^{13}C_{12}$-1,2,3,4-TCDD	100	-	-		-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	-	-		-	-

Notes:

1 If the closing standard %D exceeds the opening %D criteria, the average of the Opening and Closing RF is used instead of the Initial Calibration RF to calculate sample concentrations.

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Table 8

Methods – 23, 0023A and TO-9A
Daily Verification Standard (VER) Concentrations and Acceptance Criteria

			0023A	
	VER	23 and TO-9A	Shift Open	Shift Close[1]
Analyte	**(ng/mL)**	**%D**	**%D**	**%D**
Native PCDDs and PCDFs				
2,3,7,8-TCDD	5	±25	±20	±25
2,3,7,8-TCDF	5	±25	±20	±25
1,2,3,7,8-PeCDD	25	±25	±20	±25
1,2,3,7,8-PeCDF	25	±25	±20	±25
2,3,4,7,8-PeCDF	25	±25	±20	±25
1,2,3,4,7,8-HxCDD	25	±25	±20	±25
1,2,3,6,7,8-HxCDD	25	±25	±20	±25
1,2,3,7,8,9-HxCDD	25	±25	±20	±25
1,2,3,4,7,8-HxCDF	25	±25	±20	±25
1,2,3,6,7,8-HxCDF	25	±25	±20	±25
2,3,4,6,7,8-HxCDF	25	±25	±20	±25
1,2,3,7,8,9-HxCDF	25	±25	±20	±25
1,2,3,4,6,7,8-HpCDD	25	±25	±20	±25
1,2,3,4,6,7,8-HpCDF	25	±25	±20	±25
1,2,3,4,7,8,9-HpCDF	25	±25	±20	±25
OCDD	50	±25	±20	±25
OCDF	50	±30	±20	±25
Labeled Internal Standards				
$^{13}C_{12}$-2,3,7,8-TCDD	100	±25	±30	±35
$^{13}C_{12}$-2,3,7,8-TCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	±25	±30	±35
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	±30	±30	±35
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	±30	±30	±35
$^{13}C_{12}$-OCDD	200	±30	±30	±35
Surrogate Standards				
$^{37}Cl_4$-2,3,7,8-TCDD	5	±25	±30	±35
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	±25	±30	±35
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	±25	±30	±35
Labeled Recovery Standard				
$^{13}C_{12}$-1,2,3,4-TCDD	100	-	-	
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	-	-	

Notes:

1 If the closing standard %D exceeds the opening %D criteria, the average of the Opening and Closing RF is used instead of the Initial Calibration RF to calculate sample concentrations.

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Table 9

Method – 1613B
Initial Demonstration of Capability (IDOC) Acceptance Criteria

	Test	1613B			1613B Tetra Only	
Analyte	Conc. (ng/mL) [1]	s[2] (ng/mL) [1]	X[3] (ng/ml) [1]		s[2] (ng/mL) [1]	X[3] (ng/ml) [1]
Native PCDDs and PCDFs						
2,3,7,8-TCDD	10	2.8	8.3-12.9		2.7	8.7-12.4
2,3,7,8-TCDF	10	2.0	8.7-13.7		2.0	9.1-13.1
1,2,3,7,8-PeCDD	50	7.5	38-66		-	-
1,2,3,7,8-PeCDF	50	7.5	43-62		-	-
2,3,4,7,8-PeCDF	50	8.6	36-75		-	-
1,2,3,4,7,8-HxCDD	50	9.4	39-76		-	-
1,2,3,6,7,8-HxCDD	50	7.7	42-62		-	-
1,2,3,7,8,9-HxCDD	50	11.1	37-71		-	-
1,2,3,4,7,8-HxCDF	50	8.7	41-59		-	-
1,2,3,6,7,8-HxCDF	50	6.7	46-60		-	-
2,3,4,6,7,8-HxCDF	50	7.4	37-74		-	-
1,2,3,7,8,9-HxCDF	50	6.4	42-61		-	-
1,2,3,4,6,7,8-HpCDD	50	7.7	38-65		-	-
1,2,3,4,6,7,8-HpCDF	50	6.3	45-56		-	-
1,2,3,4,7,8,9-HpCDF	50	8.1	43-63		-	-
OCDD	100	19	89-127		-	-
OCDF	100	27	74-146		-	-
Labeled Internal Standards						
$^{13}C_{12}$-2,3,7,8-TCDD	50	18.5	14-67		17.5	16-57.5
$^{13}C_{12}$-2,3,7,8-TCDF	50	17.5	15.5-56.5		17	17.5-49.5
$^{13}C_{12}$-1,2,3,7,8-PeCDD	50	19.5	13.5-92		-	-
$^{13}C_{12}$-1,2,3,7,8-PeCDF	50	17.0	13.5-78		-	-
$^{13}C_{12}$-2,3,4,7,8-PeCDF	50	19.0	8-139.5		-	-
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	50	20.5	14.5-73.5		-	-
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	50	19.0	17-61		-	-
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	50	21.5	13.5-76		-	-
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	50	17.5	15-61		-	-
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	50	18.5	14.5-68		-	-
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	50	20.0	12-78.5		-	-
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	50	17.5	17-64.5		-	-
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	50	20.5	16-55		-	-
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	50	20.0	14-70.5		-	-
$^{13}C_{12}$-OCDD	100	47.5	20.5-138		-	-
Labeled Cleanup Standard						
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9-15.4		3.4	4.5-13.4

Notes:

1 All specifications are given as concentration in the final extract, assuming a 20-µL volume.

2 s = standard deviation of the concentration

3 X = average concentration. The acceptance range for average recovery can be normalized (shifted to center on 100% recovery) to compensate for the bias in the collaborative study used to develop the acceptance criteria.

