1. SCOPE AND APPLICATION

1.1. This method is applicable to the determination of metals by inductively coupled plasma mass spectrometry (ICP-MS) by EPA Method 6020, 6020A and EPA Method 200.8.

1.2. This method is applicable to drinking, surface, and saline waters, soil, sediment, wipe, tissue and waste samples.

1.3. Reporting Limits

The standard reporting limits for metals analyzed by ICP-MS are listed in Table 1. Upon client request, results below the standard reporting limit but above the current method detection limit (MDL) may be reported and qualified as “estimated”.

1.4. Methods are based on the requirements of SW-846 methods 6020 and 6020A.

1.5. Elements that may be determined using this procedure include: Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Si, Ag, Sr, Tl, Sn, Ti, V, Zn, Ca, Mg, K, P, Cs and Na.

Note: successful Ag analysis may require all solutions to be prepared as described, but with the addition of hydrochloric acid to 1% (v/v). This may degrade performance for As, Se and V.

1.6. For DoD QSM Version 3 requirements, refer to SOP PT-QA-025. For DoD QSM current version refer to SOP PT-QA-029.

2. SUMMARY OF METHOD

2.1. The sample solution is introduced into a pneumatic nebulizer via a peristaltic pump. The nebulizer generates a fine aerosol by bringing the solution into contact with a high velocity flow of argon gas at its tip. The nebulized sample is sorted by droplet size in the spray chamber. Large droplets are rejected, whilst smaller particles are transported with the gas stream into the plasma.

2.2. The argon plasma operates with a continuously applied radio frequency (RF) field to give a high-energy discharge consisting of argon atoms, ions and electrons. The hottest part of the plasma can attain 6000-8000 K. In the plasma, aerosol droplets undergo evaporation, atomization and ionization. Ions are sampled through an aperture in a metal cone (sampler) at atmospheric pressure, into the expansion region at about 2 mbar and subsequently through an aperture in a second metal cone (skimmer) into the intermediate chamber.

2.3. An electrostatic ion lens system focuses the ion beam through a differential aperture into the analyser chamber, at about 10-7 mbar. The ions are filtered by mass-to-charge ratio in microsecond timescales by the quadrupole. The selected mass is detected by a discrete dynode electron multiplier. The multiplier has two simultaneous modes of operation: pulse count and analogue. The combination of these two modes allows seamless detection spanning 8 - 9 orders of magnitude. A detector “cross-calibration” is required for the analogue counts to be converted to equivalent pulse counts. The output from the detector is proportional to the concentration of the element in the aspirated solution, hence the concentration of unknown samples may be calculated when the instrument response is

calibrated with standards of known concentration.

2.4. The linear range may vary from instrument to instrument and is dependant upon the sensitivity determined by the optimization parameters. This should be determined by the individual laboratory. In the test study at TestAmerica Pittsburgh, the linear ranges listed in Table 1 (below) were obtained:

2.4.1. Table 1. Test study linear ranges for the X5 ICP-MS

Analytes	Linear Range (mg/L)
Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, Se, Ag, Tl, V, Zn	0.20 – 20.0
Al, Ca, Mg, K Na, Fe	100 - 1500

2.5. Calibration standard concentrations are listed in Table 2 below.

2.5.1. Table 2. Calibration standard concentrations for analysis of water and waste

Analytes	Calibration Range (mg/L)
Al, Mn	1.0
Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Ni, Se, Ag, Tl, V, Zn	0.20
Ca, Mg, K Na, Fe	100
Fe	50
B, Mo, Sn, Sr, Ti	0.20
Si	10

3. DEFINITIONS

3.1. See Pittsburgh Laboratory Quality Assurance Manual (PT–LQM) for definitions of general terms

3.2. See appendix for Glossary of Abbreviations

4. INTERFERENCES

4.1. Isobaric interferences. Elemental isobaric interferences occur when different elements have isotopes at the same nominal mass, e.g. ^{114}Cd and ^{114}Sn. Problematic elemental isobaric interferences for these methods are listed in Table 3. The correction factors given in Table 3 are based on theoretical isotopic abundance ratios and may require adjustment.

4.2.

4.3.

Table 3 Isobaric Interferences and Correction Equations

m/z	Analyte	Interferent	Correction
58	Ni	Fe	58Ni=58M-0.0040*56Fe
64	Zn	Ni	64Zn=64M-0.0440*60Ni
82	Se	Kr	82Se=82M-1.0010*83Kr
114	Cd	Sn	114Cd=114M-0.0270*118Sn
115	In	Sn	115In=115M-0.0140*118Sn
123	Sb	Te	123Sb=123M-0.1240*125Te
138	Ba	Ce	138Ba=138M-0.0030*140Ce

4.4. Abundance Sensitivity - Abundance sensitivity is the ability of the quadrupole to separate a low intensity peak from an adjacent high intensity peak. An example of the requirement of this is the detection of low concentrations of manganese (m/z 55) in the presence of high concentrations of iron (m/z 56). Quadrupole resolution and bias can be adjusted during set-up to resolve these signals.

4.5. Isobaric Polyatomic Ion Interferences - Polyatomic ions are produced by chemical reaction in the plasma and the interface region. If these polyatomic ions have the same nominal mass to charge (m/z) ratio as an analyte a polyatomic interference is observed. The principle polyatomic species for this method are listed in Table 4. Some of the correction factors given in Table 4 are based on theoretical isotopic abundance ratios and may require adjustment. Other factors were derived empirically. The stability of the empirical factors was determined during the test study at Thermo Electron. It was found that the factors require little or no adjustment and can be transferred between similarly configured X5 instruments.

Table 4. Isobaric Polyatomic Interferences and Correction Equations

m/z	Analyte	Interferent	Correction
51	V	ClO	51V = 51M-3.0460*53ClO 53ClO = M53-0.114*52Cr
52	Cr	ArC, ClOH	52Cr = 52M-0.0050*13C
56	Fe	CaO	56Fe = 56M-0.1500*43Ca
56	Co	CaO, CaOH	59Co = 59M-0.0046*43Ca
60	Ni	CaO	60Ni = 60M-0.0020*43Ca

m/z	Analyte	Interferent	Correction
75	As	ArCl	75As = 75M-3.000*77ArCl 77ArCl = 77M-0.8000*82Se 82Se = 82M-1.0010*83Kr
111	Cd	MoO	111Cd = 111M-0.9820*108MoO 108MoO = 108M-0.712*106Cd

4.6. Physical Interferences - Physical interferences include transport effects, ionization effects and deposition effects in the sample introduction system, plasma and interface, which result in signal suppression and signal drift. Transport effects arise from variations in solution properties, e.g. viscosity or surface tension, which affect nebulization efficiency and aerosol droplet size. The concentration of dissolved matter will affect the ionization efficiency of the analytes in the plasma and will cause a mass-dependant suppression effect and contribute to space-charge effects. Dissolved matter may also condense on the cones, altering the ion beam profile. This normally manifests itself as a time-dependant downward signal drift. To reduce the severity of these effects it is advised that the total dissolved solids concentration of solutions aspirated should be limited to <0.05%. Samples known to contain higher dissolved solids concentrations should be diluted. Signal suppression and drift can be corrected, to a degree, with the use of internal standardization techniques. Since these effects can be mass-dependant and may be related to the ionization potential of the element, a multiple-element internal standard approach should be used.

4.7. Memory Effects - Memory effects occur when the signal for an analyte from a sample contributes to the signal of a subsequent sample. This effect can be severe for certain elements due to their physico-chemical properties, e.g. mercury. This effect is minimised by aspirating a wash solution between samples. A monitored wash can be used in order to ensure that analyte signals recover to the background level.

4.8. Common molecular ion interferences for ICPMS are given in Table 6.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2. Specific Safety Concerns or Requirements

5.2.1. The ICP plasma emits strong UV light and is harmful to vision. All analysts must

avoid looking directly at the plasma.

5.3. Primary Materials Used

5.4. 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.

5.5. The following specific hazards are known

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.6. Eye protection that protects against splash, laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.7. The waste pumped from the spray chamber is corrosive and must be handled with care,

especially if large volume containers are used, as these may be heavy and awkward to carry. Empty the waste vessel daily to reduce the quantity that must be disposed each time and to keep weight to a minimum. Protective clothing, including hand and eye protection must be worn when handling this waste.

5.8. The wash solution is corrosive and must be handled with care. This solution must be prepared and stored in a vessel made of a robust acid-resistant material with a tight fitting lid that it is resistant to breakage if dropped. Large volumes of this solution will be heavy and may be awkward to carry. Ensure adequate provision for transporting the vessel, i.e. suitable handles on the vessel, minimum distance between the preparation area and the instrument. Use a cart to transport the vessel where necessary or ask for assistance in carrying.

5.9. Many of the concentrated metal standard solutions are toxic and must be handled with care. Skin and eye protection should be worn when handling and inhalation of vapours must be prevented.

5.10. Fumes generated by the plasma can be hazardous and must be removed from the laboratory with an extraction system as detailed in the X Series site planning guide. If the extraction system is faulty do not attempt to use the instrument. The extraction system should be inspected on a regular basis.

5.11. The plasma emits strong UV light and is harmful to vision.

5.11.1. ***WARNING**:* AVOID looking directly at the plasma.

5.12. The plasma is a source of radio frequency (RF) radiation and intense, ultra-violet radiation that can damage the eyes. This radiation is normally contained by the system, but operators must be aware of the dangers. The instrument must be properly maintained by qualified service personnel. Never attempt to defeat hardware interlocks – they are there for your safety.

5.13. <u>WARNING: People with pacemakers should not go near the instrument while in operation</u>. DIAZOMETHANE is an extremely toxic gas with an explosion potential. Since the explosion potential is catalyzed by imperfections in glass, generation of diazomethane must be carried out in glassware free from etches, cracks, chips, and which does not have ground glass joints. Solutions of diazomethane will be kept at temperatures below 90°C. Diazomethane must be generated and handled in a fume hood.
Note: Diazomethane has not been classified as a carcinogen under the current OSHA definition.

5.14. Should the plasma need to be extinguished in an emergency, open the torch box door. This will immediately cut-off the power to the plasma RF generator, extinguishing the plasma. After extinguishing the plasma, the torch, torch box, cones and cone housing may remain very hot for some time. Operators must be aware of this fact and allow cooling time prior to handling these components.

5.15. There are high voltage components inside the instrument. Routine maintenance does not require access to any of the electronic components. If an electronic fault is suspected, a qualified service engineer must be called. Do not attempt to tamper with electronic components yourself.

5.16. 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 will be kept closed unless transfers are being made.

5.17. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.18. 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 and/or the EHSC.

6. EQUIPMENT AND SUPPLIES

6.1. Instrumentation

6.1.1. (2) X Series ICP-MSs fitted with Xi interface and Y-connector for on-line internal standard addition (supplied with this package).

6.1.2. (2) Cetac ASX-510 autosamplers.

6.2. Supplies

6.2.1. Ultrapure water system capable of delivering de-ionized, polished water of at least 18 MΩ cm

6.2.2. Yellow/orange tab peristaltic pump tubes (~0.5 mm ID)

6.2.3. White/white tab peristaltic pump tubes (~1 mm ID)

6.2.4. A range of adjustable pipettes, such as Rainin pipettes. Adjustable pipettes with a capacity of 0.1 mL, 1 mL, and 10 mL are recommended. These must be calibrated regularly to ensure accurate volumes are delivered.

6.3. Refer to Section 20 of PT-LQAM for instrument hardware/software specifications and routine instrument maintenance procedures

7. REAGENTS AND STANDARDS

7.1. General Reagents

7.1.1. **Laboratory Water** - All laboratory water used in these procedures must be of very high quality, purified with a reverse osmosis system and polished with an ion exchange system to give a final product of resistivity >18 MΩ cm.

7.1.2. **Hydrochloric Acid** (sp. gr. 1.18) - Hydrochloric acid must be at least Romil "SPA", J.T. Baker "Instra Analyzed", BDH/Merk "Analar", Fisher "Optima" - grade or equivalent. Hazards – corrosive, causes severe burns.

7.1.3. **Nitric Acid** (sp. gr. 1.42) - Nitric acid must be at least Romil "SPA", J.T. Baker "Instra Analyzed", BDH/Merk "Analar", Fisher "Optima" - grade or equivalent. Hazards – oxidising and corrosive, causes severe burns.

7.1.4. **2 % (m/v) Nitric Acid** - This reagent is used for the calibration blank, ICB, CCB, sample dilution and solution preparation. Add 5 mL of Conc of HNO3 to DI water and dilute to 250 mL.

7.1.5. For Standard preparation refer to standard log database. Composition of standards and concentration are given in Tables 2-5.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Samples are to be collected in plastic or glass containers.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2.

8.3. All soil and wipe samples must be refrigerated to $4^{o}C \pm 2^{o}C$.

8.4. Tissue samples are stored frozen until preparation.

8.5. The analytical holding time for metals by ICP-MS is 6 months.

8.6. Aqueous samples for total metals must be digested before analysis using an appropriate digestion procedure. Method 200.8 has its own digestion specifications that are followed by the laboratory. Method 3005A is used for total recoverable metals and dissolved and method 3010A is used for total metals by 6020 and 6020A. These are covered in the SOP PT-IP-003. Upon consultation with the client dissolved samples can forego digestion to help prevent contamination when very low detection limits are required.

8.7. Soil, wipe, tissue and waste samples should be digested before analysis using an appropriate digestion procedure. Method 3050B of SW846 is the appropriate digestion procedure. The SOP for 3050B is PT-IP-002.

8.8. Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

9. QUALITY CONTROL

9.1. Sample QC

9.1.1. Quality Control Batch

The batch is a set of up to 20 field samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank, an LCS and a matrix spike/matrix spike duplicate. (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 particular samples for MS/MSD, the batch may contain multiple MS/MSDs. See SOP PT-QA-021 for further definition of the batch. For QC abbreviations and criteria refer to Appendix 13.

9.1.2. Insufficient Sample

If insufficient sample is available to process a MS/MSD, then a second LCS may be processed, if precision data is required by the client. The LCS pair is then evaluated according to the MS/MSD RPD criteria.

9.1.3. Method Blank

One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that 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 must not contain any analyte of interest at or above the reporting limit (except common laboratory contaminants, see below) or at or above 10% of the measured concentration of that analyte in the associated samples, whichever is higher. Certain programs, such as USACE, may require a more stringent evaluation of the method blank, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit. **Refer to PT-QA-025 for specific DoD requirements for the method blank.** For DoD QSM current version refer to SOP PT-QA-029.

- If the analyte is a common laboratory contaminant (copper, iron, zinc), the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than five times the RL. Such action must be documented in the NCM program.
- Re-preparation and reanalysis of any samples with reportable concentrations of analytes less that 10 times the value found in the method blank is required unless other actions are agreed with the client.
- If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported. This must be documented in the NCM program.
- If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all positive results in associated samples are flagged with a "J", and appropriate comments may be made in a narrative to provide further documentation.

9.1.3.1. Refer to the QC Program document (PT-QA-021) for further details of the corrective actions.

9.1.3.2. For samples that have not been digested or matrix matched, a CCB result is reported as the method blank. The CCB analyzed immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB.

9.1.4. Laboratory Control Sample (LCS)

9.1.4.1. A laboratory control sample (LCS) is prepared and analyzed with every batch of 20 samples. All analytes must be within established control

limits. The LCS is spiked with the compounds listed in Tables 9 and 10 unless otherwise requested by the client.

9.1.4.2. If any analyte in the LCS is outside the laboratory established historical control limits, corrective action must occur:

- Check calculations,
- Check instrument performance,
- Reanalyze the LCS, and if still outside of control limits,
- Evaluate the data, and/or
- Re-prepare and reanalyze all samples in the QC batch.

9.1.4.3. Data may be reported with an anomaly in the following cases:

- The LCS recoveries are high and the analyte of concern is not detected in field samples,
- All target requested analytes are within control, but other LCS compounds are out of control,
- If no sample preparation is performed (eg., dissolved metals), the LCS may be reprepared and reanalyzed within the same sequence.

9.1.4.4. The analyst should evaluate the anomalous analyte recovery for possible trends.

9.1.4.5. If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report.

9.1.4.6. If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the LCS is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.1.4.7. For samples that have not been digested or matrix matched, a CCV result is reported as the LCS. The CCV run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCV.

9.1.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD)

A matrix spike/matrix spike duplicate (MS/MSD) is prepared and analyzed with every batch of 20 samples for methods 6020 and 6020A. For method 200.8 matrix spike is prepared and analyzed per batch of 10 samples. The MS/MSD is spiked with the same analytes as the LCS (For spiking levels see Appendix 11). **Refer to PT-QA- 025 for specific DoD requirements for the MS/MSD.** For DoD QSM current version refer to SOP PT-QA-029. Matrix spike/matrix spike duplicate recovery for methods 6020 and 6020A should be within 75-125% and the RPD ± 20%. For method 200.8 the matrix spike recovery must be within 70-130% recovery and the RPD within ± 20%.

Note: Some programs require a Matrix Spike and Matrix Replicate in lieu of an MS/MSD. When a matrix spike/matrix replicate is performed the matrix spike is evaluated for accuracy (% recovery) and the matrix replicate is evaluated for precision (RPD).

- If any individual recovery or RPD falls outside the acceptable range, corrective action must occur. The initial corrective action will be 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 may proceed. The reasons for accepting the batch must be documented.
- If the recovery for any component is outside QC limits for both the matrix spike/spike duplicate and the LCS, the process is out of control and corrective action must be taken. Corrective action will normally include re-preparation and reanalysis of the batch.
- If a MS/MSD or MS/Dup is not possible due to limited sample, then a LCS duplicate should be analyzed. RPD of the LCS and LCSD are compared to the matrix spike limits.
- The matrix spike/duplicate must be analyzed at the same dilution as the unspiked sample, even if the matrix spike compounds will be diluted out.

9.1.5.1. If the amount of an analyte found in the unspiked sample is greater than 4 times the amount of spiked analyte added, then routine control limits do not apply and recoveries are not evaluated. Other analytes in the MS and MSD must still be reported. File an NCM stating that the 4X rule was applied, and report the recovery in the LIMS as “ND MSB”. This NCM must be included in the final report.

9.1.5.2. For samples that have not been digested or matrix matched, a MS/MSD must be performed per batch of up to 20 samples by spiking two aliquots of the sample.

9.1.6. Post-Digestion Spike Samples (PDS)

9.1.6.1. For 6020, 6020A and DoD samples, a post digestion spike will be run on a sample if the if the MS/MSD for the sample falls outside of % recovery criteria. A post digestion spike is a matrix spike on a sample, which is added after the sample preparation is completed. For 6020, 6020A and DoD the default matrix spike protocol is a “post digestion spike”. However, TestAmerica Pittsburgh will perform a conventional matrix spike and spike duplicated as the default matrix QC. We will perform the “PDS” only where the conventional matrix spike fails. We believe that this approach will provide more complete matrix information than the default requirements. For methods 6020 and DoD, the spike recovery from the post digestion spiked sample should be within the range 75-125% where the spike value is greater than 25% of the indigenous analyte concentration. The post digestion spike recovery for Method 6020A

should be within 80-120%. If this spike fails, then the dilution test (Sec. 9.6 should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed. The software calculates this based on the following equation:

%Repeatability = 100 * (Spk-Orig)/Tru

where, Spk is the spiked sample result and Orig is the original sample result and Tru is the True spiked concentration value. If a result is outside the required range, the data should be assessed carefully and samples may require reanalysis. Post digestion spike is not required for method 200.8.

9.1.7. Serial Dilution Samples (SER) – CLP/20.8 or Dilution Test (6020/6020A) – CLP/200.8 - Some regulatory programs such as require a dilution test be performed for each matrix within an analytical batch determination. If the analyte concentration is sufficiently high (minimally, a factor of 10 above the lower limit of quantitation after dilution), an analysis of a 1:5 dilution should be performed. The results of the serial dilution sample(s) (SER) after dilution correction should be within the range 90-110% of the original sample, if the result for the original sample is greater than 50*IDL for CLP or greater than 50*MDL (200.8/6020/6020A) then a chemical or physical interference effect should be suspected.

9.1.7.1. The software calculates this based on the following equation:

%Repeatability = 100 * Ser/Orig

where, SER is the dilution corrected serial diluted sample result and Orig is the original sample result. If a result is outside the required range, the data should be assessed carefully and samples may require reanalysis.

9.1.8. Duplicate Samples (DUP); %RPD = ±20%: Results of the duplicate sample(s) (DUP) must be within ±20% of the results of the original sample, where the result is greater than or equal to 5*CRQL for CLP or greater than 5*RL for 200.8 or 6020/6020A. The software calculates this based on the following equation:

%RPD = (S-D) / [(S+D)/2] * 100%

where, D is the duplicate sample result and S is the original sample result.

If a result is outside the required range, the data should be assessed carefully and samples affected may need to be reanalyzed where the project requires it.

9.2. Instrument QC

9.2.1. Linear Range Verification (LR) - The linear range is determined semi-annually (2x/year) for each element on the standard list. See Section 12 for details of the linear range verification.

9.2.2. The internal standard intensities in samples must be within 60 to 125% of the IS intensities for the Calibration Blank for method 200.8, 30% to 120% for method 6020 and 70 to 120% for method 6020A. If this criterion is not met, the sample will

be diluted and reanalyzed until the IS recoveries are within the limits. If the upper control limit is exceeded, the analyst should review the data for the presence possible contribution from the native sample. Narrate any findings.

9.2.2.1. For method 6020 the internal standard intensity in the ICV, ICB, CCV and CCB should be within 20% of the IS intensity in the calibration blank of the initial calibration. If not, the analyst should check for any instrument anomalies and continue if none are noted. For method 200.8 the IS acceptance range does not vary from the 60 to 125% noted above. For method 6020A the IS acceptance range does not vary from the 70 to 120% noted above.

9.2.3. Interference Check Solutions (ICSAs) - The results of ICSA must be within ±3CRQL of the analytes "true" value or ±20% of the analytes "true" value, whichever is the greater. The "true" value will be taken as zero, unless otherwise indicated in the solution manufacturer's literature. The software automatically checks for compliance with the above, based on a "true" value of zero. If a result falls outside this range, the analysis must be terminated and the samples associated must be reanalyzed. **Refer to PT-QA-025 for specific DoD requirements for the ICSA.** For DoD QSM current version refer to SOP PT-QA-029.

9.2.4. Interference Check Solution Spike Recoveries (ICSABs) - Results of ICSAB must be within ±20% of the analytes "true" value. The software automatically checks for compliance with the above, based on the values indicated in (Tables 4 and 5). If a result falls outside this range, the analysis must be terminated and the samples associated must be reanalyzed.

9.2.5. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV must fall within ± 10% of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within ± the reporting limit (RL) from zero. (Certain programs, may require a more stringent evaluation of ICB, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit.) **Refer to PT-QA-025 for specific DoD requirements for the ICB.** For DoD QSM current version refer to SOP PT-QA-029. If either the ICV or ICB fail to meet criteria, the analytical sequence should be terminated, the problem corrected, the instrument recalibrated and the calibration re-verified.

9.2.6. CRQL Check Standard (CRI)

ILMO5.2**:** For CLP the CRI is at 2 X RL. The results of the CRI must be within the range 70-130% recovery for all analytes, except CO, Mn and Zn, which must be in the range 50-150% recovery. This is checked by the software, based on the true values.

For method 6020, the CRI is at the RL. The method does not specify criteria, however the lab uses the range 50 – 150%.

For method 6020A the CRI is at the RL. The CRI/LLICV/LLCCV must be within the 70 – 130% recovery range and analyzed at the beginning and end of the analytical sequence. For method 6020A the CRI which is the low level quantitation check sample is prepared and analyzed quarterly or as needed. The control limit is 70-130%. Please note the CRI (undigested) is still analyzed at the beginning and end of the analytical run. **For DoD refer to PT-QA-025 for specific DoD requirements**. For DoD QSM current version refer to SOP PT-QA-029.

If any analyte is outside the range indicated, the sample may be re-run once. If the results fall within the required values upon re-run, no further corrective action need be taken. If still outside the acceptable range, the analysis shall be terminated, the problem corrected and the samples reanalyzed.

9.2.7. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. Results for the CCV must be within the range 90-110% recovery. This is checked by the software, based on the true values. If outside this range, the analysis must be terminated, the problem corrected and the samples since the last valid CCV must be re-analyzed. The CCB result must fall within ± RL from zero. (Certain programs, may require a more stringent evaluation of the CCB, for instance, that the blank not contain any analytes of interest at a concentration greater than ½ the reporting limit. The analyst should refer to the project notes provided by the PM to identify when this is an issue and if so what the corrective actions to take for exceedances.) **Refer to PT-QA-025 for specific DoD requirements for the CCB.** For DoD QSM current version refer to SOP PT-QA-029. Sample results may only be reported when bracketed by valid CCV/CCB pairs. If a mid-run CCV or CCB fails, the CCV or CCB may be reanalyzed once and accepted if there is a reason for the initial out-of-control event such as carryover from a high concentration sample. Otherwise, if the CCV or CCB fails, the analysis for the affected element must be terminated, the problem corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed. (Refer to Section 10.9 for an illustration of the appropriate rerun sequence).

9.2.8. High Level Calibration Standard (HLCS) for DoD:

9.2.8.1. A high level calibration standard is analyzed after the ICSAB before any

client samples are analyzed. This standard is analyzed once for a run. The percent recovery must be within 90-110%. If not the instrument is recalibrated and instrument QC along with high level calibration standard is reanalyzed before any samples can be analyzed. Sample concentration greater than high level calibration standard for analytes listed in Table 11 will be diluted. For analytes not included in high level calibration standard, Table 11, dilutions will be determined based on instrument calibration standard, Table 2.

9.3. Nonconformance and Corrective Action:

Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the QA Manager.

9.4. Quality Assurance Summaries:

Certain clients may require specific project or program QC that may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.5. QC Program:

Further details of QC and corrective action guidelines are presented in the QC Program SOP PT-QA-021. For QC abbreviations and criteria refer to Appendix 13.

10. PROCEDURE

10.1. Sample Preparation

10.1.1. Refer to SOPs PT-IP-002, PT-IP-003 and PT-IP-005.

10.2. Calibration

10.2.1. Instrument start-up

Follow the instrument start-up procedure outlined in the Thermo X-Series ICP-MS Operator's Manual.

10.2.2. Instrument Tuning

10.2.2.1. Aspirate a 20 ppb tuning solution containing all of the tuning elements. The 6020/6020A tuning elements are Li, Co, In, and Tl. The instrument manufacturer monitors Mg, Ce, Be & Pb for instrument performance.

10.2.2.2. Mass calibration and resolution checks must be documented and included as part of the raw data package.

10.2.2.3. Resolution must be < 0.90 amu at 10% peak height for the 6 tuning (Be, Ce, Co, In, Mg, & Pb) for 6020/6020A. And the resolution must be ≤ 0.9 amu at 5% of the peak height for Method 200.8.

10.2.2.4. Mass calibration must be within ± 0.1 amu from the actual value for the

6 tuning elements (Be, Ce, Co, In, Mg, & Pb) or the mass calibration must be adjusted.

10.2.2.5. A "daily" performance check must be performed. This uses the same tuning solution as above. The 6 tuning elements must have RSDs below 5%. The oxides must be below 3.5%. If any of these conditions are not met repairs or optimization procedures must be performed until these specifications are met.

10.2.2.6. Recommended analytical isotopes and additional masses that maybe monitored are given in Table 7. Recommended isotopes and additional masses that may be monitored are given in Table 8.

10.2.3. Initial Calibration

10.2.3.1. Calibration consists of a blank and the following calibration standards (STD1, STD 2X, and STD 3X see Table 2 for concentrations) in accordance with the manufacturer's procedure. Use the average of three integrations for both calibration and sample analyses.

10.2.3.2. Following the STD, STD2X & STD3X, an ICV/ICB pair is analyzed. The ICV must be within ± 10% of the true value to be acceptable.

10.2.3.3. For 6020/6020A, following the ICV/ICB pair, the CRI/RLV is run before the ICSA is analyzed. The CRI/RLV is analyzed again at the end of the sequence.

10.2.3.4. For 6020, 6020A, following the ICSA, analyze the ICSAB. The ICSAB must be within ± 20% of the true value. For method 200.8 ICSA and ICSAB is also analyzed although not required by the method.

10.2.3.5. Internal standards are added to all standards and samples by the instrument automatically prior to analysis.

10.2.4. Continuing Calibration:

10.2.4.1. Following every 10 samples (including lab QC), analyze a CCV/CCB pair. These must be within ± 10% of the true value for analysis to continue. For methods 6020/6020A, a CCV/CCB pair should also be analyzed immediately after the ICSAB.

10.2.4.2. All samples must be bracketed by an acceptable CCV/CCB pair. Where a CCV/CCB fails the samples preceding it back to the last acceptable CCV/CCB must be reanalyzed.

10.2.5. Instrument Set-up

10.2.5.1. Configure the X Series with the standard sample introduction equipment, i.e. a glass concentric nebulizer, glass impact bead spray chamber and a one-piece torch with 1.5mm ID injector tube. A Peltier spray chamber cooling unit is optional. Ensure that the Xi interface cones are fitted. These are standard with the X5 instrument and an

option for the X7. They can be identified as follows:

Xi Sampler - 1.1 mm orifice, no nipple, no holes around the flat circumference

Xi Skimmer - Small pointed skimmer mounted in a copper adapter with two screws

Yellow/orange tab peristaltic pump tubes (6.2.2) should be used for sample and internal standard uptake. Connect the liquid output end of the peristaltic pump tubes to the 1.0 mm (OD) barbed fitting screwed into the Y connector. Note that the barbed fitting may require tightening with a pair of grips to ensure a good fluid-tight seal. The mixed output flow should be connected to the nebulizer. See diagram in Appendix 6 for plumbing schematic. A white/white tab peristaltic pump tube (6.2.3) should be connected to the spray chamber drain outlet at one end and to a tube running into a waste vessel at the other and wound on the pump to draw the waste liquid away from the spray chamber.

10.2.5.2. Perform the daily maintenance as outlined in Appendix 3.

10.2.5.3. Switch the instrument into the *Operate* state by clicking the *ON* button at the top of the screen. During the automated ignition sequence, the following processes occur:

i. Torch purge with argon gas

ii. RF power match

iii. Plasma ignition

iv. Slide valve open

v. Electronics on

This process takes about two minutes. Upon successful ignition, the software will display *Operate* in the *Instrument State* bar. If the event of unsuccessful ignition, the software will display an error message and/or place a message in the *Technician Event Log*. Upon unsuccessful ignition, inspect the sample introduction equipment and torch, ensuring a good gas-seal at each connection and ensuring the torch is not misaligned or damaged. If all appears satisfactory, the ignition may be attempted again. If the ignition process consistently fails, contact your local Thermo service agent for advice.

10.2.5.4. Once the instrument is in the *Operate* state, it should be left for 30 minutes to reach thermal equilibrium prior to starting analytical measurements. The optimization (tuning), performance testing and instrument set-up calibrations may be performed after 15 minutes. Ensure that the peristaltic pump is operated at a default analytical speed of 15%. This is done by clicking on *Instrument*, *Configurations*, *Configuration Editor*, *View Selected Accessories* (network icon),

Peristaltic Pump, *Connect* (chain icon). Set pump speed to 15% using the slider bar and adjust the *Settle Time* to 10 seconds and click on *Apply*. Click *OK* to close the dialogue box.

10.2.5.5. During the initial 15 minutes, the system can be "conditioned" by aspirating the system thoroughly with 2% nitric acid + 1% HCL solution prior to continuing.

10.2.5.6. Instrument tuning (optimization) is performed using a 20 µg/L Tune Solution, aspirated through the sample uptake tube. Optimization may not be necessary from day to day if the sample introduction system and cones have not been adjusted in any way and if the instrument fulfils the performance requirements given below. If the instrument gives performance exceeding the requirements shown below, proceed to 10.2.5.7. Otherwise, tune the instrument manually or using *Autotune* while aspirating 20 µg/L Tune Solution through both the sample and internal standard uptake tubes. *Autotune*, using an appropriately defined sequence is advised (see Appendix 4).

The final conditions must give the following:

^{9}Be	>2000cps
^{115}In	>50000cps
^{208}Pb	>25000cps
^{156}CeO/^{140}Ce	<0.02

If the above criteria are met, proceed to 10.2.5.7. If the above criteria are not met, do not proceed. Check that the tune solution was prepared properly and remake if necessary. If the sensitivity is below the minimum requirement, a new detector plateau may be required (see Appendix 6), the cones may require cleaning (see Appendix 8), or the nebulizer or sample uptake lines may have become blocked or may not be properly clamped on the peristaltic pump. If the CeO/Ce ratio is >0.025, the nebulizer gas flow can be reduced and/or the sampling depth increased, obtaining a corresponding reduction in oxide formation. Recheck the above parameters after taking any remedial action.

10.2.5.7. Save the satisfactory instrument settings by clicking on the disk icon on the Tune page. Note that this is not necessary if Autotune has been used, as the instrument settings are saved automatically (unless manual adjustments have been made after autotuning).

10.2.5.8. Set-up the resolution as described in Appendix 5.

10.2.5.9. Perform a cross-calibration (and mass-calibration and detector voltage setup if required) as explained in Appendix 6. Note that retuning may be

necessary after performing this routine.

10.2.5.10. Aspirate Tune solution and run a *Performance Report* (see Appendix 4) to confirm the mass-calibration, resolution, minimum sensitivity and maximum cerium oxide requirement and to verify instrument stability. The performance report acquires five consecutive one-minute runs and calculates the percentage relative standard deviation (RSD) of the five measurements for each isotope. The RSD of the elemental analytes in the performance report must be <5%. If the performance report passes, proceed to (10.3). If the performance report fails, check:

a. Liquid uptake tubes for kinks or other damage

b. Condition and position of the peristaltic pump tubing

c. Tightness of the peristaltic pump clamp screws (these should be just tight enough to draw liquid through the tube smoothly)

d. Joints of all sample introduction components, ensuring a good seal

e. Nebulizer for blockage

f. Salt deposition on cones

Remedy the above as necessary and repeat the test. Note that retuning may be required if any sample introduction components are adjusted or replaced.

Note: Resolution set-up may require adjustment if the resolution check fails (see Appendix 5). Note that the quadrupole and hexapole bias strongly influence abundance sensitivity (Pole Bias should be kept >+4V and Hexapole Bias <-3V).

If the measured mass position for each mass in the performance report is not within ±0.1 amu of the nominal mass position, a new mass-calibration must be performed (see Appendix 6).

10.3. Sample Analysis

10.3.1. Open the method template by clicking on *Templates* and then <TESTAMERICA PITTSBURGH ICPMS ANALYSIS>. The method template will be opened. This contains all the saved analytical parameters and only the sample list need be amended. For work flow chart refer to Appendix 12.

10.3.2. Go to *Sample List*. This grid contains all the information about calibration, QC and samples to be run. The calibration and QC concentration information is already stored. Enter all unknown samples into the list in the appropriate order below the existing calibration and QC samples by overwriting the sample label fields. Delete any QC samples that do not apply to the required method. (If sample list changes are to be made permanent to the method, save the method as a *Template*, by going to *File*, *Save as Template*. Enter a new name to create an amended method,

or use the same name to overwrite the current one.)

10.3.3. Once all the sample information is added, check the required autosampler positions have been correctly entered. Amend as necessary. To sequentially renumber positions, add the correct position required for the initiation of the sequence and right mouse click on the first correctly numbered cell. A pop-up menu will appear. Select *Renumber autosampler positions* from this. Ensure that all samples have one survey run and 3 main runs and a probe depth of 155mm.

10.3.4. Save the experiment run by clicking on the *File* menu, then *Save as*. Enter the required file name, e.g. *enviro090902* and click *Save*.

10.3.5. To print the sample list, go to *Reports* and check the *Sample List* box. Click the refresh icon. The sample list will be displayed in a printable format. Press the print icon. Note that this can only be done with PlasmaLab version 2.3 and above.

10.4. Loading the Autosampler

10.4.1. Pour the required samples into pre-cleaned 15ml polypropylene test tubes (5.1.4). To avoid contamination, a small amount of the solution to be analyzed can be poured into the tube and then discarded. This will rinse out any residual contamination.

10.4.2. Pour blanks, standards and QCs (positioned in rack 0) into pre-cleaned 50ml polypropylene tubes. To avoid contamination, a small amount of the solution to be analyzed can be poured into the tube and then discarded. This will rinse out any residual contamination. Note that **2% nitric acid** (7.1.4) is used as the calibration blank, ICB, and CCB.

10.4.3. For the **serial dilution** ("L") sample(s), dispense 2.00±0.02 mL of the original sample into a pre-cleaned 15 mL polypropylene test-tube and add 8.00±0.08 mL of 2% nitric acid (7.1.4). Mix well. This is a 5-fold dilution.

10.4.4. Place the tubes for each sample into the appropriate position in the rack according to the sample list. Note that the autosampler works on a two-dimensional grid position system by rack number (0-4). See Appendix 9 for autosampler position map.

10.5. Initiating Analysis

10.5.1. Place the sample probe into the autosampler arm and the internal standard probe into the internal standard solution.

10.5.2. Go to *Instrument*, *Tune* and click on the accessories dialog icon. Click on *Autosampler* and then on the chain icon to connect. The autosampler should initialize. Ensure that the probe is at the correct height by positioning it so that its tip just protrudes through the hole in the bottom of the arm. Click on the *Go to Wash* icon (faucet) to send the probe to the wash station. Ensure that the wash solution is being correctly delivered to the wash station via the peristaltic pump at the rear of the autosampler. Allow at least 2 minutes for the liquid to be delivered to the sample introduction system.

10.5.3. Click on the experiment to be run. Click the *Queue* icon and then *Append* and *OK*. The analysis has now been initiated.

10.5.4. To monitor the progress of the analysis, right-mouse click on the *MS* icon at the bottom-right of the screen and select *Open Service Window* from the pop-up menu. The Service Window hovers over the current application window until moved or closed and displays the current instrument activity. This window is also used **to stop an analysis** if required. This is done by clicking on the ***xQ* icon**.

10.5.5. To view results as they are generated, click on the experiment icon and go to the *Results* tab. Click on the *Refresh* button or the refresh icon (green circular arrows on a page) to calculate the results from the data obtained.

10.5.6. To view calibration plots, click on the *Calibration Data* tab. The calibration for each analyte can be viewed by clicking on the required isotope in the *Analyte* box. Each subsequent set of calibrations (calibration block) can be displayed by selecting the required calibration block from the drop-down combo box, e.g. *FQ Block 1*, *FQ Block 2*, etc. FQ denotes a Fully-Quantitative calibration and SQ denotes a Semi-Quantitative calibration, i.e. a response curve generated from the *FQ* calibrations. The SQ response curve is used to calculate semi-quantitative concentrations if required.

10.5.7. To view data, click on the *Numerical Results* tab. The *Analyte Dilution Conc.* tab is a tabular display of the calculated corrected concentrations for each analyte. These values have been corrected for internal standardization, external drift correction (if used), and dilution (where entered). The *Mass Uncorrected ICPS* tab shows the uncorrected raw data for each measured mass in units of integrated counts per second (ICPS). The *Analyte ICPS* tab shows integrated counts per second data that has been mathematically corrected for blank deduction, internal standardization, drift correction (if used), and dilution (as appropriate). The *Survey* tabs show the data integrated from the survey scan for each sample. Any concentrations displayed in the survey page will be semi-quantitative only.

10.5.8. To edit the amount of data on screen (filter the results display), click on the filter icon (funnel and lightening). Alter the numerical values or the check boxes to select the required data to display and click on *OK*. To jump directly to a particular sample of interest, find the sample in the drop-down combo box at the top of the data display and click on it.

10.5.9. To display mass-spectra, click on the *Spectra* tab. Display the spectrum for a particular sample by double-clicking on the sample name in the selection box on the left of the screen. Note that several spectra may be overlaid by double-clicking on each sample to be displayed. To zoom into a particular area, click the zoom icon (magnifying glass) and click and drag on the spectral display to zoom into the required area. The dashed-lines represent data acquired in the analogue mode of the detector whilst the solid-lines represent pulse-count data. To remove the noise associated with analogue detection at low signal levels, point at the display and right-mouse click to bring up a menu. Go to *View Options* and then click on *Eliminate Analogue Noise*. To identify a peak, click on it and wait for the options for

that mass to be displayed in the box above the spectral display. To fingerprint a spectrum, double click on the species to fingerprint in the options box. This will overlay the isotopic pattern for the selected species, based on the lowest relative intensity signal for the pattern masses. The spectra may be navigated by using the arrow buttons above the display. Allow the arrow cursor to hover over each button for an on-screen explanation of its function.

10.6. Post-Analysis Data Processing

10.6.1. Internal Standards

10.6.1.1. Check the internal standard recovery percentage for each internal standard isotope used for every sample. The percentage for each isotope must be within the range 30-120% for method 6020, 70 – 120% for method 6020A and 60 – 125% for method 200.8.

10.6.1.2. If above 120%, check that the other internal standard isotopes show similar deviation. If not, this may be due to the presence of the internal standard element in the sample. This is particularly common with the isotopes of Li, Sc and Y in environmental materials. If this is the case, the affected internal standard isotope may be excluded for the sample affected, as follows. Go to the *Sample List*.

Find the sample affected and select it in the list by clicking on the box in the left-hand column. Click *Show Advanced* and go to *Internal Standards*. Click on *New Internal Standard Set*. Select the affected isotope(s) in the *Internal Standards* box on the right. Remove the affected isotope from the *Internal Standards* box by using the left hand arrow button (<<). Recalculate the results for this sample by going back to *Results* and clicking on *Refresh*.

10.6.1.3. If any internal standard isotope is outside the range 30-120% and all other internal standard isotopes show similar values for that sample, the instrument may have drifted, or the sample may be producing a suppression or enhancement effect. Find the nearest blank following the sample in question and check its internal standard results. If these are similarly reduced or elevated, the instrument has drifted and the samples must be reanalyzed from the last compliant blank. If the blank does not exhibit similar drift, the sample must be producing a suppression or enhancement effect due to its matrix. In this case the sample must be re-analyzed after a five-fold (1+4) for CLP or a ten-fold (1+9) dilution for 6020/6020A to reduce the matrix effect.

10.7. General protocols

10.7.1. 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 shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the

client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

10.7.3. An analytical run will consist of all customer samples and quality control samples analyzed under a daily initial calibration. Each new initial calibration will begin a new analytical run.

10.7.4. Type in the QC and sample information into the autosampler table.

10.7.5. In order to use the ICP-MS data upload program into LIMS, the following naming conventions must be followed:

- Samples are identified by the 5-character work order number
- Matrix spikes, duplicates, and matrix spike duplicates are identified by the 5-character work order number followed by S (matrix spike), D (matrix spike duplicate) or X (sample duplicate).
- Prep Blanks are identified by the 5-character work order number followed by B.
- LCSs are identified by the 5-character work order number followed by C (LCS) or L (LCS Duplicate).

10.8. Initial Calibration

10.8.1. Open a new dataset using the date and instrument in the title. For instance the first run (A) on instrument 2 on JAN 1, 2003 would be X30101A.

10.8.2. Open the appropriate method if one already exists or create a new one for the analytes to be quantitated in the run. Solicit the assistance of a senior ICP-MS operator in creating a new method.

10.8.3. See Tables 7, 8, and 9 for recommended isotopes and interference equations for commonly analyzed elements.

10.8.4. If no recommended isotopes are given for the element to be analyzed, consult a senior ICP-MS operator or appropriate reference.

10.8.5. See Table 10 for commonly used internal standards.

10.8.6. All masses which could affect data quality should be monitored to determine potential interferences either simultaneously during an analytical run or in a separate scan.

10.8.7. Internal standards are added to all standards and samples by the instrument prior to analysis.

10.8.8. Use of an existing autosampler table is suggested. A read delay of 45 to 60 seconds is used between all analyses.

10.8.9. Calibration consists of a blank and a single calibration standard (STD1, see Table 2 for concentrations) in accordance with the manufacturer's procedure. Use the

average of three integrations for both calibration and sample analyses.

10.9. The order of analysis for the initial QC samples and calibration should be:

1. Rinse
2. Performance Report (Tune Check)
3. STD1 (Calibration Standard)
4. STD2 (2x Calibration Standard)
5. STD3 (3X Calibration Standard)
6. ICV (Second source, must be ± 10% of true value)
7. ICB
8. CRI / RLV/LLICV (Reporting Limit Verification Standard)
9. ICSA (Interference check solution.)
10. ICSAB (Interference check solution, ± 20% of true value)
11. CCV
12. CCB
13. Prep QC such as LCS or MB, followed by samples (up to 10 runs)
14. Rinse
15. CCV
16. CCB
17. CRI / RLV/LLCCV (Method 6020A only at the end of the analytical sequence)
18. CCV
19. CCB

10.9.1. To continue the analytical run, add an additional 10 runs followed by a rinse and CCV/CCB, and repeat for up to 24 hours.

10.9.2. Analysis sequence when out-of-control QC is observed: Recalibrate and rerun all affected samples (including initial QC)

11. CALCULATIONS / DATA REDUCTION

11.1. All pertinent calculations are performed by the Plasma LAB software. Elemental equations used to calculate results are given in Table 9.

11.2. Reporting Requirements

11.2.1. Units are ug/L or mg/L for aqueous samples and mg/kg for soil samples and ug/wipe for wipe samples.

11.2.2. If dilutions were required due to insufficient sample, interferences, or other problems, the laboratory reporting limits are multiplied by the dilution factor.

11.2.3. For results less than 10, two significant figures will be reported. For results greater than or equal to 10, three significant figures will be reported. Refer to SOP PT-QA-009 for additional information on significant figures and rounding.

11.2.4. Document any non-standard procedures or anomalies by using the anomaly program (Clouseau).

11.3. Data Package Requirements

11.3.1. A complete data package consists of: the daily tuning package, the method printout, run log, internal standard summary for 5.2 only, standards documentation, level 1 checklist, and all raw data.

11.3.2. Level I review will be completed by the analyst.

11.3.3. Level II review will be completed by a senior level laboratory analyst familiar with the technical aspects of ICP-MS and in accordance with the ICP-MS DATA REVIEW checklists. The instrument operator of an analytical run may not perform the Level II review for that run.

12. METHOD PERFORMANCE

Prior to analysis of any analyte using Method 6020/6020A, the following requirements must be met.

12.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. MDL's must be determined as detailed in SOP PT-QA-007 and in 40 CFR Part 136 Appendix B.

12.1.1. On occasion, a non-routine analyte is requested by the client. In lieu of a full MDL study, a standard containing the non-routine analyte must be analyzed. The concentration of the standard must correspond to the reporting limit or ½ the reporting limit. This is to verify that the method can satisfactorily quantify the element near the chosen reporting limit. The recovery of the standard must be between 50% and 150% of the expected value. The standard analysis should be kept with the analytical data.

12.1.2. For new analytes an MDL study should be performed and calibration curve generated before analyzing any samples.

12.2. Initial Demonstration of Capability

12.2.1. For the standard analyte list, the initial demonstration IDOC and method detection limit (MDL) studies described above must be acceptable before analysis of samples may begin.

12.2.2. For the standard analyte list, the initial demonstration consists of the preparation and analysis of four LCS samples containing all of the standard analytes for the

method, as well as a method detection limit (MDL) study (described below).

12.2.3. Four LCS samples are analyzed with the same procedures used to analyze samples, including sample preparation.

12.2.4. The mean recovery and standard deviation are calculated for each analyte of interest. These results are compared with the established or project-specific acceptance criteria. All four results must meet acceptance criteria before the method can be used to analyze samples. For further detail refer to SOP PT-QA-001. .

12.2.5. Control Limits

12.2.6. The following control limits are utilized for matrix spikes and laboratory control samples (LCS). These limits must be reviewed at least annually against current data.

QC Type	200.8	6020/6020A
LCS	85 – 115	80 – 120
MS	70 – 130	75 – 125
RPD	± 20	± 20

12.2.7. All LCS and MS recoveries must be entered into QuantIMS or other database so that accurate historical control charts can be generated. For tests without a separate extraction, matrix spikes will be reported for all dilutions.

12.2.8. Refer to the QC program document (PT-QA-021) for further details regarding control limits.

12.3. Training Qualification

12.3.1. 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.

12.4. Instrumentation Detection Limit (IDL) 6020 – IDL for each analyte must be determined for each analyte wavelength used on each instrument. The IDL must be determined quarterly for method 6020/6020A for the standard analytes listed in Appendix A. For method 200.8 IDLs will be determined annually. If the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be redetermined.

12.4.1. For 6020 the IDLs shall be determined by performing a blank analysis on 3 non-consecutive days with 7 consecutive measurements per day. The IDL is calculated by summing the standard deviations of the measurements from each day. For 200.8 the IDL is determined by performing 10 replicate blank analysis and multiplying the resulting standard deviation by 3.

12.4.2. Each measurement must be performed as though it were a separate analytical sample.

12.4.3. Each measurement must be followed by a rinse and/or any other procedure normally performed between the analyses of separate samples.

12.4.4. The IDL measurement must consist of the same number of replicates used for analytical samples with the average result used for reporting.

12.4.5. **DoD samples cannot be analyzed without a valid IDL.**

12.4.6. **For DoD, the established IDL must be less than the MDL (see below) for each analyte.**

12.5. Instrument detection limits (IDLs) 6020A – IDLs are useful means to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limit of quantitation, nor should they be used in establishing this limit. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation, however, it should be understood that the lower limit of quantitation needs to be verified according to the guidance in Section 9.2.6.

12.5.1. IDLs in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least every three months.

12.6. Linear Range Verification (LR) - The linear range is determined semi annually (2x/year) for each element on the standard list. Some regulatory programs, such as AFCEE, may require more frequent determinations.

12.6.1. To determine the linear range, analyze 3 standards at increasing concentration up to 90% of the last concentration where the element was within 10% of true value is considered the upper linear range.

12.6.2. An alternative is to prepare a higher concentration standard and run this in the analytical run. If this standard is within 10% of the expected value this value can be used as the upper linear range. If this option is chosen, then note the action in an anomaly.

13. POLLUTION CONTROL

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention.""

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1. Acid waste consisting of sample and rinse solution. This waste is collected in waste containers identified as “Acid Waste”, Waste #33. It is neutralized to a pH between 6 and 9 and then discharged down a lab sink.