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Table 10

Methods – 8290/8290A, 23, 0023A and TO-9A
Initial Demonstration of Capability (IDOC) Acceptance Criteria

Analyte	Test Conc (ng/mL) [1]	s [2] (%Rec)	X [3] (%Rec)
Native PCDDs and PCDFs			
2,3,7,8-TCDD	10	15 [4]	70-130 [4]
2,3,7,8-TCDF	10	15 [4]	70-130 [4]
1,2,3,7,8-PeCDD	50	15 [4]	70-130 [4]
1,2,3,7,8-PeCDF	50	15 [4]	70-130 [4]
2,3,4,7,8-PeCDF	50	15 [4]	70-130 [4]
1,2,3,4,7,8-HxCDD	50	15 [4]	70-130 [4]
1,2,3,6,7,8-HxCDD	50	15 [4]	70-130 [4]
1,2,3,7,8,9-HxCDD	50	15 [4]	70-130 [4]
1,2,3,4,7,8-HxCDF	50	15 [4]	70-130 [4]
1,2,3,6,7,8-HxCDF	50	15 [4]	70-130 [4]
2,3,4,6,7,8-HxCDF	50	15 [4]	70-130 [4]
1,2,3,7,8,9-HxCDF	50	15 [4]	70-130 [4]
1,2,3,4,6,7,8-HpCDD	50	15 [4]	70-130 [4]
1,2,3,4,6,7,8-HpCDF	50	15 [4]	70-130 [4]
1,2,3,4,7,8,9-HpCDF	50	15 [4]	70-130 [4]
OCDD	100	15 [4]	70-130 [4]
OCDF	100	15 [4]	70-130 [4]

Notes:
1 All specifications are given as concentration in the final extract, assuming a 20 µL volume.
2 s = standard deviation of the percent recovery
3 X = average percent recovery
4 Inhouse generated historical control limits can be used in place of the specified limit.

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Table 11

Laboratory Control Sample (LCS) Spiking Solution Component Concentrations and Acceptance Limits

Analyte	LCS Solution Conc. (ng/mL)[1]	Final Extract Conc (ng/mL)[2]	1613B LCS Conc (ng/mL)[2]	8290/8290A, 23, 0023A, TO-9A Recovery (%Rec)
2,3,7,8-TCDD	0.2	10	6.7-15.8	70-130[4]
2,3,7,8-TCDF	0.2	10	7.5-15.8	70-130[4]
1,2,3,7,8-PeCDD	1.0	50	35-71	70-130[4]
1,2,3,7,8-PeCDF	1.0	50	40-67	70-130[4]
2,3,4,7,8-PeCDF	1.0	50	34-80	70-130[4]
1,2,3,4,7,8-HxCDD	1.0	50	35-82	70-130[4]
1,2,3,6,7,8-HxCDD	1.0	50	38-67	70-130[4]
1,2,3,7,8,9-HxCDD	1.0	50	32-81	70-130[4]
1,2,3,4,7,8-HxCDF	1.0	50	36-67	70-130[4]
1,2,3,6,7,8-HxCDF	1.0	50	42-65	70-130[4]
2,3,4,6,7,8-HxCDF	1.0	50	35-78	70-130[4]
1,2,3,7,8,9-HxCDF	1.0	50	39-65	70-130[4]
1,2,3,4,6,7,8-HpCDD	1.0	50	35-70	70-130[4]
1,2,3,4,6,7,8-HpCDF	1.0	50	41-61	70-130[4]
1,2,3,4,7,8,9-HpCDF	1.0	50	39-69	70-130[4]
OCDD	2.0	100	78-144	70-130[4]
OCDF	2.0	100	63-170	70-130[4]
Tetras Only				
2,3,7,8-TCDD	0.2	10	7.3-14.6	70-130[4]
2,3,7,8-TCDF	0.2	10	8.0-14.7	70-130[4]

Notes:

1 1.0 mL of this solution is added to the LCS before extraction (see section 7.11.2).
2 The final extract concentration is based on an extract volume of 20 µL.
3 Spike concentrations are based on a 1.0 L extraction for water, 10.0g extraction for solids, and entire sample extraction for air/wipe samples.
4 Inhouse generated historical control limits can be used in place of the specified limit.

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Table 12

Method – 8290/8290A
Matrix Spike and Matrix Spike Duplicate Sample (MS/MSD) Spiking Solution Component Concentrations and Acceptance Limits[1]

Analyte	LCS Solution Conc. (ng/mL)[2]	Final Extract Conc (ng/mL)[3]	8290 Recovery (%Rec)	8290 Precision (RPD)
2,3,7,8-TCDD	0.2	10	70-130[4]	±15[4]
2,3,7,8-TCDF	0.2	10	70-130[4]	±15[4]
1,2,3,7,8-PeCDD	1.0	50	70-130[4]	±15[4]
1,2,3,7,8-PeCDF	1.0	50	70-130[4]	±15[4]
2,3,4,7,8-PeCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,6,7,8-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,7,8,9-HxCDD	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,6,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
2,3,4,6,7,8-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,7,8,9-HxCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,6,7,8-HpCDD	1.0	50	70-130[4]	±15[4]
1,2,3,4,6,7,8-HpCDF	1.0	50	70-130[4]	±15[4]
1,2,3,4,7,8,9-HpCDF	1.0	50	70-130[4]	±15[4]
OCDD	2.0	100	70-130[4]	±15[4]
OCDF	2.0	100	70-130[4]	±15[4]

Notes:
1 If insufficient sample exists for MS/MSD analysis, these limits apply to LCS/LCSD samples.
2 1.0 mL of this solution is added to the LCS before extraction (see section 1.1).
3 The final extract concentration is based on an extract volume of 20 µL.
4 Inhouse generated historical control limits can be used in place of the specified limit.

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Table 13

Methods – 1613B and 8290/8290A
Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	1613B LCS Conc (ng/mL)[2]	1613B Sample Conc (ng/mL)[2]	8290 Recovery (%Rec)
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	10.0-87.5	12.5-82.0	40-135
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	11.0-76.0	12.0-84.5	40-135
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1.0	50	10.5-113.5	12.5-90.5	40-135
$^{13}C_{12}$-1,2,3,7,8-PeCDF	1.0	50	10.5-96.0	12.0-92.5	40-135
$^{13}C_{12}$-2,3,4,7,8-PeCDF	1.0	50	6.5-164.0	10.5-89.0	40-135
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	1.0	50	10.5-96.5	16.0-70.5	40-135
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1.0	50	12.5-81.5	14.0-65.0	40-135
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1.0	50	9.5-101.0	13.0-76.0	40-135
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1.0	50	10.5-79.5	13.0-61.5	40-135
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	1.0	50	11.0-88.0	14.0-68.0	40-135
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	1.0	50	8.5-102.5	14.5-73.5	40-135
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1.0	50	13.0-83.0	11.5-70.0	40-135
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	50	10.5-79.0	14.0-71.5	40-135
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	1.0	50	10.0-93.0	13.0-69.0	40-135
$^{13}C_{12}$-OCDD	2.0	100	13.0-198.5	17.0-157	40-135
Tetras Only					
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	12.5-70.5	15.5-68.5	40-135
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	13.0-63.0	14.5-70.0	40-135

Notes:
1 1.0 mL of the Internal Standard Spiking Solution is added to each sample, method blank and LCS prior to extraction (see section 1.1).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

Table 14

Method – 1613B
Cleanup Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	1613B LCS Conc (ng/mL)[2]	1613B Sample Conc (ng/mL)[2]	1613B LCS Tetra Only Conc (ng/mL)[2]	1613B Sample Tetra Only Conc (ng/mL)[2]
$^{37}Cl_4$-2,3,7,8-TCDD	0.2	10	3.1-19.1	3.5-19.7	3.7-15.8	4.2-16.4

Notes:
1 1.0 mL of the Cleanup Standard Spiking Solution is added to each sample, method blank and LCS prior to cleanup (see section 7.11.6).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

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Table 15

Methods – 23, 0023A and TO-9A
Internal Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	23 Recovery (%Rec)	0023A Recovery (%Rec)	TO-9A Recovery (%Rec)
$^{13}C_{12}$-2,3,7,8-TCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-2,3,7,8-TCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,7,8-PeCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	1.0	50	40-130	40-135	50-120
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1.0	50	25-130	40-135	40-120
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1.0	50	25-130	40-135	40-120
$^{13}C_{12}$-OCDD	2.0	100	25-130	40-135	40-120

Notes:

1 1.0 mL of the Internal Standard Spiking Solution is added to each sample, method blank and LCS prior to extraction (see section 7.11.4).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

Table 16

Methods – 23, 0023A, and TO-9A
Surrogate Standard Spiking Solution Component Concentrations and Acceptance Limits

Labeled Analyte	Solution Conc (ng/mL)[1]	Test Conc. (ng/mL)[2]	23 Recovery (%Rec)	0023A Recovery (%Rec)	TO-9A Recovery (%Rec)
$^{37}Cl_4$-2,3,7,8-TCDD	20	100	70-130	70-130	50-120
$^{13}C_{12}$-2,3,4,7,8-PeCDF	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	20	100	70-130	70-130	50-120
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	20	100	70-130	70-130	40-120

Notes:
1 100 µL of the Surrogate Standard Spiking Solution is added to each sample train prior to sampling (see section 1.1).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

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Table 17

Methods – All
Recovery Standard Spiking Solution Component Concentrations

Labeled Analyte	Solution Conc (µg/mL)[1]	Test Conc. (ng/mL)[2]
$^{13}C_{12}$-1,2,3,4-TCDD	0.1	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0.1	100

Notes:
1 20 µL of the Recovery Standard Spiking Solution is added to each sample, method blank and LCS prior to analysis (see section 1.1).
2 Specifications given as concentration in the final extract, assuming a 20 µL volume

Table 18

Rtx-5/DB-5 Column Window Defining Standard Mixture Components

Congener	First Eluted	Last Eluted
TCDF	1,3,6,8-	1,2,8,9-
TCDD	1,3,6,8-	1,2,8,9-
PeCDF	1,3,4,6,8-	1,2,3,8,9-
PeCDD	1,2,4,6,8-/1,2,4,7,9-	1,2,3,8,9-
HxCDF	1,2,3,4,6,8-	1,2,3,4,8,9-
HxCDD	1,2,4,6,7,9-/1,2,4,6,8,9-	1,2,3,4,6,7-
HpCDF	1,2,3,4,6,7,8-	1,2,3,4,7,8,9-
HpCDD	1,2,3,4,6,7,9-	1,2,3,4,6,7,8-

Table 19

Rtx-5 (DB-5) Column Performance Standard Mixture Components

Isomer
1,2,3,7/1,2,3,8-TCDD
1,2,3,9-TCDD
2,3,7,8-TCDD

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Table 20

DB-225 (Rtx-225) Column Performance Standard Mixture Components

Isomer
2,3,4,7-TCDF
2,3,7,8-TCDF
1,2,3,9-TCDF

Table 21

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

Descriptor	Accurate Mass[1]	Ion ID	Elemental Composition	Analyte
1	292.9825 (313.9834)	LOCK	C_7F_{11} ($C_6NF_{12}^+$)	PFK (FC43)
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}Cl_4O_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9338	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	342.9792 (363.9802)	QC	C_8F_{13} ($C_7NF_{14}^+$)	PFK (FC43)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
2	330.9792 (313.9834)	LOCK	C_7F_{13} ($C_6NF_{12}^+$)	PFK (FC43)
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	380.9760 (375.9802)	QC	C_8F_{15} ($C_8NF_{14}^+$)	PFK (FC43)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCDPE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	380.9760 (375.9802)	LOCK	C_8F_{15} ($C_8NF_{14}^+$)	PFK (FC43)
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8156	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD (S)
	404.9760 (413.9770)	QC	$C_{10}F_{15}$ ($C_8NF_{16}^+$)	PFK (FC43)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE

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Table 21 (Continued)