14.1.2. Expired Metals Standards. This waste is collected in waste containers identified as “Acid Waste with Metals”, Waste #6.

15. REFERENCES

15.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update III, Method 6020, Inductively Coupled Plasma – Mass Spectrometry, Revision 0, September, 1994.

15.2. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW846, 3rd Edition, Final Update IV, Method 6020A, Inductively Coupled Plasma – Mass Spectrometry, Revision 1, February, 2007.

15.3. Thermo Electron X Series Users Manual

15.4. EPA Method 6020 CLP M, Version 8.

15.5. Methods for the Determination of Metals in Environmental Samples, Supplement 1 (EPA/600/R-94/111), Method 200.8, Determination of Trace Elements in Waters by Inductively Coupled Plasma - Mass Spectrometry, Revision 5.4, 1994

15.6. EPA Method 200.8 EMSL Office of Research & Development, Cincinnati, OH (Draft Method, Revision 4.3, August 1990).

15.7. SOP PT-QA-001, Employee Orientation and Training, current version.

15.8. SOP PT-HS-001, Waste Collection, Accumulation and Storage, current version.

15.9. SOP PT-QA-006, Procurement of Standards and Materials; Labelling and Traceability, current version.

15.10. SOP PT-QA-007, Method Detection Limits.

15.11. SOP PT-QA-009, Rounding and Significant Figures.

15.12. SOP PT-QA-011, Data Recording Requirements, current version.

15.13. SOP PT-QA-015, Maintaining Time Integrity, current version.

15.14. SOP PT-QA-016, Nonconformance & Corrective Action System, current version.

15.15. SOP PT-QA-018, Technical Data Review Requirements, current version.

15.16. SOP PT-QA-021, TestAmerica Pittsburgh QC Program, current version.

15.17. SOP PT-QA-022, Equipment Maintenance, current version.

15.18. SOP PT-QA-024, Subsampling, current version.

15.19. SOP PT-QA-025, Implementation of the DoD QSM Version 3.

15.20. SOP PT-QA-027, Sample Receiving and Chain of Custody, current version.

15.21. SOP PT-QA-029, DoD QSM Version 4.1/4.2 Requirements, current version.

15.22. PT-LQAM, Pittsburgh Laboratory Quality Assurance Manual, current version.

16. METHOD MODIFICATIONS

16.1. Not applicable.

17. ATTACHMENTS

Table 1 – Standard Analyte List and Reporting Limits

Table 2 – Composition of the CAL Standard

Table 3 – Composition of the ICV Standard

Table 4 – Composition of the ICSA Standard

Table 5 – Composition of the ICSAB Standard

Table 6 – Common Molecular Ion Interferences in ICP-MS

Table 7 – Recommended Analytical Isotopes And Additional Masses That May Be Monitored

Table 8 – Recommended Isotopes And Additional Masses That May Be Monitored

Table 9 – Elemental Equations Used To Calculate Results

Table 10 – Internal Standards And Limitations Of Use

Table 11 – High Level Calibration Standard

Appendix 1 Cleaning Procedure for Glass- and Plastic-ware

Appendix 2 Wash Solution Preparation Instructions

Appendix 3 Daily Instrument Maintenance

Appendix 4 Autotune and Performance Reports

Appendix 5 Resolution Setup

Appendix 6 Instrument Calibrations

Appendix 7 Sample Introduction Plumbing Diagram
Appendix 8 Procedure for Cleaning Sample Introduction Equipment and Cones
Appendix 9 Autosampler Position Map
Appendix 11 Spiking Levels
Appendix 12 Work Flow Chart
Appendix 13 QC Abbreviations and Criteria

18. REVISION HISTORY

18.1. Revision 5, 5/19/08:

18.1.1. Renamed SOP as PT-MT-002.

18.1.2. Changed SOP format to correspond to corporate SOP format.

18.1.3. Corrected several typographical errors and incorrect Section references.

18.1.4. All changes have been highlighted throughout the document.

18.1.5. Updated SOP References

18.1.6. Corrected As and Ni RLs for water and soil.

18.2. Revision 6:

18.2.1. Updated to method 6020A requirements. Changes are highlighted.

18.2.2. Added to section 8: Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

18.2.3. Revised Appendix 13. Corrected typos and added QC criteria for applicable method requirements. Added cross references to tables and appendices.

18.3. Revision 7:

18.3.1. Added to Section 9.2.6: For method 6020A the CRI which is the low level quantitation check sample is prepared and analyzed quarterly or as needed. The control limit is 70-130%. Please note the CRI (undigested) is still analyzed at the beginning and end of the analytical run. Updated Appendix 13.

18.3.2. Added reference to SOP PT-QA-029.

18.4. Revision 9:

18.4.1.1. Added to section 6.3. Refer to Section 20 of PT-LQAM for instrument hardware/software specifications and routine instrument maintenance procedures

18.4.1.2. Added high level CCV requirements for DoD in section 9.2.8: A high level calibration standard is analyzed after the ICSAB before any client

samples are analyzed. This standard is analyzed once for a run. The percent recovery must be within 90-110%. If not the instrument is recalibrated and instrument QC along with high level calibration standard is reanalyzed before any samples can be analyzed. Sample concentration greater than high level calibration standard for analytes listed in Table 11 will be diluted. For analytes not included in high level calibration standard, Table 11, dilutions will be determined based on instrument calibration standard, Table 2. This was also added to Appendix 13.

18.4.1.3. Added Table VIII, high level CCV for DoD.

18.4.1.4. Replaced DoD V4.1 with DoD QSM 4.1/4.2 or current version.

18.4.1.5. Removed references to CLP ILM05.2.

18.4.1.6. Deleted from section 9.2.1: The Linear Range study must be performed quarterly if doing ILM05.2.

18.4.1.7. Deleted from section 10.2.2.3: Resolution must be ≤ 0.75 amu at 5% of the peak height for ILM05.2.

18.4.1.8. Deleted ILMO5.2 requirement from the table in section 12.2.6:

QC Type	ILM05.2
LCS	80 – 120
MS	75 – 125
RPD	± 20

18.4.1.9. Removed Appendix 10 ILM05.2D Contract Required Quantitation Limits (CRQLs).

Tables:

TABLE 1								
STANDARD ANALYTE LIST AND REPORTING LIMITS*								
Element	**Symbol**	**CAS #**	**Aqueous RL mg/L**	**Aqueous QC SPIKE mg/L**	**Soil/Tissue RL mg/Kg**	**Soil/Tissue QC SPIKE mg/kg**	**Wipe RL ug/wipe**	**Wipe QC SPIKE ug/wipe**
Aluminum	Al	7429-90-5	0.03	2.0	3.0	200	1.5	100
Antimony	Sb	7440-36-0	0.002	0.50	0.2	50	0.1	25
Arsenic	As	7440-38-2	0.001	0.04	0.1	4	0.05	100
Barium	Ba	7440-39-3	0.010	2.0	1.0	200	0.5	100
Beryllium	Be	7440-41-7	0.001	0.05	0.1	5	0.05	2.5
Boron	B	7440-42-8	0.005	1.0	0.5	100	0.25	50
Cadmium	Cd	7440-43-9	0.001	0.05	0.1	5	0.05	2.5
Calcium	Ca	7440-70-2	0.10	50	10.0	5000	5.0	2500
Chromium	Cr	7440-47-3	0.002	0.2	0.2	20	0.1	10
Cobalt	Co	7440-48-4	0.0005	0.5	0.05	50	0.025	25
Copper	Cu	7440-50-8	0.002	0.25	0.2	25	0.1	12.5
Iron	Fe	7439-89-6	0.05	1.0	5.0	100	2.5	50
Lead	Pb	7439-92-1	0.001	0.02	0.1	2	0.05	25
Magnesium	Mg	7439-95-4	0.10	50	10.0	5000	5.0	2500
Manganese	Mn	7439-96-5	0.0005	0.5	0.05	50	0.025	25
Molybdenum	Mo	7439-98-7	0.005	1.0	0.5	100	0.25	50
Nickel	Ni	7440-02-0	0.001	0.5	0.1	50	0.05	25
Potassium	K	7440-09-7	0.100	50	10.0	5000	5.0	2500
Selenium	Se	7782-49-2	0.005	0.01	0.5	1	0.25	100
Silver	Ag	7440-22-4	0.001	0.05	0.1	5	0.05	2.5
Sodium	Na	7440-23-5	0.10	50	10.0	5000	5.0	2500
Strontium	Sr	7440-24-6	0.005	1.0	0.5	100	0.25	50

TABLE 1								
STANDARD ANALYTE LIST AND REPORTING LIMITS*								
Element	**Symbol**	**CAS #**	**Aqueous RL mg/L**	**Aqueous QC SPIKE mg/L**	**Soil/Tissue RL mg/Kg**	**Soil/Tissue QC SPIKE mg/kg**	**Wipe RL ug/wipe**	**Wipe QC SPIKE ug/wipe**
Tin	Sn	7440-31-5	0.005	2.0	0.5	200	0.25	100
Titanium	Ti	7440-03-26	0.005	1.0	0.5	100	0.25	50
Thallium	Tl	7440-28-0	0.001	0.05	0.1	5	0.05	100
Vanadium	V	7440-62-2	0.001	0.5	0.1	50	0.05	25
Zinc	Zn	7440-66-6	0.005	0.5	0.5	50	0.25	25

** Note: These are the routine reporting limits for most sample types. Lower reporting limits may be achievable for special projects. Difficult sample matrices may cause reporting limits to be raised.*

TABLE 2			
Composition of the Calibration Standards			
Element	**Concentration ug/mL**	**Element**	**Concentration ug/mL**
Ag	0.200	Mn	1.0
Al	1.00	Mo	0.200
As	0.200	Na	100
B	0.200	Ni	0.200
Ba	0.200	Pb	0.200
Be	0.200	Sb	0.200
Ca	100	Se	0.200
Cd	0.200	Si	10
Co	0.200	Sn	0.200
Cr	0.200	Sr	0.200
Cu	0.200	Ti	0.200
Fe	50	Tl	0.200
K	100	V	0.200
Mg	100	Zn	0.200

TABLE 3 Composition of the ICV Standard			
Element	Concentration ug/mL	Element	Concentration ug/mL
Ag	0.08	Mn	0.4
Al	0.4	Mo	0.08
As	0.08	Na	40
B	0.08	Ni	0.08
Ba	0.08	Pb	0.08
Be	0.08	Sb	0.08
Ca	40	Se	0.08
Cd	0.08	Si	4.0
Co	0.08	Sn	0.08
Cr	0.08	Sr	0.08
Cu	0.08	Ti	0.08
Fe	20	Tl	0.08
K	40	V	0.08
Mg	40	Zn	0.08

TABLE 4 Composition of the ICSA Standard			
Element	Concentration ug/mL	Element	Concentration ug/mL
Al	100	P	100
Ca	100	S	100
Fe	100	C	200
K	100	Cl^-	1000
Mg	100	Mo	2.0
Na	100	Ti	2.0

TABLE 5
Composition of the ICSAB Standard

Element	Concentration ug/mL	Element	Concentration ug/mL
Ag	0.02	Na	100
Al	100	Ni	0.02
As	0.02	Pb	0.02
B	0.05	Sb	0.02
Ba	0.02	Se	0.05
Be	0.02	Si	0.50
Ca	100	Sn	0.10
Cd	0.02	Sr	0.02
Co	0.02	Ti	2.0
Cr	0.02	Tl	0.02
Cu	0.02	V	0.02
Fe	100	Zn	0.025
K	100	P	100
Mg	100.0	S	100
Mn	0.0225	C	200
Mo	2.00	Cl-	1000

TABLE 6[1]

COMMON MOLECULAR ION INTERFERENCES IN ICP-MS

Molecular Ion	Mass	Element	Molecular Ion	Mass	Element
BACKGROUND MOLECULAR IONS					
NH^+	15		$^{38}ArH^+$	39	
OH^+	17		$^{40}ArH^+$	41	
OH_2^+	18		CO_2^+	44	
C_2^+	24		CO_2H^+	45	Sc
CN^+	26		ArC^+, ArO^+	52	Cr
CO^+	28		ArN^+	54	Cr
N_2^+	28		$ArNH^+$	55	Mn
N_2H^+	29		ArO^+	56	
NO^+	30		$ArOH^+$	57	
NOH^+	31		$^{40}Ar^{36}Ar^+$	76	Se
O_2^+	32		$^{40}Ar^{38}Ar^+$	78	Se
O_2H_+	33		$^{40}Ar_2^+$	80	Se
$^{36}ArH^+$	37				
MATRIX MOLECULAR IONS – Chloride					
$^{35}Cl0^+$	51	V	$^{37}Cl0H^+$	54	Cr
$^{35}Cl0H^+$	52	Cr	$^{35}Cl0^+$	51	V
$^{37}Cl0^+$	53	Cr	$^{35}Cl0H^+$	52	Cr
$Ar^{35}Cl^+$	75	As	$Ar^{37}Cl^+$	77	Se
MATRIX MOLECULAR IONS – Sulfate					
$^{32}SO^+$	48		$^{34}SOH^+$	51	V
$^{32}SOH^+$	49		SO_2^+, S_2^+	64	Zn
$^{34}SO^+$	50	V, Cr			
$Ar^{32}S^+$	72		$Ar^{34}S^+$	74	
MATRIX MOLECULAR IONS – Phosphate					
PO^+	47		PO_2^+	63	Cu
POH^+	48				
ArP^+	71				
MATRIX MOLECULAR IONS – Group I, II Metals					
$ArNa^+$	63	Cu	$ArCa^+$	80	
ArK^+	79				
MATRIX OXIDES[3]					
TiO	62-66	Ni. Cu. Zn	MoO	108-116	Cd
ZrO	106-112	Ag, Cd			

[1] *From Method 200.8, Section 13.2.6*
[2] *Method elements or internal standards affected by the molecular ions.*

[3]Oxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides are listed of which the analyst should be aware. It is recommended that Ti and Zr isotopes be monitored in solid waste samples, which are likely to contain high levels of these elements. Mo is monitored as a method analyte.

TABLE 7 RECOMMENDED ANALYTICAL ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED [1]			
Isotope	Element of Interest	Isotope	Element of Interest
27	Aluminum [2]	80,**78**,**82**,**76**,**77**,74	Selenium
121,123	Antimony [2]	**107**,**109**	Silver [2]
75	Arsenic [2]	**23**	Sodium [2]
138,**137**,136,**135**,134,132,130	Barium [2]	203, **205**	Thallium [2]
9	Beryllium [2]	**51**,**50**	Vanadium [2]
114,112,**111**,110,113,116,106,**108**	Cadmium [2]	**66**, **68**	Zinc [2]
42,**43**,**44**,46,48	Calcium [2]	83	Krypton
52,**53**,**50**,54	Chromium [2]	72	Germanium
59	Cobalt [2]	139	Lanthanum
63,**65**	Copper [2]	140	Cerium
56,**54**,**57**,58	Iron [2]	129	Xenon
206,207,**208**	Lead [2]	**118**	Tin
24,**25**,**26**	Magnesium [2]	105	Palladium
55	Manganese [2]	47,**49**	Titanium
98,96,92,97,94,95	Molybdenum	125	Tellurium
58,**60**,62,**61**,64	Nickel [2]	69	Gallium
39	Potassium [2]	35,37	Chlorine

[1] *From Method 6020 CLP-M, Table 9*

[2] *Element approved for ICP-MS determination by SW846 Method 6020 CLP-M*

NOTE: Isotopes recommended for analytical determination are **bolded**.

TABLE 8			
RECOMMENDED ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED			
Rare Earth Elements	**ICPMS Preferred Mass**	**Elemental Equations**	**Additional Masses**
Lanthanum	138.906		
Cerium	139.905		
Praseodymium	140.907		
Neodymium	141.908	-0.125266 * ^{140}Ce	142.910, 144.912
Samarium	151.920	-0.012780 * ^{157}Gd	144.912
Europium	152.929		
Gadolinium	157.924	-0.004016 * ^{163}Dy	156.934
Terbium	158.925		
Dysprosium	163.929	-0.047917 * ^{166}Er	
Holmium	164.930		
Erbium	165.930		
Thulium	168.934		
Ytterbium	173.939	-0.005935 * ^{178}Hf	171.937
Lutetium	174.941		

TABLE 8A			
RECOMMENDED ISOTOPES AND ADDITIONAL MASSES THAT MAY BE MONITORED			
Rare Earth Elements			
Other Elements			
Boron	11.009		
Calcium	43.956		
Cesium	132.905		
Galium	68.926		
Germanium	71.922		
Gold	196.967		
Hafnium	177.944		176.944
Holmium	164.930		
Iridium	192.963		
Lithium	7.016		
Tungsten	183.951	-0001242* ^{189}Os	
Uranium	238.050		
Yttrium	88.905		
Zirconium	238.050		
Niobium	92.906		
Palladium	104.905		
Phosphorus	30.994		
Platinum	194.965		
Rhenium	186.965	-0.099379 * ^{189}Os	
Rhodium	102.905		
Rubidium	84.912		
Ruthenium	101.904	-0.045678 * ^{105}Pd	
Scandium	44.956		
Strontium	87.906		
Tantalum	180.948		
Tellurium	127.905	-0.072348 * ^{129}Xe	
Thorium	232.03		

TABLE 9

ELEMENTAL EQUATIONS USED TO CALCULATE RESULTS

Element	Elemental Equation	Note
Al	(1.000) (^{27}C)	
Sb	(1.000) (^{121}C)	
As	(1.000) (^{75}C) - (3.1278)[^{77}C) - (1.0177)(^{78}C)]	Correction for chloride interference with adjustment for Se77. ArCl 75/77 ratio may be determined from the reagent blank.
Ba	(1.000) (^{137}C)	
Be	(1.000) (^{9}C)	
Cd	(1.000) (^{111}C) - (1.073) [(^{108}C) - (0.712) (^{106}C)]	Correction of MoO interference. An additional isobaric elemental correction should be made if palladium is present.
Cr	(1.000) (^{52}C)	In 0.4% v/v HCl, the background from ClOH will normally be small. However the contribution may be estimated from the reagent blank.
Co	(1.000) (^{59}C)	
Cu	(1.000) (^{63}C)	
Pb	(1.000) (^{206}C) + (1.000) (^{207}C) + (1.000) (^{208}C)	Allowance for isotopic variability of lead isotopes.
Mn	(1.000) (^{55}C)	
Mo	(1.000) (^{98}C) - (0.146) (^{99}C)	Isobaric elemental correction for ruthenium.
Ni	(1.000) (^{60}C)	
Se	(1.000) (^{82}C)	Some argon supplies contain krypton as an impurity. Selenium is corrected for Kr82 by background subtraction.
Ag	(1.000) (^{107}C)	
Tl	(1.000) (^{205}C)	
Th	(1.000) (^{232}C)	
U	(1.000) (^{238}C)	
V	(1.000) (^{51}C) - (3.127) [(^{53}C) - (0.113) (^{52}C)]	Correction of chloride inference with adjustment for Cr53. Cl0 51/53 ratio may be determined from the reagent blank.
Zn	(1.000) (^{66}C)	
Internal Standards		

TABLE 9 ELEMENTAL EQUATIONS USED TO CALCULATE RESULTS		
Bi	(1.000) (^{209}C)	
In	(1.000) (^{115}C) -(0.0149) (^{118}C)	Isobaric elemental correction for tin.
Ge	(1.000) (^{72}C)	
Sc	(1.000) (^{45}C)	
Tb	(1.000) (^{159}C)	
Tm	(1.000) (^{169}C)	
Y	(1.000) (^{89}C)	

* Method elements or internal standards affected by the molecular ions. C = Calibration blank subtracted counts at specified mass.

TABLE 10 INTERNAL STANDARDS AND LIMITATIONS OF USE		
Internal Standard	Mass	Possible Limitation
Lithium	6	a
Scandium	45	Polyatomic Ion Interference
Germanium	72	
Yttrium	89	a, b
Rhodium	103	
Indium	115	Isobaric Interference by Sn
Terbium	159	
Holmium	165	
Thulium	169	
Lutetium	175	
Bismuth	209	a

a May be present in environmental samples.

b In some instruments Yttrium may form measurable amounts of YO^+ (105 amu) and YOH^+ (106 amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.

Table 11	
High Level Calibration Standard for DoD	
Element	**Concentration Mg/L**
Al	500
Ba	15
Ca	1000
Cr	20
Cu	20
Fe	500
K	300
Mg	1000
Mn	20
Na	500
Pb	20
Zn	20

Appendices

Appendix 1

Cleaning Procedure for Glass- and Plastic-ware

All glassware and plastic-ware coming into contact with samples, reagents and standards must be cleaned in the following manner. Plastic pipette tips may be cleaned in the same manner by soaking them in a suitable plastic container.

1) Completely fill the container to be leached with 10% nitric acid solution (6.1.5) and fit the lid.
2) Leave soaking for at least 12 hours.
3) Empty the container of acid and rinse thoroughly with laboratory water (6.1.1). Note that the acid may be collected and re-used until it becomes too contaminated.
4) Allow the vessel to air-dry in a clean area (preferably Class-1000 or better). If no such clean area is available, the container should be allowed to dry in the cleanest possible environment, or may be emptied of residual water as much as is possible and re-capped.
5) Containers should be capped ready for use and stored in the cleanest area available.
6) If pre-cleaned containers are to be stored for long periods (weeks to months) prior to use, it is most effective to store them full of laboratory water (6.1.1). This must be discarded and the containers rinsed thoroughly with laboratory water (6.1.1) and dried before use.

Appendix 2

Wash Solution Preparation Instructions (2% Nitric Acid (v/v))

A large volume of this solution is required for supply to the autosampler rinse station in order to wash the probe between samples. These instructions detail the preparation procedure for 2.5 L of this solution that is normally sufficient for one day of analytical use. The procedure may be scaled up or down as required.

1) Into a 2.5 L container (pre-cleaned as per Appendix 1), add 500±450 mL of laboratory water (6.1.1)
2) Add 50±10 mL of concentrated nitric acid (6.1.3)
3) Make to 2.50±0.25 L with laboratory water (6.1.1)
4) Mix well

Notes:

If preparing larger quantities simply scale-up quantities proportionally.

If analyzing for Ag, add hydrochloric acid at 1% by adding 50±10 mL of concentrated hydrochloric acid (6.1.2) after step 2.

Appendix 3

Daily Instrument Maintenance

1) Wipe all instrument, autosampler and surrounding bench surfaces with a damp wipe – continual cleanliness is important for the minimization of contamination
2) Check Wash Solution volume and remake if necessary (see Appendix 2)
3) Empty Waste Vessel according to laboratory disposal policy
4) Check the condition of all peristaltic pump tubes and replace if required (it is recommended to replace these daily although this may not be necessary with lower sample loads)
5) Check condition of sample introduction system and cones and clean and/or replace as necessary (see Appendix 8)
6) Ensure instrument fume-extraction system is operational

Appendix 4

Autotune and Performance Reports

Description

Autotune is a *PlasmaLab* software tool that allows the X Series to be optimized in a consistent, routine manner, giving reproducible levels of performance and saving the operator time and effort. It works by following a pre-defined sequence, optimizing individual instrument parameters in turn. Default sequences are provided with the software upon installation and a further customized sequence is provided on the CD accompanying this productivity pack.

Performance Reports are a *PlasmaLab* software tool that allows the X Series performance to be checked on a daily basis. The *Performance Report* can be set-up to give information about instrument sensitivity, stability, background, oxide species, doubly charged species, mass-calibration validity and peak resolution. Like *Autotune*, the *Performance Report* is user definable but defaults are provided with the software. Customized *Performance Reports* are provided on the CD accompanying this package.

The philosophy of use of these tools is as follows. After the sample introduction system or the cones have been removed and replaced or upon using the instrument for the first time or following major adjustments, the full *Autotune* sequence should be used to properly optimize the system. This takes about 15 minutes. From this, an *Autotune Update* sequence can be automatically created. This is a shortened version of the optimization sequence and will take about 5 minutes to run. The performance of the X Series is, in general, very stable from day-to-day, meaning that large amounts of optimization are not normally needed on a daily basis. To check whether optimization is needed, a *Performance Report* can be run initially. The results of this tell the operator if the system requires resolution adjustment, re-mass-calibration, or re-optimization. If the required sensitivity, background, stability or oxide performance is not satisfied, an *Autotune* should be run (the faster *Autotune Update* is normally sufficient). The *Performance Report* should then be repeated to ensure that the problem has been resolved.

Installing the EPA Autotune Sequence

To install the custom Autotune sequence, follow the instructions below:

1) Insert the CD in the CD ROM drive of the instrument operating PC. Wait for it to autorun and install the Productivity Pack by following the prompts after clicking on *Install*.
2) Ensure that PlasmaLab version 2.2 (or higher) has been installed
3) In PlasmaLab, go to *Instrument*, *Tune* and click on the down arrow button next to the *Autotune* icon (musical note).
4) Point to *Tools* in the menu and then select *Import Autotune Sequences*

5) Click *Next* in the Autotune Wizard
6) Click on *Browse* and find the path

C:/Program Files/ThermoElemental/PlasmaLab/Data

7) Select *EPA Autotune Sequence* and click on *Open*
8) Click on *Next*
9) Select *EPA – Xi Interface* and click on *Next*
10) Click on *Finish*

Installing the EPA Performance Reports

To install the custom Performance Reports, follow the instructions below:

1) Ensure the Pack is installed from the CD as described above
2) Ensure that PlasmaLab version 2.2 (or higher) has been installed
3) In PlasmaLab, go to *Instrument*, *Tune* and click on the down arrow button next to the *Performance Report* icon (musical note on page).
4) Point to *Tools* in the menu and then select *Import Performance Report*
5) Click *Next* in the Performance Report Wizard
6) Click on *Browse* and find the path for the CD ROM drive

   C:/Program Files/ThermoElemental/PlasmaLab/Data

7) Select *EPA 6020 Report* and click on *Open*
8) Click on *Next*
9) Select *EPA 6020 2.1* and click on *Next*
10) Click on *Finish*

To install the second Performance Report, follow instructions 1) to 10) above, selecting the alternative Performance Report name, i.e. *EPA ILM05_2D Report*.

Running Autotune from the Tune Page

To run an Autotune Sequence, follow the instructions below:

1) In PlasmaLab go to *Instrument*, *Tune* and click on the *Autotune* icon (musical note)
2) Select *Run an Existing Autotune Sequence* and click on *Next*
3) Select the required sequence, e.g. *EPA Xi Interface*, or *EPA Xi Interface – Update* and click on *Next*

4) Ensure that the indicated solution is being aspirated (through both probes if on-line internal standard addition is being used) and allow sufficient time for the solution to be transported into the nebulizer

5) Click on *Finish*

The selected Autotune sequence will now be run. To monitor its progress, observe the processes indicated at the bottom left of the PlasmaLab screen and open the Service Window (double-click on *MS* icon at the bottom right of the screen). A printable *Autotune Report* is generated at the end of the sequence. To continue, this report must be closed. To access this report upon closure, go to *Instrument*, *Configurations*, *Configuration Editor* and point to the appropriate *Instrument Settings* line. Open a pop-up menu by right-clicking and use the *View Tune Report* selection.

Running a Performance Report from the Tune Page

To run a Performance Report, follow the instructions below:

1) In PlasmaLab go to *Instrument*, *Tune* and click on the *Performance Report* icon (musical note on a page)

2) Select *Run an Existing Performance Report* and click on *Next*

3) Select the required sequence, e.g. *EPA ILM05 / 6020*, or *EPA 6020* and click on *Next*

4) Ensure that the indicated solution is being aspirated (through both probes if on-line internal standard addition is being used) and allow sufficient time for the solution to be transported into the nebulizer

5) Click on *Finish*

   The selected *Performance Report* will now be run. To monitor its progress, open the Service Window (double-click on *MS* icon at the bottom right of the screen). A printable *Performance Report* is generated at the end of the sequence. To access this report upon closure, go to *Instrument*, *Tune*, and click on the down arrow to the right of the Performance Report icon. Point at *Tools* and then select *View Performance Report Results*. Select the required Performance Report to view and click *OK*.

Running Performance Reports and Autotune in an Experiment

It is also possible to automate the running of these procedures using an instrument setup sample within an experiment. To do this, insert an *Instrument Setup Sample* at the beginning of the Sample List by selecting the first sample and using a right-mouse-click menu to *Insert New Before*. Define the *Sample Type* for this new sample as *Instrument Setup* and click on *Show Advanced*. Click on the *Instrument Performance Tests* tab and setup the Performance Report and Autotune functions following the logic and using the drop-down combo boxes to select the next action. An example would be as follows:

Acquire Performance Report	*EPA ILM05.2 / 6020*
If mass calibration verification fails then	*Abort the Queue*

If the Performance Report fails then	*Autotune using EPA – Xi Interface*
If the Autotune fails then	*Abort the experiment*
If the Autotune passes then	*re-run the Performance Report*
If the Performance Report fails again then	*Abort the Queue*

When Performance Reports and Autotunes are acquired in this way, the results are stored as part of the experiment report. Note that since this method of acquiring the report is done using the autosampler, the solution concentration should be adjusted if on-line internal standard addition is to be used, e.g. if the addition dilutes the samples 1:1, the solution concentration should be doubled to get an accurate measure of sensitivity.

Appendix 5

Resolution Set up

With the instrument in *Operate* mode, aspirate 10-µg/L Tune solution (6.4.1) (through both probes if using on-line internal standard addition). Go to *Instrument*, *Tune* and stop the real time display (RTD) using the square stop icon. Change the display mode from *Time vs ICPS* to *ICPS on the full mass range*. Insert Be as the mass to monitor and change the spacing to 10, the dwell to 1 ms and the channels to 200. Disable all other masses in the grid. Restart the RTD by clicking on the triangular play icon. The software will display the scanned peak for mass 9, Be. To adjust the resolution, go to the *Global* tab and use the slider bar marked *Standard resolution*. This must be set up to give a peak width of less than 0.75 amu at 5% peak height. This is typically reached at a setting of between 100 and 200. If high-resolution mode is to be used, this can be setup by changing the resolution setting on the RTD to *High*. The High Resolution peak width is typically set at about 0.4 amu at 5% peak height, again with values typically between 100 and 200. Note that this method does not use High-resolution mode. Each resolution mode should be checked with several other masses across the mass range, typically 55Mn, 115In, 203Tl and 238U are used. Special attention should be paid to the resolution setup for Mn. This is measured at m/z 55, which is adjacent to both iron and argon oxide at mass 56. These high signals must be properly resolved from the low Mn signal in standard resolution mode. When the correct resolution settings are achieved, save the setting using the disk icon. **Note that a new mass-calibration must always be performed after adjustment of the resolution.**

Appendix 6

Instrument Calibrations

There are three instrument calibrations that are fundamental for obtaining good quality data on the X Series. These are:

1) Mass-calibration
2) Detector Plateau and Analogue voltage set routines
3) Detector cross-calibration.

Mass calibration sets the quadrupole scan parameters to give the correct measured mass positions. The detector plateau sets the optimum voltage on the ion or pulse counting section of the discrete dynode detector. The analogue voltage set routine applies an appropriate voltage on the analogue part of the detector to obtain a cross-calibration factor of approximately 20,000 for a mid-mass isotope. The detector calibration, or cross-calibration, calculates the correction factor, for each measured mass, between the two detector modes, pulse counting and analogue. All three calibrations may be performed in a single routine, or may be performed separately.

Mass Calibration

A mass-calibration must be performed whenever the resolution settings are adjusted, as this will affect the apparent mass position. Mass-calibration must be performed when the Performance Report shows that measured peak positions are >0.1 amu from their nominal position. Mass-calibrations are best performed using a solution containing as many elements as possible or with every analyte required for analysis at the very least. The solution should contain Li and U as these are used as low and high mass datum points. An appropriate concentration solution be used (one that gives between **100,000-1,500,000 cps** for each mass to be calibrated is appropriate). To perform a mass calibration, follow the instructions below.

1) Click *Experiment*
2) Select *Create New Experiment*
3) Click *OK*
4) Select the *Default* database
5) Click *Open*
6) Go to *Sample List*
7) Click the *Report* check box in the sample list grid
8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*
9) Click on the *Show Advanced* button

10) Click on the *Instrument Calibrations* tab

11) Check the *Mass-Calibration* box

12) There is an option to *Update current mass-calibration* or form a *New mass-calibration*. Unless a major hardware change has been performed, the *Update current mass-calibration* option should be selected.

13) Click *Queue*

14) Save the experiment with an appropriate name, e.g. *masscal 090902* and click *Save*

15) Click *Append*

16) Click *OK*

Mass-calibration will now be performed.

To view the mass-calibration results, go to *Instrument*, *Calibrations*, *Mass-Calibration*. A mass-calibration for each of the two resolution modes is displayed in the graph of Peak Width and Error (y) versus Mass (x). The current mass-calibration is indicated by the row(s) displayed in green. To display alternative mass-calibrations, click on the appropriate date/time-stamped line in the top grid. The Performance Report function can be used to check mass-calibration accuracy (see Appendix 4).

Detector Plateau and Analogue Voltage Set

These routines can be performed separately, but it is advised to run them simultaneously as described here. The necessary frequency of these calibrations depends upon the amount of signal the detector is exposed to, i.e. how many samples are analyzed, which analytes and what concentrations. For most laboratories running a moderate sample load, this procedure may be run weekly. Up to three masses may be used in this procedure, however here, the use of a single mass is described. A solution that gives a countrate of between **100,000-1,500,000 cps** is appropriate. The default mass used here is indium (m/z 115), so this must be present in the solution for the routine to work. For an X5 instrument, an appropriate concentration would typically be between 10 and 100 µg/L, depending upon the sensitivity of the system. To perform this routine, follow the instructions below.

1) Click *Experiment*

2) Select *Create New Experiment*

3) Click *OK*

4) Select the *Default* database

5) Click *Open*

6) Go to *Sample List*

7) Click in the *Report* check box in the sample list grid

8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*

9) Click on the *Show Advanced* button

10) Click on the *Instrument Calibrations* tab

11) Check *the Set analogue voltage* box

12) Set the *Number of iterations* to *2*

13) Click *Queue*

14) Save the experiment with an appropriate name, e.g. *plateau 090902* and click *Save*

15) Click *Append*

16) Click *OK*

The voltage setup will now be performed. To view the plateau, go to *Instrument*, *Calibrations*, *Detector Plateau*. A graph of signal intensity (y) versus voltage (x) is displayed. The "knee" inflexion on this plot corresponds to the plateau voltage. This is automatically selected and applied to the detector by the software.

Detector Calibration (Cross-Calibration)

This routine must be performed whenever the detector voltages are altered and daily prior to analysis of samples. The solution used must contain all the analytes to be measured as an absolute minimum. The more analytes present, the better. All analytes should ideally be set at a concentration that gives between **500,000 and 1,500,000cps**. To perform the detector calibration, follow the instructions below:

1) Click *Experiment*

2) Select *Create New Experiment*

3) Click *OK*

4) Select the *Default* database

5) Click *Open*

6) Go to *Sample List*

7) Click in the *Report* check box in the sample list grid

8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*

9) Click on the *Show Advanced* button

10) Click on the *Instrument Calibrations* tab

11) Check the *Detector Calibrate* box

12) Click *Queue*

13) Save the experiment with an appropriate name, e.g. *xcal 090902* and click *Save*

14) Click *Append*

15) Click *OK*

The detector calibration will now be performed. To view the cross-calibration grap, go to *Instrument*, *Calibrations*, *Detector Cross-Calibration*. A graph of cross-calibration factor (y) versus mass (x) is displayed. **Use the data table to check that all analytical masses of interest have been used in the cross-calibration**. If not, the cross-calibration factor will be estimated from the equation of the graph. This may result in error.

All Routines in One

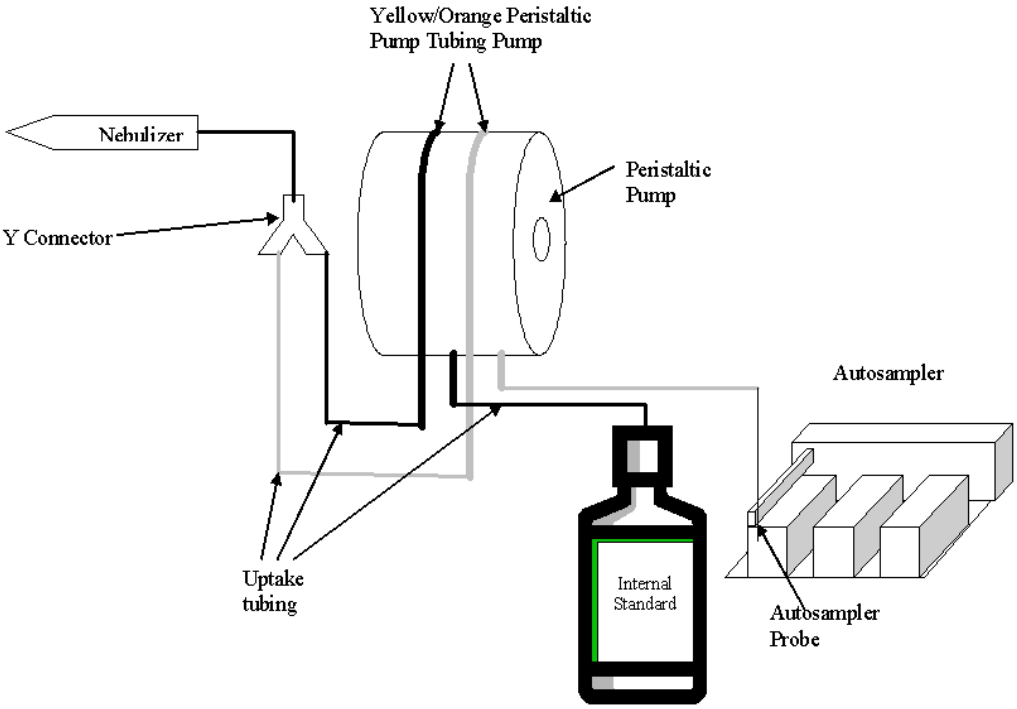
It is possible to run all three of the above routines on a single run if the solution used conforms to all of the criteria spelt out above. To do this, follow the instructions below.

1) Click *Experiment*
2) Select *Create New Experiment*
3) Click *OK*
4) Select the *Default* database
5) Click *Open*
6) Go to *Sample List*
7) Click in the *Report* check box in the sample list grid
8) Use the drop-down combo box in the *Type* column to select *Instrument Setup*
9) Click on the *Show Advanced* button
10) Click on the *Instrument Calibrations* tab
11) Check the *Mass calibration*, *Detector Calibrate* and *Set analogue voltage* boxes
12) Set the *Number of iterations* to *2*
13) Click *Queue*
14) Save the experiment with an appropriate name, e.g. *instr cal 090902* and click *Save*
15) Click *Append*
16) Click *OK*

The instrument calibrations will now be performed. Each parameter can be viewed as described above.

Appendix 7

Sample Introduction Plumbing Diagram



Appendix 8

Procedure for Cleaning Sample Introduction Equipment and Cones

1) Ensure that the instrument is in the *vacuum* or *shutdown* state (i.e. the plasma is OFF and the slide valve is SHUT)

2) Dismantle the sample introduction system as follows:

a) Remove the gas connection from the nebulizer

b) Remove the sample input plug from the nebulizer

c) Remove the metal clip on the spray chamber to elbow joint

d) Remove the drain plug from the spray chamber

e) Slide the spray chamber and nebulizer away from the elbow

f) Carefully slide the nebulizer out of the spray chamber and set both pieces aside in a safe place

g) Open the torch box and the internal Faraday cage

h) Pull the gas connections away from the torch

i) Undo the torch catch

j) Remove the metal clip on the elbow to torch joint

k) Carefully remove the torch from the load coil and set aside in a safe place

l) Remove the elbow by sliding it out of the torch box bulkhead toward spray chamber end

m) Slide the torch box away from the mass spectrometer to reveal the interface

n) Use the flat metal cone tool to undo the locking ring over the sample cone

o) Carefully remove the sample cone and set aside in a safe place

p) Carefully unscrew and remove the skimmer cone from the interface using the cylindrical aluminium tool and set aside in a safe place

3) Clean the cones as follows.

a) Carefully place the cones into a large beaker and fill with sufficient 0.05% nitric acid to cover – CAUTION: Stronger acids will corrode the cone material and reduce lifetime

b) Place the beaker in an ultrasonic bath for about 10 minutes or until surface deposition has been removed

c) Carefully remove the cones from the solution and rinse thoroughly with deionised water

d) Allow the cones to air-dry prior to refitting

4) Clean the sample introduction equipment as follows.

e) Carefully place the glass sample introduction components into a large beaker and fill with sufficient 10% nitric acid to cover all components

f) Place in an ultrasonic bath for between 20 minutes and 1 hour

g) Carefully remove the glass components and rinse thoroughly with deionised water

h) Allow to air-dry prior to refitting

5) Reassemble the components in the reverse order to disassembly

Note: Occasionally, glass sample introduction components crack when the ultrasonic cleaning procedure is used. To avoid this, the components may be soaked in acid, as above, for 12 hours, without ultrasonic treatment.

Thermo Electron cannot take any responsibility for any breakage that occurs during cleaning.

Appendix 9

Autosampler Position Map

Rack 0

Column →

Wash	1	2	3	4	5	6	7	8	9	10

Rack 1 Rack 2 Rack 3 Rack 4

Row →

↑ Column ↓	1	2	3	4	5
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
11					
12					

NB: This map is only applicable for CETAC ASX-500/510 autosamplers fitted with 60 position racks.

Appendix 10

Intentionally left blank.

Appendix 11

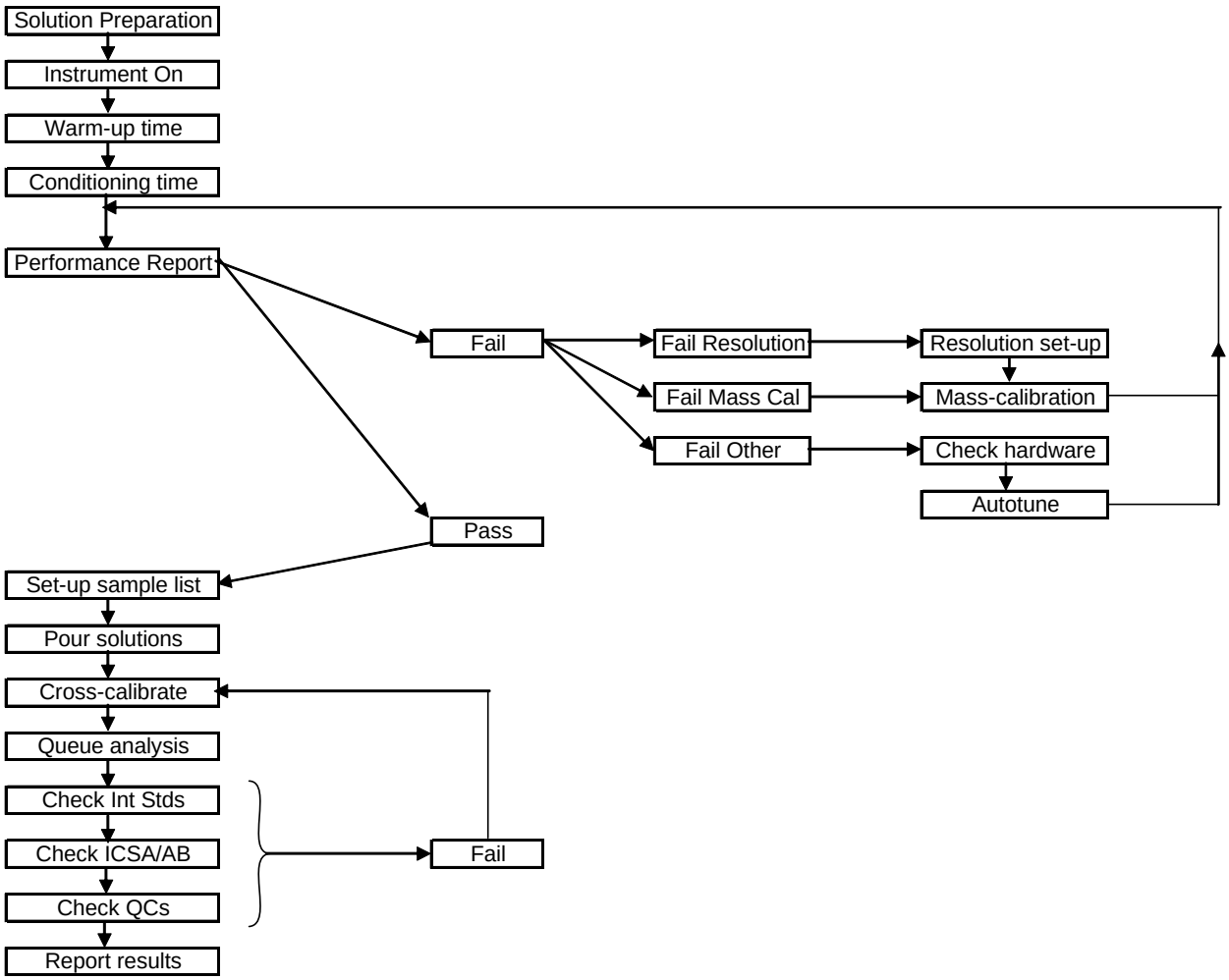
Spiking Levels

(Concentration in Final Solution Based on Instructions Within this Document)

Analyte	Spike Value (µg/L)
Al	2000
Sb	500
As	40
Ba	2000
Be	50
Cd	50
Cr	200
Co	500
Cu	250
Pb	20
Mn	500
Ni	500
Se	10
Ag	50
Tl	50
V	500
Zn	500

Appendix 12

Work Flow-Chart



Appendix 13

QC Abbreviations and Criteria

QC Code	Method(s)	QC Name	Purpose	Frequency	Limits
ICV	CLP, 6020, 6020A, 200.8, DoD	Initial Calibration Verification	Checks the calibration against a second calibration source	After initial calibration	90-110%
ICB	CLP, 6020, 6020A, 200.8, DoD	Initial Calibration Blank	Initial check of read-back at blank level	After initial calibration	<CRQL (1)
CRI/ LLICV/LLCCV[2]	CLP, 6020, 6020A, 200.8, DoD	Contract Required Quantitation Limit Check	Checks accuracy at the required limit of quantitation	After each calibration. [2]	50-150% (1) 70-130%(6020A)[2]
ICSA	CLP, 6020, 6020A, 200.8, DoD	Interference Check Solution A	Checks for freedom from interference	After initial calibration	For RL < 10 ±3 CRQL, RL > 10 ± RL or ±20% of the true value (whichever is the greater)
ICSAB	CLP, 6020, 6020A, 200.8, DoD	Interference Check Solution AB	Checks that analytes are accurately measured in an interference-producing matrix	After initial calibration	80-120% of true value
High Level Calibration Standard (DoD only)	6020 DoD	High level calibration check standard	Samples are diluted if results are above this standard and above the calibration standard, see section 9.2.8.1.	After ICSAB	90-110% of true value
CCV	CLP, 6020, 6020A, 200.8, DoD	Continuing Calibration Verification	A continuing periodic check on accuracy and drift	After each calibration and every 10 samples	90-110%
CCB	CLP, 6020, 6020A, 200.8,	Continuing Calibration Blank	A continuing periodic check	After each calibration and	<CRQL (1)

QC Code	Method(s)	QC Name	Purpose	Frequency	Limits
	DoD		on the read-back at blank levels	every 10 samples	
MB	CLP, 6020, 6020A, 200.8, DoD	Method Blank	Identify contamination	Once every 20 samples per matrix	< RL except for common lab contaminants at < 5 X RL. DoD < ½ RL, common lab contaminants < RL.
	CLP, 6020, 6020A, 200.8				
LCS	CLP, 6020, 6020A, 200.8, DoD	Laboratory Control Sample	Checks the accuracy of the entire analytical process	Once every 20 samples per matrix	80-120% 85-115% - 200.8
MS/MSD	CLP, 6020, 6020A, 200.8, DoD	Matrix Spike/Matrix Spike Duplicate	Accuracy and precision	Once every 20 samples – For 200.8 every 10 samples	75-125%, RPD ± 20%
DUP	CLP, 6020, 6020A, 200.8, DoD	Duplicate	Checks the reproducibility of results by analyzing an unknown sample in duplicate	Once every 20 samples per matrix	±20% Relative Percentage Difference (RPD)
PDS	6020, 6020A, DoD	Post Digestion Spike	Checks the recovery of analytes spiked into an unknown sample after preparation (digestion) – Performed if MS/MSD criteria not met.	Once every 20 samples per matrix	75-125% 80- 120% (6020A)
SER	CLP, 6020, 6020A, 200.8, DoD	Serial Dilution	Checks for matrix effects by assessing the variation of results for an unknown sample before and after dilution	Once every 20 samples per matrix	±10% of the original undiluted result after dilution correction for sample results ≥ 50 X MDL or IDL.

(1) For Method 6010A and 200.8, limit is 50-150%. For CLP see Section 9.2.6. For specific DoD requirements, refer to PT-QA-025. For DoD QSM current version refer to SOP PT-QA-029.

(2) For Methods 6020, 6020A & DoD requirements, the CRI is also analyzed at the end of the analytical sequence.

TITLE: Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP)

METHODS: SW-846 6010B, 6010C AND EPA 200.7

Approvals (Signature/Date):			
	07/17/09		07/20/09
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	07/07/09		07/17/09
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Controlled Source: Intranet

1. SCOPE AND APPLICATION

1.1. This procedure describes the analysis of trace elements including metals in solution by Inductively Coupled Plasma -Atomic Emission Spectroscopy (ICP-AES) using SW-846 Method 6010B, 6010C and EPA Method 200.7. Table I of Appendix A lists the elements appropriate for analysis by Methods 6010B/6010C and 200.7. Additional elements may be analyzed under Methods 6010B, 6010C and 200.7 provided that the method performance criteria presented in Section 13.0 are met. In addition to SOW ILMO4.0, this SOP is also compliant with the requirements of CLP SOWs 7/88, 3/90, ILMO1.0 and ILMO2.1.

1.2. ICP analysis provides for the determination of metal concentrations over several orders of magnitude. Detection limits, sensitivity and optimum concentration ranges of the metals will vary with the matrices and instrumentation used. For instance, in comparison to conventional ICP technique, ICP-Trace can achieve detection levels comparable to those determined using the graphite furnace atomic absorption spectroscopy (GFAAS) technique.