Ions Monitored for HRGC/HRMS Analysis of PCDDs and PCDFs

Descriptor	Accurate Mass[1]	Ion ID	Elemental Composition	Analyte
4	404.9760 (413.9770)	LOCK	$C_{10}F_{15}(C_8NF_{16}^+)$	PFK (FC43)
	407.7818	M+2	$C_{12}H\,^{35}Cl_6\,^{37}Cl\,0$	HpCDF
	409.7788	M+4	$C_{12}H\,^{35}Cl_5\,^{37}Cl_2\,0$	HpCDF
	417.8250	M	$^{13}C_{12}H\,^{35}Cl_7\,0$	HpCDF (S)
	419.8220	M+2	$^{13}C_{12}H\,^{35}Cl_6\,^{37}Cl\,0$	HpCDF (S)
	423.7767	M+2	$C_{12}H\,^{35}Cl_6\,^{37}Cl\,0_2$	HpCDD
	425.7737	M+4	$C_{12}H\,^{35}Cl_5\,^{37}Cl_2\,0_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H\,^{35}Cl_6\,^{37}Cl\,0_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H\,^{35}Cl_5\,^{37}Cl_2\,0_2$	HpCDD (S)
	442.9728 (463.9738)	QC	$C_{10}F_{17}(C_9NF_{18}^+)$	PFK (FC43)
	479.7165	M+4	$C_{12}H\,^{35}Cl_7\,^{37}Cl_2\,0$	NCDPE
5	430.9728 (425.9770)	LOCK	$C_9F_{17}(C_9NF_{16}^+)$	PFK (FC43)
	441.7428	M+2	$C_{12}\,^{35}Cl_7\,^{37}Cl\,0$	OCDF
	443.7399	M+4	$C_{12}\,^{35}Cl_6\,^{37}Cl_2\,0$	OCDF
	457.7377	M+2	$C_{12}\,^{35}Cl_7\,^{37}Cl\,0_2$	OCDD
	459.7348	M+4	$C_{12}\,^{35}Cl_6\,^{37}Cl_2\,0_2$	OCDD
	469.7780	M+2	$^{13}C_{12}\,^{35}Cl_7\,^{37}Cl\,0_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}\,^{35}Cl_6\,^{37}Cl_2\,0_2$	OCDD (S)
	480.9696 (501.9706)	QC	$C_{10}F_{19}(C_9NF_{20}^+)$	PFK (FC43)
	513.6775	M+4	$C_{12}\,^{35}Cl_8\,^{37}Cl_2\,0$	DCDPE

Notes:

1 Nuclidic masses used:

H = 1.007825	C = 12.00000	^{13}C = 13.003355	F = 18.9984
O = 15.994915	^{35}Cl = 34.968853	^{37}Cl = 36.965903	

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Table 22

Theoretical Ion Abundance Ratios and Their Control Limits for PCDDs and PCDFs

Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits Lower	Control Limits Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6 [1]	M/M+2	0.51	0.43	0.59
7	M+2/M+4	1.04/1.05[3]	0.88	1.20
7 [2]	M/M+2	0.44	0.37	0.51
8	M+2/M+4	0.89	0.76	1.02

Notes:

1 Used for ^{13}C-HxCDF (IS).
2 Used for ^{13}C-HpCDF (IS).
3 Method 1613B Theoretical Ratio

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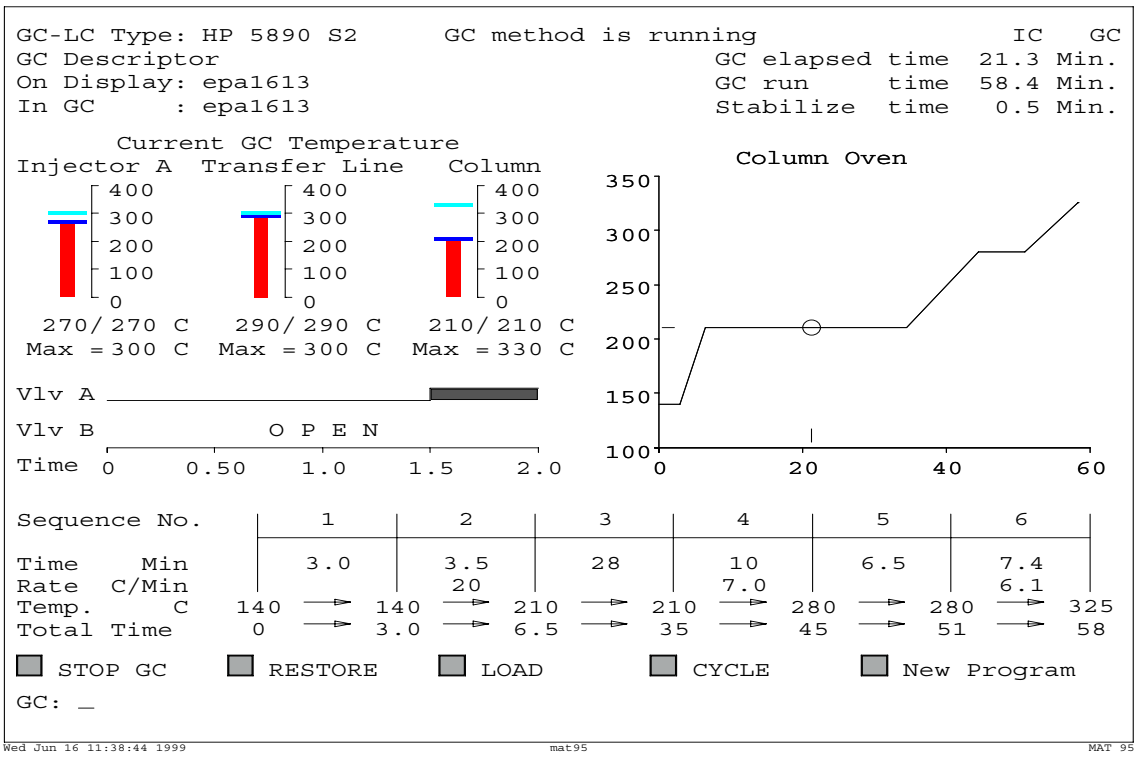
Figure 1

Rtx-5 Recommended GC Operating Conditions



DB-225 Recommended GC Operating Conditions

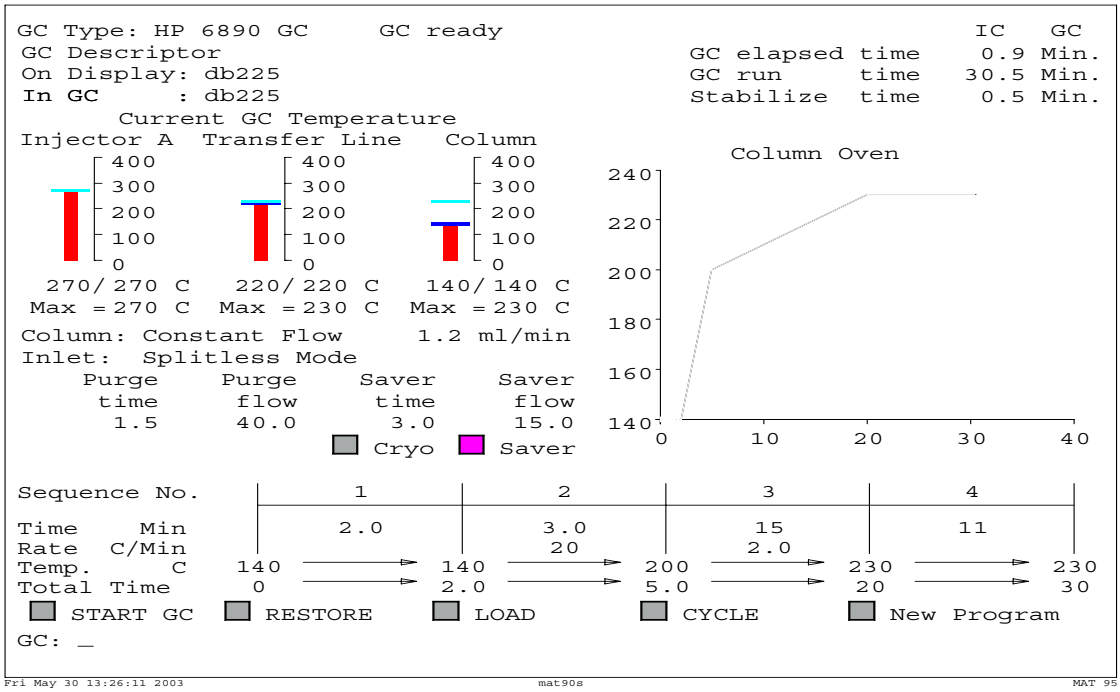


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Figure 2

Rtx-5 Recommended MID Descriptors

```
MID Set Up Parameters
 MID File                      epa1613
 Measure/lock ratio  (X)          1
 Set Damping relay   (T)      FALSE
 Width first lock    (A)       0.20  amu
 Electric jump time  (E)         10  ms
 Magnetic jump time  (D)         60  ms
 Offset              (O)        100  cts
 Electric range      (R)        300  %
 Sweep peak width    (W)       3.00
 Acq mode          (C|P)       Cent mode
 MID mode       (J|M|L|N)      Lock mode

MID  Time Windows
 #  Start  Measure  End      Cycletime
 1   8:00  28:12  36:12 min  1.00 sec
 2  36:12   7:28  43:40 min  1.00 sec
 3  43:40   5:49  49:30 min  1.00 sec
 4  49:30   5:00  54:30 min  1.00 sec
 5  54:30   3:50  58:20 min  1.00 sec
 6
 7
 8
 9

 Clear Menu      Clear Times      Clear Masses
 Stop MID        SAVE             Main

MID: _
```

```
MID Masses for Time Window   1
 #      mass    F int  gr time(ms)
 1    292.9825 l  10   1     8.19
 2    303.9016     1   1    81.92
 3    305.8987     1   1    81.92
 4    315.9419     1   1    81.92
 5    317.9389     1   1    81.92
 6    319.8965     1   1    81.92
 7    321.8936     1   1    81.92
 8    327.8847     1   1    81.92
 9    331.9368     1   1    81.92
10    333.9338     1   1    81.92
11    342.9792 c  10   1     8.19
12    375.8364     1   1    81.92
13
14
15
16
17
18
19
20
21
22
23
24

 Lock Mass   Cali Mass
```

Wed Jun 16 11:39:22 1999 mat95 MAT 95

```
MID Set Up Parameters
 MID File                      epa1613
 Measure/lock ratio  (X)          1
 Set Damping relay   (T)      FALSE
 Width first lock    (A)       0.20  amu
 Electric jump time  (E)         10  ms
 Magnetic jump time  (D)         60  ms
 Offset              (O)        100  cts
 Electric range      (R)        300  %
 Sweep peak width    (W)       3.00
 Acq mode          (C|P)       Cent mode
 MID mode       (J|M|L|N)      Lock mode

MID  Time Windows
 #  Start  Measure  End      Cycletime
 1   8:00  28:12  36:12 min  1.00 sec
 2  36:12   7:28  43:40 min  1.00 sec
 3  43:40   5:49  49:30 min  1.00 sec
 4  49:30   5:00  54:30 min  1.00 sec
 5  54:30   3:50  58:20 min  1.00 sec
 6
 7
 8
 9

 Clear Menu      Clear Times      Clear Masses
 Stop MID        SAVE             Main

MID: _
```

```
MID Masses for Time Window   2
 #      mass    F int  gr time(ms)
 1    330.9792 l  10   1     8.19
 2    339.8597     1   1    91.48
 3    341.8567     1   1    91.48
 4    351.9000     1   1    91.48
 5    353.8970     1   1    91.48
 6    355.8546     1   1    91.48
 7    357.8516     1   1    91.48
 8    367.8949     1   1    91.48
 9    369.8919     1   1    91.48
10    380.9760 c  10   1     8.19
11    409.7974     1   1    91.48
12
13
14
15
16
17
18
19
20
21
22
23
24

 Lock Mass   Cali Mass
```

Wed Jun 16 11:39:27 1999 mat95 MAT 95

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Figure 2 (Continued)