1.3. Method 6010B and 6010C are applicable to the determination of dissolved, suspended, total recoverable and total elements in ground water, aqueous samples, soils, sludges, wastes, sediments, tissues, wipes and TCLP, EP and other leachates/extracts. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples. Although digestion is not specifically required by the method, some clients and regulators may require digestion of dissolved samples and this must be clarified and documented before project initiation. Silver concentrations must be below 2.0 mg/L in aqueous samples and 100 mg/kg in solid matrix samples. Precipitation may occur in samples where silver concentrations exceed these levels and lead to the generation of erroneous data.

1.4. Method 200.7 is applicable to the determination of dissolved, suspended, total recoverable, and total elements in water, waste water, and solid wastes. All matrices require digestion prior to analysis with the exception of analyses for dissolved metals in filtered and acidified aqueous samples if the criteria in Section 11.1 are met. Silver concentrations must be below 0.1 mg/L in aqueous samples and 50 mg/kg in solid matrix samples.

1.5. For DoD QSM Version 3 requirements, refer to SOP PT-QA-025. For DoD V4.1 refer to SOP PT-QA-029.

1.6. On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.1 in the Quality Assurance Manual.

2. SUMMARY OF METHOD

2.1. This method describes a technique for the determination of multi elements in solution using sequential or simultaneous optical systems and axial or radial viewing of the plasma. The basis of the method is the measurement of atomic emission by an optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to the plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio frequency inductively coupled plasma (ICP). The spectra are dispersed by a grating spectrometer and the intensities of the emission lines are monitored by photomultiplier tubes. The photocurrents from the photomultiplier tubes are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background must be measured adjacent to analyte lines during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interferences and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences should also be recognized and appropriate actions taken. Alternatively, multivariate calibration methods may be chosen for which point selection for background correction is superfluous since whole spectral regions are processed. Consult the appropriate SOP's for details on sample preparation methods.

2.2. Refer to the appropriate SOPs for details on sample preparation methods.

3. DEFINITIONS

3.1. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (Sample is acidified <u>after</u> 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 vigorous digestion.

3.4. Total Recoverable Metals: The concentration determined on an unfiltered sample following treatment with hot, dilute mineral acid.

4. INTERFERENCES

4.1. Spectral, physical and chemical interference effects may contribute to inaccuracies in the determinations of trace elements by ICP. Spectral interferences are caused by:

- Overlap of a spectral line from another element.
- Unresolved overlap of molecular band spectra.
- Background contribution from continuous or recombination phenomena.
- Stray light from the line emission of high concentration elements.

4.1.1. Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not significant with the ICP technique but if observed can be minimized by buffering the sample, matrix matching or standard addition procedures.

4.1.2. A background correction technique is required to compensate for variable background contribution to the determination of trace elements. Background correction is not required in cases where a background corrective measurement would actually degrade the analytical result.

4.1.3. Inter-element correction factors (IECs) are necessary to compensate for spectral overlap. Inter-element interferences occur when elements in the sample emit radiation at wavelengths so close to that of the analyte that they contribute significant intensity to the analyte channel. If such conditions exist, the intensity contributed by the matrix elements will cause an excessively high (or sometimes low) concentration to be reported for the analyte. Inter-element corrections IECs must be applied to the analyte to remove the effects of these unwanted emissions.

4.1.4. Physical interferences are generally considered to be effects associated with sample transport, nebulization and conversion within the plasma. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension) or during excitation and ionization processes within the plasma itself. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If

physical interferences are present, dilution of the sample, use of a peristaltic pump, mass flow controller, use of an internal standard and/or use of a high solids nebulizer can reduce the effect.

5. SAFETY

5.1. Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.2 The ICP plasma emits strong UV light and is harmful to vision. All analysts must avoid looking directly at the plasma.

5.3 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
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.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.4 Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5 The RF generator produces strong radio frequency waves, most of which are unshielded. People with pacemakers should not go near the instrument while in operation.

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

5.7 The preparation of standards and reagents will be conducted in a fume hood or well-ventilated area.

5.8 All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor or EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Inductively Coupled Plasma Atomic Emission Spectrometer equipped with autosampler and background correction.

6.2. Radio Frequency Generator.

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

6.4. Cool flow or appropriate water cooling device.

6.5. Peristaltic Pump.

6.6. Calibrated automatic pipettes or Class A glass volumetric pipettes.

6.7. Class A volumetric flasks.

6.8. Autosampler tubes.

7. REAGENTS AND STANDARDS

7.1. Intermediate standards are purchased as custom TestAmerica multielement mixes or as single element solutions. All standards must be stored in FEP fluorocarbon or previously unused polyethylene or polypropylene bottles. Intermediate standard solutions must be replaced prior to the expiration date provided by the manufacturer. If no expiration date is provided, the intermediate solutions may be used for up to one year and must be replaced sooner if verification from an independent source indicates a problem. Expiration dates can be extended provided that the acceptance criteria described in laboratory-specific SOPs are met.

7.2. Working calibration and calibration verification solutions may be used for up to 3 months and must be replaced sooner if verification from an independent source indicates a problem. Standards should be prepared in a matrix of 5% hydrochloric and 5% nitric acids. An exception to this is in the event the Trace ICP is utilized without the internal standard. In this case, the standard acid matrix must be matched to the final preparation matrix.

7.3. Refer to Tables III, IV, IVA, V and VI (Appendix A) for details regarding the working standard concentrations for calibration, calibration verification, interference correction and spiking solutions.

7.4. Concentrated nitric acid (HNO_3), trace metal grade or better.

7.5. Concentrated hydrochloric acid (HCl), trace metal grade or better.

7.6. 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.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Sample holding times for metals are six months from time of collection to the time of analysis.

8.2. Aqueous samples are preserved with nitric acid to a pH of <2 and may be stored in either plastic or glass. If boron or silica are to be determined, plastic containers are preferred. Refrigeration is not required. Preservation must be verified prior to analysis.

8.3. Soil and wipe samples do not require preservation but must be stored at 4°C ± 2° until the time of preparation. Tissue samples are stored frozen until preparation.

8.4. Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

9. QUALITY CONTROL

9.1. Table VII (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action. See SOP PT-QA-021"TestAmerica Quality Control Program" for additional detail on criteria and corrective actions.

9.2. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 12.0.

9.3. Method Blank (MB) - One method blank must be processed with each preparation batch of up to 20 samples. The method blank consists of reagent water containing all reagents specific to the method that 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 analyte of interest at or above the reporting limit (exception: common laboratory contaminants, see below) or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 10X higher than the blank

contamination level). **Refer to PT-QA-025 for specific DoD requirements for the method blank. For DoD V4.1 refer to SOP PT-QA-029.**

- If the analyte is a common laboratory contaminant (copper, iron, lead (Trace only) or zinc) the data may be reported with qualifiers if the concentration of the analyte in the method blank is less than two times the RL. **Such action must be taken in consultation with the client and must be addressed in the project narrative.**
- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).
- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and 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.**
- For dissolved metals samples, which have not been digested, a CCB result is reported as the method blank. The CCB run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCB.

9.4. Laboratory Control Sample (LCS) - One aqueous LCS (referred to as a Laboratory Fortified Blank in 200.7) must be processed with each preparation batch of up to 20 samples. The LCS must contain all analytes of interest and must be carried through the entire analytical procedure. Aqueous LCS spike levels are provided in Table III (Appendix A). The LCS is used to monitor the accuracy of the analytical process. On-going monitoring of the LCS results provides evidence that the laboratory is performing the method within acceptable accuracy and precision guidelines.

- If any analyte is outside established control limits the system is out of control and corrective action must occur. Control limits are established, for method 6010B/6010C, a control limit of 80 - 120% (85-115% for 200.7) recovery must be applied.
- In the event that an MS/MSD analysis is not possible a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- In the instance where the LCS recovery is greater than 120% (115% for 200.7) and the sample results are < RL, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and must be addressed in the report narrative.**

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

- For dissolved metals samples, which have not been digested, a CCV result is reported as the LCS. The CCV run immediately prior to the start of the dissolved sample analyses must be used for this purpose. No more than 20 samples can be associated with one CCV.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch of up to 20 samples (6010B and 6010C) or one MS for every 10 or fewer samples (200.7). A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added (referred to as a Laboratory Fortified Matrix in 200.7). A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as 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 MS/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 Tables III and VI (Appendix A).

- If any analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. For method 6010B and 6010C, control limits of 75 - 125% (70 – 130% for 200.7) recovery and 20% RPD or historical acceptance criteria must be applied to the MS/MSD. **Refer to PT-QA-025 for specific DoD requirements for the MS.** For DoD V4.1 refer to SOP PT-QA-029. 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 MS/MSD exceeds 4x the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits

do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level.".

- If an MS/MSD is not possible due to limited sample volume then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.
- For dissolved metals samples by 200.7, which have not been digested, a MS must be performed per every 10 or fewer samples by spiking an aliquot of the sample at the levels specified in Table III (Appendix A).
- For Methods **6010B/ 6010C/DoD** samples- If the MS/MSD recoveries are unacceptable, the same sample from which the MS/MSD aliquots were prepared should also be spiked with a post digestion spike. Otherwise, another sample from the same preparation batch should be used as an alternative. An analyte spike is added to a portion of a prepared sample, or its dilution, and should be recovered to within 80% to 120% (for Method 6010C) of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the lower limit of quantitation. The spike recovery from the post digestion spiked sample **for method 6010B/DoD** the spike recovery should be within the range 75-125%. If this spike fails, then the dilution test (Sec. 9.6 should be run on this sample. If both the MS/MSD and the post digestion spike fail, then matrix effects are confirmed.

9.6 Dilution test – A dilution test is performed to determine whether significant physical or chemical interferences exist due to the sample matrix. One sample per preparation batch must be processed as a dilution test. The test is performed by running a sample at a 5x (1:5) dilution. Samples identified as field blanks cannot be used for dilution tests. The results of the diluted sample, after correction for dilution, should agree within 10% of the original sample determination when the original sample concentration is greater than 50x the MDL. If the results are not within 10%, the possibility of chemical or physical interference exists.

9.7 Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). For analyses conducted under Method 200.7, the ICV result must fall within 5% of the true value for that solution with relative standard deviation <3% from replicate readings of four exposures of the ICV standard. For Method 6010B and 6010C, the ICV must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of three) exposures. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the RL from zero. **Refer to PT-QA-025 for specific DoD requirements for the ICB. For DoD V4.1 refer to SOP PT-QA-029.** If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated

and the calibration reverified. This standard is equivalent to the Quality Control Standard (QCS) and the first Instrument Performance Check (IPC) specified in 200.7.

9.8 Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples. The CCV is a mid-range standard made from a dilution of the calibration standard. The CCV for both methods must fall within 10% of the true value for that solution with relative standard deviation <5% from replicate (minimum of three) exposures. A CCB is analyzed immediately following each CCV. The CCB result must fall within +/- RL from zero. **Refer to PT-QA-025 for specific DoD requirements for the CCB.** For DoD V4.1 refer to SOP PT-QA-029. If the blank is less than 1/10 the concentration of the action level of interest, and no sample is within 10% of the action limit, reanalysis and recalibration are not required before continuation of the run. If a mid-run CCV or CCB fails, the analytical run may be continued; however, the result(s) for the affected element(s) may only be reported when bracketed by valid CCV/CCB pairs. If analytical results for one or more elements are not bracketed by valid CCV/CCB pairs, the problem must be corrected, the instrument recalibrated, the calibration verified and the affected samples reanalyzed for those elements only.

9.9 Reporting Limit Verification Standard (RLV)/CRA or LLICV/LLCCV (6010C) – Calibration accuracy at the laboratory reporting limit is verified after the analysis of the ICB by running the RLV, CRA or LLICV/LLCCV. For method 6010C it must be analyzed at beginning and end of the analytical run. This standard is at the reporting limit. For Methods 200.7 and 6010B the control limit is 50 – 150%. For Method 6010C LLICV/LLCCV the control limit is 70-130%. For method 6010C the RLV/CRA which is the low level quantitation check sample is prepared and analyzed quarterly or as needed. The control limit is 70-130%. Please note the RLV/CRA (undigested) is still analyzed at the beginning and end of the analytical run. **Refer to PT-QA-025 for specific DoD requirements for the RLV standard.** For DoD V4.1 refer to SOP PT-QA-029.

9.10. Interference Check Analysis (ICSA/ICSAB) - The validity of the interelement correction factors is demonstrated through the successful analysis of interference check solutions. The ICSA contains only interfering elements, the ICSAB contains analytes and interferents. Refer to Table V (Appendix A) for the details of ICSA and ICSAB composition. Custom TestAmerica multielement ICS solutions must be used. All analytes should be spiked into the ICSAB solution therefore, if a non-routine analyte is required then it should be manually spiked into the ICSAB using a certified ultra high purity single element solution or custom lab-specific mix. If the ICP will display over correction as a negative number then the non-routine elements can be controlled from the ICSA as described in section 9.10.3. Elements known to be

interferents on a required analyte must be included in the ICP run when that analyte is determined. Aluminum, iron, calcium and magnesium must always be included in all ICP runs.

9.10.1. The ICSA and ICSAB solutions must be run at the beginning of the run. (See Section 10.11 for required run sequence).

9.10.2. The ICSAB results for the interferents must fall within 80 - 120% of the true value. If any ICSAB interferent result fails criteria, the analysis should be terminated, the problem corrected, the instrument recalibrated and the samples rerun.

9.10.3. ICSA results for the non-interfering elements with reporting limits ≤ 10 ug/L must fall within the TestAmerica guidelines of ± 2x RL from zero. ICSA results for the non-interfering elements with RLs > 10 µg/L must fall within the TestAmerica guidelines of ± 1x RL from zero. **Refer to PT-QA-025 for specific DoD requirements for the ICSA.** For DoD V4.1 refer to SOP PT-QA-029. If the ICSA results for the non-interfering elements do not fall within +/- 2x RL (RL ≤10) or ± 1xRL (RL>10) from zero the field sample data must be evaluated as follows:

- If the non-interfering element concentration in the ICSA is the result of contamination versus a spectral interference, and this reason is documented, the field sample data can be accepted.
- If the affected element was not required then the sample data can be accepted.
- If the interfering elements are not present in the field sample at a concentration, which would result in a false positive or negative result greater than +/- 2x RL from zero then the field sample data can be accepted.
- If the interfering element is present in the field sample at a level which would result in a false analyte signal greater than ± 2x RL from zero, the data can be accepted only if the concentration of the affected analyte in the field sample is more than 10x the analyte signal in the ICSA.
- If the data does not meet the above conditions then the IECs must be re-evaluated and corrected if necessary and the affected samples reanalyzed or the sample results manually corrected through application of the new IEC to the raw results. If the results are

recalculated manually the calculations must be clearly documented on the raw data.

9.12 Method of Standard Addition (MSA) -This technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. 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, which cause a baseline shift. Refer to Section 10.15 for additional information on when MSA is required as well as Appendix D for specific MSA requirements.

9.13 Quality Assurance/Project Summaries - Certain clients may require project- or program-specific QC, which may supersede this SOP's requirements. Quality Assurance Summaries (QASs) or equivalent documents providing project-specific requirements should be developed so that project staff clearly understands the special project requirements.

10. PROCEDURE

10.1. Calibration and Standardization

10.1.1. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required).

10.1.2. The instruments are profiled and calibrated according to the manufacturer's recommended procedures. Thermo has set up the ICP 61E to be profiled on Cu and the Trace ICPs are to be profiled on As. All other lines are preset by Thermo and should not be adjusted by the user. Flush the system with the calibration blank. The calibration curve must consist of a minimum of a blank and a standard. Refer to the facility-specific instrument SOP or ICP instrument manual for a detailed set up and operation protocols.

10.1.3. Calibration must be performed daily and each time the instrument is set up. Instrument runs may be continued over periods exceeding 24 hours as long as all calibration verification (CCV) and interference check QC criteria are met. The instrument standardization date and time must be included in the raw data.

10.1.4. Refer to Section 9.0 for calibration verification procedures, acceptance criteria and corresponding corrective actions. The NELAC requirement for verification of the initial calibration at varied concentrations is met daily since the ICVs, CCVs, and RLVs/CRA are all at different concentrations.

10.2. For 200.7 analyses, dissolved (preserved) samples must be digested unless it can be documented that the sample meets all of the following criteria:

A. Visibly transparent with a turbidity measurement of 1 NTU or less.

B. Is of one liquid phase and free of particulate or suspended matter following acidification.

C. Is NOT being analyzed for silver.

If the above criteria are met, the dissolved samples can be analyzed directly after an appropriate amount of 1:1 nitric acid is added to an aliquot of sample to adjust the acid concentration to approximately a 1% (v/v) nitric acid solution. Allowance for sample dilution should be made in the calculation.

10.3. A minimum of <u>three</u> <u>exposures</u> for each standard, field sample and QC sample is required. The average of the exposures is reported. For Trace ICP analyses, the results of the sum channel must be used for reporting.

10.4. Prior to calibration and between each sample/standard the system is rinsed with the calibration blank solution. The minimum rinse time between analytical samples is 60 seconds unless following the protocol outlined in 10.1.2 it can be demonstrated that a shorter rinse time may be used. Triton-X can be added to the rinse solution to facilitate the rinse process.

10.5. The use of an autosampler for all runs is strongly recommended.

10.6. The use of automated QC checks through the instrument software is highly recommended for all calibration verification samples (ICV, CCV, RLV/CRA/LLICV/LLCCV), blanks (ICB, CCB, PB), interference checks (ICSA, ICSAB) and field samples (linear range) to improve the data review process.

10.7. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

10.8. To facilitate the data review and reporting processes it is strongly recommended that all necessary dilutions be performed before closing out the instrument run. If any digestate for Method 200.7 has silver detected above 100 mg/L, add 1.0 ml of concentrated HCl to the digestate, mix and reanalyze. If the second analysis yields a higher value for silver, the second analysis is reported and discussed in the report narrative.

10.9. The use of an internal standard is recommended on the conventional, non-Trace ICPs as an alternative to using the method of standard additions. This technique is useful in overcoming matrix interferences especially in high solids matrices.

However, for conventional ICP techniques, internal standards may not be necessary provided that one of the following is performed to minimize physical interferences: (1) peristaltic pump is used, (2) high solids nebulizer is used, or (3) high solids samples are diluted and reanalyzed.

10.10. The use of an internal standard is **required** on any axial ICP unless the calibration and QC standards are matrix matched to each digestion procedure. The following procedural guidelines must be followed when using an internal standard:

10.10.1. Typically used internal standards are: yttrium or scandium. (Note: Any element can be used that is not typically found in environmental samples at a high rate of occurrence.)

10.10.2. The internal standard (IS) must be added to every sample and standard at the same concentration. It is recommended that the IS be added to each analytical sample automatically through use of a third pump channel and mixing coil. Internal standards should be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

10.10.3. The concentration of the internal standard should be sufficiently high to obtain good precision in the measurement of the IS analyte used for data correction and to minimize the possibility of correction errors if the IS analyte is naturally present in the sample.

10.10.4. The internal standard raw intensity counts must be printed on the raw data.

10.10.5. The analyst must monitor the response of the internal standard throughout the sample analysis run. This information is used to detect potential problems and identify possible background contributions from the sample (i.e., natural occurrence of IS analyte).

10.10.5.1. If the internal standard counts fall within ±30% of the counts observed in the ICB then the data is acceptable.

10.10.5.2. If the internal standard counts in the field samples are more than ±30% higher than the expected level, the field samples must then be:

(1) Diluted and reanalyzed;

(2) The IS concentrations must be raised; or

(3) A different internal standard must be used.

10.11. The following analytical sequence must be used for Methods 6010B/6010C and 200.7:

Instrument Calibration

ICV

ICB

RLV/CRA/LLICV

ICSA

ICSAB

7 Samples

CCV

CCB

10 samples

CCV

CCB

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

CCV

CCB

RLV/CRA/LLCCV

CCV

CCB

Refer to Quality Control Section 9.0 and Table VII (Appendix A) for Method 6010B/6010C and 200.7 quality control criteria.

10.12. Full method required QC must be available for each wavelength used in determining reported analyte results.

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

10.14. All measurements must fall within the defined linear range where spectral interference correction factors are valid. Dilute and reanalyze all samples for required analytes that exceed the linear range or use an alternate wavelength for which QC data are established. If an interelement correction exists for an analyte, which exceeds the linear range, the IEC may be inaccurately applied. Therefore, even if an overrange analyte may not be required to be reported for a sample, if that analyte is a interferent for any requested analyte in that sample, the sample must be diluted. Acid strength must be maintained in the dilution of samples.

10.15. For TCLP samples, full four-point MSA will be required if all of the following conditions are met:

- recovery of the analyte in the matrix spike is not at least 50%,
- the concentration of the analyte does not exceed the regulatory level, and,
- the concentration of the analyte is within 20% of the regulatory level.

The reporting and regulatory limits for TCLP analyses as well as matrix spike levels are detailed in Table VI (Appendix A). Appendix D provides guidance on performing MSA analyses.

10.16. Any variation in procedure shall be completely documented using instrument run logs, maintenance logs, report narratives, a Nonconformance Memo, or an anomaly report and is approved by a Supervisor/Group Leader and QA Manager. If contractually required, the client shall be notified by the Project Manager.

10.17. Nonconformance documentation shall be filed in the project file.

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

11. DATA ANALYSIS AND CALCULATIONS

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

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

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

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

11.3. RLV/CRA percent recoveries are calculated using the same equation as the ICV or CCV (replace ICV or CCV with RLV/CRA in the above equations).

11.4. 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

11.5. The relative percent difference (RPD) of matrix spike/matrix spike 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

11.6. The final concentration for a digested aqueous sample is calculated as follows:

$$mg/L = \frac{CxV1xD}{V2}$$

Where:

C = Concentration (mg/L) from instrument readout

D = Instrument dilution factor

V1 = Final volume in liters after sample preparation

V2 = Initial volume of sample digested in liters

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

$$mg/Kg, dryweight = \frac{CxVxD}{WxS}$$

Where:

C = Concentration (mg/L) from instrument readout

D = Instrument dilution factor

V = Final volume in liters after sample preparation

W = Weight in Kg of wet sample digested

S = Percent solids/100

Note: A Percent Solids determination must be performed on a separate aliquot when dry weight concentrations are to be reported. If the results are to be reported on wet weight basis the "S" factor should be omitted from the above equation.

11.8. The final concentration determined in digested wipe samples is calculated as follows:

ug/wipe = (C x V x D x 1000)

Where:

C = Concentration (mg/L) from instrument readout

V = Volume of digestate (L)

D = Instrument dilution factor

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

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

11.10. The dilution test percent difference for each component is calculated as follows:

$$\%Difference = \frac{|I - S|}{I} x100$$

Where:

I = Sample result (Instrument reading)

S = Dilution test result (Instrument reading × 5)

11.11. Appropriate factors must be applied to sample values if dilutions are performed.

11.12. Sample results should be reported with up to three significant figures in accordance with the TestAmerica significant figure policy.

12. METHOD PERFORMANCE

12.1. Initial Demonstration of Capability

12.1.1. An initial demonstration of capability for each method must be performed prior to analyzing samples. For the standard analyte list, the initial demonstration consists of the preparation and analysis of an LCS sample containing all of the standard analytes for the method, as well as a method detection limit (MDL) study (described below).

12.1.2. Four LCS samples are analyzed with the same procedures used to analyze samples, including sample preparation.

12.1.3. The mean recovery and standard deviation are calculated for each analyte of interest. These results are compared with the established or project-specific acceptance criteria. All four results must meet acceptance criteria before the method can be used to analyze samples. For further detail refer to SOP PT-QA-001.

12.2. Prior to analysis of any analyte using either Method 200.7, Method 6010B or 6010C, the following requirements must be met.

12.2.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte prior to the analysis of any client samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be determined in accordance with 40 CFR Part 136 Appendix B requirements as

detailed in TestAmerica QA SOP PT-QA-007. The result of the MDL determination must be below the TestAmerica reporting limit (RL).

12.2.2. Instrument Detection Limit (IDL) 200.7/6010B - The IDL for each analyte must be determined for each analyte wavelength used on each instrument. The IDL will be determined quarterly (every 3 months). If the instrument is adjusted in any way that may affect the IDL, the IDL for that instrument must be redetermined. The IDL shall be determined by multiplying by 3, the average of the standard deviations obtained on three nonconsecutive days from the analysis of a standard solution (each analyte in reagent water) at a concentration 3x - 5x the previously determined IDL, with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure performed between the analysis of separate samples). The IDL must be < MDL.

12.2.3. Instrument detection limits (IDLs) – Method 6010C – IDLs are useful means to evaluate the instrument noise level and response changes over time for each analyte from a series of reagent blank analyses to obtain a calculated concentration. They are not to be confused with the lower limit of quantitation, nor should they be used in establishing this limit. It may be helpful to compare the calculated IDLs to the established lower limit of quantitation, however, it should be understood that the lower limit of quantitation needs to be verified according to the guidance in Sec. 9.9.

12.2.4. IDLs in µg/L can be estimated by calculating the average of the standard deviations of three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement should be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs should be determined at least every three months.

12.2.4.1. **DoD samples cannot be analyzed without a valid IDL**.

12.2.4.2. **For DoD, the established IDL must be less than the MDL for each analyte**.

12.2.5. Linear Range Verification (LR) - The linear range will be determined on a quarterly basis for each analyte wavelength used on each instrument as per CLP requirements. Method 6010B/6010C require that the linear range only be determined semiannually. Method 200.7 requires linear ranges to be determined annually. The standards used to define the linear range limit

must be analyzed during a routine analytical run. For the **initial** determination of the upper limit of the linear dynamic range (LDR) for each wavelength, determine the signal responses from a minimum of three to five different concentration standards across the estimated range. One standard should be near the upper limit of the estimated range. The determined concentration of the linear range standards must be within 5% of the true value. The linear range is the concentration above which results cannot be reported without dilution of the sample. If the instrument is adjusted in any way that may affect the LR's, the LR's must be redetermined. The LR data must be documented and kept on file.

12.2.6. Background Correction Points - To determine the appropriate location for off-line background correction when establishing methods, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. Tests to determine spectral interference must be done using analyte concentrations that will adequately describe the interference. Background correction points must be set prior to determining IECs. Refer to the facility-specific instrument operation SOP and ICP instrument manual for specific procedures to be used in setting background correction points.

12.2.7. Inter-element Corrections (IECs) - ICP interelement correction factors must be determined prior to the analysis of samples and every six months thereafter. If the instrument is adjusted in any way that may affect the IECs, the IECs must be redetermined. When initially determining IECs for an instrument, wavelength scans must be performed to ensure that solutions in use are free from contaminants. If an IEC varies significantly from the previously determined IEC then the possibility of contamination should be investigated. The purity of the IEC check solution can be verified by using a standard from a second source or an alternate method (i.e., GFAA or ICP-MS). Published wavelength tables (e.g. MIT tables, Inductively Coupled Plasma-Atomic Spectroscopy: Prominent Lines) can also be consulted to evaluate the validity of the IECs. Refer to the facility specific instrument operation SOP and instrument manufacturer's recommendations for specific procedures to be used in setting IECs. An IEC must be established to compensate for any interelement interference which results in a false analyte signal greater than ± the RL as defined in Tables I, IA or II. To determine IECs, run a single element standard at the established linear range. To

calculate an IEC, divide the observed concentration of the analyte by the observed concentration of the "interfering element."

Note: Trace ICP IECs are more sensitive to small changes in the plasma and instrument setup conditions. Adjustments in the IECs will be required on a more frequent basis for the Trace as reflected by the ICSA response.

12.2.8. Rinse Time Determination - Rinse times must be determined whenever a new instrument is set up. . To determine the appropriate rinse time for a particular ICP system, the linear range verification standard should be aspirated as a regular sample followed by the analysis of a series of rinse blanks. The length of time required to reduce the analyte signals to < RL will define the rinse time for a particular ICP system. For some analytes it may be impractical to set the rinse time based on the linear range standard result (i.e., analyte not typically detected in environmental samples at that level and an excessive rinse time would be required at the linear range level). Until the required rinse time is established, the method recommends a rinse period of at least 60 seconds between samples and standards. If a memory effect is suspected, the sample must be reanalyzed after a rinse period of sufficient length. Rinse time studies can be conducted at additional concentration levels. These additional studies must be documented and kept on file, if a concentration other than the linear range level is used to set the rinse time. The concentration levels used to establish the rinse time must be taken into consideration when reviewing the data. Linear Range Verifications are performed at a minimum of every six months. Whenever Linear Range Verifications are performed the suitability of the rinse time settings will be evaluated and the rinse time determination will be repeated when necessary.

12.3. Method performance is determined by the analysis of matrix spike and matrix duplicate samples as well as preparation blanks and laboratory control samples. The matrix spike recovery should fall within +/- 25 % and the matrix duplicates should compare within 20% RPD. Preparation blanks must meet the criteria specified in Section 9.3. The LCS should recover within 20% of the true value for aqueous LCS and within the control limits supplied by the manufacturer of the soil LCS.

12.4. Training Qualification:

12.4.1. 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.

13. POLLUTION PREVENTION

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

13.2. This method does not contain any specific modifications that serve to minimize or prevent pollution.

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to CW-E-M-001. The following waste streams are produced when this method is carried out.

14.1.1. Acid waste consisting of sample and rinse solution, this waste is collected in waste containers identified as "Acid Waste", Waste #33.

14.1.2. Expired Metals Standards – This waste is collected in containers identified as "Acid Waste with Metals", Waste #6.

15. REFERENCES/CROSS REFERENCES

15.1. 40 CFR Part 136, Appendix B, 7-5-95, Determination of Method Detection Limits.

15.2. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update III, Method 6010B,Revision 2, December 1996.

15.3. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update IV, Method 6010C, Revision 3, February, 2007.

15.4. Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry, Revision 4.4, May 1994. Method 200.7.

15.5. Standard Methods 20th Edition 2340B; Hardness by Calculation.

15.6. SOP PT-QA-001, Employee Orientation and Training, current version.

15.7. SOP PT-HS-001, Waste Collection, Accumulation and Storage, current version.

15.8. SOP PT-QA-007, Determination of Method Detection Limits (MDLs), current version.

15.9. SOP PT-QA-009, Rounding and Significant Figures.

15.10. SOP PT-QA-016, Nonconformance & Corrective Action System, current version.

15.11. SOP PT-QA-018, Technical Data Review Requirements, current version.

15.12. SOP PT-QA-021, Quality Control Program, current version.

15.13. SOP PT-QA-025, Implementation of the DoD QSM Version 3, January 2006, current version.

15.14. SOP PT-QA-029, DoD QSM Version 4.1 Requirements, current version.

16. METHOD MODICATIONS

16.1. Modifications/Interpretations from reference method

16.1.1. Modifications/interpretations from both Methods 6010B and 200.7.

16.1.1.1. TestAmerica laboratories use mixed calibration standard solutions purchased from approved vendors instead of using individual mixes prepared in house as recommended by the subject methods.

16.1.1.2. Methods 200.7 and 6010B state that if the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution should fall within a specific concentration range around the calibration blank. In determining IECs, because of lack of definition clarification for "concentration range around the calibration blank," TestAmerica has adopted the procedure in EPA CLP ILM04.1.

16.1.1.3. Section 8.5 of Method 6010B and Section 9.5 of Method 200.7 recommend that whenever a new or unusual matrix is encountered, a series of tests be performed prior to reporting concentration data for that analyte. The dilution test helps determine if a chemical or physical interference exists. Because TestAmerica laboratories receive no prior information from clients regarding when to expect a new or unusual matrix, TestAmerica may select to perform a dilution test on one sample in each prep batch. According to the method, the post digestion spike (PDS) determines any potential matrix interferences. At TestAmerica labs, matrix interference is determined by evaluating data for the LCS and MS/MSD. TestAmerica requires documented, clear guidance when a new or

unusual matrix will be received for a project and a request to perform the dilution test or PDS on a client-identified sample.

16.1.2. Modifications from Method 200.7.

16.1.2.1. The calibration blank is prepared in an acid matrix of 5% HNO_3/5% HCl instead of the specified 2% HNO_3/10% HCl matrix as the former matrix provides for improved performance relative to the wide variety of digestate acid matrices which result from the various EPA preparation protocols applied.

16.1.2.2. Section 7.12 of 200.7 indicates that the QCS (ICV) should be prepared at a concentration near 1 ppm. The ICV specified in this SOP accommodates the 1 ppm criteria for the majority of analytes. For the remaining analytes, this SOP specifies ICV concentrations, which are appropriate to the range of calibration. The intent of the ICV, verification of calibration standard accuracy, is independent of the ICV concentration used.

16.1.2.3. The ICS criteria applied by this SOP differ from those stated in the method. Method 200.7 section 10.4 states that results should fall within the established control limits of 3 times the standard deviation of the calibration blank for that analyte. TestAmerica Pittsburgh follows the CLP ICS procedures because it is applicable to a wider number of programs. Therefore, we feel it is a more conservative approach.

16.1.2.4. Method 200.7 section 9.3.4 states the CCB should be less than the IDL, but > the lower 3-sigma control limit of the calibration blank. The intent of this requirement is to ensure that the calibration is not drifting at the low end. TestAmerica has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. SOP section 9.8 provides the detailed corrective action criteria that must be followed. **Refer to PT-QA-025 for specific DoD requirements for the CCB.** For DoD V4.1 refer to SOP PT-QA-029.

16.1.3. Modifications from Method 6010B.

16.1.3.1. 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 the reporting limit. Common lab contaminants are allowed up to two times the reporting limit in the blank following consultation with the client. **Refer to PT-QA-025 for specific DoD**

requirements for the method blank. For DoD V4.1 refer to SOP PT-QA-029.

16.1.3.2. Method 6010B section 8.6.1.3 states that the results of the calibration blank are to agree within 3x the IDL. If not, repeat the analysis two or more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples. The intent of this requirement is to ensure that the calibration is not drifting at the low end. TestAmerica has adopted an absolute control limit of +/- RL from zero for calibration blank criteria. See SOP Section 9.8 for a detailed description of the required corrective action procedures. **Refer to PT-QA-025 for specific DoD requirements for the calibration blanks.** For DoD V4.1 refer to SOP PT-QA-029.

17. ATTACHMENTS

17.1. Documentation and Record Management

- The following documentation comprises a complete ICP raw data package:
- Raw data (direct instrument printout).
- Relevant sample preparation benchsheets.
- Run log printout from instrument software where this option is available (TJA) or manually generated run log (i.e., Ward WSL printout).
- Data review checklist - See Appendix B.
- Standards documentation (including prep and expiration dates, source, and lot #).
- Nonconformance/anomaly documentation (if applicable).

17.2. FIGURE 1 – FLOW DIAGRAM

17.3. APPENDIX A - TABLES

17.4. APPENDIX B - TESTAMERICA ICP DATA REVIEW CHECKLIST

17.5. APPENDIX C - TROUBLESHOOTING GUIDE

17.6. APPENDIX D - CONTAMINATION CONTROL GUIDELINES

17.7. APPENDIX E - PREVENTIVE MAINTENANCE

18. REVISION HISTORY

18.1. Revision 10, 03/31/09

18.1.1. Updated into the new Corporate format; added the appropriate Corporate text to the Scope, Safety, Waste Management and Pollution Control sections; added text to section 9 concerning the Initial Demonstration of Capability being moved to section 12; changed STL to TestAmerica throughout the SOP; updated reference numbers and SOP references throughout the document; updated the Reference section SOP numbers; in section 9.3 changed 20X to 10X; in section 10.10 changed the Trace to any axial ICP.

18.1.2. 6010C method reference added. SOP references updated.

18.1.3. Updated SOP for requirement of Method 6010C, see SOP areas highlighted referring to 6010C.

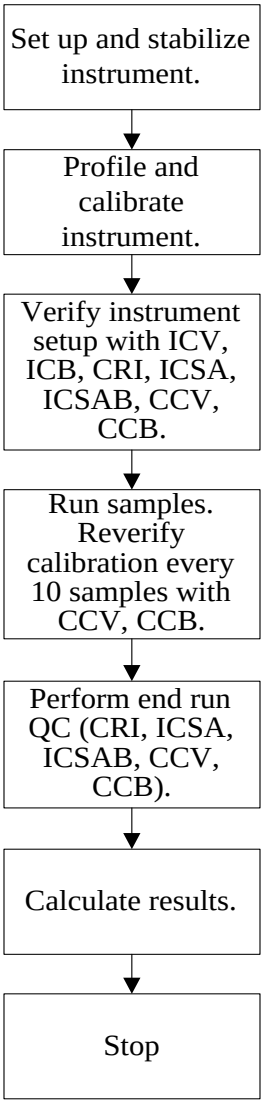
18.1.4. Added to section 8: Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

18.2. Revision 11:

18.2.1. Added to section 9.9: For method 6010C the RLV/CRA which is the low level quantitation check sample is prepared and analyzed quarterly or as needed. The control limit is 70-130%. Please note the RLV/CRA (undigested) is still analyzed at the beginning and end of the analytical run.

18.2.2. Added references to SOP PT-QA-029.

Figure 1. Flow Diagram



APPENDIX A

TABLES

TABLE I. Method 200.7, 6010B and 6010C Target Analyte List

ELEMENT	Symbol	CAS #	6010B/6010 C analyte	200.7 analyte	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil	Reporting Limit (ug/wipe) Wipe
Aluminum	Al	7429-90-5	X	X	200	20	10
Antimony	Sb	7440-36-0	X	X	60	6	3
Arsenic	As	7440-38-2	X	X	300	30	15
Barium	Ba	7440-39-3	X	X	200	20	10
Beryllium	Be	7440-41-7	X	X	4	0.4	0.25
Boron	B	7440-42-8	X	X	200	20	10
Cadmium	Cd	7440-43-9	X	X	5	0.5	0.25
Calcium	Ca	7440-70-2	X	X	5000	500	250
Chromium	Cr	7440-47-3	X	X	10	1	0.5
Cobalt	Co	7440-48-4	X	X	50	5	2.5
Copper	Cu	7440-50-8	X	X	25	2.5	1.25
Iron	Fe	7439-89-6	X	X	100	10	5
Lead	Pb	7439-92-1	X	X	100	10	5
Lithium	Li	7439-93-2	X	X	50	5	2.5
Magnesium	Mg	7439-95-4	X	X	5000	500	250
Manganese	Mn	7439-96-5	X	X	15	1.5	0.75
Molybdenum	Mo	7439-98-7	X	X	40	4	2
Nickel	Ni	7440-02-0	X	X	40	4	2
Phosphorus	P	7723-14-0	X	X	300	30	NA
Potassium	K	9/7/7440	X	X	5000	500	250
Selenium	Se	7782-49-2	X	X	250	25	12.5
Silicon	Si	7631-86-9	X	X	500	N/A	N/A
Silver	Ag	7440-22-4	X	X	10	1	0.5
Sodium	Na	7440-23-5	X	X	5000	500	250
Strontium	Sr	7440-24-6	X	X	50	5	2.5
Thallium	Tl	7440-28-0	X	X	2000	200	100
Vanadium	V	7440-62-2	X	X	50	5	2.5
Zinc	Zn	7440-66-6	X	X	20	2	1

Note: Where reporting “Hardness” by ICP use the following equations per SM20th ed. 2340B:

Calcium Hardness = 2.497 [Ca, mg/L]
Total Hardness = 2.497 [Ca, mg/L] + 4.118 [Mg, mg/L]
Where reporting "Silica" by ICP use the following equation:

Silica = Silicon * 2.14

TABLE IA. Method 200.7, 6010B and 6010C Trace ICP Target Analyte List

ELEMENT	Symbol	CAS #	Reporting Limit (ug/L) Water	Reporting Limit (mg/kg) Soil	Reporting Limit (ug/wipe) Wipe
Arsenic	As	7440-38-2	10	1.0	0.5
Lead	Pb	7439-92-1	3.0	0.3	0.15
Selenium	Se	7782-49-2	5.0	0.5	0.25
Thallium	Tl	7440-28-0	10	1.0	0.5
Antimony	Sb	7440-36-0	10	1.0	0.5
Cadmium	Cd	7440-43-9	5.0	0.5	0.25
Silver	Ag	7440-22-4	5.0	0.5	0.25
Chromium	Cr	7440-47-3	5.0	0.5	0.25

TABLE II. Non-Routine Analyte List

			Reporting	Reporting	Reporting

ELEMENT	Symbol	CAS #	Limit (ug/L) Water	Limit (mg/kg) Soil	Limit (ug/wipe) Wipe
Tin	Sn	7440-31-5	100	10	5
Titanium	Ti	7440-32-6	50	5	2.5

TABLE III. Matrix Spike and Aqueous Laboratory Control Sample Levels

ELEMENT	LCS Level (ug/L)	Matrix Spike Level (ug/L)
Aluminum	2000	2000
Antimony	500	500
Arsenic	2000	2000
Barium	2000	2000
Beryllium	50	50
Cadmium	50	50
Calcium	50000	50000
Chromium	200	200
Cobalt	500	500
Copper	250	250
Iron	1000	1000
Lead	500	500
Lithium	1000	1000
Magnesium	50000	50000
Manganese	500	500
Molybdenum	1000	1000
Nickel	500	500
Potassium	50000	50000
Selenium	2000	2000
Silver	50	50
Sodium	50000	50000
Strontium	1000	1000
Thallium	2000	2000
Vanadium	500	500
Zinc	500	500

ELEMENT	LCS Level (ug/L)	Matrix Spike Level (ug/L)
Boron	1000	1000
Silicon	10000	10000
Tin	2000	2000
Titanium	1000	1000

TABLE IV. ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	100000	200	25000	50000
Antimony	10000	60	1000	5000
Arsenic	10000	300	1000	5000
Barium	10000	200	1000	5000
Beryllium	10000	4	1000	5000
Cadmium	10000	5	1000	5000
Calcium	100000	5000	25000	50000
Chromium	10000	10	1000	5000
Cobalt	10000	50	1000	5000
Copper	10000	25	1000	5000
Iron	100000	100	25000	50000
Lead	10000	100	1000	5000
Lithium	10000	50	1000	5000
Magnesium	100000	5000	25000	50000
Manganese	10000	15	1000	5000
Molybdenum	10000	40	1000	5000
Nickel	10000	40	1000	5000
Potassium	100000	5000	25000	50000
Selenium	10000	250	1000	5000
Silver	2000	10	500	1000
Sodium	100000	5000	25000	50000
Strontium	10000	50	1000	5000
Thallium	20000	2000	5000	10000
Vanadium	10000	50	1000	5000
Zinc	10000	20	1000	5000

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Boron	10000	200	1000	5000
Silicon	10000	500	1000	5000
Tin	10000	100	1000	5000
Titanium	10000	50	1000	5000

TABLE IVA. Trace ICP Calibration and Calibration Verification Standards

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Aluminum	50000	200	12500	25000
Antimony	1000	10	250	500
Arsenic	1000	10	250	500
Barium	4000	10	1000	2000
Beryllium	4000	4	1000	2000
Cadmium	1000	5	250	500
Calcium	100000	5000	25000	50000
Chromium	4000	5	1000	2000
Cobalt	4000	50	1000	2000
Copper	4000	25	1000	2000
Iron	50000	100	12500	25000
Lead	1000	3	250	500
Magnesium	100000	5000	25000	50000
Manganese	4000	15	1000	2000
Molybdenum	4000	40	1000	2000
Nickel	4000	40	1000	2000
Potassium	250000	5000	50000	125000
Selenium	1000	5	250	500
Silver	2000	5	500	1000
Sodium	250000	5000	50000	125000
Thallium	2000	10	500	1000
Vanadium	4000	50	1000	2000
Zinc	4000	20	1000	2000
Boron	4000	200	1000	2000

Element	Calibration Level	RL (ug/L)	ICV (ug/L)	CCV (ug/L)
Silicon	4000	500	1000	2000
Tin	4000	100	1000	2000
Titanium	4000	50	1000	2000

TABLE V. Interference Check Sample Concentrations*

Element	ICSA (ug/L)	ICSAB (ug/L)
Aluminum	500000	500000
Antimony	-	1000
Arsenic	-	1000
Barium	-	500
Beryllium	-	500
Cadmium	-	1000
Calcium	500000	500000
Chromium	-	500
Cobalt	-	500
Copper	-	500
Iron	200000	200000
Lead	-	1000
Magnesium	500000	500000
Manganese	-	500
Molybdenum	-	1000
Nickel	-	1000
Potassium	-	10000
Selenium	-	1000
Silver	-	1000
Sodium	-	10000
Thallium	-	10000**
Vanadium	-	500
Zinc	-	1000
Tin	-	1000

* Custom TestAmerica solutions contain common analytes. Non-routine elements not listed above should be spiked into the ICSAB at 1000 ug/L.
** Thallium level for Trace ICP should be at 1000 ug/L.

TABLE VI. TCLP Reporting Limits, Regulatory Limits and Matrix Spike Levels

ELEMENT	Reporting Level (ug/L)	Regulatory Limit (ug/L)	Spike Level (ug/L)
Arsenic	500	5000	5000
Barium	10000	100000	50000
Cadmium	100	1000	1000
Chromium	500	5000	5000
Lead	500	5000	5000
Selenium	250	1000	1000
Silver	500	5000	1000

TABLE VII. Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Two-point Initial Calibration	Beginning of every analytical run, every 24 hours, whenever instrument is modified, or CCV criterion is not met	RSD between duplicate exposures ≤5%	Terminate analysis; Correct the problem; Prepare new standards; Recalibrate following system performance.
ICV	Beginning of every analytical run.	Method 200.7: 95 - 105 % recovery. Method 6010B & 6010C: 90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate.
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero. (1)	Terminate analysis; Correct the problem; Recalibrate.
RLV/CRA/LLICV/LLCCV	Beginning of every analytical run, immediately following the ICB. Method 6010C also requires analysis at the end of the analytical sequence.	50 – 150% recovery. (1) Method 6010C: 70 – 130% recovery	Terminate analysis; Correct the problem; Recalibrate.
CCV	Every 10 samples and at the end of the run.	Method 200.7, 6010B & 6010C: 90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV.
CCB	Immediately following each CCV.	The result must be within +/- RL from zero. (1)	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB.

TABLE VII. Summary of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICSA	Beginning of every run	See Section 9.10.3 (1)	See Section 9.10.3.
ICSAB	Immediately following each ICSA.	Results must be within 80 - 120% recovery.	See Section 9.10.2.
Dilution Test	One per prep batch.	For samples > 50x MDL, dilutions must agree within 10%.	Narrate the possibility of physical or chemical interference per client request.
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. (1) Common lab contaminants may be accepted up to 2x the RL after consultation with the client (See 9.3). Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL may not require redigestion or reanalysis (see Section 9.3).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.3 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits. (85-115% for 200.7)	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS.

TABLE VII. Summary of Quality Control Requirements			
QC PARAMETER	**FREQUENCY**	**ACCEPTANCE CRITERIA**	**CORRECTIVE ACTION**
		Samples for which the contaminant is < RL and the LCS results are > 120% (115% for 200.7) may not require redigestion or reanalysis (see Section 9.4)	
Matrix Spike	One per sample preparation batch of up to 20 samples (6010B/6010C) or one per every 10 or fewer samples (200.7).	75 - 125 % (6010B & 6010C) or 70 – 130% (200.7) recovery or in-house control limits. (1) For TCLP See Section 10.15.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. For TCLP see Section 10.15.
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery; RPD ≤ 20%. (1)	See Corrective Action for Matrix Spike.

(1) For specific DoD requirements, refer to PT-QA-025. For DoD V4.1 refer to SOP PT-QA-029.

APPENDIX B

TESTAMERICA ICP DATA REVIEW CHECKLIST

TestAmerica
THE LEADER IN ENVIRONMENTAL TESTING

TestAmerica Pittsburgh ICP Data Review Checklist

Run Date: _____ 3. _____ 10. _____ 17. _____ 24. _____ 31. _____
Analyst: _____ 4. _____ 11. _____ 18. _____ 25. _____ 32. _____
Inst: _____ 5. _____ 12. _____ 19. _____ 26. _____ 33. _____
Meth: _____ 6. _____ 13. _____ 20. _____ 27. _____ 34. _____
Lots Analyzed: 7. _____ 14. _____ 21. _____ 28. _____ 35. _____
1. _____ 8. _____ 15. _____ 22. _____ 29. _____ 36. _____
2. _____ 9. _____ 16. _____ 23. _____ 30. _____ 37. _____

Review Item	Yes (✓)	No (✓)	N/A (✓)	2nd Lv (✓)	Comments
A. Calibration/Instrument Run QC 1. Instrument calibrated per manufacturer's instructions and at SOP specified levels?					
2. ICV/CCV analyzed at appropriate frequency and within control limits? (6010B, CLP=90-110%, 200.7=95-105%[ICV])?					
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?					
4. CRA/RLV/CRI analyzed? (CRI for CLP only)					
5. ICSA/ICSAB run at required frequency and within SOP limits?					
B. Sample Results 1. Were samples with concentrations > the linear range for any parameter diluted and reanalyzed?					
2. All reported results bracketed by in control QC?					
3. Sample analyses done within holding time?					
C. Preparation/Matrix QC 1. LCS done per prep batch and within QC limits?					
2. Method blank done per prep batch and < RL or CRDL (CLP)?					
3. MS run at required frequency and within limits?					
4. MSD or DU run at required frequency and RPD within SOP limits?					
5. Dilution Test done per prep batch (or per SDG for CLP)?					
6. Post digestion spike analyzed if required (CLP only)?					
D. Other 1. Are all nonconformances documented appropriately?					
2. Current IDL/LR/IEC data on file?					
3. Calculations checked for error?					
4. Transcriptions checked for error?					
5. All client/project specific requirements met?					
6. Date/Time of analysis verified as correct?					