Rtx-5 Recommended MID Descriptors

```
MID Set Up Parameters
 MID File                      epa1613
 Measure/lock ratio  (X)          1
 Set Damping relay   (T)      FALSE
 Width first lock    (A)       0.20  amu
 Electric jump time  (E)         10  ms
 Magnetic jump time  (D)         60  ms
 Offset              (O)        100  cts
 Electric range      (R)        300  %
 Sweep peak width    (W)       3.00
 Acq mode          (C|P)       Cent mode
 MID mode       (J|M|L|N)      Lock mode

MID  Time Windows
 #  Start  Measure  End      Cycletime
 1   8:00  28:12  36:12 min  1.00 sec
 2  36:12   7:28  43:40 min  1.00 sec
 3  43:40   5:49  49:30 min  1.00 sec
 4  49:30   5:00  54:30 min  1.00 sec
 5  54:30   3:50  58:20 min  1.00 sec
 6
 7
 8
 9

 Clear Menu      Clear Times     Clear Masses
 Stop MID        SAVE            Main

MID: _
```

```
MID Masses for Time Window   3
#      mass    F int  gr time(ms)
1    373.8208      1   1    91.48
2    375.8178      1   1    91.48
3    380.9760 l   10   1     8.19
4    383.8639      1   1    91.48
5    385.8610      1   1    91.48
6    389.8156      1   1    91.48
7    391.8127      1   1    91.48
8    401.8559      1   1    91.48
9    403.8529      1   1    91.48
10   404.9760 c   10   1     8.19
11   445.7555      1   1    91.48
12
13
14
15
16
17
18
19
20
21
22
23
24
     Lock Mass     Cali Mass
```

```
Wed Jun 16 11:39:32 1999          mat95                    MAT 95
```

```
MID Set Up Parameters
 MID File                      epa1613
 Measure/lock ratio  (X)          1
 Set Damping relay   (T)      FALSE
 Width first lock    (A)       0.20  amu
 Electric jump time  (E)         10  ms
 Magnetic jump time  (D)         60  ms
 Offset              (O)        100  cts
 Electric range      (R)        300  %
 Sweep peak width    (W)       3.00
 Acq mode          (C|P)       Cent mode
 MID mode       (J|M|L|N)      Lock mode

MID  Time Windows
 #  Start  Measure  End      Cycletime
 1   8:00  28:12  36:12 min  1.00 sec
 2  36:12   7:28  43:40 min  1.00 sec
 3  43:40   5:49  49:30 min  1.00 sec
 4  49:30   5:00  54:30 min  1.00 sec
 5  54:30   3:50  58:20 min  1.00 sec
 6
 7
 8
 9

 Clear Menu      Clear Times     Clear Masses
 Stop MID        SAVE            Main

MID: _
```

```
MID Masses for Time Window   4
#      mass    F int  gr time(ms)
1    404.9760 l   10   1     8.19
2    407.7818      1   1    91.48
3    409.7788      1   1    91.48
4    417.8250      1   1    91.48
5    419.8220      1   1    91.48
6    423.7767      1   1    91.48
7    425.7737      1   1    91.48
8    435.8169      1   1    91.48
9    437.8140      1   1    91.48
10   442.9728 c   10   1     8.19
11   479.7165      1   1    91.48
12
13
14
15
16
17
18
19
20
21
22
23
24
     Lock Mass     Cali Mass
```

```
Wed Jun 16 11:39:37 1999          mat95                    MAT 95
```

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Figure 2 (Continued)

Rtx-5 Recommended MID Descriptors

```
MID Set Up Parameters
 MID File                      epa1613
 Measure/lock ratio (X)            1
 Set Damping relay  (T)        FALSE
 Width first lock   (A)        0.20 amu
 Electric jump time (E)          10 ms
 Magnetic jump time (D)          60 ms
 Offset             (O)         100 cts
 Electric range     (R)         300 %
 Sweep peak width   (W)        3.00
 Acq mode         (C|P)        Cent mode
 MID mode      (J|M|L|N)       Lock mode

MID  Time Windows
 #  Start  Measure  End      Cycletime
 1   8:00  28:12  36:12 min  1.00 sec
 2  36:12   7:28  43:40 min  1.00 sec
 3  43:40   5:49  49:30 min  1.00 sec
 4  49:30   5:00  54:30 min  1.00 sec
 5  54:30   3:50  58:20 min  1.00 sec
 6
 7
 8
 9

 Clear Menu     Clear Times    Clear Masses
 Stop MID       SAVE           Main

MID: _
```

```
MID Masses for Time Window   5
 #      mass    F int  gr time(ms)
 1    430.9728 l  10   1    10.92
 2    441.7428     1   1   120.15
 3    443.7399     1   1   120.15
 4    457.7377     1   1   120.15
 5    459.7348     1   1   120.15
 6    469.7780     1   1   120.15
 7    471.7750     1   1   120.15
 8    480.9696 c  10   1    10.92
 9    513.6775     1   1   120.15
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

 Lock Mass   Cali Mass
```

Wed Jun 16 11:39:43 1999 mat95 MAT 95

DB-225 Recommended MID Descriptor

```
MID Set Up Parameters
 MID File                      db225
 Measure/lock ratio (X)            1
 Set Damping relay  (T)         TRUE
 Width first lock   (A)        0.20 amu
 Electric jump time (E)          10 ms
 Magnetic jump time (D)          60 ms
 Offset             (O)         100 cts
 Electric range     (R)         300 %
 Sweep peak width   (W)        3.00
 Acq mode         (C|P)        Cent mode
 MID mode      (J|M|L|N)       Lock mode

MID  Time Windows
 #  Start  Measure  End      Cycletime
 1   8:00  22:30  30:30 min  1.00 sec
 2
 3
 4
 5
 6
 7
 8
 9

 Clear Menu     Clear Times    Clear Masses
 Start MID      RESTORE        Main

MID: _
```

```
MID Masses for Time Window   1
 #      mass    F int  gr time(ms)
 1    292.9825 l  10   1     8.19
 2    303.9016     1   1    81.92
 3    305.8987     1   1    81.92
 4    315.9419     1   1    81.92
 5    317.9389     1   1    81.92
 6    319.8965     1   1    81.92
 7    321.8936     1   1    81.92
 8    327.8847     1   1    81.92
 9    331.9368     1   1    81.92
10    333.9338     1   1    81.92
11    342.9792 c  10   1     8.19
12    375.8364     1   1    81.92
13
14
15
16
17
18
19
20
21
22
23
24

 Lock Mass   Cali Mass
```

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Figure 3

Example Sample Data Review Checklist

TestAmerica Knoxville Dioxin GC/MS Initial Calibration Data Review / Narrative Checklist
Method: 8290/8290A - KNOX-ID-0004-R9