General Comments: _____

Analyst & Date: _____ Second-Level Review & Date: _____

APPENDIX C

CROSS REFERENCE OF TERMS USED IN METHODS 6010B, 6010C, 200.7 AND BY TESTAMERICA

CROSS REFERENCE OF TERMS COMMONLY USED IN

METHODS EPA 200.7, SW846 6010B/6010C AND TESTAMERICA INC. SOP

EPA 200.7	SW6010B/6010C	TestAmerica Inc. SOP
Calibration blank (CB)	Calibration blank	Initial and continuing calibration blanks (ICB/CCB)
Dilution test	Dilution test	Dilution Test
Instrument detection limit (IDL)	Instrument detection limit (IDL)	Instrument detection limit (IDL)
Instrument performance check (IPC)	Continuing calibration verification (CCV)	Continuing calibration verification (CCV)
Internal standard	Internal standard	Internal standard (IS)
Laboratory duplicates	n/a	n/a
Laboratory fortified blank (LFB)	n/a	Laboratory control sample (LCS)
Laboratory fortified sample matrix (LFM)	Matrix spike and matrix spike duplicate (MS/MSD)	Matrix spike and matrix spike duplicate (MS/MSD)
Laboratory reagent blank (LRB)	Method blank	Method or Prep blank (MB)
Linear dynamic range (LDR)	Linear dynamic range (LDR)	Linear dynamic range (LDR)
Method detection limit (MDL)	Method detection limit (MDL)	Method detection limit (MDL)

EPA 200.7	SW6010B/6010C	TestAmerica Inc. SOP
Quality control sample (QCS)	Check standard or Initial calibration verification (ICV)	Initial calibration verification (ICV)
Spectral interference check solution (SIC)	Interference check solution (ICS)	Interference check solution (ICSA/ICSAB)

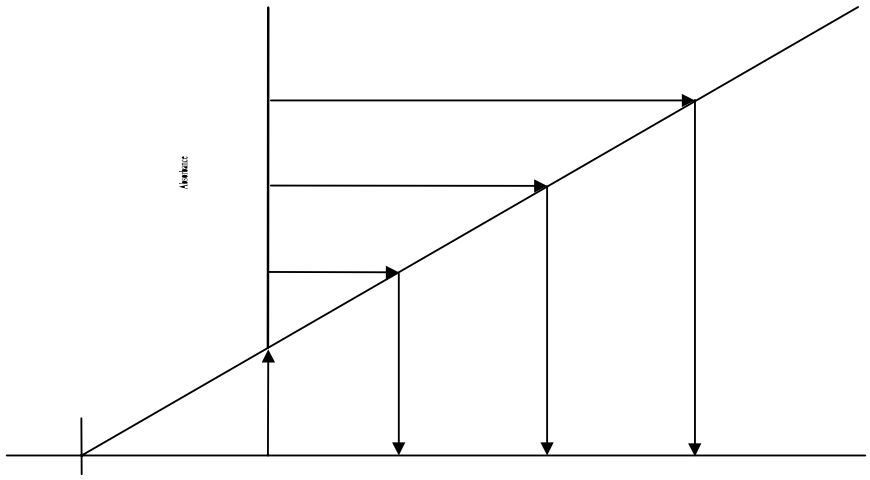
APPENDIX D

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 standard should be the same.

In order to determine the concentration of analyte in the sample, the analytical value of each solution is determined and a plot or linear regression performed. On the vertical axis the analytical value is plotted versus the concentrations of the standards on the horizontal axis. 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.



- 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.

APPENDIX E

TROUBLESHOOTING GUIDE

Problem	Possible Cause/Solution
High Blanks	Increase rinse time Clean or replace tip Clean or replace torch Clean or replace sample tubing Clean or replace nebulizer Clean or replace mixing chamber Lower Torch
Instrument Drift	RF not cooling properly Vacuum level is too low Replace torch (Crack) Clean or replace nebulizer (blockage) Check room temperature (changing) Replace pump tubing Room humidity too high Clean torch tip (salt buildup) Check for argon leaks Adjust sample carrier gas Reprofile Horizontal Mirror Replace PA tube
Erratic Readings, Flickering Torch or High RSD	Check for argon leaks Adjust sample carrier gas Replace tubing (clogged) Check drainage(back pressure changing) Increase uptake time (too short) Increase flush time (too short) Clean nebulizer, torch or spray chamber Increase sample volume introduced Check that autosampler tubes are full Sample or dilution of sample not mixed Increase integration time (too short) Realign torch Reduce amount of tubing connectors
Cu/Mn Ratio Outside Limits or Low Sensitivity	Plasma conditions changed Clean nebulizer, torch or spray chamber Replace tubing (clogged)

Problem	Possible Cause/Solution
	Realign torch Check IECs
Standards reading twice normal absorbance or concentration	Incorrect standard used Incorrect dilution performed

APPENDIX F

CONTAMINATION CONTROL GUIDELINES

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 glassware should be washed with detergent and tap water and rinsed with 20% 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.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

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

Yellow pipette tips and volumetric caps can sometimes contain cadmium.

Some sample cups have been found to contain lead.

The markings on glass beakers have been found to contain lead. If acid baths are in use for glassware cleaning, they should be periodically checked for contaminants since contaminant concentrations will increase over time.

New glassware especially beakers can be a source of silica and boron.

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

Improper cleaning of glassware can cause contamination.

Latex gloves contain over 500 ppb of zinc.

APPENDIX G

PREVENTATIVE MAINTENANCE

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, time and instrument 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.

Daily
Change sample pump tubing and pump windings
Check argon gas supply level
Check rinse solution and fill if needed
Check waste containers and empty if needed
Check sample capillary tubing is clean and in good condition
Check droplet size to verify nebulizer is not clogged.
Check sample flow for cross flow nebulizer
Check Cu/Mn ratio-should be 30% of value at date that IECs were performed
Check pressure for vacuum systems

As Needed
Clean plasma torch assembly to remove accumulated deposits
Clean nebulizer and drain chamber; keep free-flowing to maintain optimum performance
Replace peristaltic pump tubing, sample capillary tubing, and autosampler sipper probe

Weekly
Apply silicon spray on autosampler tracks
Check water level in cool flow

Monthly
Clean air filters on back of power unit to remove dust
Check D mirror for air instruments

Bi-yearly
Change oil for vacuum systems
Replace coolant water filter (may require more or less frequently depending on quality of cooling water)

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN SOLID SAMPLES BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY

METHOD: SW846 7471A AND 7471B

Approvals (Signature/Date):			
	6/23/2010		6/17/2010
Larry Matko Technical Manager	Date	Steve Jackson Health & Safety Manager / Coordinator	Date
	06/23/10		6/23/2010
Nasreen K. DeRubeis Quality Assurance Manager	Date	Larry Matko Laboratory Director	Date

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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 7471A and 7471B.

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. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

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

1.4. The TestAmerica reporting limit for mercury in solid matrices is 0.033 mg/kg based a 0.6 g sample aliquot (wet weight). The TestAmerica reporting limit for wipes is 0.02 ug/wipe.

1.5. For DoD QSM Version 3 requirements, refer to SOP PT-QA-025, current revision.

1.6. For DoD QSM Version 4.1 requirements, refer to SOP PT-QA-029, current revision.

1.7. On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.1 in the Quality Assurance Manual.

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

4. INTERFERENCES

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

4.1. Potassium permanganate, which is used to breakdown 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.

4.2. 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.

4.3. 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 at least 15 minutes. Some samples may require dilution prior to digestion due to extremely high concentrations of chloride.

4.4. 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.

4.5. 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.

4.6. The most common interference is laboratory contamination, which 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 Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

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

5.3. 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 in Reagent)	Oxidizer Corrosive Poison	0.1 Mg/M3 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/M3-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/M3 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.
Stannous Chloride	Irritant	2 Mg/M3 TWA as Tin	Causes irritation to the respiratory tract. Can irritate skin and eyes. Symptoms include coughing and shortness of breath. Contact with skin and/or eyes may cause redness, itching and pain.
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. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of

getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution 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:

5.5.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.5.2. Iodine, 0.25%, in a 3% KI solution.

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

5.7. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.8. 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.

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

5.10. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor and/or the EH&S coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Hot blocks capable of maintaining temperature of 95 $\pm$ 5 °C.

6.2. Leeman HYDRA AA Automated Mercury Analysis System.

6.3. Disposable Sealable Sample Containers (Corning).

6.4. Argon gas supply (ultrahigh purity-grade).

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.

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 (1000 ppm) mercury standards (in 10% HNO_3) are purchased as custom TestAmerica 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 stock mercury standard (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. This 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 intermediate mercury standard (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. This acid (150 uL of

concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot. A second source working standard is prepared at 0.1 ppm for preparation of the ICV.

7.5. The calibration standards must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into sample prep bottles and proceeding as specified in Section 11.1. The 0, .5, 1.0, 5.0 and 10 standards are recommended by Thermo Electron. The 0.2 standard level was selected to include a standard at the RL. See Table 1 (Appendix A) for the preparation of the ICV, CCV and RLV standards.

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. For example, automated mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard (ICV) must be made from a different stock solution than that of the calibration standards.

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.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

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

7.9.1. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

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

7.11. Stannous chloride solution: Add 200 g of stannous chloride to 2 L of 10% hydrochloric acid.

Note: Stannous sulfate may be used in place of stannous chloride. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

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.

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, SHIPMENT AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of sample analysis.

8.2. Soil and wipe samples do not require preservation but must be stored at 4° C ± 2° C until the time of analysis. Tissue samples are stored frozen.

8.3. Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. 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 LCS and a matrix spike/matrix spike duplicate. 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 specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

9.2. 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.

9.3. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that 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 analyte of interest at or above the reporting or at or above 5% of the measured concentration of that analyte in associated samples, whichever is higher (sample result must be a minimum of 20 times higher than the blank contamination level). **Refer to PT-QA-025 or PT-QA-029 for specific DoD requirements for method blank.**

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. **Such action must be taken in consultation with the client and 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.**

9.4. Laboratory Control Sample (LCS) - One aqueous LCS must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going 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. The CCV results can be reported as the LCS results since all CCVs (as well as all other standards) are processed through the sample preparation step with the field samples. No more than 20 samples can be associated with one CCV used for the purpose of reporting LCS data.

- If the LCS is outside established control limits the system is out of control and corrective action must occur. Until in-house control limits are established, a control limit of 80 - 120% recovery must be applied.

- In the instance where the LCS recovery is > 120% and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative.

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.5. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as 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 MS/MSD's. 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 (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 75 - 125 % 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. **Refer to PT-QA-025 or PT-QA-029 for specific DoD requirements for the MS/MSD.**

- If the native analyte concentration in the MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual

recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.6. Initial Calibration Verification (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 that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. **Refer to PT-QA-025 or PT-QA-029 for specific DoD requirements for the ICB.** If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the associated samples.

9.7. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples and at the end of the analytical sequence. The CCV must be a mid-range standard at a concentration other than that of the ICV. The CCV result must fall within 20% of the true value for that solution. A CCB is analyzed immediately following each CCV. The CCB result must fall within +/- RL from zero. **Refer to PT-QA-025 or PT-QA-029 for specific DoD requirements for the CCB.** 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 ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, 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 the corrective action will include repreparation of the associated samples.

9.8. Reporting Limit Verification Standard (RLV) – Calibration accuracy at the laboratory reporting limit is verified after the analysis of the ICB. Until in-house control limits are established, a control limit of 50 - 150% recovery will be applied.

9.9. 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, which cause a baseline shift. Refer to Section 10.3.11 for

additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. PROCEDURE

10.1. Calibration and Standardization

10.1.1. Calibration standards must be processed through the preparation procedure as described in Section 10.2.

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

10.1.3. 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.

10.1.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to the facility specific instrument SOP and CVAA instrument manual for detailed setup and operation protocols.

10.1.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the TestAmerica 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.

10.1.6. The calibration curve must have a correlation coefficient of $\geq$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.

10.1.7. Refer to Section 9.0 and Table II for calibration verification procedures, acceptance criteria and corrective actions. The NELAC requirement for

verification of initial calibration at varied concentrations is met daily since the ICVs, CCVs, and RLVs are all at different concentrations.

10.2. Standard and Sample Preparation:

10.2.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB, RLV) are processed through the digestion procedure as well as the field samples.

10.2.2. Transfer 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working standard (7.5) into a series of sample digestion bottles.

Note: Alternate volumes of standard may be prepared as long as the accuracy and final standard concentrations as detailed in Table I are maintained.

10.2.3. Add reagent water to each standard bottle to make a total volume of 10 mL. Continue preparation as described under 10.2.5 or 10.2.6 below.

10.2.4. Transfer triplicate, 0.2 g portions of a well mixed sample into a clean sample digestion bottle. Refer to PT-QA-024 for subsampling procedures. For wipes, add the entire contents of the sample jar into a clean sample digestion container. Continue preparation as described under 10.2.5 or 10.2.6 below.

10.2.5. Hot Block protocol (default procedure):

10.2.5.1. Add 5 mL concentrated of H_2SO_4 and 2 mL of concentrated HNO_3.

10.2.5.2. To the LCS, add 2.5 mL, and to the MS, and MSD, add 1.0 mL of 0.1 ppm working standard (7.4)

10.2.5.3. Add 5 mL of saturated potassium permanganate solution.

10.2.5.4. Add 8 mL of potassium persulfate solution.

10.2.5.5. Cover digestion bottle with aluminum foil or screw cap loosely applied.

10.2.5.6. Heat the samples at 95 $\pm$ 5 °C for 2 hours.

10.2.5.7. Cool.

10.2.5.8. Add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce excess permanganate.

Note: Alternate final volumes may be used as long as the standards and sample are treated the same way and reagents are adjusted proportionally.

10.2.5.9. Make up to volume of 100 mL with reagent water.

10.2.5.10. Continue as described under Section 10.3.

10.3. Sample Analysis:

10.3.1. Refer the instrument manual for detailed setup and operation protocols for the Hydra AA.

10.3.2. All labs are required to detail the conditions/programs utilized for each instrument within the facility specific instrument operation SOP.

10.3.3. Automated determination: Follow instructions provided by instrument manufacturer.

10.3.4. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. ug of mercury. 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.

10.3.5. All measurements must fall within the defined calibration range to be valid. When sample concentrations exceed the upper limit of the calibration curve, the samples will be diluted and reanalyzed (if possible) to bring them within calibration curve. When reported sample concentrations either exceed the upper limit of the curve (i.e. cannot be rerun) or fall below the reporting limit, the data will be qualified as estimated.

10.3.6. 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.

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

10.3.8. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

10.3.9. The following analytical sequence must be used with 7471A and 7471B:

Instrument Calibration

ICV

ICB

RLV

Maximum 10 samples

CCV

CCB

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

CCV

CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7471A and 7471B.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

10.3.10. The following run sequence is consistent with 7471A, 7471B and CLP and may be used as an alternate to the sequence in 10.3.9. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration

ICV

ICB

RLV or CRA*

CCV

CCB

10 samples

CCV

CCB

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

CCV

CCB

Refer to the appropriate CLP SOP (CORP-MT-0008) for quality control requirements for QC samples.

* Refer to the CLP SOP for information on the CRA.

10.3.11. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

Appendix C provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

10.4. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

10.5. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and parts maintenance. For instrument troubleshooting, use the autodiagnostics software. If a the problem cannot be determined using the software, place a call to service personnel

10.6. 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 shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

11. CALCULATIONS / DATA REDUCTION

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

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

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

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

11.3. RLV percent recoveries are calculated using the same equation as the ICV or CCV (replace ICV or CCV with RLV in the above equations).

11.4. 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

11.5. 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

11.6. For automated determinations, the final concentration determined in solid samples when reported on a dry weight basis is calculated as follows:

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

Where:

C = Concentration (ug/L) from instrument readout

V = Volume of digestate (L)

D = Instrument dilution factor

W = Weight in g of wet sample digested

S = Percent solids/100

Note: A Percent Solids determination must be 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 should be omitted from the above equation.

11.7. For automated determinations, the final concentration determined in wipe samples is calculated as follows:

ug/wipe = (C x V x D)

Where:

C = Concentration (ug/L) from instrument readout

V = Volume of digestate (L)

D = Instrument dilution factor

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

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

11.9. Sample results should be reported with up to three significant figures in accordance with the TestAmerica significant figure policy.

12. METHOD PERFORMANCE

12.1. Prior to the analysis of Hg using 7471A or 7471B, the following requirements must be met:

12.2. Initial Demonstration of Capability

12.2.1. An initial demonstration of capability for each method must be performed prior to analyzing samples. For the standard analyte list, the initial demonstration consists of the preparation and analysis of four LCS samples containing all of the standard analytes for the method, as well as a method detection limit (MDL) study (described below).

12.2.2. Four LCS samples are analyzed with the same procedures used to analyze samples, including sample preparation.

12.2.3. The mean recovery and standard deviation are calculated for each analyte of interest. These results are compared with the established method acceptance criteria. All four results must meet acceptance criteria before the method can be used to analyze sample. The results of the initial demonstration study must be acceptable before analysis of samples may begin For further detail refer to SOP PT-QA-001.

12.2.4. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, and have been carried through the entire analytical procedure. MDLs are determined in accordance with 40 CFR Part 136 Appendix B requirements and SOP PT-QA-007. The result of the MDL determination must be below the TestAmerica reporting limit.

12.3. Method performance is determined by the analysis of method blank, laboratory control sample, matrix spike and matrix spike duplicate samples. The matrix spike recovery

should fall within +/- 25 % and the matrix spike duplicates should compare within 20% RPD. **Refer to PT-QA-025 or PT-QA-029 for specific DoD requirements for the MS.** The method blanks must meet the criteria in Section 9.3. **Refer to PT-QA-025 or PT-QA-029 for specific DoD requirements for the method blank.** The laboratory control sample should recover within 20% of the true value until in house limits are established.

12.4. Training Qualification:

12.4.1. 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.

13. POLLUTION CONTROL

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

13.2. This method does not contain any specific modifications that serve to minimize or prevent pollution.

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1. Extracted sample containing less than 1 ppb Hg. This waste is collected in waste containers identified as “Acid Waste”, Waste #33. It is neutralized to a pH between 6 and 9 and is disposed down a lab sink.

14.1.2. Unused Standards. This waste collected in containers identified as “Mercury Standards Waste”, Waste #4.

14.1.3. Extracted sample containing greater than 1 ppb Hg. This waste collected in containers identified as “Mercury Standards Waste”, Waste #4.

14.1.4. Mercury Analyzer Waste. Waste discharged from mercury analyzer is collected in containers identified as “Mercury Standards Waste”, Waste #4.

15. REFERENCES / CROSS-REFERENCES

15.1. Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7471A (Mercury).

15.2. Mercury In Solid Or Semisolid Waste (Manual Cold-Vapor Technique), Test Methods for Evaluating Solid Waste , Physical/Chemical Methods, SW-846, 3rd Edition, Final Update IV, Revision 2, February 2007, Method 7471B (Mercury).

15.3. U.S.EPA Statement of Work for Inorganics Analysis, ILM04.0.

15.4. SOP PT-QA-001, Employee Orientation and Training, current version.

15.5. SOP PT-HS-001, Waste Collection, Accumulation and Storage, current version.

15.6. SOP PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability, current version.

15.7. SOP PT-QA-007, Detection Limits, current version.

15.8. SOP PT-QA-009, Rounding and Significant Figures, current version.

15.9. SOP PT-QA-016, Nonconformance & Corrective Action System, current version.

15.10. SOP PT-QA-018, Technical Data Review Requirements, current version.

15.11. SOP PT-QA-021, Quality Assurance Program, current version.

15.12. SOP PT-QA-022, Equipment Maintenance, current version.

15.13. SOP PT-QA-024, Subsampling, current version.

15.14. SOP PT-QA-025, DoD QSM Version 3, current version.

15.15. SOP PT-QA-027, Sample Receiving and Chain of Custody, current version.

15.16. SOP PT-QA-029, QA/QC Requirements for DoD QSM Version 4.1, April 2009, current version.

16. METHOD MODIFICATIONS:

16.1. Modifications/Interpretations from reference method.

16.1.1. Modifications from 7471A.

16.1.1.1. 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.

16.1.1.2. The alternate run sequence presented in Section 10.3.10 is consistent with method requirements.

16.1.1.3. Chapter 1 of SW846 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. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

16.1.1.4. 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 the reporting limit.

16.1.2. Modifications from Revision 4: Safety Section 5.0, Pollution Prevention Section 14.0 and Waste Management Section 15.0 updated. References to DoD criteria were added. Wipe samples were added to the SOP.

17. ATTACHMENTS

17.1. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

18. REVISION HISTORY

18.1. Revision 7, 01/15/09

18.1.1. Updated the Section headers to the new format; changed STL to TestAmerica throughout the SOP; updated section and SOP reference numbers; added text from the new template in the Safety, Pollution Control and Waste Management Sections; added Section 8.3 concerning lab filtered and preservation sample procedure; Updated the Reference Section.

18.1.2. Added references to Method 7471B.

18.1.3. Added: Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

18.2. Revision 8, 10/8/2009

18.2.1. Removed reference to the autoclave throughout the SOP and added reference to the hot block procedure.

18.2.2. Added the appropriate references to SOP PT-QA-029 where necessary throughout the SOP. Added reference to SOP PT-QA-022, Equipment Maintenance.

18.2.3. Updated Appendix F to be consistent with PT-QA-022.

18.3. Revision 9

18.3.1. Removed reference of the LEEMAN PS200II Mercury Analyzer from sections 6.2, 10.3.1 and Appendix F since this instrument has been removed from service.

18.3.2. Removed section 10.2.5 Water Bath Protocol since only Hot Blocks are used for soils.

18.3.3. Removed Figure 2 detailing the Water Bath Procedure since only Hot Blocks are used for soil digestion.

18.3.4. In section 6.1 removed the Water Bath Temperature requirement since only Hot Blocks are used for soil digestion.

18.3.5. Removed section 7.11 Aqua Regia since soils are digested by hotblock and not wath bath.

Figure 1. Solid Sample Preparation for Mercury - Hot Block Procedure (Default)

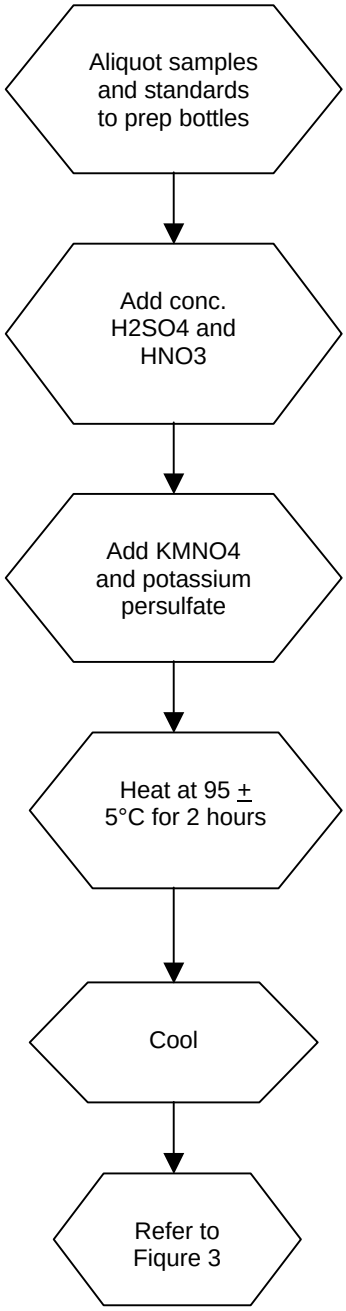
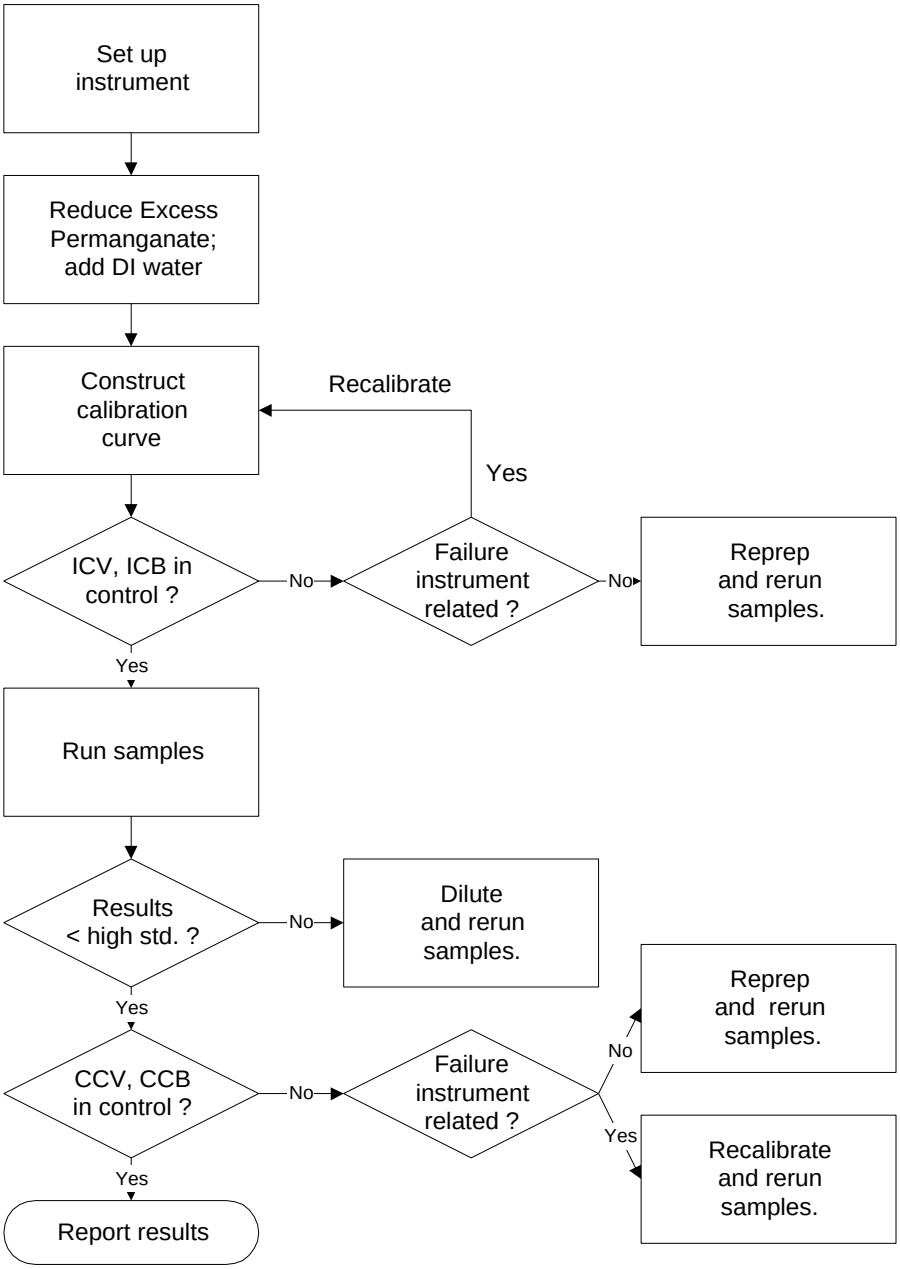


Figure 2. CVAA Mercury Analysis



APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS

Method	Reporting Limit	
SW846 7471A/7471B	0.033 mg/kg or 0.02 ug/wipe	
Standard or QC sample	**mLs of 0.1 ppm Working Standard**	**Concentration (mg/L) *** **
Std 0	0	0
Std 1	0.2	0.0002
Std 2	0.5	0.0005
Std 3	1.0	0.001
Std 4	5.0	0.005
Std 5	10.0	0.010
ICV	2.5 **	0.0025
CCV	5.0	0.005
RLV	0.2	0.0002
LCS	2.5	0.0025
MS	1.0	0.001

* SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements. Deviations from specified calibration levels must be documented in the facility specific instrument operation SOP and must be approved by the facility technical manager and Quality Assurance Manager.

** Prepared from a second source 0.1 ppm working standard.

*** When brought to a 100 mL final volume.

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	90 - 110 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero.(1)	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
RLV	Beginning of every analytical run, immediately following the ICB.	50 - 150 % recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.9).
CCV	Every 10 samples and at the end of the run.	80 - 120 % recovery.	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.8).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero.(1)	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.8).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL.(1) Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4)	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Matrix Spike	One per sample preparation batch of up to 20 samples.	75 - 125 % recovery or in-house control limits.(1) If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 10.3.11
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % recovery or in-house control limits; RPD ≤ 20%.(1) (See MS)	See Corrective Action for Matrix Spike.

(1) For specific DoD requirements, refer to PT-QA-025 or PT-QA-029.

APPENDIX B

TESTAMERICA PITTSBURGH Hg DATA REVIEW CHECKLIST

TestAmerica Pittsburgh Example Data Review Checklist – Mercury

Run Date: _____ Lots Analyzed: 4. _____ 8. _____ 12. _____

Analyst: _____ 1. _____ 5. _____ 9. _____ 13. _____

Instrument: _____ 2. _____ 6. _____ 10. _____ 14. _____

Methods: _____ 3. _____ 7. _____ 11. _____ 15. _____

Review Item	Yes ( )	No ( )	N/A ( )	2nd Level Review ( )	Comments
A. Calibration/Instrument Run QC 1. Instrument calibrated per manufacturer's instructions and at SOP specified levels?					
2. ICV/CCV analyzed at appropriate frequency and within control limits?					
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?					
4. CRA run? (CLP only)					
B. Sample Results 1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?					
2. All reported results bracketed by in control QC?					
3. Sample analyses done within holding time?					
C. Preparation/Matrix QC 1. LCS done per prep batch and within QC limits?					
2. Method blank done per prep batch and < RL or CRDL (CLP)?					
3. MS run at required frequency and within limits?					

Review Item	Yes ( )	No ( )	N/A ( )	2nd Level Review ( )	Comments
4. MSD or DU run at required frequency and RPD within SOP limits?					
D. Other 1. Are all nonconformances documented appropriately?					
2. Current IDL/MDL data on file?					
3. Calculations and transcriptions checked for error?					
4. All client/project specific requirements met?					
5. Date/Time of analysis verified as correct?					

General Comments:_____
_____

Analyst & Date: _____**Second-Level Review & Date:** _____

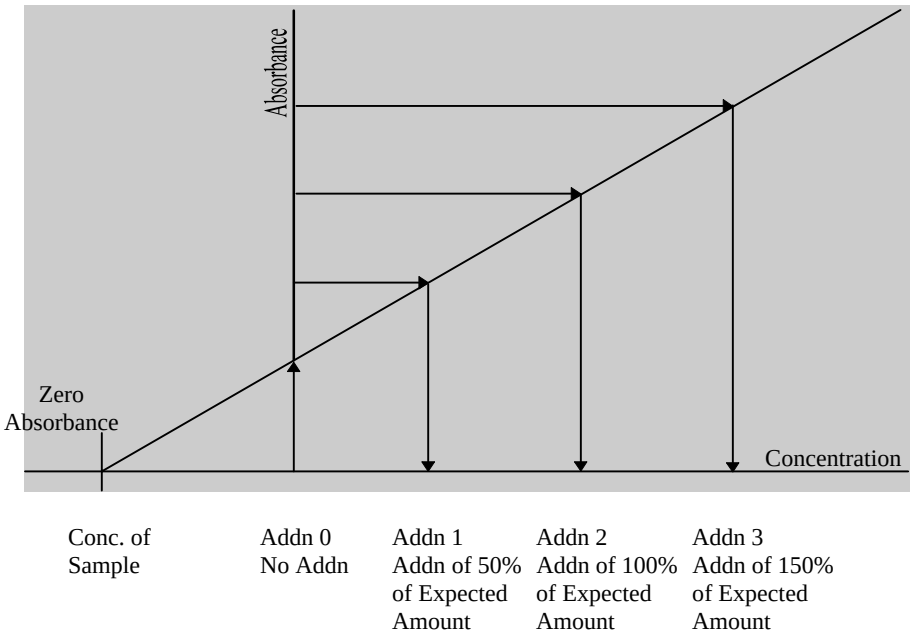
APPENDIX C. MSA GUIDANCE

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.

APPENDIX D. PARTS MAINTENANCE GUIDE

Maintenance Schedule

The software offers a simple to use online Scheduled Maintenance page. To view the page go to Instrument:Scheduled Maintenance (F1 Menu, I, S). A page displaying all items necessary to keep the instrument well maintained is shown (see figure 6.1A).

```
RunProt:
RunFold:          Seq: 0    Batch:
                  Prnt: R/T Off
                  Rev: 3.390  15:40:47 14 Jan 1996 Xmit: Off  Gas:        LPM
 None                                                User:            A/S: On
INSTRUMENT:  Scheduled Maintenance
                                  Uses left     Last service    Next service
 replace: Pump tubing               200          14-Jan-96       24-Jan-96
          Waste drain tubing       2500          14-Jan-96       29-Dec-96
          Liquid/gas separator     5000          14-Jan-96       14-Mar-96
          puMp head               10000            N/A             N/A
          Hg lamp                   N/A          14-Jan-96       12-Jun-96
          Reductant bottle          400          14-Jan-96       12-Jul-96
          prOcess tubing           5000            N/A             N/A
 Clean optical cell                 300            N/A             N/A
 clean External optics              N/A          14-Jan-96       12-Jul-96

* - needs maintenance

For help on <hotkey> press Shift <hotkey>
```

Figure 6.1a. Scheduled maintenance screen

Each scheduled maintenance item has a usage counter, timed usage, or both (N/A indicates that the usage counter or the timed usage is not applicable for that item). If either condition expires for a given item a maintenance message will alert the user at the top of the status box.

Maintenance Procedures

An asterisk(*) will appear next to the item requiring maintenance on the Scheduled Maintenance screen. To clear the message hit <Tab> or replace, clean, or replenish the item using the hot key for the item on the Scheduled Maintenance page. To perform the maintenance on a given item simply type the hot key (e.g. Type <P> for Pump tubing) and follow the directions. Once the directions are followed to completion, the usage counter and timed usage gets updated.

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.

All glassware should be washed with detergent and tap water and rinsed with 20% 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.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

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.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

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, time and instrument 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.

Cold Vapor Atomic Absorption (Hydra AA)

Daily	As Needed	Annually
Clean lens windows with methanol.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture reading.	Check pump tubing/drain tubing.	Check liquid/gas separator.
Check argon flow/pressure.	Clean optical cell	
Check tubing and replace, if needed.	Lubricate pump	
Check drain.		
Replace drying tube.		

This is a Controlled Document. When Printed it becomes Uncontrolled.

TITLE: PREPARATION AND ANALYSIS OF MERCURY IN AQUEOUS SAMPLES BY COLD VAPOR ATOMIC ABSORPTION

METHODS: SW846 7470A AND MCAWW 245.1

Approvals (Signature/Date):

	01/13/2012		12/6/2011
William T. Reinheimer	Date	Steve Jackson	Date
Technical Manager		Health & Safety Manager / Coordinator	
	01/05/12		12/8/2011
Nasreen DeRubeis	Date	Deborah L. Lowe	Date
Quality Assurance Manager		Laboratory Director	

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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. Both the water bath digestion and the hot block digestion are available at the TestAmerica Pittsburgh facility, however the default practice is the hot block digestion for 7470A and 245.1. Both procedures are described in this SOP.

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. Detection limits, sensitivity and optimum concentration ranges for mercury analysis will vary with the matrices, instrumentation and volume of sample used.

1.3. Method 7470A is applicable to the preparation and analysis of mercury in ground water, aqueous samples, wastes, wipes, TCLP, EP and other leachates/extracts. Certain solid and sludge type wastes may also be analyzed, however Method 7471A/B (see PT-MT-007) is usually the method of choice. 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 TestAmerica reporting limit for mercury in aqueous matrices is 0.0002 mg/L.

1.6. For DoD QSM Version 3 requirements, refer to SOP PT-QA-025 and for DoD QSM Version 4.1 requirements, refer to SOP PT-QA-029.

1.7. On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in Section 12.1 in the Quality Assurance Manual.

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 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. Dissolved Metals: Those elements which pass through a 0.45 um membrane. (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.

4. INTERFERENCES

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

4.1. Potassium permanganate, which is used to breakdown 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.

4.2. 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.

4.3. 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 head space 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.

4.4. 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.

4.5. 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.

4.6. The most common interference is laboratory contamination, which 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 Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

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

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

5.4. 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 in Reagent)	Oxidizer Corrosive Poison	0.1 Mg/M3 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/M3-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/M3 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.
Stannous Chloride	Irritant	2 Mg/M3 TWA as Tin	Causes irritation to the respiratory tract. Can irritate skin and eyes. Symptoms include coughing and shortness of breath. Contact with skin and/or eyes may cause redness, itching and pain.
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.			

5.5. Eye protection that protects against splash, laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Cut resistant gloves must be worn doing any other task that presents a strong possibility of getting cut. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.6. Mercury is a highly toxic element that must be handled with care. The analyst must be aware of the handling and clean-up techniques before working with mercury. Since mercury vapor is toxic, precaution 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:

5.6.1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or

5.6.2. Iodine, 0.25%, in a 3% KI solution.

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

5.8. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.9. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor or EH&S coordinator.

5.10. 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.

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

6. EQUIPMENT AND SUPPLIES

6.1. Temperature controlled water bath (capable of maintaining a temperature of 90-95 °C) or hot block capable of maintaining a temperature of 95 ± 5°C for 2 hours.

6.2. Leeman HYDRA AA Automated Mercury Analysis System.

6.3. Disposable Sealable Sample Containers (Corning).

6.4. Argon gas supply (ultrahigh purity-grade).

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.

7.2. Stock (1000 ppm) mercury standards (in 10% HNO_3) are purchased as custom TestAmerica 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 stock mercury standard (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. This 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 intermediate mercury standard (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. This acid (150 uL of concentrated HNO_3) must be added to the flask/bottle before the addition of the stock standard aliquot. A second source working standard is prepared at 0.1 ppm for preparation of the ICV.

7.5. The calibration standards listed in Table I must be prepared fresh daily from the working standard (7.4) by transferring 0, 0.2, 0.5, 1.0, 5.0 and 10.0 mL aliquots of the working mercury standard into 100 mL flasks and diluting to volume with reagent water. The 0, .5, 1.0, 5.0 and 10 standards are recommended by Thermo Electron. The 0.2 standard level was selected to include a standard at the RL. See Table 1 (Appendix A) for the preparation of the ICV, CCV and RLV standards.

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. For example, automated

mercury systems do not require 100 mL of standard and therefore smaller volumes may be generated to reduce waste generation.

7.6. The initial calibration verification standard (ICV) must be made from a different stock solution than that of the calibration standards.

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.

Note: If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

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

7.9.1. Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated H_2SO_4 to 1 liter with reagent water.

7.10. Stannous chloride solution: Add 200 g of stannous chloride to 2 L of 10% hydrochloric acid.

7.11. Stannous sulfate may be used in place of stannous chloride. This mixture is a suspension and should appear cloudy. This solution should be made daily and should be stirred continuously during use.

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.

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, SHIPMENT AND STORAGE

8.1. Sample holding time for mercury is 28 days from time of collection to the time of analysis. For TCLP leachates, the holding time is 28 days from the time of TCLP extraction to the time of analysis.

8.2. 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 analysis.

8.3. Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

9. QUALITY CONTROL

Table II (Appendix A) provides a summary of quality control requirements including type, frequency, acceptance criteria and corrective action.

9.1. Each laboratory must have initial demonstration of performance data on file for each analyte of interest as described in Section 12.0.

9.2. Preparation Batch - A group of up to 20 samples composed of the same matrix and processed together using the same procedures and reagents. The preparation batch must contain a method blank, a LCS and a matrix spike/matrix spike duplicate for 7470A or a matrix spike (one per 10 or fewer samples) for 245.1. 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 specific samples for MS/MSD, the batch may contain multiple MS/MSD pairs.

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

9.4. Method Blank (MB) - One method blank must be processed with each preparation batch. The method blank consists of reagent water containing all reagents specific to the method that 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 analyte of interest at or above the reporting limit, or above 10% of either the measured concentration of that analyte in associated samples or the regulatory limit. See SOP PT-QA-021 for more detail on criteria and corrective actions. In addition, blank contamination should always be evaluated against project specific requirements. **Refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1) for specific DoD requirements for the method blank.**

- Repreparation and reanalysis of all samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples (see exception noted above).

- If there is no analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action must be taken in consultation with the client and 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 aqueous LCS (referred to as a Laboratory Fortified Blank in 245.1) must be processed with each preparation batch. The LCS is used to monitor the accuracy of the analytical process. On-going 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. The CCV results can be reported as LCS results since all CCVs (as well as all other standards) are processed through the sample preparation step with the field samples. No more than 20 samples can be associated with one CCV used for the purpose of reporting LCS data.

- If the LCS is outside established control limits the system is out of control and corrective action must occur. Corrective action will result in the batch being re-prepped and re-analyzed. In-house control limits are 80 - 120% for SW-846 method 7470A and 85 – 115% for EPA method 245.1.

- In the instance where the LCS recovery is > 120% (7470A) or > 115% (245.1) and the sample results are < RL, the data may be reported with qualifiers. Such action must be taken in consultation with the client and must be addressed in the case narrative.

- In the event that an MS/MSD analysis is not possible, a Laboratory Control Sample Duplicate (LCSD) must be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

- Corrective action will be repreparation and reanalysis of the batch unless the client agrees that other corrective action is acceptable.

9.6. Matrix Spike/Matrix Spike Duplicate (MS/MSD) - One MS/MSD pair must be processed for each preparation batch of up to 20 samples for 7470A or a MS must be processed for every 10 or fewer samples for 245.1. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added (referred to as a Laboratory Fortified Matrix in 245.1). A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked identically as 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 MS/MSD's. 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 (Appendix A).

- If analyte recovery or RPD falls outside the acceptance range, the recovery of that analyte must be in control for the LCS. Until in-house control limits are established, a control limit of 75 - 125 % (7470A) or 70 – 130% (245.1) recovery and 20% RPD must be applied to the MS/MSD. **Refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1) for specific DoD requirements for 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 MS/MSD exceeds 4 times the spike level for that analyte, the recovery data are reported as NC (i.e., not calculated). If the reporting software does not have the ability to report NC then the actual recovery must be reported and narrated as follows: "Results outside of limits do not necessarily reflect poor method performance in the matrix due to high analyte concentrations in the sample relative to the spike level."

- If an MS/MSD is not possible due to limited sample volume, then a laboratory control sample duplicate (LCSD) should be analyzed. The RPD of the LCS and LCSD must be compared to the matrix spike RPD limits.

9.7. Initial Calibration Verification (ICV/ICB) - Calibration accuracy is verified by analyzing a second source standard (ICV). The ICV result must fall within 10% (7470A) or 5% (245.1) of the true value for that solution. An ICB is analyzed immediately following the ICV to monitor low level accuracy and system cleanliness. The ICB result must fall within +/- the reporting limit (RL) from zero. **Refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1) for specific DoD requirements for the ICB.** If either the ICV or ICB fail to meet criteria, the analysis should be terminated, the problem corrected and the instrument recalibrated. If the cause of the ICV or ICB failure was not directly instrument related the corrective action will include repreparation of the associated samples. The ICV is equivalent to the Quality Control Sample (QCS) and the first Initial Performance Check (IPC) specified in 245.1.

9.8. Continuing Calibration Verification (CCV/CCB) - Calibration accuracy is monitored throughout the analytical run through the analysis of a known standard after every 10 samples and at the end of the analytical sequence. The CCV must be a mid-range

standard at a concentration other than that of the ICV. **The CCV result must fall within 10% (7470A and 245.1) of the true value for that solution.** If both methods are analyzed in the same sequence the tighter criteria of 10% is used for the CCV. A CCB is analyzed immediately following each CCV. The CCB result must fall within +/- RL from zero. **Refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1) for specific DoD requirements for the CCB.** 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 ICV/CCV and ICB/CCB pairs. If a mid-run CCV or CCB fails, the analysis must be terminated, the problem corrected, 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 the corrective action will include repreparation of the associated samples.

9.9. Reporting Limit Verification Standard (RLV) – Calibration accuracy at the laboratory reporting limit is verified after the analysis of the ICB. Until in-house control limits are established, a control limit of 50 – 150% recovery will be applied.

9.10. 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 which cause a baseline shift. Refer to Section 10.3.11 for additional information on when full 4 point MSA is required as well as Appendix C for specific MSA requirements.

10. PROCEDURE

10.1. Calibration and Standardization

10.1.1. Calibration standards must be processed through the preparation procedure as described in Section 10.2.

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

10.1.3. 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.

10.1.4. Set up the instrument with the operating parameters recommended by the manufacturer. Allow the instrument to become thermally stable before beginning calibration (approximately 30 minutes of warm-up is required). Refer to CVAA instrument manual for detailed setup and operation protocols.

10.1.5. Calibrate the instrument according to instrument manufacturer's instructions, using a minimum of five standards and a blank. One standard must be at the TestAmerica 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.

10.1.6. 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.

10.1.7. Refer to Section 9.0 and Table II for calibration verification procedures, acceptance criteria and corrective actions. The NELAC requirement for verification of the initial calibration at varied concentrations is met daily since the ICVs, CCVs, and RLVs are all at different concentrations.

10.2. Sample Preparation:

10.2.1. All calibration and calibration verification standards (ICV, ICB, CCV, CCB, RLV) are processed through the digestion procedure as well as the field samples. *An exception to this is for Method 245.1 samples. The calibration curve samples are* ***not*** *heated.*

10.2.2. Transfer 50 mL of well-mixed sample or standard to a clean sample digestion bottle. Refer to PT-QA-024 for subsampling procedures.

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.

10.2.3. Add 2.5 mL of concentrated H_2SO_4 and 1.25 mL of concentrated HNO_3 mixing after each addition.

Note: All spiking (LCS, MS, MSD) should be done after the initial addition of acids (see Appendix A, Table 1).

10.2.4. 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 15 mL additional permanganate the color does not persist, sample dilution prior to reanalysis may be required.

Note: When performing analyses using automated vs. manual techniques the sample dilution resultant from the addition of more than the original aliquot of permanganate solution must be compensated for by the addition of the same volume of permanganate to all associated samples, standards, *and QC samples (e.g. LCS and blank)* in the run. In instances, where this is not feasible, the addition of excess reagent can be addressed through mathematical correction of the results to account for the resultant dilution effect.

10.2.5. Add 4 mL of potassium persulfate solution for a 50 mL sample and heat for two hours in a hot block at 95 ± 5°C . (**Note:** 8 mL of potassium persulfate solution would be used for a 100 mL sample, etc. for proportional volumes).

NOTE: Alternatively, for analyses using 7470A and 245.1, samples may be digested using a water bath capable of maintaining a temperature of 90 - 95 °C for 2 hours.

10.2.6. Cool samples.

10.2.7. Samples are adjusted to a final volume of 50 ml after digestion.

10.2.8. **NOTE:** All Safety Kleen Total and TCLP waters are prepared a 10 fold dilution, 5 mls of sample diluted to a final volume of 50 mls.

10.2.9. For the procedure in how to make a dilution, refer to work Instruction PT-QA-W-006.

10.3. Sample Analysis:

10.3.1. Refer to the SOP PT-MT-010 and the instrument manuals for detailed setup and operation protocols for the LEEMAN Hydra AA.

10.3.2. Refer to CVAA instrument manual for detailed setup and operation protocols.

10.3.3. When ready to begin analysis, add 6 mL of sodium chloride-hydroxylamine hydrochloride “clearing solution” to the samples to reduce the excess permanganate (the permanganate has been reduced when no purple color remains). Add this solution in 6 mL increments until the permanganate is completely reduced i.e. colorless.

10.3.4. Automated determination: Follow instructions provided by instrument manufacturer.

10.3.5. Perform a linear regression analysis of the calibration standards by plotting maximum response of the standards vs. concentration of mercury. 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.

10.3.6. All measurements must fall within the defined calibration range to be valid. When sample concentrations exceed the upper limit of the calibration curve, the samples will be diluted and reanalyzed (if possible) to bring them within calibration curve. When reported sample concentrations either exceed the upper limit of the curve (i.e. cannot be rerun) or fall below the reporting limit, the data will be qualified as estimated. 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.

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

10.3.8. Baseline correction is acceptable as long as it is performed after every sample or after the CCV and CCB; resloping is acceptable as long as it is immediately preceded and followed by a compliant CCV and CCB.

10.3.9. The following analytical sequence must be used with 7470A and 245.1:

Instrument Calibration

ICV

ICB

RLV

Maximum 10 samples

CCV

CCB

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

CCV

CCB

Refer to Quality Control Section 9.0 and Table II (Appendix A) for quality control criteria to apply to Methods 7470A and 245.1.

Note: Samples include the method blank, LCS, MS, MSD, duplicate, field samples and sample dilutions.

10.3.10. The following run sequence is consistent with 7470A, CLP and 245.1 and may be used as an alternate to the sequence in 10.3.9. This run sequence is recommended if multiple method requirements must be accommodated in one analytical run:

Instrument Calibration

ICV

ICB

RLV or CRA*

CCV

CCB

10 samples

CCV

CCB

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

CCV

CCB

Refer to the appropriate CLP SOPs (PT-MT-006) for quality control requirements for QC samples.

* Refer to the CLP SOPs for information on the CRA.

10.3.11. For TCLP samples, full four point MSA will be required if all of the following conditions are met:

1) recovery of the analyte in the matrix spike is not at least 50%,

2) the concentration of the analyte does not exceed the regulatory level, and,

3) the concentration of the analyte is within 20% of the regulatory level.

The reporting and matrix spike levels for TCLP analyses are detailed in Table I (Appendix A). Appendix E provides guidance on performing MSA analyses. For TCLP mercury determinations, MSA spikes must be added prior to sample preparation.

10.4. To facilitate the early identification of QC failures and samples requiring rerun it is strongly recommended that sample data be reviewed periodically throughout the run.

10.5. Guidelines are provided in the appendices on procedures to minimize contamination of samples and standards, preventive maintenance and parts maintenance. For instrument troubleshooting, use the auto diagnostics software. If the problem cannot be determined using the software, place a call to service personnel.

10.6. 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 shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

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

11. DATA ANALYSIS AND CALCULATIONS

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

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

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

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

11.3. RLV percent recoveries are calculated using the same equation as the ICV or CCV (replace ICV or CCV with RLV in the above equations).

11.4. 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

11.5. 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

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

mg/L = C x D

Where:

C = Concentration (mg/L) from instrument readout

D = Instrument dilution factor

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

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

11.8. Appropriate factors must be applied to sample values if dilutions are performed.

11.9. Sample results should be reported with up to three significant figures in accordance with the TestAmerica significant figure policy.

12. METHOD PERFORMANCE

12.1. Initial Demonstration of Capability

Prior to the analysis of any analyte using 7470A or the 245.1, the following requirements must be met.

12.1.1. Method Detection Limit (MDL) - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest, that have been carried through the entire analytical procedure. MDLs must be determined in accordance with 40 CFR Part 136 Appendix B requirements and SOP PT-MT-007. The result of the MDL must be below the TestAmerica reporting limit.

12.1.2. Initial Demonstration Study - This requires the analysis of four LCS samples. The LCS sample is a well characterized laboratory generated sample used to monitor method performance. The results of the initial demonstration study must be acceptable before analysis of samples may begin. Refer to SOP PT-QA-001.

12.1.2.1. Four aliquots of the LCS are prepared and analyzed using the procedures detailed in this SOP and the determinative SOPs.

12.2. Method performance is determined by the analysis of method blanks, laboratory control samples, matrix spike and matrix spike duplicate samples. The matrix spike recovery should fall within +/- 25 % (7470A) or +/- 30% (245.1) and the matrix spike duplicates should compare within 20% RPD. The method blanks must meet the criteria in Section 9.4. **Refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1) for specific DoD requirements for the method blank and MS.** The laboratory control sample should

recover within 20% (7470A) or 15% (245.1) of the true value until in house limits are established.

12.3. Training Qualification:

12.3.1. 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.

13. POLLUTION PREVENTION

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

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

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1. Extracted sample containing less than 1 ppb Hg. This waste is collected in waste containers identified as "Acid Waste", Waste #33. It is neutralized to a pH between 6 and 9 and is disposed down a lab sink.

14.1.2. Unused Standards. This waste collected in containers identified as "Mercury Standards Waste", Waste #4.

14.1.3. Extracted sample containing greater than 1 ppb Hg. This waste collected in containers identified as “Mercury Standards Waste”, Waste #4.

14.1.4. Mercury Analyzer Waste. Waste discharged from mercury analyzer is collected in containers identified as “Mercury Standards Waste”, Waste #4.

15. REFERENCES/CROSS-REFERENCES

15.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Final Update II, Revision I, September 1994, Method 7470A (Mercury).

15.2. “Methods for the Chemical Analysis of Water and Wastes”, EPA-600/4-79-020, U.S.EPA, 1994, Method 245.1, Revision 3.0.

15.3. U.S.EPA Statement of Work for Inorganics Analysis, ILM04.1.

15.4. PT-QA-001, Employee Orientation and Training.

15.5. PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability.

15.6. PT-QA-007, Method Detection Limits.

15.7. PT-QA-009, Rounding and Significant Figures.

15.8. PT-QA-016, Nonconformance & Corrective Action System.

15.9. PT-QA-018, Technical Data Review Requirements.

15.10. PT-QA-021, Quality Assurance Program.

15.11. PT-QA-022, Equipment Maintenance

15.12. PT-QA-024, Subsampling.

15.13. PT-QA-025, DoD QSM Version 3.

15.14. PT-QA-027, Sample Receiving and Chain of Custody.

15.15. PT-QA-029, QA/QC Requirements for DoD QSM Version 4.1.

15.16. PT-MT-010, Operation of Leeman PS200 (Automated) for Mercury Analysis.

15.17. PT-LQAM- Pittsburgh Laboratory Quality Assurance Manual.

15.18. PT-QA-W-006, Metals Dilution Calculation Table.

16. **METHOD MODIFICATIONS:**

16.1. Modifications/Interpretations from reference method.

16.1.1. Modifications from both 7470A and 245.1.

16.1.1.1. The 200 series methods and Chapter 1 of SW846 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. This SOP requires that reagent water must be free of the analytes of interest as demonstrated through the analysis of method blanks.

16.1.1.2. 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."

16.1.1.3. The alternate run sequence presented in Section 10.3.10 is consistent with method requirements.

16.1.2. Modifications from Method 7470A

16.1.2.1. 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 the reporting limit. **Refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1) for specific DoD requirements for the method blank.**

16.1.2.2. Documentation is on file from EPA's Office of Solid Waste (Oliver Fordham 11/28/95) regarding the acceptance of the autoclave as an equivalent heating device to the water bath. In his letter, Mr. Fordham

cited the CLP water protocol 245.1 CLP-M and therefore the operating parameters from that method were adopted for 7470A (15 minutes at 120 °C and 15 lbs.).

16.1.3. Modifications from 245.1

16.1.3.1. 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. TestAmerica reports all Hg results under this SOP to two significant figures.

17. ATTACHMENTS

17.1. Documentation and Record Management

The following documentation comprises a complete CVAA raw data package:

- Raw data (direct instrument printout)
- Run log printout from instrument software where this option is available or manually generated run log. (A bench sheet may be substituted for the run log as long as it contains an accurate representation of the analytical sequence).
- Data review checklist - See Appendix B
- Standards Documentation (source, lot, date).
- Copy of digestion log.
- Non-conformance summary (if applicable).

17.2. APPENDIX A - TABLES

17.3. APPENDIX B - TestAmerica Hg DATA REVIEW CHECKLIST

17.4. APPENDIX C - MSA GUIDANCE

17.5. APPENDIX D – PARTS MAINTENANCE GUIDE

17.6. APPENDIX E- CONTAMINATION CONTROL GUIDELINES

17.7. APPENDIX F - PREVENTIVE MAINTENANCE

18. REVISION HISTORY

18.1. Revision 8, 9/2/2008

18.1.1. Updated the Headers to the new Corporate format; updated SOP and section references throughout the SOP; added Corporate text to the Scope, Safety, Pollution Control and Waste Management sections; changed STL to TestAmerica throughout the SOP; updated the Reference section.

18.1.2. Addedto Section 8.3: Dissolved metals samples that are filtered and preserved at the laboratory with concentrated Nitric acid will be held for 24 hours before digestion.

18.2. Revision 9, 10/8/2009

18.2.1. Removed all reference to the autoclave and add the reference for the hot block digestion requirements throughout the SOP.

18.2.2. Added the SOP reference for DoD QSM 4.1, PT-QA-029 in the appropriate areas within the SOP. Added reference to SOP PT-QA-022, Equipment Maintenance.

18.2.3 In section 10.2.2 changed 100 mL to 50 mL.

18.2.4 In section 10.2.3 changed 5 mL to 2.5 mL and 2.5 mL to 1.25 mL.

18.2.5 In section 10.2.4 changed 15 mL to 7.5 mL.

18.2.6 In section 10.2.5 changed 8 mL to 4 mL.

18.2.7 Updated Figure 1/Figure 2 to remove the autoclave requirements and add the hot block requirements.

18.2.8 Updated Table 1 to separate out the Working Standard requirements for 7470A and 245.1.

18.3. Revision 10

18.3.1. Updated the SOP reference for 7471A/B to PT-MT-007 in section 1.3.

18.3.2. Removed reference to the LEEMAN PS200II Mercury Analyzer in sections 6.2 and 10.3.1 since this instrument has been taken out of service.

18.3.3. Added to section 9.8: If both methods are analyzed in the same sequence the tighter criteria of 10% is used for the CCV.

18.3.4. In section 10.2.5, corrected the potassium persulfate portion to 4 mL for a 50 mL sample.

18.4. Revision 11

18.4.1. Updated CCV criteria to ±10% for 7470A in section 9.8 and Table II.

18.5. Revision 12

18.5.1. Updated section 1.1, added method 245.1 to be prepared using hot block. Default prep for both method is hot block. Removed "the water bath procedure is always used for 245.1".

18.5.2. Updated section 10.2.5 and Figure 1 to indicate that digestion for both Method 7470A and 245.1 can be performed using a hot block. Indicated in a NOTE under this section that using a water bath for digestion is an alternative digestion procedure.

18.6. Revision 13

18.6.1. Added to section 10.2.7: Samples are adjusted to a final volume of 50 ml after digestion.

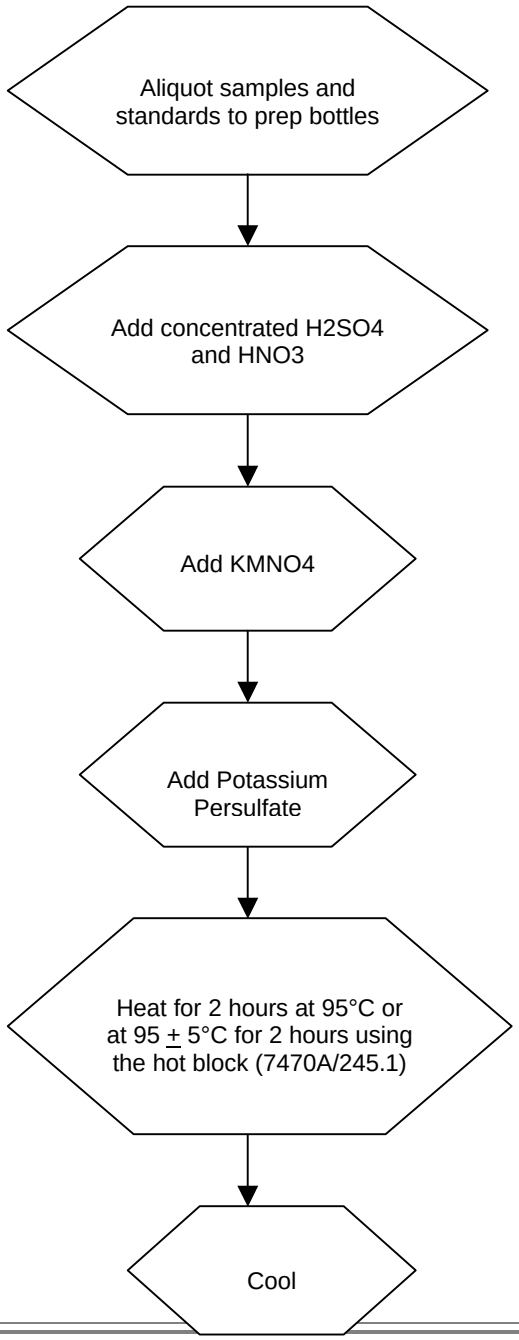
18.6.2. Added section 10.2.8 to note how Safety Kleen samples are handled for mercury preparation.

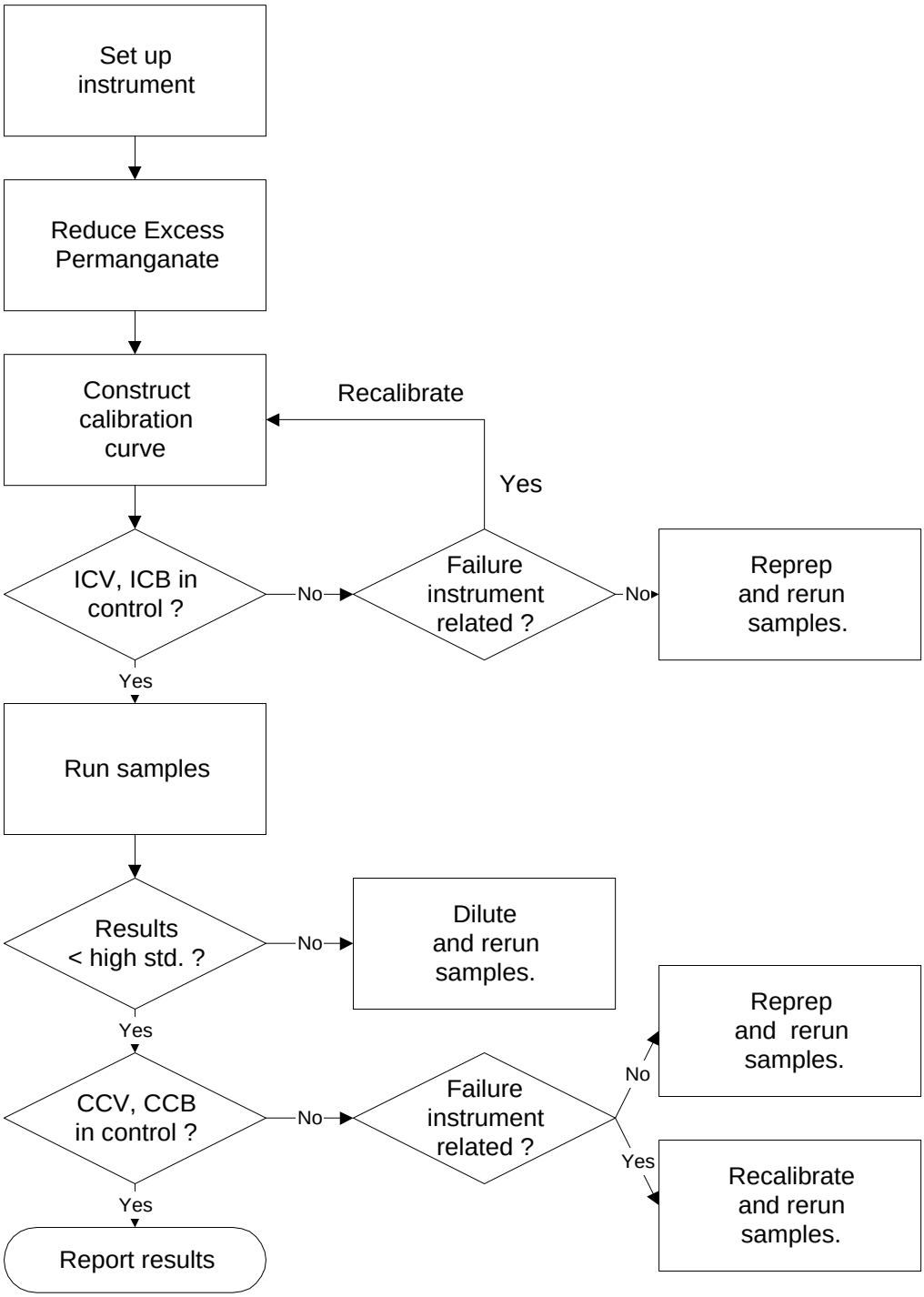
18.6.3. Added to section 10.2.9: For a procedure in how to make a dilution, refer to work Instruction PT-QA-W-006.

18.6.4. Added to section 15.18: PT-QA-W-006, Metals Dilution Calculation Table

18.6.5. Replaced Larry Matko with Bill Reinheimer as the Technical Manager.

18.6.6. **Figure 1**. Aqueous Sample Preparation – Mercury / **Figure 2**. CVAA Mercury Analysis




Set up instrument
Reduce Excess Permanganate
Construct calibration curve
Recalibrate
Yes
ICV, ICB in control ?
No
Failure instrument related ?
No
Reprep and rerun samples.
Yes
Run samples
Results < high std. ?
No
Dilute and rerun samples.
Yes
CCV, CCB in control ?
No
Failure instrument related ?
No
Reprep and rerun samples.
Yes
Recalibrate and rerun samples.
Yes
Report results

APPENDIX A

TABLES

TABLE I . MERCURY REPORTING LIMITS, CALIBRATION STANDARD*, QC STANDARD AND SPIKING LEVELS (MG/L)

Method		Reporting Limit	
SW846 7470A		0.0002 mg/ L	
SW846 7470A (TCLP)		0.0002 mg/ L	
MCAWW 245.1		0.0002 mg/ L	
Standard or QC sample	**7470A mLs of 0.1 ppm Working Standard**	**245.1 mLs of 0.1 ppm Working Standard**	**Concentration (mg/L)*** **
Std 0	0	0	0
Std 1	0.1	0.2	0.0002
Std 2	0.25	0.5	0.0005
Std 3	0.5	1.0	0.001
Std 4	2.5	5.0	0.005
Std 5	5.0	10.0	0.010
ICV	1.25	2.5**	0.0025
CCV	2.5	5.0	0.005
RLV	0.1	0.2	0.0002
LCS	1.25	2.5	0.0025
Aqueous MS	0.5	1.0	0.001
TCLP MS	0.25	5.0	0.005

* SOP specified calibration levels must be used unless prevented by the instrument configuration or client specific requirements.

** Prepared from a second source 0.1 ppm working standard.

*** When brought to a 100 mL final volume.

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
ICV	Beginning of every analytical run.	7470A: 90 - 110 %. 245.1: 95 – 105%	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
ICB	Beginning of every analytical run, immediately following the ICV.	The result must be within +/- RL from zero. (1)	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.7).
RLV	Beginning of every analytical run, immediately following the ICB.	50 – 150% recovery.	Terminate analysis; Correct the problem; Recalibrate or reprep batch (see Section 9.9).
CCV	Every 10 samples and at the end of the run.	7470A: 90 - 110%. 245.1: 90 – 110%	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCV or reprep batch (see Section 9.8).
CCB	Immediately following each CCV.	The result must be within +/- RL from zero. (1)	Terminate analysis; Correct the problem; Recalibrate and rerun all samples not bracketed by acceptable CCB or reprep batch (see Section 9.8).
Method Blank	One per sample preparation batch of up to 20 samples.	The result must be less than or equal to the RL. (1) Sample results greater than 20x the blank concentration are acceptable. Samples for which the contaminant is < RL do not require redigestion (See Section 9.4).	Redigest and reanalyze samples. Note exceptions under criteria section. See Section 9.4 for additional requirements.

TABLE II. Summary Of Quality Control Requirements

QC PARAMETER	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Laboratory Control Sample (LCS)	One per sample preparation batch of up to 20 samples.	Aqueous LCS must be within 80 - 120% (7470A) or 85 – 115% (245.1) recovery or in-house control limits.	Terminate analysis; Correct the problem; Redigest and reanalyze all samples associated with the LCS (see Section 9.5).
Matrix Spike	One per sample preparation batch of up to 20 samples (7470A) or one for every 10 or fewer samples (245.1).	75 - 125 % (7470A) or 70 – 130% (245.1) recovery or in-house control limits. (1) If the MS/MSD is out for an analyte, it must be in control in the LCS.	In the absence of client specific requirements, flag the data; no flag required if the sample level is > 4x the spike added. (see Section 9.6) For TCLP see Section 10.3.11
Matrix Spike Duplicate	See Matrix Spike	75 - 125 % (7470A) or 70 – 130% (245.1) recovery or in-house control limits; RPD ≤ 20%. (1) (See MS)	See Corrective Action for Matrix Spike.

(1) For specific DoD requirements, refer to PT-QA-025 (QSM 3.0) or PT-QA-029 (QSM 4.1).

APPENDIX B
Example Hg DATA REVIEW CHECKLIST

Run Date: _____ Lots Analyzed: 4. _____ 8. _____ 12. _____

Analyst: _____ 1. _____ 5. _____ 9. _____ 13. _____

Instrument: _____ 2. _____ 6. _____ 10. _____ 14. _____

Methods: _____ 3. _____ 7. _____ 11. _____ 15. _____

Review Item	Yes (✓)	No (✓)	N/A (✓)	2nd Level Review (✓)	Comments
A. Calibration/Instrument Run QC 1. Instrument calibrated per manufacturer's instructions and at SOP specified levels?					
2. ICV/CCV analyzed at appropriate frequency and within control limits?					
3. ICB/CCB analyzed at appropriate frequency and within +/- RL or +/- CRDL (CLP)?					
4. CRA run? (CLP only)					
B. Sample Results 1. Were samples with concentrations > the high calibration standard diluted and reanalyzed?					
2. All reported results bracketed by in control QC?					
3. Sample analyses done within holding time?					
C. Preparation/Matrix QC 1. LCS done per prep batch and within QC limits?					
2. Method blank done per prep batch and < RL or CRDL (CLP)?					
3. MS run at required frequency and within limits?					
4. MSD or DU run at required frequency and RPD within SOP limits?					
D. Other 1. Are all nonconformances documented appropriately?					
2. Current IDL/MDL data on file?					

This is a Controlled Document. When Printed it becomes Uncontrolled.

APPENDIX B - DATA REVIEW CHECKLIST

Review Item	Yes (✓)	No (✓)	N/A (✓)	2nd Level Review (✓)	Comments
3. Calculations and transcriptions checked for error?					
4. All client/project specific requirements met?					
5. Date/Time of analysis verified as correct?					

General

Comments:_____

Analyst & Date: _____ Second-Level Review & Date: _____

Controlled Source: Intranet
Company Confidential & Proprietary

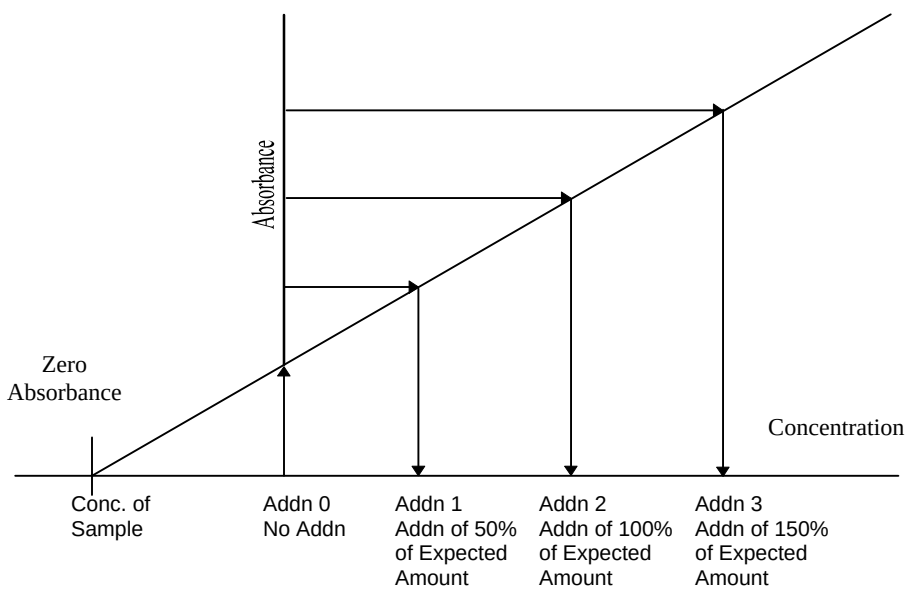
APPENDIX C. MSA GUIDANCE

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.

APPENDIX D. PARTS MAINTENANCE GUIDE

Maintenance Schedule

The software offers a simple to use online Scheduled Maintenance page. To view the page go to Instrument:Scheduled Maintenance (F1 Menu, I, S). A page displaying all items necessary to keep the instrument well maintained is shown (see figure 6.1A).

```
RunProt:
RunFold:          Seq: 0    Batch:
                  Prnt: R/T Off
                  Rev: 3.390  15:40:47 14 Jan 1996 Xmit: Off  Gas:        LPM
 None                                              User:            A/S: On
INSTRUMENT:  Scheduled Maintenance
                                  Uses left     Last service    Next service
 replace: Pump tubing               200          14-Jan-96       24-Jan-96
          Waste drain tubing       2500          14-Jan-96       29-Dec-96
          Liquid/gas separator     5000          14-Jan-96       14-Mar-96
          pump head               10000            N/A             N/A
          Hg lamp                   N/A          14-Jan-96       12-Jun-96
          Reductant bottle          400          14-Jan-96       12-Jul-96
          process tubing           5000            N/A             N/A
 Clean optical cell                300            N/A             N/A
 clean External optics             N/A          14-Jan-96       12-Jul-96

* - needs maintenance

For help on <hotkey> press Shift <hotkey>
```

Figure 6.1a. Scheduled maintenance screen

Each scheduled maintenance item has a usage counter, timed usage, or both (N/A indicates that the usage counter or the timed usage is not applicable for that item). If either condition expires for a given item a maintenance message will alert the user at the top of the status box.

Maintenance Procedures

An asterisk(*) will appear next to the item requiring maintenance on the Scheduled Maintenance screen. To clear the message hit <Tab> or replace, clean, or replenish the item using the hot key for the item on the Scheduled Maintenance page. To perform the maintenance on a given item simply type the hot key (e.g. Type <P> for Pump tubing) and follow the directions. Once the directions are followed to completion, the usage counter and timed usage gets updated.

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.

All glassware should be washed with detergent and tap water and rinsed with 20% 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.

Glassware should be periodically checked for cracks and etches and discarded if found. Etched glassware can cause cross contamination of any metallic analytes.

Autosampler trays should be covered to reduce the possibility of contamination. Trace levels of elements being analyzed in the samples can be easily contaminated by dust particles in the laboratory.

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.

Improper cleaning of glassware can cause contamination.

Separate glassware if an unusually high sample is analyzed and soak with sulfuric acid prior to routine cleaning.

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, time and instrument 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.

Cold Vapor Atomic Absorption (Hydra AA)

Daily	As Needed	Annually
Clean lens windows with methanol.	Check Hg lamp intensity.	Change Hg lamp.
Check aperture reading.	Check pump tubing/drain tubing.	Check liquid/gas separator.
Check argon flow/pressure.	Clean optical cell	
Check tubing and replace, if needed.	Lubricate pump	
Check drain.		
Replace drying tube.		

Title: Acid Volatile Sulfides (AVS) and Simultaneously Extracted Metals (SEM) in Sediment

Approvals (Signature/Date):

Mike Wesoloski Technical Specialist	11/18/2011 Date	Steve Jackson Health & Safety Manager / Coordinator	10/5/2011 Date
Nasreen DeRubeis Quality Assurance Manager	10/28/2011 Date	Deborah Lowe Laboratory Director	11/2/2011 Date

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1. SCOPE AND APPLICATION

1.1. This method describes the procedure for the determination of acid volatile sulfides (AVS) and for metals that are solubilized during the acidification step (Simultaneously Extracted Metals, SEM). The conditions used have been reported to measure amorphous or moderately crystalline monosulfides. As a precipitant of toxic heavy metals, sulfide is important in controlling the bioavailability of metals in anoxic sediments. If the molar ratio of toxic metals measured by SEM to AVS exceeds one, the metals are potentially bioavailable. Because the relative amounts of AVS and SEM are important in the prediction of potential metal bioavailability, it is important to use the SEM procedure for sample preparation for metal analysis. This uses the same conditions for release of both sulfide and metal from the sediment and thus provides the most predictive means of assessing the amount of metal associated with the sulfide.

1.2. Method 9034 is used to quantify the concentration of sulfide and Method 6010B is used to quantify the concentration of the routine SEM metals (arsenic, cadmium, chromium, copper, lead, nickel, silver and zinc). If mercury is requested as a SEM, Method 7470A is used for quantification. Reporting limits are listed in Attachment 1.

2. SUMMARY OF METHOD

2.1. The AVS in the sample is first converted to hydrogen sulfide (H2S) by acidification with hydrochloric acid at room temperature. The H2S is then purged from the sample and trapped. The amount of sulfide that is trapped is then determined titrimetrically following Method 9034. The SEM are metals liberated from the sediment during the acidification. These are determined following Method 6010B after filtration of the sample (plus 7470A if mercury is required).

3. DEFINITIONS

3.1. Acid Volatile Sulfides (AVS): Amorphous, moderately crystalline monosulfides, and other sulfides that form hydrogen sulfide under the conditions of this test.

3.2. Simultaneously Extracted Metals (SEM): Metals which form less soluble sulfides than do iron or manganese, and which are at least partially soluble under the conditions of this test. The routine SEMs are cadmium, copper, lead, nickel, and zinc. Mercury may also be determined on a project specific basis.

3.3. ICV: Initial Calibration Verification: An undistilled standard prepared by adding 1 mL of a 1000 ppm (or standardized concentration) sodium sulfide standard (different source than the standard used for the LCS and MS/MSD) to 50 mL of reagent water (20 ppm concentration).

3.4. ICB: Initial Calibration Blank: undistilled blank consisting of 50 mL of reagent water.

3.5. PBW: Prep Blank Water or Method Blank.

3.6. CCV: Continuing Calibration Verification: preparation is the same as the ICV.

3.7. CCB: Continued Calibration Blank: preparation is the same as the ICB.

3.8. LCS: Laboratory Control Sample.

4. INTERFERENCES

4.1. Oxygen in the reagents and apparatus is the primary interference reported. Samples must be taken with minimum aeration to avoid volatilization of sulfide or reaction with oxygen, which oxidizes sulfide to sulfur compounds that are not detected. Use deoxygenated, deionized water and reagents.

4.2. Reduced sulfur compounds, such as sulfite and hydrosulfite, may decompose in acid and form sulfur dioxide. This gas may carry over to the zinc acetate solutions and subsequently react with iodine during the titration, thus causing a positive bias to the results.

4.3. The iodometric method suffers interference from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds.

4.4. The pH of the sample after the addition of the acid and during the purge process must be below 3.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1. Specific Safety Concerns or Requirements

5.1.1. Hydrogen sulfide (H_2S) gas is generated by the addition of sulfuric acid. Inhalation of H_2S gas can cause headache, dizziness, nausea and unconsciousness and potentially death.

5.2. 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
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.
Iodine	Poison Corrosive Oxidizer	0.1 ppm-Ceiling	Vapors severely irritate and can burn the mucous membranes and respiratory tract. Liquid contact may cause blistering burns, irritation, and pain. Vapors may be severely irritating to the skin. Vapors are severely irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Dichromate	Oxidizer Corrosive Carcinogen	0.1 Mg/M3 TWA as CrO3	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. May cause ulceration and perforation of the nasal septum. Symptoms of redness, pain, and severe burn can occur. Dusts and strong solutions may cause severe irritation. Contact can cause blurred vision, redness, pain and severe tissue burns. May cause corneal injury or blindness.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Sulfide	Corrosive	10 ppm-TWA 15 ppm-STEL	Will form Hydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal. Symptoms include painful conjunctivitis, headache, nausea, dizziness, coughing and, in extreme cases, pulmonary edema and possible death. Irritant. Contact with skin can produce serious caustic burns with painful inflammation and possible destruction of tissue. Inflammation, tearing and pain may be expected. Severe contact can cause destruction of tissue.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Procedures shall be carried out in a manner that protects the health and safety of all TestAmerica associates.

5.4. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.6. 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 will be kept closed unless transfers are being made.

5.7. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

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

6. EQUIPMENT AND SUPPLIES

6.1. Instrumentation

6.1.1. Not Applicable.

6.2. Supplies

6.2.1. Boiling tube.

6.2.2. Inlet adapter.

6.2.3. Dropping funnel.

6.2.4. Gas inlet.

6.2.5. Impinged bubbler.

6.2.6. Fritted bubbler.

6.2.7. Bubbler vessels.

6.2.8. WestClips®

6.2.9. Gas line "T" connector.

6.2.10. Class A Volumetric flasks, pipettes, and burettes.

6.2.11. High purity nitrogen gas.

6.2.12. Regulator.

6.2.13. 100 mL and 300 mL graduated disposable flasks.

6.2.14. 100 mL disposable beaker

6.2.15. Hot plate stirrer.

6.2.16. 50mL burette.

6.2.17. Parafilm

6.2.18. Filtering apparatus and 0.45 μm filter membrane.

7. REAGENTS AND STANDARDS

7.1. Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee of Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2. Reagent water (Super Q/DI Water). All references to water in this method refer to reagent water.

7.3. Zinc acetate for the scrubber. Zinc acetate solution (approximately 0.5M). Dissolve about 110g zinc acetate dihydrate in 200mL of reagent water. Add 1mL hydrochloric acid (concentrated), to prevent precipitation of zinc hydroxide. Dilute to 1L.

7.4. Acid to acidify the sample. 6 M Hydrochloric acid, 1:1 HCl:reagent water. Purge with nitrogen for at least 30 minutes prior to use.

7.5. UHP/zero grade nitrogen gas. Gas chromatographic grade with two-stage regulator.

7.6. Starch indicator. 0.5%. Purchased.

7.7. 0.0250N $Na_2S_2O_3$. Purchased.

7.8. 0.025N Iodine. Purchased.

7.9. 1000ppm Sodium sulfide prepared by adding approximately 3.75g $Na_2S \bullet 9H_20$ to 500mL reagent water. May be commercially available.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Samples must be cooled to 4°C and stored headspace free. Typically a separate 4 oz jar is filled specifically for this test.

8.2. The acidification of the sample (H_2S generation) and sulfide determination must be performed within 14 days from the date of collection. The routine SEMs are stable up to six months after sample collection (28 days for mercury, if required).

8.3. If after distillation, the AVS distillate can not be immediately titrated it may be stored at ≤ 6°C for up to 24 hours before final titration provided the 7 day holding time is not exceeded.

9. QUALITY CONTROL

9.1. Sample QC

9.1.1. A Laboratory Control Sample (LCS) must be analyzed with each batch of 20 or fewer samples. A separate sulfide (AVS) LCS and metals (SEM) LCS is performed.

9.1.1.1. The LCS and ICV are the same standard. Therefore the ICV/LCS acceptance criteria are 85 to 115 percent. If the LCS is not used as the ICV, then the LCS must meet a 75 to 125 percent recovery criterion.

9.1.2. A matrix spike and a matrix spike duplicate (MS/MSD) must be analyzed with each batch of 20 or fewer samples. A separate sulfide (AVS) MS/MSD and metals (SEM) MS/MSD is performed.

9.1.2.1. The percent recovery for matrix spike and matrix spike duplicate should be ± 25 percent. If this criterion is not met, evaluate method process. If no errors are found, document in a Non-Conformance Memo (NCM).

9.1.2.2. The relative percent difference (RPD) between the MS and MSD must be within ± 20 percent. If this criterion is not met, then repeat the analysis once. The results with the better RPD will be reported. If the results for the reanalysis are the same as the original analysis, then report the original analysis.

9.1.3. A method blank must be analyzed with each batch of 20 samples or fewer processed at the same time. The prep blank (or method blank) can be used as the ICB if it meets the ICB acceptance criteria. The processing of a method blank will assure non-contamination of the reagents. The ICB result must be less than the Reporting Limit. The method blank result must be less than two times the Reporting Limit, otherwise all samples must be reprepared and reanalyzed. If this is not possible due to limited sample quantity (or there is no sample left) the corresponding samples will be flagged and the PM will be notified. If repreparation and reanalysis happen to be outside holding time, then approval from the client must be obtained before any reanalysis is performed.

9.2. Instrument QC

9.2.1. A sulfide run will consist of the following sequence: ICV, ICB, and up to 10 samples followed by a CCV and a CCB. See the appropriate metals SOP for the SEM analyses.

9.2.2. This can be followed by up to 10 more samples, followed by a CCV and CCB.

9.2.3. Repeat 9.2.1 and 9.2.2 sequence for additional samples.

9.2.4. The following QC requirements must be met for the sulfide (AVS) analyses:

9.2.4.1. The ICV must be within ± 15 percent. If this criterion is not met, then recalibrate and reanalyze the samples. The LCS can be used as an ICV if it meets the ICV acceptance criteria of 85 to 115 percent. If the LCS is not used as the ICV, then the LCS must meet a 75 to 125 percent recovery criterion.

9.2.4.2. The CCV must be within ± 15 percent. If this criterion is not met, then reanalyze the samples with a valid CCV. If the analysis sequence shows ICV, ICB, and 10 samples followed by CCV, CCB, and this CCV fails, then all those 10 samples must be reanalyzed. If with the above sequence 10 additional samples are analyzed following a CCV and a CCB and this second CCV fails, then all the samples up to the last acceptable CCV must be reanalyzed. The CCB criteria are the same as ICB.

9.3. All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by or under supervision of experienced analysts.

9.4. All sample preparation and analysis information will be documented on laboratory bench sheets, computer printouts, standard logbooks, etc. All the documents associated with an analysis will be forwarded for reporting and for inclusion in the project files.

10. PROCEDURE

10.1. Sample Preparation

10.1.1. Place the boiling tube containing approximately 10 grams of sample (record to the nearest 0.1 grams) and 50 mL of reagent water in the heater block (used as a holder only) and assemble the acid soluble sulfide distillation apparatus as shown in Figure 1. The sample can be weighed on a 2” x 2” piece of Parafilm and placed into the boiling tube.

10.1.2. Spike the sulfide (AVS) LCS, MS, and MSD with 1 mL of the 1000 ppm sodium sulfide solution (7.11) which is equivalent to 100 mg/Kg in a 10 gram sample. Spike the metals (SEM) LCS, MS, and MSD with 2.5 mLs of the metals ICP MS solution. If mercury is required, a mercury spike will need to be added to the LCS, MS, and MSD.

10.1.3. Place 2.0mL of 0.5M zinc acetate solution and 20.0mL of deionized water in each of two bubbler vessels. Place an impinged bubbler in the first (front) and second (back) vessel, and seal them with size 24/40 WestClips®. The sealed vessels and impingers function as the gas scrubbers. Connect the first scrubber to the inlet adapter and place the second bubbler vessel in the bubbler vessel rack. Connect the two impingers in series using Tygon® tubing.

10.1.4. Close stopcock of dropping funnel. Place 20 mL of the nitrogen purged 6 M hydrochloric acid in the dropping funnel.

10.1.5. Connect a high-purity (GC grade) nitrogen gas source to the main inlet of the gas manifold of the aluminum heater block as specified in the Heater Block Operation Manual. Use a two-stage gas tank regulator and set the pressure into the gas manifold to 20psi.

10.1.6. Connect a black gas line from each gas manifold valve to a "T" connector and a tygon gas line from the "T" to each of the two gas inlets of the apparatus. One at the top of the dropping funnel and one at the inlet adapter as shown in Figure 1.

10.1.7. Purge assembled apparatus with high-purity nitrogen for 10 minutes to remove atmospheric oxygen from the apparatus and contained solutions. During purge, adjust nitrogen flow such that 2-3 bubbles per second exit the base of the inlet adapter.

10.1.8. Open stopcock of dropping funnel and allow all of the 6M hydrochloric acid to drip into the boiling tube. Once dropping funnel is empty, close the stopcock to ensure sample is not lost into the funnel.

10.1.9. Purge the sample for 1 hour at room temperature. After the 1 hour purging period, remove the bubbler vessels. Turn off the nitrogen flow. Carefully combine the gas scrubber solutions in a 100 mL graduated disposable flask. Do not shake or mix solutions to avoid loss of sulfide. Bring up to 50 mL with reagent water. Determine the concentration of acid volatile sulfide in the zinc acetate gas scrubber solutions by using the Titrimetric-iodine method (9034)—proceed to Section 10.3.

10.1.10. After the generation of sulfide has been completed, the sediment suspension remaining in the boiling tube is filtered through a 0.45 μm membrane filter. The pH of the solution is determined using narrow range pH strips to verify that the pH is less than 3. If the pH is not less than 3, the group supervisor and QA Manager should be consulted. Document all actions in a Nonconformance Memo (NCM). The solution is brought up to a final volume of 250 mL in a 300 mL graduated disposable flask. This solution is analyzed directly by ICP for the routine SEMs (see SOP PT-MT-001). If mercury is required, an aliquot of this solution is prepared following Method 7470A and analyzed by CVAA (see SOP PT-MT-005).

10.2. Calibration

NOTE: All periodic standardizations of titrants can be found in the Wet Chemistry standardization logbook. Daily standardizations are found on the bench worksheet.

10.2.1. Stock sulfide standard is titrated daily before each distillation of sample sets. The stock standard must be reprepared every week.

10.2.2. Sodium thiosulfate (0.0250N) standardization—performed daily.

10.2.2.1. Use 0.0250 N Biiodate titrant: dissolve 0.8124g potassium biiodate (dried 2 hours) in Super-Q water and dilute to 1 L.

10.2.2.2. Place 2g KI in 250mL beaker and add 100mL Super-Q water and stir. Add 10mL 1:4 H_2SO_4 and 10mL biiodate.

10.2.2.3. Place in the dark for 5 minutes. Dilute to 150mL and add starch indicator (Section 7.8)

10.2.2.4. Titrate with $Na_2S_2O_3$ (7.9) to clear endpoint. Repeat procedure two additional times. Determine the normality of the $Na_2S_2O_3$ as follows:

$$N\ Na_2S_2O_3 = \frac{10\ \text{mL biiodate} \times 0.025\ \text{N biiodate}}{\text{mL}\ Na_2S_2O_3\ \text{titrant}}$$

10.2.3. Iodine standardization: performed daily

10.2.3.1. Place 20mL .0250N iodine in Erlenmeyer flask. Add 2mL 6 N HCl.

10.2.3.2. Titrate with $Na_2\ S_2O_3$ (7.9) to a pale yellow color.

10.2.3.3. Add starch indicator (7.8) and titrate with $Na_2S_2O_3$ (7.9) to clear endpoint. Determine the normality of the iodine (I) as follows:

$$N\ I = \frac{N Na_2S_2O_3 \times \text{mL}\ Na_2S_2O_3\ \text{titrant}}{\text{mL I solution}}$$

10.3. Sample Analysis

10.3.1. Pipette a known amount of standardized 0.025N iodine solution the 100mL disposable sample beaker, adding an amount in excess of that needed to oxidize the sulfide.

10.3.2. Add 2mL of 6N HCl to the iodine.

10.3.3. If at any point the amber/orange color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be added to the amount from Section 10.3.1 for calculations. Record the total volume of standardized 0.025N iodine solution used.

10.3.4. Add enough starch indicator (approximately 1 mL) for the solution to turn a dark blue color.

10.3.5. Titrate the solution in the flask with standard 0.025N sodium thiosulfate solution until the dark blue color disappears. Record the volume of titrant used.

10.3.6. For metals, the solution is analyzed directly by ICP for the routine SEMs (see SOP PT-MT-001). If mercury is required, an aliquot of this solution is prepared following Method 7470A and analyzed by CVAA (see SOP PT-MT-005).

11. CALCULATIONS / DATA REDUCTION

11.1. One mL of 0.0250 N standard iodine solution reacts with 0.4mg sulfide present in titration vessel.

11.2. AVS mg/Kg-dry $= \dfrac{[(A \times B) - (C \times D)] \times 16000}{E \times F}$

A = mL of iodine solution
B = N of iodine solution
C = mL of $Na_2S_2O_3$ solution
D = N of $Na_2S_2O_3$ solution
E = weight of sample (grams or mls)
F = Percent solids as decimal fraction (i.e., 50% solid is 0.50)

11.3. To convert the AVS concentration from mg/Kg-dry to μmoles/gram-dry, divide by 32.066 (molecular weight of sulfur).

11.4. Enter the completed data work sheet into computer program, sulfide analysis worksheet, for final results.

11.5. For each SEM, first determine concentration in mg/Kg-dry as follows:

SEM mg/Kg-dry $= \dfrac{A \times B}{C \times D}$

A = conc. of metal in solution as determined by 6010B or 7470A (mg/L)
B = final volume of solution in liters—typically 0.25 liters.
C = weight of sample in Kg.
D = Percent solids as decimal fraction (i.e., 50% solid is 0.50)

11.6. To convert the concentration of each SEM from mg/Kg-dry to μmoles/gram-dry, divide by the molecular weight of that metal (cadmium = 112.411; copper = 63.546; lead = 207.2; mercury = 200.59; nickel = 58.69; and zinc = 65.39).

11.7. Calculate the Total SEM molar concentration of the sample by summing each of the individual SEM concentrations in units of μmoles/gram-dry. If any one of the SEMs is not detected (ND), it is considered a zero (0) in the summation.

11.8. Calculate the molar ratio of SEM over AVS as follows:

SEM/AVS = A/B

A = Total SEM molar concentration (μmoles/gram-dry).
B = AVS molar concentration (μmoles/gram-dry).

Note: If AVS is not detected (ND), the molar ratio cannot be determined.

11.9. Matrix Spike percent recovery:

$$Theoretical\ Spike\ Conc. = \frac{\begin{pmatrix} Spike \\ Conc. \end{pmatrix} \times \begin{pmatrix} Vol.\ of \\ Spike\ Added \end{pmatrix}}{Final\ Vol.\ Spiked}$$

$$\%\ \mathrm{Recovery} = \frac{\begin{pmatrix} Final \\ Spike + Sample \end{pmatrix} - Sample\ \mathrm{Result} \begin{pmatrix} \dfrac{Vol.\ Sample\ Spiked}{Final\ Vol.\ Spiked} \end{pmatrix}}{Theoretical\ Spike\ Conc.} \times 100$$

12. METHOD PERFORMANCE

12.1. Method Detection Limit Study (MDL)

12.1.1. Method Detection Limit (MDL) for Titrimetric Procedures - The detection limit for titrimetric procedures can be defined by the smallest amount of reagent that can be added during a titration to cause a chemical change. This is typically determined by the smallest size of the drop that can be produced on a particular burette or other titrating device. Drop size can be estimated by averaging the size of several (5 to 10 is a good number) repeated drops. The detection limit can then be calculated based on the titrant concentration, the sample size, and the minimum drop size.

12.1.2. Method Detection Limit (MDL) for Metals - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. Either an annual MDL study or quarterly MDL Verification can be done. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest that have been carried through the entire analytical procedure. MDLs must be determined in accordance with 40 CFR Part 136 Appendix B requirements as detailed in SOP: PT-QA-007. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the TestAmerica reporting limit.

12.2. Demonstration of Capabilities

12.2.1. Prior to analysis of any samples using this SOP, the following requirements must be met: Initial Demonstration Study: This requires the analysis of four QC check samples. The QC check sample is a well-characterized, laboratory-generated sample used to monitor method performance, which should contain the analyte(s) of interest. The results of the initial demonstration study must be acceptable before analysis of samples under this SOP may begin. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP. Acceptance criteria for the LCS are given in Section 9.1.1.1.

12.3. Training Qualifications

12.3.1. The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. The group/team leader must document the training and PE performance and submit the results to the QA Manager for inclusion in associate training files.

13. POLLUTION CONTROL

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental

Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

13.2. This method does not contain any specific modifications that serve to minimize or prevent pollution.

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1. Acidic waste generated by sample titration. This waste is collected in a waste container identified as "Acid Waste", Waste #33. This waste is neutralized to a final pH between 6 and 9 and discharged down into a lab sink.

14.1.2. Unused sample distillate. This waste is collected in a waste container identified as "Acid Waste", Waste #33. This waste is neutralized to a final pH between 6 and 9 and discharged down into a lab sink.

14.2. Waste generated in the procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Coordinator should be contracted if additional information is required.

15. REFERENCES

15.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed.; U.S. EPA. Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1997; SW-846.

15.2. Allen, H.E. and F. Gongmin et al. 1991. Determination of Acid Volatile Sulfide and Simultaneously Extractable Metals in Sediment, April 1991 (Draft Analytical Method for the Determination of Acid Volatile Sulfide in Sediment, U.S. EPA Office of Water and Office of Science and Technology, Health and Ecological Criteria Division, Washington, D.C., August 1991.

15.3. SOP PT-MT-001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analyses, SW-846 Method 6010B, 6010C and EPA Method 200.7, current revision.

15.4. SOP PT-MT-005, Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW-846 7470A and MCAWW 245.1, current revision.

15.5. SOP PT-WC-010, Total Sulfide as Acid Soluble Sulfide, Method 9030B/9034, SM 20th Ed. 4500S-$^{2-}$F and EPA Method 376.1, current revision.

15.6. SOP PT-QA-007, Detection Limits, current revision.

15.7. SOP PT-QA-003, Glassware Clean-up for Organic/Inorganic Procedures, current version.

15.8. SOP PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability, current version.

15.9. SOP PT-QA-008, Thermometer Calibration and Temperature Monitoring, current version.

15.10. SOP PT-QA-011, Data Recording Requirements, current version.

15.11. SOP PT-QA-012, Selection and Calibration of Balances and Weights, current version.

15.12. SOP PT-QA-016, Nonconformance & Corrective Action System, current version.

15.13. SOP PT-QA-021, Quality Assurance Program, current version.

15.14. SOP PT-QA-022, Equipment Maintenance, current version.

15.15. SOP PT-QA-027, Sample Receiving and Chain of Custody, current version.

15.16. PT-LQAM, current version.

16. METHOD MODIFICATIONS

16.1. Not applicable.

17. ATTACHMENTS

17.1. Figure 1 – Acid Volatile Sulfide generation apparatus.

17.2. Attachment 1 – SEM and AVS Reporting Limits. MDLs listed in the two attachments for metals and sulfide are subject to change.

18. REVISION HISTORY

18.1. Revision 1, 5/16/08.

18.1.1. Renamed SOP as PT-WC-008.

18.1.2. Changed laboratory name to TestAmerica.

18.1.3. Updated SOP format to match corporate SOP format.

18.1.4. Corrected some typographical errors and several Section references that were incorrect.

18.1.5. Revised section 9.1.1.1: The LCS and ICV are the same standard. Therefore the ICV/LCS acceptance criteria are 85 to 115 percent. If the LCS is not used as the ICV, then the LCS must meet a 75 to 125 percent recovery criterion.

18.1.6. Added to Section 12.1.1: Method Detection Limit (MDL) for Titrimetric Procedures - The detection limit for titrimetric procedures can be defined by the smallest amount of reagent that can be added during a titration to cause a chemical change. This is typically determined by the smallest size of the drop that can be produced on a particular burette or other titrating device. Drop size can be estimated by averaging the size of several (5 to 10 is a good number) repeated drops. The detection limit can then be calculated based on the titrant concentration, the sample size, and the minimum drop size.

18.1.7. Modified Section 12.1.2 to add either annual MDL Study or quarterly MDL Verification can be done for metals..

18.1.8. All revisions are highlighted throughout the SOP.

18.2. Revision 2

18.2.1. Updated SOP reference numbers throughout the SOP.

18.2.2. Added TestAmerica Pittsburgh's SOP References in section 15.

18.3. Revision 3

18.3.1. Section 1.2, added As, Cr and Ag for ICP. Added: Reporting limits are in Attachment 1.

18.3.2. Formaldehyde is not used in executing this SOP, thus references to formaldehyde in sections 4.2, the Table under 5.2, 7.3 and 10.1.3.

18.3.3. Section 8.3 was added to clarify that a distillate will be refrigerated no more than 24 hours before final titration provide the 7 day holding time is still met.

18.3.4. In section 10.1.1, corrected the volume of reagent water added to the heater block from 100 ml to 50 ml.

18.3.5. Added section 10.3.5: For metals, the solution is analyzed directly by ICP for the routine SEMs (see SOP PT-MT-001). If mercury is required, an aliquot of this solution is prepared following Method 7470A and analyzed by CVAA (see SOP PT-MT-005).

18.3.6. In section 11.2, correct variable E to read weight of sample (grams or mLs).

18.3.7. In Section 15 References/Cross-References, references were added to all pertinent QA SOP's and the PT-LQAM.

18.4. Revision 4

18.4.1. Removed reference to the use of H_2SO_4 in the Table under section 5.2 and in section 7.5 since it is not used in this SOP.

18.4.2. In section 7.9, added "approximately" before 3.75 g.

18.4.3. In section 10.3.3 added amber/orange color.

18.4.4. Added section 10.3.4 to clarify that starch indicator is added to the sample to turn it dark blue before it is titrated with sodium thiosulfate in section 10.3.5.