Mass Res. ✓ Date/Time:		Inst:		Win Filename:		Col Perf Filename:	

CS1 Filename	CS2 Filename	CS3 Filename	CS4 Filename	CS5 Filename

Review Items	N/A	Yes	No	If No, why is data reportable?	2nd Level
1. Was the mass resolution documented before beginning the initial calibration?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 or FC43 m/z 313.9838 and m/z 363.9807?					
3. Was the measured exact mass of m/z 380.9760 (PFK) or 363.9807 (FC43) within 5 ppm at reduced accelerating voltage?					
4. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
5. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer?					
6. Were the five calibration standard solutions, at the concentrations specified in Table 5 of the SOP, analyzed?					
7. Was date/time of analysis verified between analysis header and logbook as correct?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound (Table 5), quantitation ions (Table 22), and formula (Section 10.2.6)?					
9. Are the relative retention times of all PCDDs/PCDFs and all labeled compounds within the limits specified in Table 3?					
10. Are %RSD ≤20% for all unlabeled native analytes?					
11. **8290**, are %RSD ≤30% for all labeled internal standards?					
12. **8090A**, are %RSD ≤20% for all labeled internal standards?					
13. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
14. Are the ion abundance ratios for all labeled and unlabeled analytes within the control limits specified in Table 22 of the SOP?					
15. Was the second source (Wellington) ICV standard analyzed, and the %D calculated and within the acceptance criteria of < ±35%?					
16. If manual integrations were performed, are they clearly identified, initialed and dated?					
17. Were before/after chromatograms reviewed to determine whether the software and manual integrations were appropriate?.					
18. Were manual integrations performed properly?.					
19. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
20. Does the ICAL folder contain **complete** data in the following order? Data review checklist, a **complete** runlog, Avg. %RSD summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation; Total RIC, EICP's and manual integration - for window and all standards, in order from low to high standard, ICV Summary Table, Calculation Summary, and chromatograms?					

Analyst:	Date:	2nd Level Reviewer :	Date:
Comments:		Comments:	

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Figure 3 (Continued)

Example Data Review Checklist

TestAmerica Knoxville Dioxin GC/MS Continuing Calibration Review / Narrative Checklist
Method: 8290/8290A - KNOX-ID-0004-R9

Start Mass Res. ✓:		**Ver Filename:**		**Inst:**	
End Mass Res. ✓:		**Win Filename:**		**ICAL Date:**	
		Col Perf Filename:			
		End Ver Filename:			

Review Items	**N/A**	**Yes**	**No**	**If No, why is data reportable?**	**2nd Level**
1. Was the mass resolution documented at both the beginning and end of the 12 hour shift?					
2. Was the instrument resolution >10,000 (<100 ppm) on PFK m/z 304.9824 and m/z 380.9760 or FC43 m/z 313.9838 and m/z 363.9807?					
3. Was the measured exact mass of m/z 380.9760 (PFK) or 363.9807 (FC43) within 5 ppm at reduced accelerating voltage?					
4. Was date/time of analysis verified between analysis header and logbook as correct?					
5. Was the Window Defining Mixture analyzed and the MID switchpoints set to encompass the retention time windows of each congener group?					
6. Was the Column Performance solution analyzed and the %Valley ≤25 for separation between 2378-TCDD/F and the closest eluting non-2378 isomer?					
7. Were continuing calibrations performed at the beginning and end of the 12-hour period, with successful mass resolution and GC resolution performance checks?					
8. Were the response factors calculated for each labeled standard and unlabeled native analyte using the SOP specified reference compound (Table 3), quantitation ions (Table 22), and formula (Section 10.2.6)?					
9. Are the measured RRFs for each compound within the specified control limits in Table 7 for all PCDDs/PCDFs?					
10. Are the relative retention times of all PCDDs/PCDFs and all labeled compounds within the limits specified in Table 3?					
11. Are all S/N ratios ≥10 for the GC signals in each EICP (extracted ion chromatographic profile) including internal standards?					
12. Are the ion abundance ratios for all labeled and unlabeled analytes within the control limits specified in Table 22 of the SOP?					
13. If manual integrations were performed, are they clearly identified, initialed and dated?					
14. Were before/after chromatograms reviewed to determine whether the software and manual integrations were appropriate?.					
15. Were manual integrations performed properly?.					
16. If criteria were not met, was a NCM generated, approved by supervisor, and copy included in folder?					
17. Does the CCAL folder contain **complete** data in the following order: Data review checklist, a **complete** runlog, CCAL summary, Ratio summary, Calculation summary, PFK resolution/peak match documentation; Total RIC, EICP's and manual integration - for window and all standards?					

Analyst:	**Date:**	**2nd Level Reviewer :**	**Date:**
Comments:		**Comments:**	

ID022R13.doc, 072710

Figure 3 (Continued)

Example Data Review Checklist

TestAmerica Knoxville Dioxin GC/MS Data Review / Narrative Checklist LOT #_____
Method: 8290/8290A- KNOX-ID-0004-R9 Page 1 of 1 Batch#_____