18.4.5. In section 10.3.1 added the word sample between disposable and beaker.

18.4.6. Removed sentence one from 10.3.3 and removed "in transferring the zinc acetate solution" from sentence two in section 10.3.3.

Attachment 1 – Reporting Limits

TAL Reference Data Summary

Structured Analysis Code: **A-**-OS-8G-03**
Target Analyte List: All Analytes

Matrix: SOLID
Extraction: None specified.
Method: Simultaneously Extractable Metals in Sediment
QC Program: MARINE\SEDIMENT
Location: TestAmerica Pittsburgh

Analyte List		Detection Limits					Check List 3008							Spike List 3009						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
140	Arsenic	0.003337	umoles/gn	0.00038	umoles/gn	20061013	C	Y	0.6673	umoles/g	80	120	20	C	Y	0.667	umoles/g	75	125	20
411	Cadmium	0.001112	umoles/gn	0.00003	umoles/gn	20061013	C	Y	0.0111	umoles/g	80	120	20	C	Y	0.0111	umoles/g	75	125	20
2952	Chromium	0.002404	umoles/gn	0.00021	umoles/gn	20061013	C	Y	0.0961	umoles/g	80	120	20	C	Y	0.0961	umoles/g	75	125	20
643	Copper	0.009835	umoles/gn	0.00088	umoles/gn	20061013	C	Y	0.0983	umoles/g	80	120	20	C	Y	0.0983	umoles/g	75	125	20
1605	Lead	0.0007239	umoles/gn	0.00023	umoles/gn	20061013	C	Y	0.0603	umoles/g	80	120	20	C	Y	0.0603	umoles/g	75	125	20
1701	Mercury	0.0000623	umoles/gn	0.00000	umoles/gn	20061013	C	Y	0.0001	umoles/g	80	120	20	C	Y	0.0001	umoles/g	60	120	20
1956	Nickel	0.01704	umoles/gn	0.00049	umoles/gn	20061013	C	Y	0.2129	umoles/g	80	120	20	C	Y	0.2129	umoles/g	75	125	20
2285	Silver	0.001159	umoles/gn	0.00013	umoles/gn	20061013	C	Y	0.0115	umoles/g	80	120	20	C	Y	0.0115	umoles/g	75	125	20
2649	Zinc	0.03823	umoles/gn	0.00282	umoles/gn	20061013	C	Y	0.1911	umoles/g	80	120	20	C	Y	0.1911	umoles/g	75	125	20

Attachment 1 – Cont.

TAL Reference Data Summary

Structured Analysis Code: **A-**-P7-8G-03**
Target Analyte List: All Analytes

Matrix: SOLID
Extraction: None specified.
Method: Acid Volatile Sulfide in Sediment (AVS)
QC Program: MARINE\SEDIMENT
Location: TestAmerica Pittsburgh

Analyte List		Detection Limits					Check List 3000							Spike List 3001						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
3735	Acid Volatile Sulfide	0.499	umoles/gn	0.155	umoles/gn	20050101	C	Y			85	115	20	C	Y			75	125	25

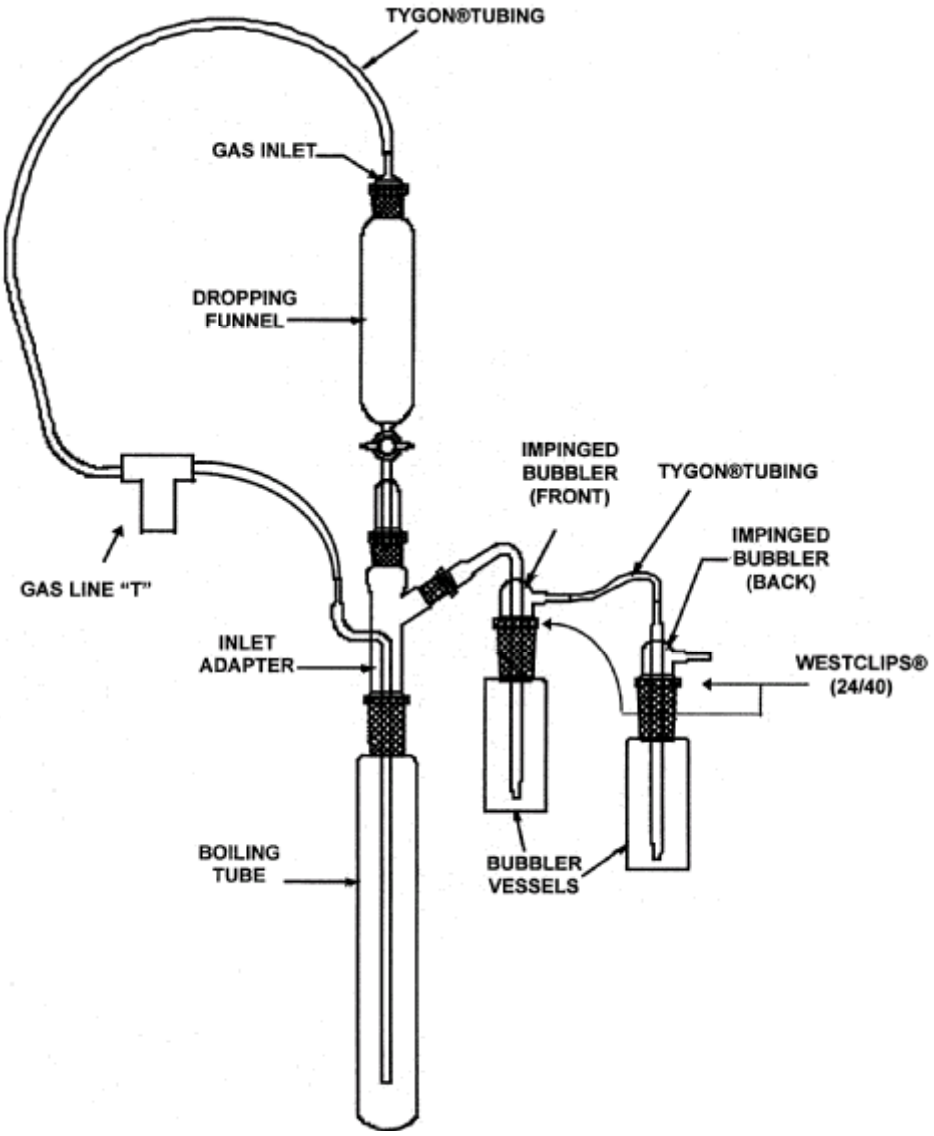


Figure 1 – Acid Volatile Sulfide generation apparatus.

EPA 8015B

DIESEL RANGE ORGANICS

1 SCOPE AND APPLICATION

1.1 This method is designed to measure the concentration of diesel range organics (DRO) in water and soil samples. This method should not be used to report hydrocarbon results in States where an alternative method has been mandated without approval from the regulatory authority.

Compound	CAS Number
DRO	Not Applicable

1.2 Instrumentation: HP 5890 Gas Chromatograph (GC) equipped with a flame ionization detector (FID) and a LEAP Technologies CTC A200S autosampler and Agilent Chemstation data acquisition software.

1.3 The method is primarily designed to measure mid-range petroleum products such as fuel oil. DRO corresponds to a hydrocarbon range of C_{10} - C_{28} and a boiling point range between approximately 170°C and 430°C. Hydrocarbons greater than C_{28} present in products such as motor oils or lubricating oils are also detectable under the conditions of this method. If, based on a review of the chromatogram, the presence of these heavier hydrocarbon products is noted, an additional analysis under different conditions may be necessary. An alternate analytical procedure is provided for heavier hydrocarbons.

1.4 Second column confirmation is not required for this method. If based on review of the chromatogram, it appears that it is likely that a major contribution to the DRO result is not a typical hydrocarbon pattern, a case narrative note should be made.

1.5 The estimated method detection limit (MDL) for DRO in sand and water is listed in Table 1. The detection limits given may vary based on sample size or sample matrix and/or regulatory requirements. The low standard, equal to 40 mg/kg for soil and 100 µg /L for water, is used as the reporting limit unless another reporting convention is required based on project or regulatory requirements.

1.6 Typical Demonstration of Capability (DOC) studies for sand and water are listed in Table 2.

1.7 This method is restricted to use by, or under the supervision of, analysts experienced in the use of a gas chromatograph and skilled in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2 SUMMARY OF METHOD

2.1 This method provides gas chromatographic conditions for the detection of semi-volatile petroleum fractions such as diesel, #2 fuel oil, or kerosene. Samples are extracted and injected into a capillary column gas chromatograph with FID. An alternate analytical approach is provided for heavier hydrocarbons such as motor oil or hydraulic oil.

2.2 Soil samples are dried with sodium sulfate and extracted with hexane. Water samples are extracted with hexane, solvent evaporated, and made to volume with hexane.

2.3 The extract is transferred to injection vials and analyzed by GC-FID.

3 DEFINITIONS AND ACRONYMS

3.1 There are many terms and acronyms used throughout this document. Check the definitions and acronyms sections of the Quality Manual for complete explanations.

4 INTERFERENCES

4.1 All materials including solvents, reagents, glassware and other sample processing materials must be demonstrated to be free from interferences under conditions of the analysis by analyzing method blanks. All glassware used to extract and analyze samples will be single use and disposable, which should eliminate typical glassware contamination problems associated with DRO analysis. However, even single use glassware may have potential interferences from the manufacturing and distribution process.

4.2 Because the FID is a “universal” detector there is a potential for many interferences, such as naturally occurring organics, fats, or phthalates. In most cases, prior site data will indicate that a potential problem may exist. Experienced analysts will aid the project in identifying interferences from true petroleum hydrocarbon results.

5 SAFETY

5.1 Employees must abide by the policies and procedures in the ECCS Chemical Hygiene Plan (CHP), and this document. Refer to the CHP for more detailed safety information or for information not listed in this document.

5.2 Eye protection that protects against splash and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled during this procedure. Lab coats are recommended.

5.3 Employees must handle glassware and equipment carefully in order to prevent injury and accidents. Any damaged or broken glassware is to be discarded or moved to the glass repair box.

5.4 ECCS maintains a Material Safety Data Sheet (MSDS) for every chemical used in the

laboratory. The MSDS file is kept in the main laboratory.

6 APPARATUS AND MATERIALS

6.1 Gas Chromatograph (GC)

6.1.1 Gas Chromatograph: HP5890
Autosampler: LEAP Technologies A200S
Detector: Flame Ionization
Injector: Split/splitless Injector
Data system: Agilent Chemstation Data Acquisition Software

6.1.2 Columns

6.1.2.1 Column 1: MXT-1, 30 m x 0.53 mm ID, 0.25 µm film thickness or equivalent

NOTE: This column is the preferred column for normal DRO analyses.

6.1.2.2 Column 2: MXT-1HT Sim Dist, 5 m x 0.53 mm ID, 0.1 µm film thickness or equivalent

NOTE: This column is the preferred column for heavier hydrocarbons such as motor oil or hydraulic fluids.

6.1.3 Injection hardware: Restek standard 4mm gooseneck liner and stainless steel cross seal.

6.2 Balances:

6.2.1 Top loader balance capable of weighting to 0.01 g

6.2.2 Analytical balance capable of weighting to 0.0001 g

6.3 Vials:

6.3.1 2 mL amber gas chromatograph injection vials with Teflon lined crimp seals

6.4 Bottles: 1000 ml amber glass bottles with Teflon lined screw caps

6.5 Volumetric flasks, various sizes

6.6 Pipettes, various sizes

6.7 Syringes: Gas-tight, various sizes

6.8 Disposable glass transfer pipettes and 2 mL rubber bulbs

6.9 Compressed Gas

6.9.1 Helium, Grade 5

6.9.2 Hydrogen, Grade 5

6.9.3 Air, standard

6.10 Refrigerator capable of maintaining 4 °C

6.11 Freezer capable of maintaining temperatures below -15 °C

7 REAGENTS

7.1 Solvents

7.1.1 Hexane

7.2 Solid Reagents – Not Applicable to this method

7.3 Acids and Bases

7.3.1 12 N Hydrochloric acid (HCl)

7.3.2 1:1 HCl

7.3.2.1 Add approximately 40 mL of de-ionized water to a 100 mL volumetric flask. Add 50 mL of 12 N HCl with a 50 mL pipette. Fill to the mark with de-ionized water, cap and mix. Fill to the mark again, mix, and transfer to a 100-mL bottle with LIMS label.

7.4 Stock Standards

7.4.1 Primary DRO stock standard (10 components) is purchased from Absolute Standards at certified solutions of 10,000 µg/mL for each of the 10 components (Part No. 91034).

7.4.2 Alternative stock standards such as fuel oil, motor oil, etc. can be utilized to accommodate specific project objectives.

7.5 Intermediate Standards – 5000 µg/mL total concentration

7.5.1 The intermediate DRO standard, each component at 500 µg/mL is prepared in a 50 mL volumetric flask by combining 5 mL of surrogate stock solution (7.7.2) with 2.5 mL of stock DRO solution (7.4.1) and bringing to the mark with hexane. The solution is documented in LIMS and transferred to LIMS labeled 40 mL VOA vials for refrigerated storage.

NOTE: The stock ampule(s) should be sonicated prior to use to insure the standard components are in solution.

7.5.2 If alternative standards are prepared for mixtures of hydrocarbons such as fuel oil or motor oil, the recommended concentration of intermediate standards is 2x or 10,000 µg/mL.

7.6 Calibration Standards

7.6.1 Calibration standards for DRO are prepared at seven concentrations 20, 50, 100, 200, 500, 1000, and 5000 µg/mL by serial dilution and use of the intermediate standard. See Table 6 for dilution scheme. The solutions are documented in LIMS and transferred to LIMS labeled 40 mL VOA vials for refrigerated storage.

7.7 Surrogate Spike

7.7.1 Surrogate stocks

7.7.1.1 Purchase neat n-nonane from Chem Service, Part No. F-1099

7.7.1.2 Purchase neat n-triacontane from Chem Service, Part No. O-2268.

7.7.2 Surrogate Spike Mix

7.7.2.1 Prepare the surrogate spike mix at 5,000 µg/mL by weighing 0.125 g of neat n-nonane and 0.125 g of n-triacontane into a 25 mL volumetric flask. Bring to the mark with hexane. The solution is documented in LIMS and transferred to LIMS labeled 40 mL VOA vials for refrigerated storage.

7.7.3 Concentrations and spiking volumes may be changed based on project specific goals and different final volumes. These changes must be documented.

7.8 Laboratory Control Sample (LCS) Spike

7.8.1 The LCS spike mix is the stock standard (7.4.1) at 10,000 µg/mL for each of the 10 components. For a final extract volume of 10 mL, spike with 50 µl for a nominal 100% DRO recovery of 500 µg/mL (each component 50 µg/mL).

7.9 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Spike

7.9.1 The MS/MSD spike mix is the stock standard (7.4.1) at 10,000 µg/mL for each of the 10 components. For a final extract volume of 10 mL, spike with 50 µl for a nominal 100% DRO recovery of 500 µg/mL (each component 50 µg/mL).

7.10 Second Source Calibration Standards

7.10.1 Second source DRO stock standards are purchased from Restek at certified solutions of 2,000 µg/mL for each of the 10 components (Part No. 31064).

7.10.2 Second source calibration check standard.

7.10.2.1 Prepare a second source calibration standard at 500 µg/mL total DRO. Using a gas tight syringe, aliquot 625 µL of second source stock (2,000 µg/mL) into a 25 mL volumetric flask. Dilute to volume with hexane. The solution is documented in LIMS and transferred to LIMS labeled 40 mL VOA vials for refrigerated storage.

7.11 Internal Standard – Not applicable to this method

8 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

8.1 Water samples should be collected in 1 L amber glass bottles with Teflon lined caps containing 5 mL of 1:1 hydrochloric acid for preservation. Water samples must be extracted within 7 days of collection.

8.2 Soil samples should be collected in 4 ounce or larger amber glass jars with Teflon lined caps. Soil samples must be extracted within 14 days of collection.

8.3 All samples should be stored on ice or refrigerated at 4 °C immediately after collection. In the laboratory, store samples at 4 °C.

8.4 Extracts are stored in the freezer and must be analyzed within 40 days of extraction.

9 PROCEDURE

9.1 Water samples should be extracted in accordance with PRE-001, Separatory Funnel Extraction.

9.2 Soil samples should be extracted in accordance with PRE-003, Micro-scale Soil Extraction.

9.3 Water samples should be concentrated in accordance with PRE-001, Separatory Funnel Extraction. Soil sample extracts prepared in accordance with PRE-003, Micro-scale Soil Extraction, do not require concentration.

9.4 Clean-up and/or derivatization procedures do not apply to this method.

9.5 Instrument Conditions

9.5.1 MXT-1 Column (or equivalent)

<u>Temperature Program</u>

Initial Temp:	55 °C
Initial Hold:	3 min
Initial Rate:	22 °C/min
Final Temp (1):	360 °C
Hold Time (1):	5 min
Injector Temp:	350 °C

Detector Temp:	380 °C
Carrier Gas:	Helium
Head Pressure:	~7 PSI
Make up Gas:	Helium
Flow Rate:	~30 mL/min
Oven Max	380° C
Splitless Valve	Splitless box not checked
On time	0.2 min
Off time	Initial value is off

9.5.2 MXT-1HT Sim Dist Column

<u>Temperature Program</u>

Initial Temp:	60 °C
Initial Hold:	1 min
Initial Rate:	15 °C/min
Final Temp (1):	390 °C
Hold Time (1):	2.0 min
Injector Temp:	400 °C
Detector Temp:	400 °C
Carrier Gas:	Helium
Head Pressure:	~7 PSI
Make up Gas:	Helium
Flow Rate:	~30 mL/min
Oven Max	450° C
Splitless Valve	Splitless box not checked
On time	0.3 min
Off time	24.5 min

9.6 Preventive Maintenance

9.6.1 Routine maintenance consists of clipping the column, replacing the liner and seal, cleaning the hat, and installing a new septum.

9.6.2 Change the septum as needed based on age or number of injections that have been made on the GC. When operating continuously, change the septum daily.

9.6.3 Carryover on the GC is usually caused by a worn out injection syringe. When replacing the syringe, if a burr exists, use fine sandpaper to remove. Rinse the inside and outside of the syringe with hexane to remove any grit left in the syringe tip.

9.7 Calibration

9.7.1 For standard DRO analysis, prepare an initial calibration (ICAL) consisting of all six calibration standards; 20, 50,100, 200, 500, 1000, and 5000 µg/mL. Quantitation of DRO is performed by the external standard technique.

NOTE: For heavier hydrocarbons prepare a 5+ point calibration curve of the standard that best suits the data quality objective.

9.7.2 Inject each calibration standard using the technique that will be used to introduce the actual samples into the gas chromatograph. The concentration of DRO in the sample is determined from a summation of the total response within the range of 0.1 minutes before the onset of elution of n-decane to 0.1 minutes after the end of the elution of n-octacosane using the initial calibration curve.

9.7.2.1 Integration should be baseline to baseline defined as a flat baseline parallel to the x-axis of the chromatogram that includes all responses within the retention time window. The optimal baseline placement would be a horizontal line drawn through the lowest point in the chromatogram. The lowest point is generally the baseline immediately after injection, but before the solvent elutes. A baseline hold integration event at approximately 0.7 minutes is generally used for a consistent and accurate baseline.

9.7.3 Regression

9.7.3.1 Plot the area summation against the concentration of the calibration standard using linear regression with a weighting factor of 1/concentration. The coefficient of determination (r^2) must be ≥0.990, which corresponds to a correlation coefficient of (r) of ≥0.995.

$$Y = AX^B \quad \text{or} \quad \ln Y = B \ln X + \ln A$$

Where: Y = area summation
X = Concentration in µg/mL
A = Constant
B = Exponent

9.7.4 Continuing calibration verification (CCV) The working calibration curve is verified on each working day by the injection of a 500 µg/mL CCV. If the response for any CCV varies from theory by more than ± 20%, a new calibration curve must be injected, and/or data is qualified.

$$Percent\ Difference = \frac{R2 - R1}{R1} \times 100$$

Where: R1 = Theoretical concentration.
R2 = Concentration from CCV.

9.8 Retention Time Windows

9.8.1 Retention times for the area summation and surrogates are obtained from the ICAL and used throughout the analytical run.

9.8.2 The surrogates are set as reference peaks. Retention windows for the surrogates are usually set as 0.06 minutes.

9.9 Sample Analysis

9.9.1 Set up the GC system using the conditions described in Section 9.5.1 or 9.5.2.

9.9.2 Samples are analyzed in a group referred to as an analysis sequence which is generated in LIMS to match the Chemstation data system sequence.

9.9.2.1 The initial calibration sequence will consist of a solvent blank followed by the ICAL standards, an initial calibration check standard (ICV), and the second source standard verification (SCV). Sample and quality control extracts are the added to the sequence interspersed with CCV standard every 10 injection and at the end of the run.

9.9.2.2 If a previous ICAL will be used, a new sequence is created in LIMS referencing that ICAL. The new sequence will consist of a solvent blank, an ICV, and a low level standard equal to or below the required reporting limit. Sample and quality control extracts are the added to the sequence interspersed with CCV standard every 10 injection and at the end of the run.

9.9.2.3 NOTE: The low level standard is analyzed to assure the previous ICAL is valid at the reporting limit.

9.9.3 Transfer an aliquot of each sample to 2 mL injection vials. Inject the samples and collect and process the data using the ChemStation data system.

9.9.4 Injection – Inject approximately 2 µL of each extract.

9.9.5 If any of the sample responses exceeds the theoretical value of the highest ICAL standard, dilute the extract and re-inject. Dilute the sample so expected concentration is in the upper half of the standard curve range.

9.9.6 Data Package Assembly and Review

9.9.6.1 The data package is to be assembled and reviewed in accordance with GEN-016, Data Review Procedures.

9.10 Calculations

9.10.1 The concentration of DRO in the sample extract is determined from the calibration curve in µg/ml through reverse extrapolation from the area summation

response in the sample using power regression. The concentration in µg/L or µg/kg is then calculated as follows:

9.10.1.1 Water Samples (µg/L)

$$Concentration\ (\mu g/L) = \frac{A_x \times D \times V_e}{V_s}$$

Where: A_x = Concentration of compound in the extract in µg/mL
D = Dilution factor, if applicable
V_e = Volume of extract in mL
V_s = Volume of sample extracted in Liters

9.10.1.2 Soil Samples (µg/kg)

$$Concentration\ (\mu g/g) = \frac{A_x \times D \times V_e}{W_s}$$

Where: A_x = Concentration of compound in the extract in µg/mL
D = Dilution factor, if applicable
V_e = Volume of extract in mL
W_s = Volume of sample extracted in kilograms

10 QUALITY CONTROL

10.1 Refer to Method 8000 for general quality control procedures for chromatography methods.

10.2 An analytical batch consists of 20 or fewer samples. Batch quality control samples should be analyzed with each set with the following frequency:

Blanks - One per 20 or fewer samples, minimum one per day
LCSs - One per 20 or fewer samples, minimum one per day
MS/MSDs - One MS/MSD per 20 or fewer samples, minimum one set per day

Note: If an MS/MSD cannot be prepared because of limited sample volume, a second LCS must be prepared.

10.3 Method blanks consist of an aliquot of laboratory reagent water or silica sand that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure. If target analytes or interferences are present at concentrations that impact the analytical results for samples, the samples (including quality control samples) should be re-extracted or appropriately qualified in accordance with GEN-015, Qualification of Data.

10.4 LCSs consist of an aliquot of laboratory reagent water or silica sand spiked with the target analytes, prepared and processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure. LCS control limits for precision and accuracy are established on at least a yearly basis through the use of at least 20 data points. Interim control limits are 70-130%. If the recovery of any of the target analytes is outside control limits, the samples (including quality control samples) should be re-extracted or appropriately qualified in accordance with GEN-015, Qualification of Data.

10.5 MS/MSD samples consist of duplicate aliquots of sample spiked with the target analytes, prepared and processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure. MS/MSD control limits for precision and accuracy are established on at least a yearly basis through the use of at least 20 data points. MS/MSD control limits are advisory. Interim control limits are 60-140%. If the recovery or RPD of any of the target analytes is outside control limits, data should be appropriately qualified in accordance with GEN-015, Qualification of Data.

10.6 Initial calibration (ICAL) is performed using the internal/external standard technique by injecting a minimum of 5 of the available calibration standards. The lowest calibration point must be at or below the reporting limit. An acceptable calibration curve has a coefficient of determination (r^2) of 0.990 or greater.

10.7 The working calibration curve must be verified on each working day by the injection of one or more CCV standards. If the response for any analyte varies from the theoretical concentration by more than 20%, a new calibration curve must be prepared or data appropriately qualified in accordance with GEN-015, Qualification of Data.

10.8 Surrogates are added to every sample and QC sample. Surrogate control limits are generated on at least a yearly basis. Interim control limits are 60-140%. If a surrogate recovery is outside of control limits, the sample should be re-extracted and re-analyzed, if possible. If not, the data should be appropriately qualified in accordance with GEN-015, Qualification of Data.

10.9 A second source calibration verification standard must be analyzed with every initial calibration. The accepted limits are 70-130% for all analytes. If an SCV fails, immediate corrective action is required before proceeding with sample analysis. Affected data should be qualified according to GEN-015, Qualification of Data.

11 METHOD PERFORMANCE

11.1 Estimated MDLs for eight replicates of silica sand and water are listed in Table 1.

11.2 Performance data for four replicates of silica sand and water spiked at an LCS concentration are listed in Table 2.

12 CONTINGENCIES FOR HANDLING OUT-OF-CONTROL OR UNACCEPTABLE DATA

12.1 Contingencies for out-of-control data should be evaluated on a case-by-case basis. A Corrective Action Form (CAF) must be completed for those times that acceptable QC results cannot be achieved. The CAF must be completed by the analyst and filed with the Quality Manager. Analytical results shall be qualified as necessary.

13 WASTE MANAGEMENT / POLLUTION PREVENTION

13.1 All waste will be disposed of in accordance with federal, state, and local regulations. This method has been prepared to minimize the waste produced and the potential for pollution of the environment. All ECCS employees shall follow this method and the guidance provided in the ECCS Health and Safety manual.

14 REFERENCES

14.1 Method 8015B, “Nonhalogenated Organics Using GC/FID,” SW 846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, December 1996

14.2 “Modified DRO, Method for Determining Diesel Range Organics,” Wisconsin DNR, September 1995.

TABLE 1

DRO MDLS
DB-1 COLUMN

WATER

Compound	Spike Conc. (µg/L)	Average (µg/L)	Average Rec (%)	Standard Deviation	RSD (%)	MDL (µg/L)
DRO	Not available when SOP was prepared.					

NOTES: [1] 10 component standard mix used as spike

SOIL

Compound	Spike Conc. (mg/kg)	Average (mg/kg)	Average Rec (%)	Standard Deviation	RSD (%)	MDL (mg/kg)
DRO	Not available when SOP was prepared.					

NOTES: [1] 10 component standard mix used as spike

TABLE 2

DEMONSTRATION OF CAPABILITY

WATER

Compound	Spike Conc. (µg/L)	Average (µg/L)	Average Rec (%)	Standard Deviation	RSD (%)	MDL (µg/L)
DRO [1]	Not available when SOP was prepared.					

NOTES: [1] 10 component standard mix used as spike

SOIL

Compound	Spike Conc. (mg/kg)	Average (mg/kg)	Average Rec (%)	Standard Deviation	RSD (%)	MDL (mg/kg)
DRO [1]	Not available when SOP was prepared.					

NOTES: [1] 10 component standard mix used as spike

TABLE 3

RETENTION TIMES

Compound	**MXT-1**
n-Nonane (Surr)	2.73
n-Decane	4.28
n-Octacosane	14.7
n-Triacontane (Surr)	15.19

TABLE 4

STOCK STANDARD SOLUTION CONCENTRATION

Compound	**Concentration (µg/mL)**
DRO[1]	100,000

NOTES: [1] 10 component standard mix (7.4.1)

TABLE 5

INTERMDEDIATE STANDARD CONCENTRATIONS

Compound	**Concentration (µg/mL)**
DRO[1]	5000

NOTES: [1] 10 component standard mix (7.5.1)

TABLE 6

INITIAL CALIBRATION CURVE PREPARATION

Concentration (µg/mL)

	L-1	**L-2**	**L-3**	**L-4**	**L-5**	**L-6**	**L-7**
DRO	20	50	100	200	500	1000	5000
Stock ID	L-4	L-5	Inter[1]	Inter[1]	Inter[1]	Inter[1]	See 6.5.1
Aliquot (mL)	5	5	1	2	5	10	N/A
Final Volume[2] (mL)	50	50	50	50	50	50	N/A

NOTES: [1] Intermediate 10 component stock standard (7.5.1)

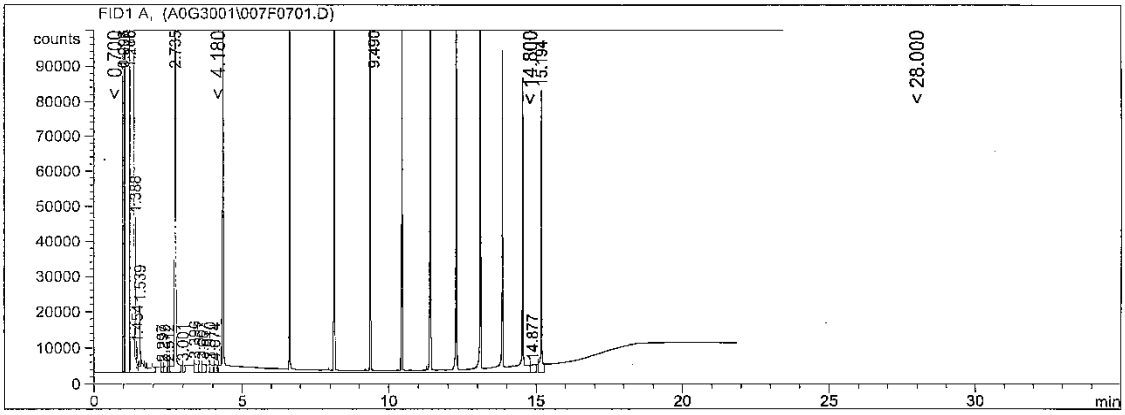
N/A – not applicable

FIGURE 1

EXAMPLE L-5 STANDARD CHROMATOGRAM – MXT-1 COLUMN

```
Data File C:\CHEM32\3\DATA\A0G3001\007F0701.D
Sample Name: A0G3001-CAL5
    ==================================================================
    Acq. Operator    : cps                              Seq. Line :   7
    Acq. Instrument  : 3336A54843                        Location : Vial 7
    Injection Date   : 7/30/2010 6:14:33 PM                   Inj :   1
                                                       Inj Volume : Manually
    Acq. Method      : C:\CHEM32\3\DATA\073010\072910 2010-07-30 15-17-48\DRO1.M
    Last changed     : 7/30/2010 11:02:19 AM by CJM
    Analysis Method  : C:\CHEM32\3\METHODS\DROQ.M
    Last changed     : 8/3/2010 2:01:40 PM by cps
                       (modified after loading)
    Method Info      : DRO C9-C30, Nonane, Triacontane Surrogate

    ==================================================================
```




```
    ==================================================================
                          External Standard Report
    ==================================================================

    Sorted By              :      Retention Time
    Calib. Data Modified   :      8/3/2010 2:03:34 PM
    Multiplier:                    :      1.0000
    Dilution:                      :      1.0000
    Use Multiplier & Dilution Factor with ISTDs

    Signal 1: FID1 A,

    RetTime Sig Type     Area      Amt/Area    Amount   Grp   Name
     [min]            counts*s                [ug/mL]
    -------|--|------|----------|----------|----------|--|---------------
      2.735  1 HH     2.78208e5  1.81707e-4   50.55246    Nonane
      9.490  1 HHA+   2.64366e6  1.82950e-4  483.65800    DRO
     15.194  1 HH     1.62175e5  3.09106e-4   50.12932    Triacontane

    Totals :                                  584.33978

    ==================================================================
                          *** End of Report ***

3336A54843 8/3/2010 2:05:37 PM cps                          Page   1 of 1
```

The signatures below indicate the following individuals have reviewed this document in its entirety and authorize its use to supersede prior revisions as of the effective date of this SOP.

Reviewed By:

Chris Sauer, GC/MS Team Leader — Date: 02/18/11

Michael Linskens, Quality Manager — Date: 02/18/11

Approved By:

Nick Nigro, President — Date: 02/18/11

Title: Determination of Diesel Range Organics (DRO) and Petroleum Range Organics (PRO) [8015B, 8015C, 8015D, FL PRO, TN DRO, and Others]

Approvals (Signature/Date):

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Steve Wilhite — Date	Stephanie Wilson — Date
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1.0 Scope and Application

To provide the procedures necessary for the determination of Diesel Range Organics (DRO) and Petroleum Range Organics (PRO).

1.1 Analytes, Matrix(s), and Reporting Limits

This SOP applies to the analysis of a variety of matrices analyzed within the GC/Organic department. This method is designed to measure the concentration of diesel range organics in water and soil.

The method reporting limits for soils and waters are 2.5 mg/kg and 100 µg/L, respectively. Method detection limits (MDLs) for this method can be found in the laboratory Quality Assurance Manual (QAM).

On occasion clients may request modifications to this SOP. These modifications are handled following the procedures outlined in the Quality Assurance Manual.

2.0 Summary of the Method

2.1 When no state requirements exist, this corresponds to an alkane range of C_{10}-C_{28} and a boiling point range between approximately 170°C and 480°C. This method provides an extraction procedure and the chromatographic conditions for the detection of fuel hydrocarbons in the carbon range of C_{10}-C_{28} or state-specified carbon range. A weighed amount of the solid matrix is extracted using methylene chloride as the extraction solvent. A measured volume of aqueous matrix is extracted with methylene chloride. Quantitative analysis is done using direct injection of 1.0 µl of sample extract into a gas chromatograph (GC). A temperature program is used in the GC to separate the organic compounds. Detection is achieved by a flame ionization detector (FID). Quantitation is performed by comparing the total chromatographic area between n-C_{10} and n-C_{28} (or state-specified carbon range), including resolved and unresolved components, to the response of a multi-component calibration standard. Otherwise, the following carbon ranges apply:

Table 1

State	Petroleum Range Organics	Diesel Range Organics
Alabama		Any recognized 8015 method
Arkansas		Any recognized 8015 method
Colorado		Any recognized 8015 method
Florida	C_8-C_{40} (FL PRO)	C_{10}-C_{28}
Illinois		C_{10}-C_{28}
Indiana		Any recognized 8015 method
Iowa		IDNR OA-2 (entire response integrated)
Louisiana		C_{10}-C_{28}
Kansas		Any recognized 8015 method
Massachusetts		MADEP EPH (see SOP PS-GCS-011)
Mississippi		C_{10}-C_{25}
New Jersey		C_{10}-C_{28}
North Carolina		Modified MADEP EPH (see SOP PS-GCS-011)
North Dakota		Any recognized 8015 method

State	Petroleum Range Organics	Diesel Range Organics
Ohio		compare to free product standard
Oklahoma		OK DRO (C_{10}-C_{28})
Oregon		C_{10}-C_{28}
Pennsylvania		C_{10}-C_{28}
Rhode Island		C_{10}-C_{28}
Tennessee		C_{12}-C_{40}
Texas	C_6-C_{10}, >C_{10}-C_{28}	C_{10}-C_{28}
Virginia		WI DNR modified DRO (C_{10}-C_{28})
West Virginia		C_{10}-C_{28}

2.2 The method is designed to measure mid-range petroleum products such as diesel or fuel oil. Components greater than C_{28} present in products such as motor oils or lubricating oils are detectable under the conditions of the method. If, based on a review of the chromatogram, the presence of these product types is suspected, additional efforts may be performed including, but not limited to, analysis of additional reference materials. These additional efforts are not contained in this SOP.

3.0 Definitions

3.1 Diesel Range Organics (DRO)**:** All chromatographic peaks eluting between decane (n-C_{10}) and octacosane (n-C_{28}). Quantitation is based on direct comparison of the area within this range to the total area of the 10-components in the Total Petroleum Hydrocarbon standard.

3.2 Petroleum Range Organics (PRO): All chromatographic peaks eluting between octane (n-C_8) and Tetracontane (n-C_{40}). Quantitation is based on direct comparison of the area within this range to the total area of the 17-components in the Total Petroleum Hydrocarbon standard.

3.3 Additional definitions and acronyms may be found in the QAM.

4.0 Interferences

Other organic compounds; including chlorinated hydrocarbons, phenols, and phthalate esters are measurable. As defined in the method, the DRO results include these compounds.

The flame ionization detector (FID) is a non-selective detector. There is a potential for many non-target compounds present in samples to interfere with this analysis.

5.0 Safety

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), Radiation Safety Manual and this document.

5.1 Specific Safety Concerns Or Requirements

The gas chromatograph contains 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.

There are areas of high voltage in both the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.2 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
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. May be absorbed through skin.
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 may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Diesel Fuel	Flammable	N/A	A slight irritant to the mucous membranes. Toxic effects exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

Equipment maintenance is described in the manufacturer's manuals. All maintenance is documented per SOP PS-LAB-004 (Logbook Format, Review and Control).

Refer to the instrument operating manual for maintenance requirements and suggestions.

Refer to the QAM for the maintenance schedule.

6.1 Instrumentation

- Gas chromatograph HP 5890 flame ionization detector (FID).
- Computer with Enviroquant Software
- Gas chromatographic column and operating conditions for the instrument are:

  - Flash column RTX-5 capillary column or RTX-1 capillary column, 5 meters, 0.25 mm id, 0.25 µm film thickness.
  - Detector: flame ionization detector
  - Injection method: Splitless mode
  - Program temperature:
    Initial temperature = 45°C, hold = 20 seconds;
    Rate = 315°C/75 seconds, hold 270 seconds;
    Total run time 4.5 minutes.
  - Gas flows:

Hydrogen	= 30 ml/minute
Air	= 300 ml/minute
Slit (He)	= 100 ml/minute
Septum Sweep	= 5 ml/minute

  - Column pressure = 12 psi

6.2 Supplies

- 2000 ml separatory funnels
- Zymark Turbo Vap
- 1 ml Endpoint Tubes for use with Turbo Vap
- Spatula
- 4 and 8 ml glass vials
- Water bath
- Sonic disrupter
- 250 ml beakers
- Gas-tight syringes
- Autosampler vials – 1.8 ml
- Drying oven
- Mettler balance (top loader) - Calibration of balances is performed per SOP PS-QAD-016 (Calibration of Laboratory Balances and Laboratory Weights).

7.0 Reagents and Standards

All standards and surrogate solutions are prepared in methylene chloride and/or carbon disulfide. Standards are prepared, labeled, and stored in accordance with the guidelines in EPA SW846 Method 8000. NIST standards are used whenever available.

7.1 Methylene chloride - Pesticide quality

7.2 Carbon disulfide – low benzene

CAUTION

Carbon disulfide is extremely flammable. Vapor may cause a flash fire. Harmful if swallowed, inhaled, or absorbed through the skin. Causes eyes, skin, and respiratory tract irritation.

7.3 Sodium sulfate (Na_2SO_4) - granular, kiln dried

7.4 Reagent water: reagent water is defined as water free of analyte(s) of interest [i.e., analyte(s) of interest not observed at MDL] when employed in this procedure.

7.5 Silica Gel, 28 to 200 mesh, reagent grade 12 or equivalent (deactivated with 1 to 2% water).

7.6 Total petroleum hydrocarbon standard - A seventeen (C_8-C_{40}) component blend of typical petroleum components (Attachment 1) containing the even numbered carbons. This standard serves as a quantitation standard and a retention time window defining mix for diesel and petroleum range organics. Additional components that may be added include C_6, C_9, and C_{19}. If these are added it will alter the total amounts in each standard.

7.7 Fuel (Diesel) Standard - Diesel purchased from a local service station or obtained from the sample site or from a commercial standards vendor. Prepare the Fuel standard by weighing out 2500 mg of diesel into a 250 ml volumetric flask and dilute to volume with methylene chloride. This yields a 10000 µg/ml stock calibration standard.

7.8 Custom Florida TRPH standard

7.9 Surrogate standards - The surrogate standards ortho ter phenyl (OTP) and nonatriacontane (C_{39}) are purchased as neat compounds. Stock (intermediate) standards are made by diluting 1000 mg of OTP into 100 ml methylene chloride and 150 mg of C_{39} into 100 ml of carbon disulfide The resulting concentrations are 10000 µg/ml OTP and 1500 µg/ml C_{39}. A working standard is prepared by diluting both 6.25 ml of the stock OTP standard and 16.67 ml of the stock C_{39} standard into 250 ml of methylene chloride with 10-15% carbon disulfide to help keep the C_{39} in solution. This will produce a working standard with a 250 µg/ml concentration of OTP and 100 µg/ml concentration of C_{39}. If the surrogate is also to be used for North Carolina and Massachusetts EPH analyses, 1-Chlorooctadecane (COD) should be prepared and added the same way as the OTP.

7.10 The required working (calibration) standards and surrogate standards are prepared in the following proportions:

Optional	Optional	Optional						
C_6 (10000 µg/ml)	C_9 (10000 µg/ml)	C_{19} (10000 µg/ml)	TPH Standard (5000 µg/ml)	OTP Stock (10000 µg/ml)	COD Stock (10000 µg/ml)	C_{39} Stock (1500 µg/ml)	Final Conc.	Final Volume
1 ml	1 ml	1 ml	2 ml	1 ml	1 ml	6.67 ml	400 µg/ml	25 ml
0.5 ml	0.5 ml	0.5 ml	1 ml	0.5 ml	0.5 ml	3.33 ml	200 µg/ml	25 ml
1 ml	1 ml	1 ml	2 ml	1ml	1ml	6.67 ml	100 µg/ml	100 ml
0.125 ml	0.125 ml	0.125 ml	0.25 ml	0.125 ml	0.125 ml	0.83 ml	50 µg/ml	25 ml
0.05 ml	0.05 ml	0.05 ml	0.1 ml	0.05 ml	0.05 ml	0.333 ml	20 µg/ml	25 ml
0.0125 ml	0.0125 ml	0.0125 ml	0.025 ml	0.125 ml	0.125 ml	0.083 ml	5 µg/ml	25 ml

8.0 Sample Collection, Preservation, Shipment, and Storage

Matrix	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Waters	Glass	1000 mLs	Cool 4 ± 2°C	7/40 Days	40 CFR Part 136.3
Soils	Glass	30 grams	Cool 4 ± 2°C	14/40 Days	N/A

[1] To Extraction/To Analysis.

Holding Times, Preservation and Container Requirements:
State DRO, PRO, - Aqueous

STATE	METHOD	CONTAINER	PRESERVATION Temp	PRESERVATION Chemical	HOLDING TIME
Florida	FL PRO	1 liter glass, Teflon cap	4°C	HCl or H_2SO_4 to pH < 2	Extraction 7 days Analysis 40 days
Iowa	Method for Determination of DRO	One liter glass, Teflon caps	4°C	None	Extraction 7 days Analysis 40 days
Kansas	Extractable Petroleum Products	1 liter glass, Teflon lid	4°C	None	Extraction 7 days Analysis 40 days
Kentucky	Methods for sample collection, sample preservation, chain of custody (COC), sampling equipment, decontamination procedures, sample containers, sample sizes, and maximum sample holding times shall be conducted according to 40 CFR 260.11, specifically, US EPA SW-846.				
Maine	Modified DRO	1 liter amber bottles, Teflon cap	4 ± 2°C	1:1 HCl or $NaHSO_4$ to pH < 2	7 days
Mississippi	Method for Determination of Diesel Hydrocarbons	1 liter glass, Teflon lid	4°C	None	Extraction 7 days Analysis 40 days
Montana	Method for Determination of DRO	1 liter glass containers	4°C	Acidified to pH 2	Extraction 7 days Analysis 40 days
New York	Petroleum Fingerprint Identification	1 liter glass mason jar, Teflon cap	4°C	None	Transport to lab within 24 hours
Oklahoma	DRO	1 liter amber, Teflon cap	4°C	5ml of 50% HCl	Extraction 7 days Analysis 40 days
Tennessee	Method of Determination of EPH by GC/FID	1 liter glass	4°C	Acid	Extract 7 days Analysis 40 days
Virginia	Refer to Wisconsin Methods				
Wisconsin	Modified DRO[1]	One liter amber glass, Teflon cap	4°C	5 ml 50% HCl at time of collection	Extraction 7 days Analysis 47 days

Key to Table

1. Acid can be added to bottle prior to adding sample. Samples from carbonate aquifers should be preserved with sodium azide or extracted unpreserved within 48 hours. These samples must be flagged on the COC

9.0 Quality Control

Please refer to the QAM for quality parameters not addressed in this SOP.

Refer to SOP PS-QAD-017 (Non-conforming Events) for corrective action procedures.

Quality Controls	Frequency	Control Limit	Corrective Action[5]
Method Blank (MB)	1 in 20 or fewer samples	< Rpt. Limit	MB > ½ the RL. Request re-extracts.
Laboratory Control Sample (LCS)/(LCSD)[1]	1 in 20 or fewer samples	Statistical Limits [4]	LCS is outside limits, request re-extract.
Matrix Spike (MS)[2]	1 in 20 or fewer samples	Statistical Limits [4]	
MS Duplicate (MSD)[2]	1 in 20 or fewer samples	Statistical Limits [4]	MS/MSD if the samples confirm flag the data and report. If they do not "match" re-extract.
Surrogates	every sample[3]	Statistical Limits [4]	Outside control limits high – 1) no hits = flag and report. Hits, request re-extracts. Low – request re-extract unless matrix interference is evident.

[1] LCS Duplicate (LCD) is required when MS/MSD is not available to determine precision.
[2] The sample selection for MS/MSD are randomly selected, unless specifically requested by a client.
[3] Analytical and QC samples (MB, LCS, MS/MSD)
[4] Statistical control limits are updated annually and are updated into LIMS.
[5] For a complete description of Corrective Actions refer to PS-QAD-017 (Non-conforming Events).

10.0 Procedures

10.1 Sample Preparation

- Aqueous matrices are extracted and concentrated using SOP PS-EXT-001 (Continuous Liquid-Liquid Extraction) or SOP PS-EXT-002 (Separatory Funnel Liquid-Liquid Extraction); however, the final concentrate volume is adjusted to 5 ml (2 ml final volume for FLPRO only, 1 ml final volume for OA-2 and Wisconsin).
- Solid matrices are extracted and concentrated using SOP PS-EXT-005 (Preparation of Soil/Sediment by Pulsed Sonication for the Analysis of Semivolatile Organic Compounds), but final concentrate volume is adjusted to 5 ml (2 ml final volume for FLPRO only, 1 ml final volume for OA-2 and Wisconsin).
- Silica Gel Cleanup (Mandatory for FLPRO analysis) - Add 0.3 g of loose silica gel to the extract and shake the mixture for five (5) minutes. Transfer cleaned extract to a labeled vial with a sealed Teflon-lined septum vial for analysis.

NOTE
When using loose silica gel, filter the extract through a plug of precleaned silanized glass wool in a disposable glass pipette or allow to settle and decant extract into appropriate vial.

10.2 Calibration (if state method does not specify) - External Standard Method

A calibration curve should be run initially or when a new column is put in place, major maintenance takes place, or if the CCV will not pass criteria. The initial calibration correlation coefficient must be **≥ 0.995** or meet relative standard deviation **(%RSD)** criteria (see 10.2.3) for 8015B in order to proceed with analysis.

10.2.1 Calibrate the GC with an initial six-point calibration using the TPH standards listed in section 7.10. See Attachment 3 for calibration point concentrations.

For 8015B, the initial calibration is generated using the diesel standard discussed in section 7.7. For all other DRO methods including FLPRO, the initial calibration curve is generated using the TPH standard.

10.2.3 Tabulate the concentration injected against the area response of the 10 components (C_{10}-C_{28}) for DRO and the 17 components (C_8-C_{40}) for FLPRO. If C_6, C_9 and/or C_{19} were added to the standards, the number of expected components will increase to include these. The ratio of the concentration injected to the area response, defined as the calibration factor (CF), can be calculated for the standard at each concentration. If the percent relative standard deviation (%RSD) is less the 25% over the working range, linearity through the origin can be assumed, and the average continuing calibration factor can be used in place of a calibration curve.

$$CF = \frac{\text{concentration of standard (mg/L)}}{\text{total area of TPH components}}$$

NOTE
For Iowa, 8015B %RSD must be less than 20%.

10.2.4 The working calibration factor or calibration curve must be verified on each working day by the injection of a continuing calibration verification standard - CCV (100 μg/ml mid-point). The CCV is run every 10 samples and followed by an instrument blank. If the response for this standard varies from the predicted response by more than ± 25% (or other as noted below), the CCV analysis must be repeated. Second exceedence requires initial calibration and/or corrective action.

$$\text{Percent difference (\%D)} = \frac{R_1 - R_2}{R_{avg}} \times 100$$

where:

R_1 = Average CF from the calibration curve
R_2 = Calibration Factor from CCV
$R_{avg} = (R_1 + R_2)/2$

NOTE
For El Paso work, 85%-115% will be used for continuing calibration checks for all GC methods.
For Iowa, the %D must not vary by more than ± 20%.

10.3 Sample Analysis

10.3.1 Retention Time Windows

Retention time (RT) windows are established for all compounds of interest. Retention time windows are calculated according to the procedure in SW846 method 8000B, section 7.6. The retention times of all analytes in all verification standards must fall within the absolute RT windows. If an analyte falls outside the RT window in a calibration verification standard, new absolute RT windows must be calculated, unless instrument maintenance corrects the problem.

- The TPH alkane standard is injected after the calibration curve and as frequently as needed throughout the run for retention time verification (RTV) of individual hydrocarbon ranges.
- Samples, blanks and QC samples are analyzed by GC/FID. Suggested injection volumes are 1.0 µl using the conditions established in section 7.9.
- If initial calibration has been performed, verify the calibration by analysis of a mid-point CC.
- The mid-point standard must also be analyzed every 10 injections and at the end of each sequence.
- A methylene chloride blank must be run in every sequence to determine the area generated on normal baseline bleed under the conditions prevailing in the 24 hour period. Methylene chloride blanks should also be run as needed after samples suspected of being highly concentrated to prevent carryover.
- If the product concentration exceeds the linear range of the method in the final extract, the extract must be diluted and reanalyzed.