Review Items **A. Initial Calibration**	N/A	Yes	No	Why is data reportable?	2nd Level
1. Was the correct ICAL used for quantitation? (Check 1-2 compounds for batch by manually calculating concentration using the ICAL avg. RF.)					
B. Continuing Calibration	N/A	Yes	No		2nd
1. Has a Continuing Calibration Checklist been completed for each analytical batch?					
C. Client Sample AND QC Sample Results	N/A	Yes	No		2nd
1. Were all special project requirements met?					
2. Were the header information, prep factors, and dilution factors verified?					
3. Is logbook date/time of analysis correct?					
4. Sample analyses done within preparation and analytical holding time (HT)? *If no, list samples:*_____				HT expired upon receipt. * Client requested analysis after HT expired. Re-extraction done after HT expired.	
5. Are internal standards within QC limits specified in Table 13? *If no, list samples and reason (e.g.,* **sur1***):* Sample Reason Sample Reason _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____ _____				* **[sup]** Ion suppression due to matrix. * **[low]** Low recovery. S/N >10 and EDL<ML. **[sam]** Not enough sample to re-extract. **[dil]** Dilution showed acceptable %R. **[mtx]** Obvious matrix interference. Further cleanup not possible. * **[unk]** At client's request, data was flagged as estimated and released without further investigation.	
6. Were reported PCDD/Fs which did not meet the criteria below, properly calculated and reported as EMPCs?: • RT of 2378 isomers within -1 to +3 seconds of associated labeled isomer. • RT of non-2378 isomers within established first/last windows. • Both native ions maximized within ±2 seconds. • Ion abundance ratios within the control limits specified in Table 22. • No corresponding peak at PCDPE mass.					
7. Were all 2378-TCDF hits ≥ ML confirmed by analysis on DB-225?					
8. Are positive results > ML within calibration range? *If no, list samples:* _____				OCDD/F or non-2378 exceeded calibration range Sample extracted at lowest possible volume	
9. Are all manual integrations performed properly and clearly identified and approved?					
10. Were before/after chromatograms reviewed to determine whether the software and manual integrations were appropriate?.					
11. Final report acceptable? (Results correct, DLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.)					
12. Was a narrative prepared and all deviations noted?					
D. Preparation/Matrix QC	N/A	Yes	No	Why is data reportable?	2nd
1. LCS(OPR) done per prep batch and all analytes within the limits specified in QuantIMS reference data?				* Reanalysis not possible-insufficient sample. LCS %R high and affected analyte(s) were <ML in associated samples.	
2. Method blank done per prep batch, method/instrument blank analyzed with each sequence and analytes present in the method blank ≤ ML? *If no, list blank ID:* _____				Sample results are > 20x higher than blank. * There is no analyte > RL in the samples associated with method blank. * Reanalysis not possible-insufficient sample	
3. MS/MSD recoveries and RPDs within laboratory generated QC limits? *If no, list MS/MSD* _____				LCS acceptable, indicating sample matrix effects. LCS acceptable, high analyte concentration. LCS acceptable, lack of sample homogeneity.	
E. Other	N/A	Yes	No		2nd
1. Are all nonconformances documented appropriately and copy included with deliverable?					

Analyst:	**Date:**	**Analyst:**	**Date:**
Comments:		**Comments:**	

* Such action must be taken in consultation with client.

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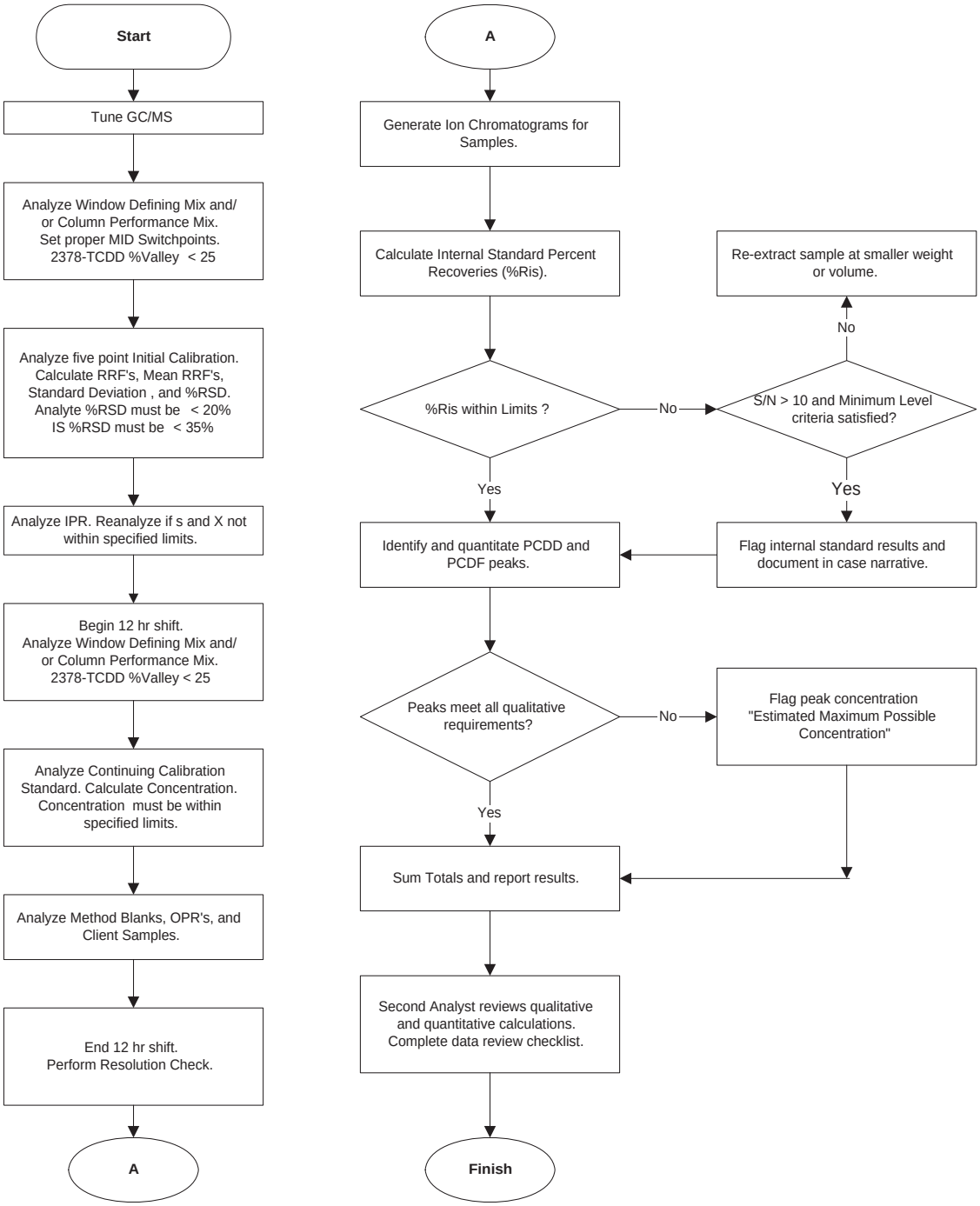
Figure 4

Analysis of PCDDs and PCDFs by HRGC/HRMS