11.0 Calculations and Data Reduction

The concentration of hydrocarbons in an extracted sample is calculated by using a total area sum between C_{10} and C_{28}. The area of the surrogate OTP is subtracted from the total sample when applicable.

11.1 Soil Samples

$$\text{Concentration (mg/kg)} = \frac{(CF)(V)(T)(d)}{(D)\ \text{(amount of soil extracted)}}$$

11.2 Water Samples

$$\text{Concentration (mg/L)} = \frac{(CF)(T)(d)}{(C)}$$

Where: C = concentration factor, i.e., the volume of sample divided by the volume of the extract (ml).
CF = Calibration Factor
D = dry weight of soil sample (in kilograms)
d = dilution factor, if samples extract was diluted
T = total response area of sample

V = volume of sample extract (in liters)

11.3 Results are reported as ND (no detection) if the sample results are below the reporting limits described in section 1.1.

11.4 Linear regression: If this method is used, employ software to calculate sample results using the linear regression equations.

11.5 Enviroquant automatically calculates surrogate recovery.

$$\text{OTP \% Recovery} = \frac{\text{Amount of OTP in Sample}}{250 \text{ (surr. Spiked into sample)}} \times 100$$

$$C_{39} \text{ \% Recovery} = \frac{\text{Amount of } C_{39} \text{ in Sample}}{100 \text{ (surr. Spiked into sample)}} \times 100$$

11.6 QC calculations are discussed in the laboratory QAM.

11.7 Acceptance criteria is available in the laboratory LIMS and in the Quality Assurance Manual.

11.8 Calculations for calibration curves may be found in Corporate SOP CA-Q-S-005, Calibration Curves.

12.0 Method Performance

12.1 Method Detection Limit Study (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL procedure of the QAM. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method requirements require a greater frequency.

12.2 Demonstration of Capabilities

Refer to the QA Manual for general procedures and specific concentrations that must be used. Also, reference SOP PS-QAD-021 (Demonstrations of Capability).

12.3 Training Requirements

The QA Manual or the Training SOP PS-LAB-014 (Training Program and Documentation) should be referenced for training requirements.

13.0 Data Reporting

- Iowa requires product type identification of common petroleum products.

14.0 Pollution Control

It is the laboratory's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

15.0 Waste Management

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to laboratory SOP PS-LAB-015 (Waste Handling and Disposal Practices).

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

- Solvent waste generated in the department is placed in a 4 liter satellite waste container labeled Organic Waste and stored in a secondary waste container. The containers are dumped in the Hazardous waste room in the Organic Solvent Waste Drum and recorded in the hazardous waste book.
- The samples vials are disposed of in the sample vial drum located in the hazardous waste room and the recorded in the hazardous waste book.
-

16.0 References / Cross-References

16.1 Florida DEP Method for Determination of Petroleum Range Organics (Method # FL-PRO).

16.2 The Mississippi Method for the Determination of Diesel Hydrocarbons.

16.3 Tennessee Department of Health and Environment's Analysis of Gasoline and Other Petroleum Products for Total Petroleum Hydrocarbons Using Gas Chromatography.

16.4 Virginia DEQ Petroleum Program Manual.

16.5 Modified DRO, Method for Determining Diesel Range Organics, Wisconsin DNR, September 1995.

16.6 Iowa DNR, OA-2, Method for Extractable Petroleum Products and Related Low Volatility Organic Compounds, Revision 7/27/93)

16.7 Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846), Third Edition, September 1986, Final Update I, July 1992, Final Update IIA, August 1993, Final Update II, September 1994; Final Update IIB, January 1995; Final Update III, December 1996, Final Update IV, 2008. (8015B, 8015C, 8015D)

16.8 Standard Methods for the Examination of Water and Wastewater, 18th/19th /20th edition /Online; Eaton, A.D. Clesceri, L.S. Greenberg, A.E. Eds; American Water Works

Association, Water Pollution Control Federation, American Public Health Association: Washington, D.C.

16.9 Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act, and Appendix A-C; 40 CFR Part 136, USEPA Office of Water. Revised as of July 1, 1995, Appendix A to Part 136 - Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater (EPA 600 Series)

16.10 Laboratory Quality Assurance Manual, PS-QAM-001.

16.11 Laboratory SOP, PS-LAB-004 Logbook Format, Review and Control.

16.12 Laboratory SOP, PS-QAD-017 Non-conforming Events.

16.13 Laboratory SOP, PS-QAD-016 Calibration of Laboratory Balances and Laboratory Weights.

16.14 Laboratory SOP, PS-LAB-015 Waste Handling and Disposal Practices

16.15 Corporate SOP, CA-Q-S-001 Solvent and Acid Testing and Approval.

16.16 Corporate SOP, CA-Q-S-005 Calibration Curves.

16.17 Corporate SOP, CW-E-M-001 Corporate Environmental Health and Safety Manual.

17.0 Method Modifications

N/A

18.0 Attachments

Attachment 1: TPH Standard
Attachment 2: Acceptance criteria for QC Samples
Attachment 3: Total Amount of TPH in Standards
Attachment 4: El Paso Technical Requirements

19.0 Revision History

- Revision 0, dated 01/21/2008.
  - Add El Paso Technical Requirements

- Revision 1, dated 01/16/2009.
  - Updated State carbon ranges in Table 1
  - Revised layout to be consistent with TA Template Method SOP R1
  - Corrected typographical errors
  - Corrected internal and external references
  - Removed obsolete state references and requirements
  - Added caution note for Carbon disulfide

- Revision 2, dated 07/16/2010.
  - Added Holding Times, Preservation and Container Requirements: State DRO, PRO, - Aqueous to Section 8.

- Updated Reference Section 16

Attachment 1

TPH Standard

Component	Mid-point Concentration (mg/L)	Component	Mid-point Concentration (mg/L)
Octane	100	Hexacosane	100
Decane	100	Octacosane	100
Dodecane	100	Triacontane	100
Tetradecane	100	Dotriacontane	100
Hexadecane	100	Tetratriacontane	100
Octadecane	100	Hexatriacontane	100
Eicosane	100	Octatriacontane	100
Decosane	100	Tetracontane	100
Tetracosane	100		

Attachment 2

Acceptance criteria for QC Samples

01/27/00	FLPRO		8015/DRO-TNEPH		TX 1005	
	WATER	SOIL	WATER	SOIL	WATER	SOIL
RL (ppb)	100	2500	100	2500	5000	50000
SPK TV (ppb)	3400	113333	10,000	333,333		
LCS CLs (%)	41-133	50-124	55-142	56-152	70-130	70-130
MS/D CLs (%)	41-101	11-154	21-144	36-156	70-130	70-130
MS/D RPD CLs (%)	20	50	33	40	30	30
OTP CLs (%)	49-143	50-121	65-144	68-141	50-150	50-150
C39 CLs (%)	20-176	37-138				

01/27/00	NC/MA TPH (C19-C36)		NC/MA TPH (C9-C18)		NC/MA PAH (C11-C22)	
	WATER	SOIL	WATER	SOIL	WATER	SOIL
RL (ppb)	50	1,600	50	1,600	50	1,600
SPK TV (ppb)	100	3,333	150	5,000	250	8,333
LCS CLs (%)	40-140	40-140	40-140	40-140	40-140	40-140
LCS CLs (ppb)	40-140	1,333-4,667	60-210	2,000-7,000	60-210	2,000-7000
MS/D CLs (%)	40-140	40-140	40-140	40-140	40-140	40-140
MS/D CLs (ppb)	40-140	1,333-4,667	60-210	2,000-7,000	60-210	2,000-7000
MS/D RPD CLs (%)	50	50	50	50	50	50
MS/D RPD CLs (ppb)	50	1,667	75	2,500	75	2,500
OTP TV (ug/ml)					125	125
OTP CLs (%)					40-140	40-140
OTP CLs (ug/ml)					50-175	50-175
COD TV (ug/ml)	125	125	125	125		
COD CLs (%)	40-140	40-140	40-140	40-140		
COD CLs (ug/ml)	50-175	50-175	50-175	50-175		
FBP TV (ug/ml)					100	100
FBP CLs (%)					40-140	40-140
FBP CLs (ug/ml)					40-140	40-140
2BN TV (ug/ml)					100	100
2BN CLS (%)					40-140	40-140
2BN CLS (ug/ml)					40-140	40-140

Attachment 3

Total Amount of TPH in Standards

#Peaks	calibration point concentrations (ppm/peak)					
1	5	20	50	100	200	400
2	10	40	100	200	400	800
3	15	60	150	300	600	1200
4	20	80	200	400	800	1600
5	25	100	250	500	1000	2000
6	30	120	300	600	1200	2400
7	35	140	350	700	1400	2800
8	40	160	400	800	1600	3200
9	45	180	450	900	1800	3600
10	50	200	500	1000	2000	4000
11	55	220	550	1100	2200	4400
12	60	240	600	1200	2400	4800
13	65	260	650	1300	2600	5200
14	70	280	700	1400	2800	5600
15	75	300	750	1500	3000	6000
16	80	320	800	1600	3200	6400
17	85	340	850	1700	3400	6800
18	90	360	900	1800	3600	7200
19	95	380	950	1900	3800	7600
20	100	400	1000	2000	4000	8000

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Attachment 4

El Paso GC Semivolatile TPH Tech Requirements

General

Dual column/detector confirmation not required for VOA or GRO
Ret Time Window reset only once per 24hr.

QC Requirements

LCS

All targets must pass LCS (If LCSD, all targets must pass both LCS and LCSD) Contact PM if no extra volume for re-analysis

- Ok to report if LCS high and sample ND
- Re-analyze LCS only once; if fail again re-prep/analyze samples if in hold
- Re-analyze for all low LCS

Surrogate

Re-analyze for any Surr failure

- Unless MS/MSD out on Elpaso sample, or
- Surr high and sample ND, or
- Obvious, documentable matrix interference….
- If re-analysis ok and in hold, report re-analysis only
- If re-analysis also fails or is run out of hold; report both runs

Blanks

Blank Criteria →

- no hit above RL; Surr pass
- hit ok if ND in sample or if sample hit > 10x blank hit
- can re-analyze blank once; if still hit re-prep/analyze samples (with same hit) if in hold
- If samples out of hold or if re-prep/analysis still has blank hit, report original analysis and notify PM

Instrument Blanks OK, but cannot use only before CCV.

Matrix Spikes

MS/MSD failure ok if LCS good; NCM probable matrix interference
Spike Elpaso if >10 samples in Batch

Calibration

IC RSD ≤ 20% for avg RF
Linear R ≥ 0.99; Quadratic R^2 ≥ 0.99; force thru 0; cannot use 0 as point
Cannot use Grand Mean
CCV/ICV ≤ 15%D
CCV every 10 samples

- Reanalyze samples bracketed by failing CCV

TESTAMERICA KNOXVILLE

STANDARD OPERATING PROCEDURE

TITLE: Isotope Dilution Analysis of Selected Semivolatile Organic Compounds and Alkylated PAHs by Gas Chromatography/Mass Spectrometry - Selected Ion Monitoring (GC/MS-SIM)

(SUPERSEDES: KNOX-ID-0016, Rev. 7)

Prepared By: _____

Reviewed By: _____
Technical Specialist

Approved By: _____ 08/19/10
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Approved By: _____ 8-17-10
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Approved By: _____ 8-19-10
Laboratory Director

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1. Scope and Application

1.1. This procedure is used for the determination of selected semivolatile organic compounds and alkylated polynuclear aromatic hydrocarbons (PAHs) in water, soil, sediment, sludge, tissue, emissions from stationary sources and other sample matrices.

1.2. The individual compounds and homologue groups listed in Table 1 may be determined by this procedure.

1.3. The standard reporting limits for this method are approximately 10 ng/L for aqueous samples, 1 ng/g for soil/sediment/tissue samples, and 10 ng/g for air (XAD & filter) samples. Some analytes have higher reporting limits (refer to Table 1). Reporting limits will be proportionately higher for samples and extracts that require dilution.

1.4. This procedure is written for use by analysts who are experienced with residue analysis and skilled in GC/MS SIM.

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 PAHs and other target compounds. 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 capillary column gas chromatography/mass spectrometry (GC/MS) techniques. The mass spectrometer is operated in the selected ion monitoring (SIM) mode.

2.2. Samples are spiked with a solution of known amounts of the isotopically labeled internal standards listed in Table 4. The samples are then extracted using matrix specific extraction and cleanup techniques. The final extract is prepared by adding a known amount of the labeled recovery standard and concentrating to the final volume.

2.3. An aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a mass spectrometer.

2.4. The identification of the target compounds is based on their retention time relative to the labeled internal standards as established during routine calibration and the simultaneous detection of a quantitation and confirmation ion.

2.5. Quantitation of the target compounds is based on their relative response to the internal standards. A multipoint calibration is performed to establish mean response factors for the target analytes. Alkylated homologues are quantitated on the basis of response factors of the parent PAH. The instrument performance is routinely checked by the analysis of continuing calibration standards. Method performance is demonstrated by the analysis of method blanks and laboratory control samples (LCS), as well as an initial demonstration of capability.

3. Definitions

3.1. Alternate Surrogate Standard - A labeled compound which is used in 2 cases: (1) It is added to source air impinger contents prior to extraction to estimate the extraction efficiency for PAHs and other target compounds in the impinger sample. It is only used when the impinger extract is to be combined with the XAD sample extract prior to analysis. (2) It is added to the second liter of aqueous sample when the extracts from two separatory funnel extractions are to be combined for analysis.

3.2. Continuing Windowing Standard (Win) – A dilute mixture of coal tar and crude oils, selected for light, medium and heavy molecular weight distributions. This standard is used to verify and update the retention times of the characteristic peaks of PAH homologue groups (e.g., C2 Alkylnaphthalenes and C3 Alkylnaphthalenes). The solution is analyzed at the beginning of each shift during which homologue data is to be acquired.

3.3. Data Acquisition Parameters – Parameters affecting the scanning operation and conversion of the analytical signal to digitized data files. These include the configuration of the ADC circuitry, the ion dwell time, the MID cycle time, and acquisition modes set up for the method. Examples of acquisition modes for the MS include SIM mode, and Low Mass Resolution mode.

3.4. Labeled 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.

3.5. Recovery Standard - Labeled compounds which are added to every sample, blank, and quality control spike sample extract prior to analysis. They are used to measure the recovery of the internal standards and the alternate surrogate standard.

3.6. Sampling Surrogate Standard - A labeled compound added in a known amount to the XAD-2 resin of the sampling train, and allowed to equilibrate with the matrix before sampling is performed. The sampling surrogate standard has to be a component that can be completely resolved, is not present in the sample, and does not have any interference effects. Its measured concentration in the extract is an indication of how effectively the sampling train retains the target compounds collected on the XAD-2 resin. The recovery of the sampling surrogate standards in the field blanks can be used to determine whether there are any matrix effects caused by time or conditions under which the sample is transported and stored prior to analysis.

3.7. Additional definitions can be found in the TestAmerica Knoxville QAM glossary.

4. Interferences

4.1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may 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 should avoid using PVC gloves, powdered gloves, or gloves with measurable levels of phthalates.

4.2. The use of high purity reagents and solvents helps minimize interference problems.

4.3. Transformation of PAHs and the formation of artifacts can occur in the sampling train. PAH degradation and transformation on sampling train filters have been demonstrated. Certain reactive PAHs such as benzo(a)pyrene, benz(a)anthracene, and fluoranthene when trapped on filters can readily react in corrosive matrices. These PAHs are transformed by reaction with low levels of nitric acid and higher levels of nitrogen oxides, ozone, and sulfur oxides.

4.4. Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed with solvent between samples. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

4.5. Non-target interferences may cause peaks on selected ion current profiles (SICPs) intended for PAHs and their alkylated homologues. Pattern recognition must be employed for identifying interfering peaks that should not be considered for the homologue or target PAH under consideration. Analysts should be intimately familiar with both parent and alkyl PAH analyses in complex environmental samples. This procedure is particularly important for newer operators. See Figure 3 for chromatograms for identifying alkyl PAHs.

4.6. Atmospheric contamination can cause significant background peaks, especially for lower molecular weight parent and alkyl PAHs. The source of contamination can be significant in areas containing atmospheric PAHs (e.g., from diesel exhaust). Quality control requirements for the blank and appropriately qualifying the data are discussed in section 9.3.

5. Safety

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

5.2. Safety Concerns or Requirements.

5.2.1. The preparation of all standards and reagents, and glassware cleaning procedures that involve solvents such as methylene chloride will be conducted in a fume hood with the sash closed as far as the operations will permit.

5.2.2. 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 pass through an appropriate filter.

5.2.3. Training: Workers must complete the new employee Corporate Safety Manual safety orientation prior to working in the laboratory.

5.2.4. Personal Hygiene: Thoroughly washing of hands and forearms is recommended after each manipulation and before breaks.

5.2.5. Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans.

5.2.6. Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

5.3. 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[1]**	**Signs and symptoms of exposure**
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable, Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause light-headedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Isooctane	Flammable, Toxic, Irritant	None Established	Inhalation of vapors may cause respiratory tract irritation. Overexposure may cause drowsiness and dizziness. Toxic if absorbed through skin. May cause skin irritation. May cause eye irritation. May be harmful if swallowed.
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. May be absorbed through skin.
1 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3.1. Chemicals that have been classified as carcinogens, or potential carcinogens, under OSHA include the following PAHs: benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, and indeno(1,2,3-cd)pyrene. The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be kept to a minimum.

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

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

5.6. The autosampler, 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.

5.7. The mass spectrometer is under high vacuum. The mass spectrometer must be brought to atmospheric pressure prior to working on the source.

5.8. 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.

6. Equipment and Supplies

6.1. Gas Chromatograph/Mass Spectrometer (GC/MS) System – Analytical system complete with a temperature-programmable gas chromatograph suitable for split/splitless injection and all required accessories, including syringes, autosampler, analytical columns, and gases. The GC capillary column is directly coupled to the MS source.

6.2. GC column - 30m x 0.25mm ID x 25µm film thickness. RTX-5MS with Integra-guard fused silica capillary column, or equivalent.

6.3. Mass Spectrometer - Electron impact ionization with the filament eVs optimized for best instrument sensitivity, stability and signal to noise ratio, shall be capable of repetitively selectively monitoring 20 exact masses minimum during a period of approximately 1 second.

6.4. Data System - A computer system must be interfaced to the mass spectrometer. The system must allow the continuous acquisition and storage on machine readable media of all mass spectra obtained throughout the duration of the chromatographic program. Target™ software is used and can search any GC/MS data file for ions of a specific mass and that can plot such ion abundances versus time or scan number. This type of plot is defined as the Extracted Ion Current Profile (EICP). This software allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIH Mass Spectral Library is recommended

6.5. Carrier gas - Ultra high purity helium.

6.6. Volumetric flask (class A) of appropriate sizes with ground-glass stoppers.

6.7. Balance capable of weighing 0.0001g.

6.8. Syringe: various sizes, Hamilton Laboratory grade syringes or equivalent.

6.9. Glass bottles with PTFE-lined screw caps or crimp tops.

7. Reagents and Standards

7.1. Acetone, pesticide quality, or equivalent.

7.2. Methylene chloride, pesticide quality, or equivalent.

7.3. Hexane, pesticide quality, or equivalent.

7.4. Isooctane, pesticide quality, or equivalent.

7.5. Perfluorotributylamine (FC-43) is used in neat form to tune and calibrate the mass spectrometer. Scientific Instruments Services Catalog No. FC-43-100, or equivalent.

7.6. Standards and Calibration Solutions: Obtained as individual solutions and prepared solutions from Cambridge Isotope Laboratories (CIL), Cerilliant, Accustandard, Supelco or equivalent. Refer to Table 4 for details.

7.6.1. Refer to SOP KNOX-QA-0001, “Standard/Reagent Labeling and Documentation”, current revision, for guidance on standard documentation and labeling.

7.6.2. Initial Calibration Standards: CS1-CS7. See Table 3 for a complete list of compounds and their concentrations. Solutions are prepared with hexane as the solvent.

7.6.3. Initial Calibration Verification Standard (ICV): A second source calibration standard different from that used to prepare the initial calibration. A 0.5 µg/mL solution is prepared and combined with internal standard stock solutions in order to prepare a second source standard (the same concentration as a CS4 standard; see Table 3).

7.6.4. Continuing Windowing Standard:

7.6.4.1. The Crude Oil Intermediate solution is prepared by weighing 2.5 g of stock crude oil into 100 mL of hexane (final conc. = 25,000 µg/mL).

7.6.4.2. The Coal Tar Intermediate solution (stock solution = 20% coal tar in 83% alcohol/5%Polysorbate-80) is prepared by taking a known amount of solution and concentrating on a water bath/nitrogen stream to remove as much alcohol as possible, then bringing back to volume with isooctane. A 2 % solution (20,000 µg/mL) is then prepared by diluting a portion with isooctane.

7.6.4.3. 10 mL of each of these are put through a silica gel clean-up and brought back to volume with hexane.

7.6.4.4. The Alkyl Window Spiking solution is prepared by combining 100 µL of the 25,000 µg/mL crude oil stock and 100 µL of the 20,000 µg/mL coal tar stock into 1 mL of hexane. The final

concentration of the crude oil and the coal tar is 2,500 µg/mL and 2,000 µg/mL, respectively.

7.6.5. LCS Spiking Solutions: See Table 4 for a complete list of compounds and their concentrations. Solutions are prepared with acetone as the solvent.

7.6.6. Internal Standard Spiking Solutions: See Table 4 for a complete list of compounds and their concentrations. Solutions are prepared with acetone as the solvent.

7.6.7. Recovery Standard Spiking Solution: See Table 4 for a complete list of compounds and their concentrations. Solution is prepared with hexane as the solvent.

7.6.8. Alternate Surrogate Standard Spiking Solution: See Table 4 for a complete list of compounds and their concentrations. Solution is prepared with acetone as the solvent.

7.6.9. Sampling Surrogate Standard Spiking Solution: See Table 4 for a complete list of compounds and their concentrations. Solution is prepared with hexane as the solvent.

7.6.10. Stability of Solutions: Sealed standard solutions used for quantitative purposes expire 3 years from the date received or on the manufacturer's expiration date, unless otherwise specified by program requirements. Lab prepared stock solutions expire 2 years after preparation; lab prepared spiking solutions expire 1 year after preparation. No daughter solution expiration date can exceed the parent expiration date. Standards are stored at 6°C or less, or per manufacturer's recommendation.

7.6.11. Since the alkyl window standard is used for qualitative purposes only, the coal tar and crude oil stock materials and intermediate solutions have no expiration date. The alkyl window spiking solution expires 1 year after preparation. If degradation of any alkyl window pattern is observed, a new spiking solution is to be prepared. If degradation is still observed, a new intermediate solution is to be prepared.

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. All extracts must be analyzed within 40 days from the start of extraction.

8.3. Store extracts in the dark at 4±2°C.

8.4. Sample holding times:

8.4.1. Solid samples have a 14 day holding time from collection to extraction. Water samples have a 7 day holding time from extraction to extraction.

Tissue samples have a 1 year holding time from collection to extraction. Air samples collected using method CARB 429 have a 21 day holding time from collection to extraction, whereas, air samples collected using SW-846 method 0010 have a 14 day holding time from collection to extraction.

9. Quality Control

9.1. Initial Demonstration of Capability and Method Detection Limit Studies: For the standard analyte list (Table 1), the initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin. Refer to Table 7 for the initial demonstration of capability acceptance criteria.

9.2. Internal standards are spiked into all samples, blanks, and LCS (LCSD and MS/MSD, if requested) to assess method performance on the sample matrix.

9.2.1. See Table 7 for the acceptance criteria for the recoveries of the internal standards and spiked compounds in field samples, method blanks, and other QC samples.

9.2.2. The isotope dilution technique assumes that results are independent of internal standard recovery (i.e., the target analyte is expected to behave similarly to the internal standard, thus the quantitation of the target analyte should not be impacted by the recovery of the internal standard).

9.2.3. If the recovery of any internal standard is not within the specified limits, one or more of the following steps may be useful in diagnosing the problem and determining the impact to the data:

9.2.3.1. Determine if the outlying recoveries are associated with a pattern, such as 1) an association of the outliers with a specific recovery standard or 2) a trend of low bias early in the chromatogram.

9.2.3.2. Verify that the selection and integration of the recovery standard and the internal standard is appropriate.

9.2.3.3. Verify that the calculations are correct.

9.2.3.4. Inspect the extract volume for discrepancies. Inspect the extraction notes for problems encountered during extraction.

9.2.3.5. Verify that the instrument sensitivity and retention time has not been compromised. Inspect the area counts of the recovery standards for diagnosis. An acceptable bracketing analysis may be used to determine that the instrument was in control and only that specific analysis is suspect.

9.2.3.6. If matrix interference is suspected, a dilution to reduce the matrix effect may be warranted.

9.2.3.7. High internal standard recovery may indicate matrix interferences on the internal standard or a suppression of the recovery standard.

9.2.3.8. Low internal standard recovery may also indicate matrix interferences on the internal standard, or a high recovery of the recovery standard. If a low internal standard recovery is determined to be due to a loss of instrument sensitivity, the impact on the ability to support the reporting limit should be considered.

9.2.3.9. If the poor internal standard recovery is judged to be a result of sample matrix interferences, a reduced portion of the sample may be re-extracted or additional cleanups may be employed.

9.2.4. If it has been determined that the data has been impacted due to the recovery of the internal standard being outside limits, reanalysis at a dilution or a re-extraction of the sample should be performed

9.2.5. If it has been determined that the data has not been impacted, generate a nonconformance memo and discuss the situation in the case narrative. This should be done in consultation with the client.

9.3. Method Blank: A method blank must be extracted with each extraction batch of 20 or fewer samples. The method blank (or an instrument blank) must be analyzed before the samples and must not contain any of the compounds of interest at a concentration above the reporting limit or 10 percent of the analyte concentration in the field samples.

9.3.1. Samples associated with a contaminated method blank must be re-extracted and reanalyzed with an acceptable method blank. The project manager may consult the client to determine project needs. If the client prefers that the original data be reported, the associated data may be reported in lieu of reanalysis. A nonconformance memo and narrative addressing the analytical issues must be generated.

9.3.2. If there is no target analyte greater than the RL in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be taken in consultation with the client.

9.4. A laboratory control sample (LCS) is extracted and analyzed along with each extraction batch of 20 or fewer samples. LCS spike components, and control limits are listed in Table 7.

9.4.1. If any LCS compounds of interest are calculated outside the control limits, the associated samples must be re-extracted and reanalyzed with a compliant LCS. (Refer to QA-003 for additional guidance.) The project manager may consult the client to determine project needs. If the client prefers that the original data be reported, the associated data may be reported in lieu of reanalysis. A nonconformance memo and narrative

addressing the analytical issues must be generated.

9.5. Client-specified matrix spike / matrix spike duplicate samples may be analyzed to provide additional precision and accuracy data.

9.6. Nonconformance and Corrective Action: Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the QA Manager.

9.7. Quality Assurance Summaries: Certain clients or regulatory programs may require specific project or program QC that may supersede these method requirements. Quality Assurance Summaries are developed to address these requirements.

10. Calibration and Standardization

10.1. Refer to CA-Q-S-002, current revision, Acceptable Manual Integration Practices and the TestAmerica Knoxville attachment for information on manual integration practices and documentation requirements.

10.2. Setup the autosampler, GC/MS, and establish the instrument operating conditions. Example GC/MS instrument conditions are shown in Figure 1.

10.3. Tune the mass spectrometer as needed using perfluorotributylamine (PFTBA) and the instrument data system autotune program. Select the DFTPP tune optimization profile for the autotune program.

10.4. 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 calibration solution (CS4). No samples are to be analyzed until acceptable initial and continuing calibrations are demonstrated and documented.

10.5. Setup the MS to acquire data in MID mode. Setup MID descriptors using the masses listed in Table 6.

10.5.1. Prior to analyzing initial calibration standards for the first time and afterwards as needed, analyze the Continuing Alkyl Window standard and CS4 standard in full scan mode to determine the elution retention time window of the target alkyl PAH groups and target parent analytes.

10.5.2. Use the retention times from the full scan analyses to set the MID switchpoints so that the target analytes and alkyl PAH retention time windows fall within their respective MID groups.

10.6. Initial Calibration

10.6.1. Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 3.

10.6.2. The 12-hour time period begins at the moment of injection of the first

calibration analysis that is used to demonstrate the linearity. The time period ends when 12 hours has elapsed according to the system clock. Analysis may proceed until 12 hours from the injection of the calibration have passed.

10.6.3. Analyze 1µL of each of the seven calibration standards and calculate the relative response factor (RRF) of each analyte vs. the appropriate internal standard and each internal standard vs. the appropriate recovery standard listed in Table 5 using the following equation:

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

Where:

As = area of the quantitation ion of the compound of interest.
Ais = area of the quantitation ion of the appropriate reference standard.
Cis = concentration of the appropriate reference standard.
Cs = concentration of the compound of interest.

NOTE: Alkylated PAH homologues are assigned the RRF calculated for the parent PAH. See table 8 for parent response factor assignment for the alkylated homologues.

10.6.4. Calculate the mean relative response factor and the standard deviation of the relative response factors for each calibration standard solution using the following equations:

$$\overline{RRF} = \frac{1}{n}\sum_{i=1}^{n}(RRF)_i$$

Where:

RRF_i = RRF calculated for calibration solution "i" using the equation in section 10.6.3.
n = The number of calibration points in the curve.

$$\%RSD = \frac{SD}{\overline{RRF}} \times 100$$

Where:

$\overline{RRF}$ = Mean relative response factor calculated above.
SD = the sample standard deviation of the relative response factors used to calculate the mean RRF.

$$SD = \sqrt{\sum_{i=1}^{N}\frac{\left(RFi - \overline{RF}\right)^2}{N-1}}$$

Where:

RFi = RF for each of the calibration levels.

N = Number of RF values.

10.6.5. Criteria for Acceptable Calibration - The percent relative standard deviation (%RSD) for the mean relative response factors for both the target analytes and the internal standards must not exceed 30 percent.

10.6.5.1. 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 an abnormal disruption of an individual acquisition (e.g., low injection volume or the instrument inadvertently loses communication during elution), repeat the individual analysis and recalculate the percent relative standard deviation. (See the current revision of P-T-001, "Selection of Calibration Points".) If the calibration is acceptable, document the problem and proceed; otherwise repeat the initial calibration.

10.6.6. Initial Calibration Verification Standard (2nd source standard)

Prepare the ICV as described in section 7.6.3. The ICV must contain all the target analytes analyzed in the initial calibration.

Analyze 1µL of the ICV standard under the same conditions as the initial calibration. Calculate the concentration of the ICV using the average RRFs from the initial calibration. Calculate the percent recovery (%R) between the expected and the calculated ICV concentration. The %R must not exceed ± 30% (see Table 7).

10.7. Continuing Calibration

10.7.1. Continuing calibration is performed at the beginning of a 12-hour period. The 12-hour time period begins at the moment of injection of the continuing calibration standard (CCAL). The time period ends when 12 hours has elapsed according to the system clock. Analyses may proceed until 12 hours from the injection of the CCAL have passed. A sample injected less than 12 hours after the CCAL is acceptable.

10.7.2. Analyze 1µL of the CS4 continuing calibration standard (see Table 3). Use the same data acquisition parameters as those used during the initial calibration. Check for GC resolution and peak shape.

10.7.3. If total homologues are to be acquired during the analytical shift, analyze 1µL of the Continuing Alkyl Windowing Standard Solution (section 7.6.4). Use the same data acquisition parameters as those used during the continuing calibration.

Examine and identify the presence of first and last peaks for the isomers of any total homologues to be quantified during the shift. Representative selected ion chromatograms for alkyl PAH windows are shown in Figure 3.

10.7.4. Criteria for Acceptable Calibration - The criteria listed below for acceptable calibration must be met at the beginning of each 12 hour period during which samples are analyzed. If continuing calibration criteria are not met, identify the root cause, perform corrective action and repeat the continuing calibration. If the second consecutive continuing calibration does not meet acceptance criteria, additional corrective action must be performed. Acceptable performance must be demonstrated after two consecutive failing continuing calibrations by the analysis of two consecutive acceptable continuing calibrations or by analysis of a new initial calibration.

10.7.4.1. The measured RRFs of all target analytes and internal standards must be within 30 percent difference or drift of the mean values established during the initial calibration. If this criterion is not satisfied, a new initial calibration curve must be established before sample extracts can be analyzed.

$$\%\text{Drift} = \frac{C_{actual} - C_{found}}{C_{actual}} \times 100$$

Where:

C_{actual} = Known concentration in standard
C_{found} = Measured concentration

$$\%\text{Difference} = \frac{\overline{RF} - RF}{\overline{RF}} \times 100$$

Where:

$\overline{RF}$ = Average analyte response factor from initial calibration
RF = Measured analyte response factor from calibration verification

10.7.4.2. The recovery standard response must be within 50-200% of the response in the corresponding CS4 calibration level of the initial calibration.

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 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.

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

11.3. GC/MS Analysis

11.3.1. Calibrate the instrument as described in Section 10.

11.3.2. Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 1 µL into the GC/MS and acquire data until benzo(ghi)perylene has eluted from the column.

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

- Date of analysis
- Time of analysis
- Instrument data system filename
- Analyst
- Lab sample identification
- Bench dilution factor

Additional information may be recorded in the logbook if necessary.

11.3.4. Generate ion chromatograms for the masses listed in Table 6 that encompass the expected retention windows of the target analytes. Integrate the selected ion current profiles of the quantitation ions shown in the table. Representative selected ion chromatograms for alkyl PAH windows are shown in Figure 3.

11.3.5. Dilutions: If the response for any compound exceeds the working range of the GC/MS system, a dilution of the extract is prepared and analyzed. An appropriate dilution should be in the upper half of the calibration range. Samples may be screened to determine the appropriate dilution for the initial run. If the initial diluted run has no hits or hits below 20% of the calibration range and the matrix allows for analysis at a lesser dilution, the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12. Data Analysis and Calculations

12.1. Qualitative identification criteria for individual analytes: For a gas chromatographic peak to be identified as a target analyte, it must meet all of the following criteria:

12.1.1. The quantitation ion must be present.

12.1.2. The internal standard quantitation ions must be present.

12.1.3. The relative intensities of confirmation ions should agree to within ±30% between the standard and sample spectra. (Example: For an ion with an abundance of 50% in the standard spectra, the corresponding sample abundance must be between 20% and 80%). The absence of confirmation ions should be considered carefully when making decisions regarding qualitative identification. Confirmation ions may have lower response than

quantitation ions and may not always be present at lower concentrations. Their absence in this case may not be cause for determining that the analyte is not present. The absence of confirmation ions at higher levels where they should have been detectable may be cause for determination that an analyte is not present.

12.1.4. The sample component retention time must compare to within ± 0.2 min. of the retention time of the internal standard component. For reference, the standard must be run within the same 12 hour period as the sample.

12.1.5. If a compound cannot be verified by all the above criteria, but in the technical judgment of the analyst the identification is correct, the analyst shall report that identification and proceed with quantitation.

12.2. Qualitative identification criteria for total homologue groups (e.g., total C2 or C3 alkylnaphthalenes) - For gas chromatographic peaks to be identified as a member of the homologue, it must meet all of the following criteria:

12.2.1. The retention time (RT) of the analyte must be no more than 5 seconds before and no more than 5 seconds after the expected RT of the first and last isomer in the homologue, based on the continuing windowing solution analysis.

12.2.2. Manual integration of the alkyl PAH homologues (e.g., total C2 or C3 alkylnaphthalenes) by an experienced analyst is required. Proper identification of the alkyl clusters is critical, as is the proper identification and elimination of non-target compounds that occur at the same nominal mass. Retention time window criterion alone is insufficient for correctly identifying alkyl PAH clusters and non-target compounds. Pattern recognition must be used to avoid including non-target species that may occur at the same mass and within the retention time window as the target alkyl PAHs. All alkyl clusters should be integrated baseline to baseline to sum the total area of the cluster (adjusting the baseline for detector drift), but not valley to valley. Manual control and adjustment of the integration parameters is required for proper integration.

12.3. Quantitation for Target Analytes.

12.3.1. Calculate the internal standard recoveries (Ris) relative to the recovery standard according to the following equation:

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

Where:

Ais	=	area of the quantitation ion of the appropriate internal standard
Ars	=	area of the quantitation ion of the recovery standard
Qrs	=	ng of recovery standard added to the extract
Qis	=	ng of internal standard added to the sample

RRFis = mean relative response factor of internal standard obtained during initial calibration
S = Prep split factor, i.e., the inverse of the proportion of extract used after the addition of internal standards and before the addition of recovery standard.

Example:

Ais = 104067
Ars = 63273
Qrs = 10,000 ng/mL x 0.025 mL = 250 ng
Qis = 250 ng/mL x 3 mL = 750 ng/mL
RRFis = 2.12963
S = 3 (i.e., 1/3 of extract was taken through cleanup after the addition of internal standards)

$$\text{Ris} = \frac{104067 \times 250\,\text{ng} \times 3}{63273 \times 2.12963 \times 750\,\text{ng/mL}} \times 100\% = 77.2\%$$

12.3.2. See Table 7 for the acceptance criteria for recoveries of the internal standards and spiked compounds in field samples, method blanks, and other QC samples. See section 9.2 for guidance for corrective action when internal standards are outside control limits.

12.3.3. Calculate the concentration of individual target analytes according to the following equation:

$$\text{Concentration} = \frac{\text{As} \times \text{Qis}}{\text{Ais} \times \text{RRF} \times \text{W} \times \%\text{S}}$$

Where:

As = area of the quantitation ion of the compound of interest. In the case of total homologues, As = the sum of areas of all peaks which meet the qualitative criteria listed in Section 12.2.
Ais = area of the quantitation ion of the appropriate internal standard
Qis = ng of internal standard added to the sample
RRF = mean relative response factor of compound obtained during initial calibration
W = amount of sample extracted (grams or mL)
%S = % solids decimal fraction (i.e., % solids/100)

Example:

As = 2082058
Ais = 104067
Qis = 250 ng/mL x 3 mL = 750 ng
RRF = 0.92745
W = 30 g
%S = 0.750

$$\text{Concentration} = \frac{2082058 \times 750\text{ng}}{104067 \times 0.92745 \times 30\text{g} \times 0.750} = 719\ \text{ng/g}$$

NOTE: Alkylated PAH homologues are assigned the RRF calculated for the parent PAH. See table 8 for parent response factor assignment for the alkylated homologues.

12.3.4. If the concentration in the final extract of any target analyte exceeds the upper method calibration level, a dilution of the extract or a re-extraction of a smaller portion of the sample must be performed. Dilutions of up to 50x may be performed on the extract. Since the internal standards are diluted in the extracts, the internal standards that are used for calculation should be inspected to ensure that they are not diluted below a 10 to 1 signal to noise ratio. If the compounds which exceed the calibration range cannot be brought within the calibration range by a 50x dilution, extraction of a smaller aliquot of sample may be performed or the sample may be analyzed by a more appropriate analytical technique such as full scan GC/MS. Consultation with the client should occur before any re-extraction is performed.

12.3.5. The isotope dilution technique accounts for the dilution factor in the extract. If a sample extract is diluted, the internal standard and recovery standard are also diluted, so a dilution factor is not used in the equation. However, the analyst must apply the dilution factor in QuantIMS to adjust the RL and MDL appropriately.

12.4. Flag all compound results in the sample which were detected in the method blank with a “B” qualifier.

12.5. Flag all compound results in the sample which are below the reporting limit and above the MDL with a “J” qualifier. See Table 1.

12.6. Flag all compound results in the sample which are above the upper calibration limit with an “E” qualifier.

12.7. Total alkyl homologue concentrations are considered estimated and are qualified with the EST flag. The qualitative criteria for these homologues are not as rigorous as they are for individual targets (i.e., the retention times of all the compounds are not known). The compounds are identified as eluting within a retention time window established by examining a variety of coal tar and crude oil standards.

12.8. Data Review

12.8.1. The analyst who performs the initial data calculations must initial and date the QuantIMS data review form.

12.8.2. Refer to Figure 2 for an example data review checklist 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. The analyst who performs the initial data calculations must

initial and date the data review checklist.

12.8.3. All qualitative peak identifications must be verified by a second analyst. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.8.4. All hand calculations and data entries into calculation programs, databases, or spreadsheets must be checked by a second analyst 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.

12.8.5. The analyst that performed the second level review must fill out, initial and date the data review checklist.

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 (this does not apply to alkyl homologues). 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. Demonstration of capability for both soil and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method.

13.2.1. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample is listed in Table 7.

13.2.2. Calculate the average recovery and relative standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in Table 7. Historical matrix specific laboratory control sample acceptance criteria may also be used for evaluation of method demonstrations.

13.2.3. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

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. All attempts will be made to minimize 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 policies in section 13 of the Corporate Safety Manual for "Waste Management and Pollution Prevention."

15.2. The following waste streams are produced when this procedure is carried out.

- Solvent waste shall be placed in the flammable waste stream, contained in a steel satellite accumulation container type or flammable solvent container.
- Miscellaneous disposable glassware, chemical resistant gloves, bench paper and similar materials shall be placed in the incinerable laboratory waste stream, contained in a steel or poly satellite accumulation container type.

16. References

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

16.2. Method 429 - Determination of Polycyclic Aromatic Hydrocarbon (PAH) emissions from Stationary Sources, California Environmental Protection Agency Air Resources Board, Adopted: September 12, 1989, Amended: July 28, 1997.

16.3. NOAA Technical Memorandum NOS ORCA 130, National Status and Trends Program for Marine Environmental Quality, Sampling and Analytical Methods of the National Status and Trends Program Mussel Watch Project: 1993-1996 Update, March 1998.

17. Miscellaneous

17.1. Deviations from reference methods: Not applicable. This TestAmerica Knoxville laboratory SOP was developed using information from various sources, including the reference methods listed in section 16. This stand alone procedure is not intended to be compliant with all requirements of the reference methods.

17.2. The NOAA Technical Memorandum NOS ORCA 130 document is used to reference the alkyl groups only and not used for calibration, etc.

17.3. List of appendices, tables and figures referenced in the body of the SOP.

17.3.1. Table 1 – Target Analytes and Reporting Limits

17.3.2. Table 1A – Additional Analytes and Reporting Limits

17.3.3. Table 2 – Matrix, Sample Size, IS Spiking Level, and Final Volume

17.3.4. Table 3 – Concentration of Target Analytes in Calibration Solutions

17.3.5. Table 4 – Concentration of Stock Standards and Spiking Solutions

17.3.6. Table 5 – Quantitation References

17.3.7. Table 6 – Selected Ion Monitored and SIM Groups

17.3.8. Table 7 – Acceptance Criteria for Performance Tests and QC Samples

17.3.9. Table 8 – Response Factor Assignment for the Alkylated Homologues

17.3.10. Figure 1 – Recommended GC and GC/MS Conditions

17.3.11. Figure 2 – Example Data Review Checklist

17.3.12. Figure 3 – C1-C4 Alkyl Homologue Peak Patterns

Table 1 - Standard Target Analytes and Reporting Limits

Analyte	CAS No.	Aqueous (ng/L)	Solid/Sediment and Tissue (ng/g)	Air (Filter) (ng/sample)	Air (XAD) (ng/sample)	Air (Combined) (ng/sample)
Naphthalene	91-20-3	50	20	50	400	400
2-Methylnaphthalene	91-57-6	20	10	20	50	50
1-Methylnaphthalene	90-12-0	10	5	20	50	50
Acenaphthylene	208-96-8	10	1	20	20	20
Acenaphthene	83-32-9	10	1	20	20	20
Fluorene	86-73-7	10	1	10	10	10
Phenanthrene	85-01-8	20	1	20	30	30
Anthracene	120-12-7	10	1	10	10	10
Fluoranthene	206-44-0	10	1	10	10	10
Pyrene	129-00-0	10	1	60	20	60
Benz(a)anthracene	56-55-3	10	1	10	10	10
Chrysene	218-01-9	10	1	10	10	10
Benzo(b)fluoranthene	205-99-2	10	1	10	100	100
Benzo(k)fluoranthene	207-08-9	10	1	10	100	100
Benzo(e)pyrene	192-97-2	10	1	10	10	10
Benzo(a)pyrene	50-32-8	10	1	10	10	10
Perylene	198-55-0	10	1	10	10	10
Indeno(1,2,3-c,d)-pyrene	193-39-5	10	1	10	10	10
Dibenz(ah)anthracene	53-70-3	10	1	10	10	10
Benzo(ghi)perylene	191-24-2	10	1	10	10	10
C2 Naphthalenes	NA	10	2	NA	NA	NA
C3 Naphthalenes	NA	10	2	NA	NA	NA
C4 Naphthalenes	NA	10	1	NA	NA	NA
C1 Fluorenes	NA	10	1	NA	NA	NA
C2 Fluorenes	NA	10	1	NA	NA	NA
C3 Fluorenes	NA	10	1	NA	NA	NA
C1 Phenanthrenes & Anthracenes	NA	10	1	NA	NA	NA
C2 Phenanthrenes & Anthracenes	NA	10	1	NA	NA	NA
C3 Phenanthrenes & Anthracenes	NA	10	1	NA	NA	NA
C4 Phenanthrenes & Anthracenes	NA	10	1	NA	NA	NA
C1 Fluoranthenes & Pyrenes	NA	10	1	NA	NA	NA
C1 Benz(a)anthracenes & Chrysenes	NA	10	1	NA	NA	NA
C2 Benz(a)anthracenes & Chrysenes	NA	10	1	NA	NA	NA
C3 Benz(a)anthracenes & Chrysenes	NA	10	1	NA	NA	NA
C4 Benz(a)anthracenes & Chrysenes	NA	10	1	NA	NA	NA

Table 1A - Additional Analytes and Reporting Limits

Analyte	CAS No.	Aqueous (ng/L)	Solid/Sediment and Tissue (ng/g)	Air (Filter) (ng/sample)	Air (XAD) (ng/sample)	Air (Combined (ng/sample)
Biphenyl	92-52-4	10	1	20	50	50
1-Methylphenanthrene	832-69-9	10	1	10	10	10
2,6-Dimethylnaphthalene	581-42-0	10	2	20	30	30
2,3,5-Trimethylnaphthalene	2245-38-7	10	2	10	10	10
Dibenzothiophene	132-65-0	10	1	10	10	10
C1 Dibenzothiophenes	NA	10	1	NA	NA	NA
C2 Dibenzothiophenes	NA	10	1	NA	NA	NA
C3 Dibenzothiophenes	NA	10	1	NA	NA	NA
C4 Dibenzothiophenes	NA	10	1	NA	NA	NA

Table 2 - Matrix, Sample Size, IS Spiking Level and Final Volume

	Water	**Soil/ Sediment**	**Tissue**	**Wipe**	**Air**	**Waste**
Weight/volume/ sample amount	1 L	10 g	10 g	Entire Sample	Entire Sample	1 g
IS Spiking Levels	250 ppt	25 ppb	25 ppb	250 ng	250 ng	250 ng
Final Extract Vol. (mL)	0.5	0.5	0.5	0.5	0.5	0.5

Table 3 - Concentration of Target Analytes in Calibration Solutions

Analyte	CS1 (µg/mL)	CS2 (µg/mL)	CS3 (µg/mL)	CS4 (µg/mL)	CS5 (µg/mL)	CS6 (µg/mL)	CS7 (µg/mL)
Naphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Biphenyl	0.02	0.10	0.25	0.50	1.0	2.5	5.0
2-Methylnaphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
1-Methylnaphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Acenaphthylene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Acenaphthene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Fluorene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Phenanthrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
1-Methylphenanthrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
2,3,5-Trimethylnaphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Anthracene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
2,6-Dimethylnaphthalene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Fluoranthene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Pyrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benz(a)anthracene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Chrysene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(b)fluoranthene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(k)fluoranthene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(e)pyrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(a)pyrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Perylene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Indeno(1,2,3-cd)pyrene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Dibenz(ah)anthracene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Benzo(ghi)perylene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Dibenzothiophene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Sampling Surrogates							
d_{10}-Fluorene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
d_{14}-p-Terphenyl	0.02	0.10	0.25	0.50	1.0	2.5	5.0
^{13}C-Fluorene	0.02	0.10	0.25	0.50	1.0	2.5	5.0
Internal Standards							
d_{10}-Anthracene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_4-1,4-Dichlorobenzne	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_8 Naphthalene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-2-Methylnaphthalene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-1-Methylnaphthalene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_8-Acenaphthylene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-Phenanthrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-2,6-Dimethylnaphthalene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-Fluoranthene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benz(a)anthracene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Chrysene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(b)fluoranthene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(k)fluoranthene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(a)pyrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Perylene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Indeno(1,2,3-cd)pyrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{14}-Dibenz(ah)anthracene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(ghi)perylene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_8-Dibenzothiophene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Recovery Standards							
d_{10}-Acenaphthene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{10}-Pyrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
d_{12}-Benzo(e)Pyrene	0.50	0.50	0.50	0.50	0.50	0.50	0.50
Alternate Surrogate							
$^{13}C_6$-Anthracene	0.50	0.50	0.50	0.50	0.50	0.50	0.50

Table 4 - Concentration of Stock Standards and Spiking Solutions

Compound	Recommended Sources*	Catalog Number	Vendor Conc (µg/mL)	Stock Solution (µg/mL)	Spiking Solution (µg/mL)
Native Analytes					
Naphthalene	Supelco	21084612	100	50	0.25
Biphenyl	Supelco	21084612	100	50	0.25
2-Methyl naphthalene	Supelco	21084612	100	50	0.25
1-Methyl naphthalene	Supelco	21084612	100	50	0.25
Acenaphthylene	Supelco	21084612	100	50	0.25
Acenaphthene	Supelco	21084612	100	50	0.25
Fluorene	Supelco	21084612	100	50	0.25
Phenanthrene	Supelco	21084612	100	50	0.25
1-Methylphenanthrene	Supelco	21084612	100	50	0.25
2,3,5-Trimethylnaphthalene	Supelco	21084612	100	50	0.25
Anthracene	Supelco	21084612	100	50	0.25
2,6-Dimethylnaphthalene	Supelco	21084612	100	50	0.25
Fluoranthene	Supelco	21084612	100	50	0.25
Pyrene	Supelco	21084612	100	50	0.25
Benz(a)anthracene	Supelco	21084612	100	50	0.25
Chrysene	Supelco	21084612	100	50	0.25
Benzo(b)fluoranthene	Supelco	21084612	100	50	0.25
Benzo(k)fluoranthene	Supelco	21084612	100	50	0.25
Benzo(e)pyrene	Supelco	21084612	100	50	0.25
Benzo(a)pyrene	Supelco	21084612	100	50	0.25
Perylene	Supelco	21084612	100	50	0.25
Indeno(1,2,3-cd)pyrene	Supelco	21084612	100	50	0.25
Dibenz(a,h)anthracene	Supelco	21084612	100	50	0.25
Benzo(ghi)perylene	Supelco	21084612	100	50	0.25
Dibenzothiophene	Supelco	21084612	100	50	0.25
Internal Standards					
d_8-Naphthalene	Accustandard	S-18004	200	10	0.25
d_{10}-2-Methyl naphthalene	Accustandard	S-18004	200	10	0.25
d_{10}-1-Methyl naphthalene	Accustandard	S-18004	200	10	0.25
d_8-Acenaphthylene	Accustandard	S-18004	200	10	0.25
d_{10}-Phenanthrene	Accustandard	S-18004	200	10	0.25
d_{12}- 2,6-Dimethylnaphthalene	Accustandard	S-18004	200	10	0.25
d_{10}-Fluoranthene	Accustandard	S-18004	200	10	0.25
d_{12}-Benz(a)anthracene	Accustandard	S-18004	200	10	0.25
d_{12}-Chrysene	Accustandard	S-18004	200	10	0.25
d_{12}-Benzo(b)fluoranthene	Accustandard	S-18004	200	10	0.25
d_{12}-Benzo(k)fluoranthene	Accustandard	S-18004	200	10	0.25
d_{12}-Benzo(a)pyrene	Accustandard	S-18004	200	10	0.25
d_{12}-Perylene	Accustandard	S-18004	200	10	0.25
d_{12}-Indeno(1,2,3-cd)pyrene	Accustandard	S-18004	200	10	0.25
d_{14}-Dibenz(a,h)anthracene	Accustandard	S-18004	200	10	0.25
d_{12}-Benzo(ghi)perylene	Accustandard	S-18004	200	10	0.25
d_8-Dibenzothiophene	Accustandard	S-18004	200	10	0.25
d_{10}-Anthracene	Accustandard	S-18004	200	10	0.25
Recovery Standards					
d_{10}-Acenaphthene	CIL	DLM-108-S	200	NA	10
d_{10}-Pyrene	CIL	DLM-155-S	200	NA	10
d_{12}-Benzo(e)pyrene	CIL	DLM-257-S	200	NA	10
Alternate Surrogate					
$^{13}C_6$-Anthracene	Cerilliant	CLM-1333-1.2	100	10	0.25
Sampling Surrogates					
$^{13}C_6$-Fluorene	Cerilliant	CLM-3596-1.2	100	20	5.0
d_{10}-Fluorene	CIL	DLM-1123-S	200	20	5.0
d_{14}-p-Terphenyl	CIL	DLM-382-S	200	20	5.0

* Other sources of standards may be used.

Table 5 – Quantitation References

Analyte	Analyte Type	Quantitation Standard (QS)	QS Type
Naphthalene	Native Analyte	d_8-Naphthalene	IS
Biphenyl	Native Analyte	d_{10}-2-Methylnaphthalene	IS
2-Methylnaphthalene	Native Analyte	d_{10}-2-Methylnaphthalene	IS
1-Methylnaphthalene	Native Analyte	d_{10}-1-Methylnaphthalene	IS
Acenaphthylene	Native Analyte	d_8-Acenaphthylene	IS
Acenaphthene	Native Analyte	d_8-Acenaphthylene	IS
Fluorene	Native Analyte	d_{10}-Phenanthrene	IS
Dibenzothiophene	Native Analyte	d_8-Dibenzothiophene	IS
Phenanthrene	Native Analyte	d_{10}-Phenanthrene	IS
1-Methylphenanthrene	Native Analyte	d_{10}-Phenanthrene	IS
2,3,5-Trimethylnaphthalene	Native Analyte	d_{12}-2,6-Dimethylnaphthalene	IS
Anthracene	Native Analyte	d_{10}-Anthracene	IS
2,6-Dimethylnaphthalene	Native Analyte	d_{12}-2,6-Dimethylnaphthalene	IS
Fluoranthene	Native Analyte	d_{10}-Fluoranthene	IS
Pyrene	Native Analyte	d_{10}-Fluoranthene	IS
Benz(a)anthracene	Native Analyte	d_{12}-Benz(a)anthracene	IS
Chrysene	Native Analyte	d_{12}-Chrysene	IS
Benzo(b)fluoranthene	Native Analyte	d_{12}-Benzo(b)fluoranthene	IS
Benzo(k)fluoranthene	Native Analyte	d_{12}-Benzo(k)fluoranthene	IS
Benzo(e)pyrene	Native Analyte	d_{12}-Benzo(a)pyrene	IS
Benzo(a)pyrene	Native Analyte	d_{12}-Benzo(a)pyrene	IS
Perylene	Native Analyte	d_{12}-Perylene	IS
Indeno(1,2,3-cd)pyrene	Native Analyte	d_{12}-Indeno(1,2,3-cd)pyrene	IS
Dibenz(ah)anthracene	Native Analyte	d_{14}-Dibenz(ah)anthracene	IS
Benzo(ghi)perylene	Native Analyte	d_{12}-Benzo(ghi)perylene	IS
C2 Naphthalenes	Alkyl Group	d_8-Naphthalene*	IS
C3 Naphthalenes	Alkyl Group	d_8-Naphthalene*	IS
C4 Naphthalenes	Alkyl Group	d_8-Naphthalene*	IS
C1 Fluorenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C2 Fluorenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C3 Fluorenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C1 Dibenzothiophene	Alkyl Group	d_8-Dibenzothiophene*	IS
C2 Dibenzothiophene	Alkyl Group	d_8-Dibenzothiophene*	IS
C3 Dibenzothiophene	Alkyl Group	d_8-Dibenzothiophene*	IS
C4 Dibenzothiophene	Alkyl Group	d_8-Dibenzothiophene*	IS
C1 Phenanthrenes & Anthracenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C2 Phenanthrenes & Anthracenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C3 Phenanthrenes & Anthracenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C4 Phenanthrenes & Anthracenes	Alkyl Group	d_{10}-Phenanthrene*	IS
C1Fluoranthenes & Pyrenes	Alkyl Group	d_{10}-Fluoranthene*	IS
C1 Benz(a)anthracenes & Chrysenes	Alkyl Group	d_{12}-Chrysene *	IS
C2 Benz(a)anthracenes & Chrysenes	Alkyl Group	d_{12}-Chrysene *	IS
C3 Benz(a)anthracenes & Chrysenes	Alkyl Group	d_{12}-Chrysene *	IS
C4 Benz(a)anthracenes & Chrysenes	Alkyl Group	d_{12}-Chrysene *	IS
d_{10}-Fluorene	Sampling Surrogate	d_{10}-Phenanthrene	IS
d_{14}-p-Terphenyl	Sampling Surrogate	d_{10}-Fluoranthene	IS
$^{13}C_6$-Fluorene	Sampling Surrogate	d_{10}-Phenanthrene	IS

* Response factor for alkyls taken from parent PAH. See Table 8.

Table 5 – Quantitation References (continued)

Analyte	Analyte Type	Quantitation Standard (QS)	QS Type
d_{-8}-Naphthalene	IS	d_{10}-Acenaphthene	RS
d_{10}-2-Methylnaphthalene	IS	d_{10}-Acenaphthene	RS
d_{10}-1-Methylnaphthalene	IS	d_{10}-Acenaphthene	RS
d_{12}-2,6-Dimethylnaphthalene	IS	d_{10}-Acenaphthene	RS
d_{8}-Acenaphthylene	IS	d_{10}-Acenaphthene	RS
d-8 dibenzothiophene	IS	d_{10}-Pyrene	RS
d_{10}-Phenanthrene	IS	d_{10}-Pyrene	RS
d_{10}-Anthracene	IS	d_{10}-Pyrene	RS
d_{10}-Fluoranthene	IS	d_{10}-Pyrene	RS
d_{12}-Benz(a)anthracene	IS	d_{10}-Pyrene	RS
d_{12}-Chrysene	IS	d_{10}-Pyrene	RS
d_{12}-Benzo(b)fluoranthene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Benzo(k)fluoranthene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Benzo(a)pyrene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Perylene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Indeno(1,2,3-cd)pyrene	IS	d_{12}-Benzo(e)pyrene	RS
d_{14}-Dibenz(ah)anthracene	IS	d_{12}-Benzo(e)pyrene	RS
d_{12}-Benzo(ghi)perylene	IS	d_{12}-Benzo(e)pyrene	RS
$^{13}C_6$-Anthracene	Alternate Surrogate	d_{10}-Pyrene	RS

IS = Labeled Internal Standard
RS = Recovery Standard

Table 6 - Selected Ions Monitored and SIM Groups

Analyte	Classification	Quantitation	Confirmation	SIM Group
d_8-Naphthalene	Internal Standard	136	134	2
Naphthalene	Native Analyte	128	102	2
d_{10}-2-Methylnaphthalene	Internal Standard	152	151	3
2-Methylnaphthalene	Native Analyte	142	141	3
d_{10}-1-Methylnaphthalene	Internal Standard	152	151	3
1-Methylnaphthalene	Native Analyte	142	141	3
Biphenyl	Native Analyte	154	152	4
C2-naphthalenes	Alkyl Group	156	141	4,5
d_{12}-2,6-Dimethylnaphthalene	Internal Standard	168	167	4
2,6-Dimethylnaphthalene	Native Analyte	156	155	4
C3-naphthalenes	Alkyl Group	170	155	5,6
d_8-Acenaphthylene	Internal Standard	160	158	5
Acenaphthylene	Native Analyte	152	151	5
d_{10}-Acenaphthene	Recovery Standard	164	163	5
Acenaphthene	Native Analyte	154	153	5
C4-Naphthalenes	Alkyl Group	184	169	5,6,7
2,3,5-Trimethylnaphthalene	Native Analyte	170	169	6
d_{10}-Fluorene	Sampling Surrogate	176	174	6
$^{13}C_6$-Fluorene	Sampling Surrogate	171	172	6
Fluorene	Native Analyte	166	165	6
C1-Fluorenes	Alkyl Group	180	165	6,7
Dibenzothiophene	Native Analyte	184	139	7
d_8-Dibenzothiophene	Internal Standard	192	191	7
d_{10}-Phenanthrene	Internal Standard	188	184	7
Phenanthrene	Native Analyte	178	176	7
C2-Fluorenes	Alkyl Group	194	179	7
d_{10}-Anthracene	Internal Standard	188	184	7
Anthracene	Native Analyte	178	176	7
$^{13}C_6$-Anthracene	Alternate Surrogate	184	182	7
C1-Dibenzothiophenes	Alkyl Group	198	197	7,8
C3-Fluorenes	Alkyl Group	208	193	7,8,9
C1-Phenanthrenes_Anthracenes	Alkyl Group	192	191	7,8
1-Methylphenanthrene	Native Analyte	192	191	8
C2-Dibenzothiophenes	Alkyl Group	212	211	8,9
C2-Phenanthrenes_Anthracenes	Alkyl Group	206	191	8,9
C3-Dibenzothiophenes	Alkyl Group	226	211	8,9
d_{10}-Fluoranthene	Internal Standard	212	208	9
Fluoranthene	Native Analyte	202	200	9
C3-Phenanthrenes_Anthracenes	Alkyl Group	220	205	9
C4-Dibenzothiophenes	Alkyl Group	240	225	8,9
d_{10}-Pyrene	Recovery Standard	212	208	9
Pyrene	Native Analyte	202	200	9
C4-Phenanthrenes_Anthracenes	Alkyl Group	234	219	9

Table 6 - Selected Ions Monitored and SIM Groups (continued)

Analyte	Classification	Quantitation	Confirmation	SIM Group
d_{14}-Terphenyl	Sampling Surrogate	244	242	9
C1-Fluoranthenes_Pyrenes	Alkyl Group	216	215	9
d_{12}-Benz(a)anthracene	Internal Standard	240	236	10
Benz(a)anthracene	Native Analyte	228	226	10
d_{12}-Chrysene	Internal Standard	240	236	10
Chrysene	Native Analyte	228	226	10
C1-Benz(a)anthracenes_Chrysenes	Alkyl Group	242	241	10,11
C2-Benz(a)anthracenes_Chrysenes	Alkyl Group	256	241	10,11
C3-Benz(a)anthracenes_Chrysenes	Alkyl Group	270	255	10,11
d_{12}-Benzo(b)fluoranthene	Internal Standard	264	260	11
Benzo(b)fluoranthene	Native Analyte	252	253	11
d_{12}-Benzo(k)fluoranthene	Internal Standard	264	260	11
Benzo(k)fluoranthene	Native Analyte	252	253	11
C4-Benz(a)anthracenes_Chrysenes	Alkyl Group	284	269	11
d_{12}-Benzo(e)pyrene	Recovery Standard	264	260	11
Benzo(e)pyrene	Native Analyte	252	253	11
d_{12}-Benzo(a)pyrene	Internal Standard	264	260	11
Benzo(a)pyrene	Native Analyte	252	253	11
d_{12}-Perylene	Internal Standard	264	260	11
Perylene	Native Analyte	252	253	11
d_{14}-Dibenz(ah)anthracene	Internal Standard	292	288	12
Dibenz(ah)anthracene	Native Analyte	278	139	12
d_{12}-Indeno(1,2,3-cd)pyrene	Internal Standard	288	284	12
Indeno(1,2,3-cd)pyrene	Native Analyte	276	138	12
d_{12}-Benzo(ghi)perylene	Internal Standard	288	284	12
Benzo(ghi)perylene	Native Analyte	276	138	12

Table 7 - Acceptance Criteria for Performance Tests and QC Samples

Analyte	IDOC Test Conc[1] (ng/µL)	IDOC %RSD	IDOC %R	ICV %R	LCS %R	Method Blank %R	Sample %R
Naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
2-Methyl naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
1-Methyl naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
Biphenyl	0.5	30	60-140	70-130	60-140	NA	NA
2,6-Dimethyl naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
Acenaphthylene	0.5	30	60-140	70-130	60-140	NA	NA
Acenaphthene	0.5	30	60-140	70-130	60-140	NA	NA
2,3,5-Trimethyl naphthalene	0.5	30	60-140	70-130	60-140	NA	NA
Fluorene	0.5	30	60-140	70-130	60-140	NA	NA
Phenanthrene	0.5	30	60-140	70-130	60-140	NA	NA
Anthracene	0.5	30	60-140	70-130	60-140	NA	NA
1-Methyl phenanthrene	0.5	30	60-140	70-130	60-140	NA	NA
Fluoranthene	0.5	30	60-140	70-130	60-140	NA	NA
Pyrene	0.5	30	60-140	70-130	60-140	NA	NA
Benz(a)anthracene	0.5	30	60-140	70-130	60-140	NA	NA
Chrysene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(b)fluoranthene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(k)fluoranthene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(e)pyrene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(a)pyrene	0.5	30	60-140	70-130	60-140	NA	NA
Perylene	0.5	30	60-140	70-130	60-140	NA	NA
Indeno(1,2,3-cd)pyrene	0.5	30	60-140	70-130	60-140	NA	NA
Dibenz(ah)anthracene	0.5	30	60-140	70-130	60-140	NA	NA
Benzo(ghi)perylene	0.5	30	60-140	70-130	60-140	NA	NA
Dibenzothiophene	0.5	30	60-140	70-130	60-140	NA	NA
Internal Standards							
d_8-Naphthalene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-2-Methyl naphthalene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-1-Methyl naphthalene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-2,6-Dimethyl naphthalene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_8-Acenaphthylene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-Phenanthrene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-Fluoranthene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benz(a)anthracene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Chrysene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benzo(b)fluoranthene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benzo(k)fluoranthene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benzo(a)pyrene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Perylene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Indeno(1,2,3-cd)pyrene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{14}-Dibenz(a,h)anthracene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{12}-Benzo(ghi)perylene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_{10}-Anthracene	0.5	30	60-140	70-130	60-140	60-140	30-120
d_8-Dibenzothiophene	0.5	30	60-140	70-130	60-140	60-140	30-120
Alternate Surrogate							
$^{13}C_6$-Anthracene	0.5	30	60-140	70-130	60-140	60-140	30-120
Sampling Surrogate							
d_{10}-Fluorene	NA	NA	NA	NA	NA	NA	50-150
d_{14}-p-Terphenyl	NA	NA	NA	NA	NA	NA	50-150
$^{13}C_6$-Fluorene	NA	NA	NA	NA	NA	NA	50-150

[1]Test concentration in the final extract, assuming a 0.5 mL volume.

Table 8 – Response Factor Assignment for the Alkylated Homologues

Alkyl Group	Parent to reference for RF
C2 Naphthalenes	Naphthalene
C3 Naphthalenes	Naphthalene
C4 Naphthalenes	Naphthalene
C1 Fluorenes	Fluorene
C2 Fluorenes	Fluorene
C3 Fluorenes	Fluorene
C1 Dibenzothiophene	Dibenzothiophene
C2 Dibenzothiophene	Dibenzothiophene
C3 Dibenzothiophene	Dibenzothiophene
C4 Dibenzothiophene	Dibenzothiophene
C1 Phenanthrenes & Anthracenes	Phenanthrene
C2 Phenanthrenes & Anthracenes	Phenanthrene
C3 Phenanthrenes & Anthracenes	Phenanthrene
C4 Phenanthrenes & Anthracenes	Phenanthrene
C1Fluoranthenes & Pyrenes	Pyrene
C1 Benz(a)anthracenes & Chrysenes	Chrysene
C2 Benz(a)anthracenes & Chrysenes	Chrysene
C3 Benz(a)anthracenes & Chrysenes	Chrysene
C4 Benz(a)anthracenes & Chrysenes	Chrysene

Figure 1 Recommended GC & GC/MS Conditions

```
                              INSTRUMENT CONTROL PARAMETERS:    MP
                              ------------------------------------

   C:\MSDCHEM\1\METHODS\KNX_00161.M
      Tue Sep 15 10:30:44 2009

Control Information
------- -----------

Sample Inlet      :  GC
Injection Source  :  GC ALS
Mass Spectrometer :  Enabled

==============================================================================
                                 6890 GC METHOD
==============================================================================


OVEN
   Initial temp:  45 'C (On)                Maximum temp:  375 'C
   Initial time:  0.50 min                  Equilibration time:  0.50 min
   Ramps:
      #  Rate  Final temp  Final time
      1 30.00      240        0.00
      2 21.00      310        0.00
      3  4.00      320        0.10
      4 35.00      335        2.64
      5   0.0(Off)
   Post temp:  0 'C
   Post time:  0.00 min
   Run time:  16.00 min


FRONT INLET (SPLIT/SPLITLESS)           BACK INLET (UNKNOWN)
   Mode:  Pulsed Splitless
   Initial temp:  250 'C (On)
   Pressure:  15.73 psi (On)
   Pulse pressure:  25.0 psi
   Pulse time:  0.50 min
   Purge flow:  10.0 mL/min
   Purge time:  1.25 min
   Total flow:  14.2 mL/min
   Gas saver:  Off
   Gas type:  Helium


COLUMN 1                                COLUMN 2
   Capillary Column                        (not installed)
   Model Number:  Restek 12623-124
   Rtx-5MS w/Integra-Guard
   Max temperature:  360 'C
   Nominal length:  30.0 m
   Nominal diameter:  250.00 um
   Nominal film thickness:  0.25 um
   Mode:  constant flow
   Initial flow:  1.2 mL/min
   Nominal init pressure:  15.73 psi
   Average velocity:  26 cm/sec
   Inlet:  Front Inlet
   Outlet:  MSD
   Outlet pressure:  3.80 psi


FRONT DETECTOR (NO DET)                 BACK DETECTOR (NO DET)


SIGNAL 1                                SIGNAL 2

KNX_00161.M Tue Sep 15 10:30:43 2009 Test America Knoxville                Page: 2
```

Figure 1 Recommended GC & GC/MS Conditions (continued)

```
   Data rate:  20 Hz                          Data rate:  20 Hz
   Type:  test plot                           Type:  test plot
   Save Data:  Off                            Save Data:  Off
   Zero:  0.0 (Off)                           Zero:  0.0 (Off)
   Range:  0                                  Range:  0
   Fast Peaks:  Off                           Fast Peaks:  Off
   Attenuation:  0                            Attenuation:  0

COLUMN COMP 1                             COLUMN COMP 2
   (No Detectors Installed)                   (No Detectors Installed)

THERMAL AUX 2                             AUX PRESSURE 3
   Use:  MSD Transfer Line Heater             Description:  Quick Swap
   Description:                               Gas Type:  Helium
   Initial temp:  300 'C (On)                 Initial pressure:  0.00 psi (Off)
   Initial time:  0.00 min
      #  Rate  Final temp  Final time
      1   0.0(Off)

AUX PRESSURE 4                            AUX PRESSURE 5
   Description:                               Description:
   Gas Type:  Helium                          Gas Type:  Helium
   Initial pressure:  0.00 psi (Off)          Initial pressure:  0.00 psi (Off)

                                          POST RUN
                                             Post Time: 0.00 min

TIME TABLE
   Time       Specifier                        Parameter & Setpoint


                              GC Injector

     Front Injector:
        Sample Washes                 0
        Sample Pumps                  6
        Injection Volume           1.00 microliters
        Syringe Size               10.0 microliters
        PreInj Solvent A Washes       0
        PreInj Solvent B Washes       0
        PostInj Solvent A Washes      3
        PostInj Solvent B Washes      3
        Viscosity Delay               1 seconds
        Plunger Speed              Fast
        PreInjection Dwell         0.00 minutes
        PostInjection Dwell        0.00 minutes

     Back Injector:
No parameters specified

 Column 1 Inventory Number : 915849
 Column 2 Inventory Number :

                              MS ACQUISITION PARAMETERS

General Information
------- -----------

Tune File                 : dftpp.u

KNX_00161.M Tue Sep 15 10:30:43 2009 Test America Knoxville                Page: 3
```

Figure 1 Recommended GC & GC/MS Conditions (continued)

```
Acquistion Mode          : Scan/SIM

MS Information
-- -----------

Solvent Delay            : 4.40 min

EMV Mode                 : Relative
Relative Voltage         : 141
Resulting EM Voltage     : 1647

[Scan Parameters]

Low Mass                 : 35.0
High Mass                : 550.0
Threshold                : 500
Sample #                 : 1       A/D Samples    2
[Sim Parameters]

GROUP 1
Group ID                 : 1
Resolution               : Low
Plot 1 Ion               : 146.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (146.00,     40) (148.00,     40) (150.00,     40)
                         (152.00,     40)

GROUP 2
Group ID                 : 2
Resolution               : Low
Group Start Time         : 5.52
Plot 1 Ion               : 102.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (102.00,     40) (128.00,     40) (134.00,     40)
                         (136.00,     40)

GROUP 3
Group ID                 : 3
Resolution               : Low
Group Start Time         : 6.12
Plot 1 Ion               : 141.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (141.00,     35) (142.00,     35) (151.00,     35)
                         (152.00,     35) (156.00,     35)

GROUP 4
Group ID                 : 4
Resolution               : Low
Group Start Time         : 6.50
Plot 1 Ion               : 152.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (141.00,     15) (152.00,     15) (154.00,     15)
                         (155.00,     15) (156.00,     15) (167.00,     15)
                         (168.00,     15)

GROUP 5
Group ID                 : 5
Resolution               : Low
Group Start Time         : 6.81
Plot 1 Ion               : 151.00
Ions/Dwell In Group      (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                         (141.00,     10) (151.00,     10) (152.00,     10)
                         (153.00,     10) (154.00,     10) (155.00,     10)
                         (156.00,     10) (158.00,     10) (160.00,     10)
                         (163.00,     10) (164.00,     10) (169.00,     10)
                         (170.00,     10) (184.00,     10)

GROUP 6

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```

Figure 1 Recommended GC & GC/MS Conditions (continued)

```
Group ID                  : 6
Resolution                : Low
Group Start Time          : 7.30
Plot 1 Ion                : 165.00
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                          (139.00,     10) (155.00,     10) (165.00,     10)
                          (166.00,     10) (169.00,     10) (170.00,     10)
                          (171.00,     10) (172.00,     10) (174.00,     10)
                          (176.00,     10) (180.00,     10) (184.00,     10)

GROUP 7
Group ID                  : 7
Resolution                : Low
Group Start Time          : 8.00
Plot 1 Ion                : 139.00
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                          (139.00,      5) (165.00,      5) (169.00,      5)
                          (176.00,      5) (178.00,      5) (179.00,      5)
                          (180.00,      5) (182.00,      5) (184.00,      5)
                          (186.00,      5) (188.00,      5) (191.00,      5)
                          (192.00,      5) (193.00,      5) (194.00,      5)
                          (197.00,      5) (198.00,      5) (208.00,      5)

GROUP 8
Group ID                  : 8
Resolution                : Low
Group Start Time          : 8.80
Plot 1 Ion                : 191.00
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                          (191.00,     10) (192.00,     10) (193.00,     10)
                          (197.00,     10) (198.00,     10) (206.00,     10)
                          (208.00,     10) (211.00,     10) (212.00,     10)
                          (225.00,     10) (226.00,     10) (240.00,     10)

GROUP 9
Group ID                  : 9
Resolution                : Low
Group Start Time          : 9.20
Plot 1 Ion                : 200.00
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                          (191.00,      5) (193.00,      5) (200.00,      5)
                          (202.00,      5) (205.00,      5) (206.00,      5)
                          (208.00,      5) (211.00,      5) (212.00,      5)
                          (215.00,      5) (216.00,      5) (219.00,      5)
                          (220.00,      5) (225.00,      5) (226.00,      5)
                          (234.00,      5) (240.00,      5) (242.00,      5)
                          (244.00,      5)

GROUP 10
Group ID                  : 10
Resolution                : Low
Group Start Time          : 10.70
Plot 1 Ion                : 226.00
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                          (226.00,     25) (228.00,     25) (236.00,     25)
                          (240.00,     25) (241.00,     25) (242.00,     25)

GROUP 11
Group ID                  : 11
Resolution                : Low
Group Start Time          : 11.20
Plot 1 Ion                : 252.00
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                          (241.00,     30) (242.00,     30) (252.00,     30)
                          (253.00,     30) (255.00,     30) (256.00,     30)
                          (260.00,     30) (264.00,     30) (269.00,     30)
                          (270.00,     30) (284.00,     30)

GROUP 12
```

Figure 1 Recommended GC & GC/MS Conditions (continued)

```
Group ID                  : 12
Resolution                : Low
Group Start Time          : 14.00
Plot 1 Ion                : 292.00
Ions/Dwell In Group       (  Mass,  Dwell) (  Mass,  Dwell) (  Mass,  Dwell)
                          (138.00,     25) (139.00,     25) (276.00,     25)
                          (278.00,     25) (284.00,     25) (288.00,     25)
                          (292.00,     25)

[MSZones]

MS Source                 : 230 C   maximum 250 C
MS Quad                   : 150 C   maximum 200 C


                              END OF MS ACQUISITION PARAMETERS


                               TUNE PARAMETERS for SN: US81839504
                           ----------------------------

 Trace Ion Detection is OFF.

 EMISSION    :      34.610
 ENERGY      :      69.922
 REPELLER    :      29.620
 IONFOCUS    :      87.310
 ENTRANCE_LE :       0.000
 EMVOLTS     :    1505.882
                                Actual EMV  :    1647.06
                                GAIN FACTOR :       2.04
 AMUGAIN     :    1914.000
 AMUOFFSET   :     125.688
 FILAMENT    :       1.000
 DCPOLARITY  :       0.000
 ENTLENSOFFS :     19.325@  3    19.325@ 50    15.561@ 69    16.816@131    16.565@219    17.06
7@414    16.816@502    16.816@1049
 MASSGAIN    :    -652.000
 MASSOFFSET  :     -44.000

                             END OF TUNE PARAMETERS
                        ------------------------------------


PostRun InstCntl macro(s) exist: msacq2.mac


                              END OF INSTRUMENT CONTROL PARAMETERS
                              ------------------------------------


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```

Figure 2 Example Data Review Checklist

TestAmerica Knoxville GC/MS-SIM Initial Calibration Data Review / Narrative Checklist
Method: PAHs and Selected SVOCs - KNOX-ID-0016, Revision 8

Analysis Date:		Instrument::		ICAL Batch/Scan Name:		Scanned ☐

A. Review Items	N/A	Yes	No	Why is data reportable?	2nd √
1. Were all standards injected within 12 hr of first calibration standard?					
2. Was date/time of analysis verified between header and logbook?					
3. Are peak integrations appropriate?					
4. Were ≥ 5 levels of each analyte/IS analyzed?					
5. Was the high point standard checked for saturation?					
6. Was low level standard at or below RL?					
7. Are all %RSD ≤30% ?					
8. Are the MID descriptors properly set?					
9. Are correct RFs listed in ICAL summary?					
10. Was ICAL summary form processed using the correct method?					
11. Are the ICAL start and end dates/times correct on ICAL summary?					
12. Elution order checked on isomeric pairs?					
• 2-methylnaphthalene before 1-methylnaphthalene (& d10 isomers)					
• acenaphthylene before acenaphthene (& d10 isomers)					
• dibenzothiophene before anthracene					
• phenanthrene before anthracene (& d10 isomers)					
• fluoranthene before pyrene (& d10 isomers)					
• benzo(a)anthracene before chrysene (& d12 isomers)					
• benzo(b)fluoranthene before benzo(k)fluoranthene (& d12 isomers)					
• benzo(e)pyrene before benzo(a)pyrene benzo(a)pyrene before perylene (& d12 isomers)					
• Indeno(1,2,3-cd)pyrene before benzo(g,h,I)perylene (& d12 isomers)					
13. Is the 2nd source ICV with +/- 30% of the expected value?					
14. Are the Alkyl RFs correct (i.e., same as the parent RF)?					
15. If criteria were not met, was a NCM generated and approved by supervisor?					
16. Does the ICAL folder contain **complete** data in the following order? ICAL data review checklist, runlog, Target Initial Calibration Report, followed by the quan report and chromatograms for all calibration and 2nd source standards.					

1st Level Reviewer:	Date:
Comments:	

2nd Level Reviewer:	Date:
Comments:	

ID028R20.doc, 081810

Figure 2 Example Data Review Checklist (continued)

TestAmerica Knoxville GC/MS-SIM Continuing Calibration Review / Narrative Checklist
Method: LRPAH PAHs and Selected SVOCs - KNOX-ID-0016, Revision 8

Analysis Date:		CCAL Batch/ Scan Name:		Instrument:		ICAL Batch/ Scan Name:		Scanned ☐

A. Review Items	N/A	Yes	No	Why is data reportable?	2nd √
1. Were all injections in sequence within 12 hr of CCAL?					
2. Was date/time of analysis verified between header and logbook?					
3. Are peak integrations appropriate?					
4. Is the %D or drift <30% for all analytes					
5. Are the recovery standards within 50-200% of the ICAL CS4 level?					
6. Are the MID descriptors properly set?					
7. Are correct RFs listed in CCAL summary?					
8. Was the correct ICAL used for quantitation? (Verify 1 RF.)					
9. Elution order checked on isomeric pairs/coeluters?					
• 2-methylnaphthalene before 1-methylnaphthalene (& d10 isomers)					
• acenaphthylene before acenaphthene (& d10 isomers)					
• dibenzothiophene before anthracene					
• phenanthrene before anthracene (& d10 isomers)					
• fluoranthene before pyrene (& d10 isomers)					
• benzo(a)anthracene before chrysene (& d12 isomers)					
• benzo(b)fluoranthene before benzo(k)fluoranthene (& d12 isomers)					
• benzo(e)pyrene before benzo(a)pyrene benzo(a)pyrene before perylene (& d12 isomers)					
• Indeno(1,2,3-cd)pyrene before benzo(g,h,l)perylene (& d12 isomers)					
10. Were the first/last RTs for each alkyl PAH homologue group properly identified and indicated on the chromatogram?					
11. If criteria were not met, was a NCM generated and approved by supervisor?					
12. Does the CCAL folder contain **complete** data in the following order? CCAL data review checklist, runlog, Target Continuing Calibration Report, followed by the quan report and chromatograms for the CCAL and window standard.					

1st Level Reviewer:	Date:
Comments:	
2nd Level Reviewer:	Date:
Comments:	

ID028R20.doc, 081810

Figure 2 Example Data Review Checklist (continued)

TestAmerica Knoxville GC/MS-SIM Data Review / Narrative Checklist
Method: PAHs and Selected SVOCs - KNOX-ID-0016, Revision 8
Page 1 of 3

Lot Number:			Instrument:		
Scanned Filenames:					

A. Tune / Calibration	N/A	Yes	No	Why is data reportable?	2nd √
1. Were all samples injected within 12 hr of CCAL?					
2. Was the correct ICAL used for quantitation? (Check 1 RF per sample/QC sample.)					
B. Sample Results	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd √**
1. Were all special project requirements met?					
2. Were sample preparation and analytical HTs met? If no, list NCM#_____				☐ [ht1] HT expired upon receipt. ☐ [ht2] Client requested analysis after HT expired.* ☐ **Re-extraction done after HT expired.**	
3. Was prep info (sample amount, final vol, split factors, units, prep dates/times) verified?					
4. For sediment samples, were the RLs and MDLs adjusted for % moisture using QuantIMS DF?					
5. Was date/time of analysis verified between header and logbook?					
6. Was header information (WO#, data file, initial wt/vol, extract vol, DF) verified?					
7. Were peaks properly identified?					
8. Are peak integrations appropriate?					
9. Were alkyl group start/end times and patterns verified?					
10. Are internal standards (30-120% R), alternate standards and sampling surrogates (30-140% R) within QC limits for samples and matrix spikes? Sample Reason Sample Reason _____				☐ **[is1] IS above QC limits.** ☐ **[is2] IS below QC limts.** ☐ **[sur1] Surrogates outside QC limits.**	
11. If amount extracted was <80% of nominal amount, were the RLs/MDLs adjusted? List samples:_____				☐ [elev6] Elevated RLs for all analytes due to insufficient sample amount received.	
12. For initial analysis that's a dilution, was the largest analyte >20% of calibration range? List dilutated samples and reason (e.g elev1) Sample Reason Sample Reason _____				☐ [elev1] Elevated RL for (ANALYTE) due to sample matrix interferences. ☐ [elev2] Elevated RL for (ANALYTE) due to interfering analyte. ☐ [elev3] Elevated RLs for all analytes due to difficult sample matrix. ☐ [elev4] Diluted based on screening results. ☐ [elev5] Elevated RLs for all analytes due to presence of non-target compounds.	

NOTE: Nonconformance memos are required for **bold** autotext statements.

Figure 2 Example Data Review Checklist (continued)

TestAmerica Knoxville GC/MS-SIM Data Review / Narrative Checklist
Method: LRPAH PAHs and Selected SVOCs - KNOX-ID-0016, Revision 8
Page 2 of 3

Lot Number:					
13. If bench dilutions were required, were results within calibration range? Sample Reason Sample Reason _____				☐ [E1] 1 g reprep performed. ☐ [E2] 1 g multi-spike reprep performed. ☐ [E3] Post-extraction spike performed. ☐ [E4] E values reported per client.	
14. For secondary diluted analyses to bring compounds in calibration range, was the largest analyte targeted to be above 50% of calibration range? List diluted samples and reason (e.g., dil1): Sample Reason Sample Reason _____				☐ [dil1] Conc. of (ANALYTE) > calibration range. RLs adjusted accordingly. ☐ [dil2] Conc. of several compounds > calibration range. RLs adjusted accordingly. ☐ [dil3] Conc. of (ANALYTE) > calibration range. Both analyses reported to provide lowest RLs. ☐ [dil4] Conc. of several compounds > calibration range. Both analyses reported to provide lowest RLs.	
15. Was the upper calibration range (UCL) calculated correctly and were hits >UCL flagged with "E"?					
16. If manual integrations were performed, are they clearly identified, initialed, dated and reason given?				Reasons: 1) Corrected split peak; 2) Unresolved peak; 3) Tailing; 4) RT shift; 5) Wrong peak selected; 6) Other	
17. Have alternate hits and manual integrations been verified as correct?					
C. Preparation/Matrix QC Results	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd √**
1. LCS native analyte %R within QC limits (60-140%)? If no, list NCM#:: _____				☐ **[lcs1] Insufficient sample for reanalysis.** ☐ **[lcs2] Samples consumed during prep.** ☐ **[lcs3] LCS %R high but analyte <RL in associated samples.**	
2. LCS IS %R within QC limits (60-140%)?				☐ **[is3] IS above QC limits.** ☐ **[is4] IS below QC limts.**	
3. Method blank done per prep batch and method blank or instrument blank analyzed with each sequence?					
4. Method blank IS %R within QC limits (60-140%)?.				☐ **[is5] IS above QC limits.** ☐ **[is6] IS below QC limts.**	
5. Are all analytes present in the method blank ≤ RL?				☐ **[mb1] Reported blank after client consultation.** ☐ **[mb3] Analyte < RL in associated samples.** ☐ **[mb4] Sample results >10x blank.** ☐ **[mb5] Insufficient sample for reanalysis.** ☐ **[mb7] Samples consumed during prep.**	
6. Were MS run #'s assigned correctly?					
7. Are MS/MSD recoveries and RPDs within QC limits?				☐ [ms1] LCS acceptable. High native analyte concentration relative to spike level and/or lack of sample homogeneity.	
D. Final Report	**N/A**	**Yes**	**No**	**Why is data reportable?**	**2nd √**
1. Final report acceptable? (Results correct, RLs calculated correctly, units correct, IS %R correct, appropriate flags used, dilution factor correct, and extraction/ analysis dates correct.)					

Figure 2 Example Data Review Checklist (continued)

TestAmerica Knoxville GC/MS-SIM Data Review / Narrative Checklist
Method: LRPAH PAHs and Selected SVOCs - KNOX-ID-0016, Revision 8
Page 3 of 3

Lot Number:					
2. If samples were split, are the dilution factors & prep factors applied properly & MDL/RLs adjusted				☐ [elev7] Elevated RLs for all analytes due to split; list samples: _____ _____	
3. For alkyl PAHs, are hits fagged with EST?					
4. Were all non-associated internal standards turned to 'NA'?					
5. Was a narrative prepared and all deviations noted?					
6. Are all non-conformances documented appropriately and copy included with deliverable?					
7. Are the correct scanned file names listed?					
8. Were all CCALs and window standards scanned?					
1st Level Reviewer:		**Date:**			
Comments:					
2nd Level Reviewer:		**Date:**			
Comments:					

Figure 3: C1-C4 Alkyl Homologue Peak Patterns

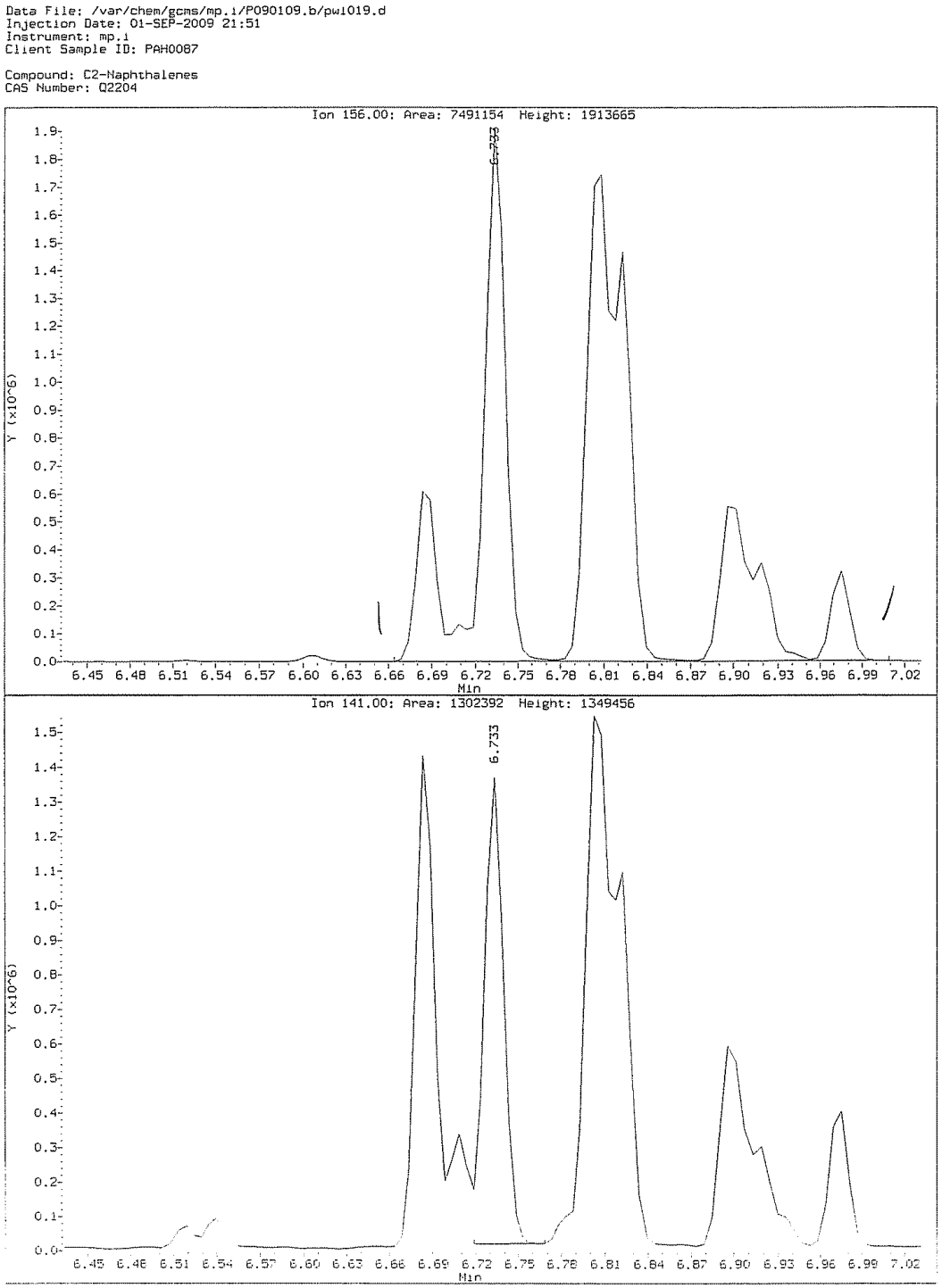

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

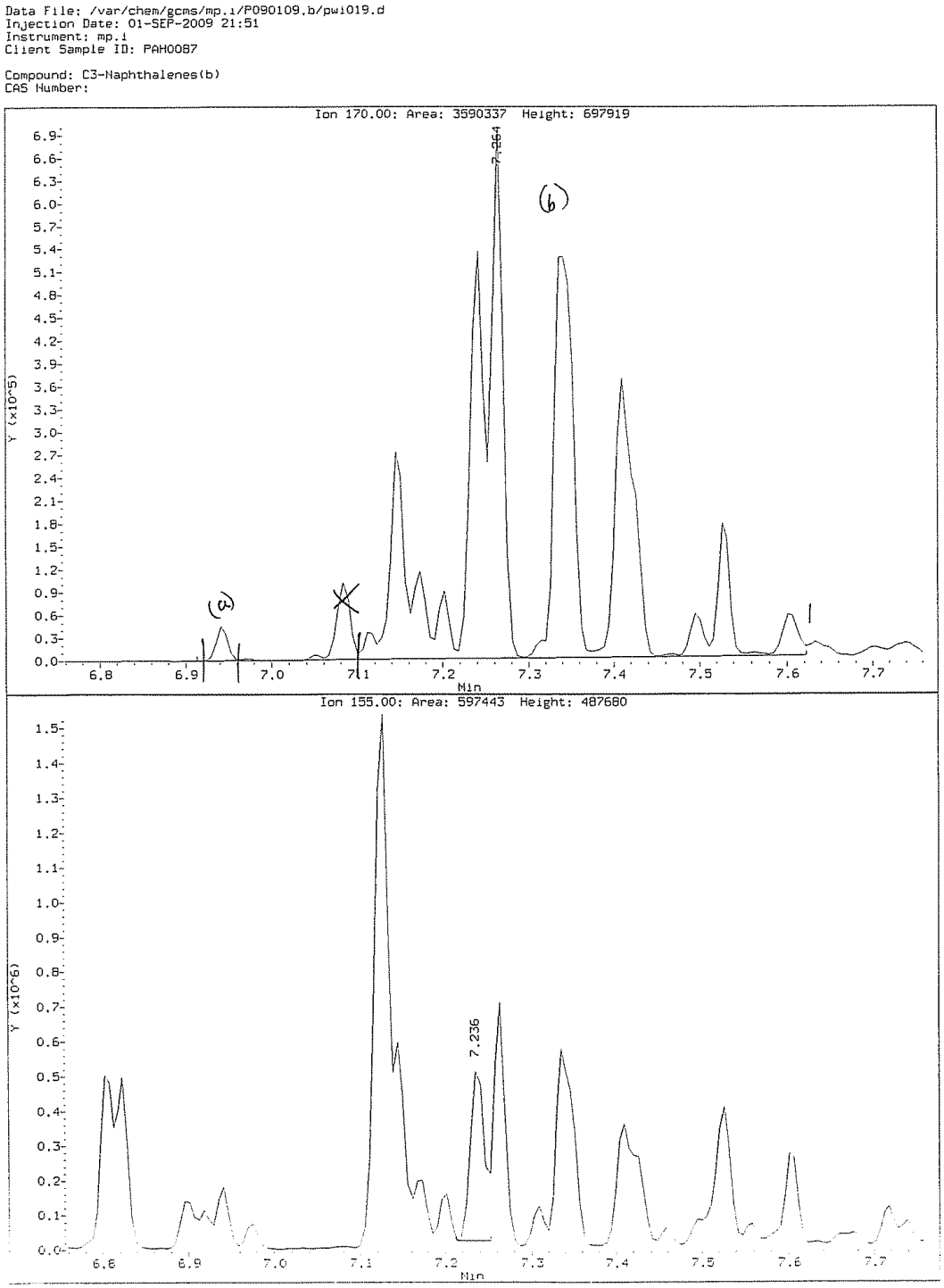

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

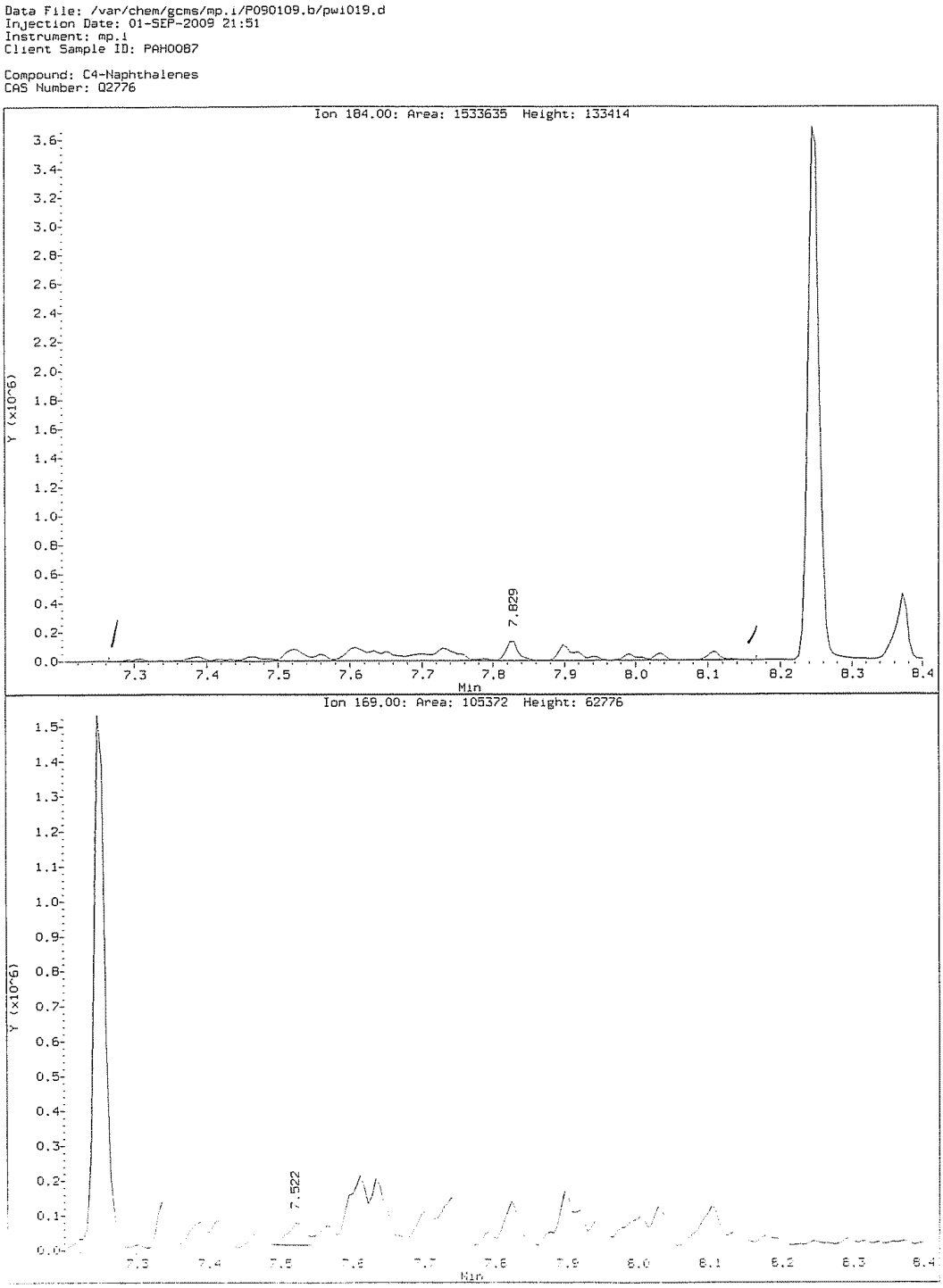

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

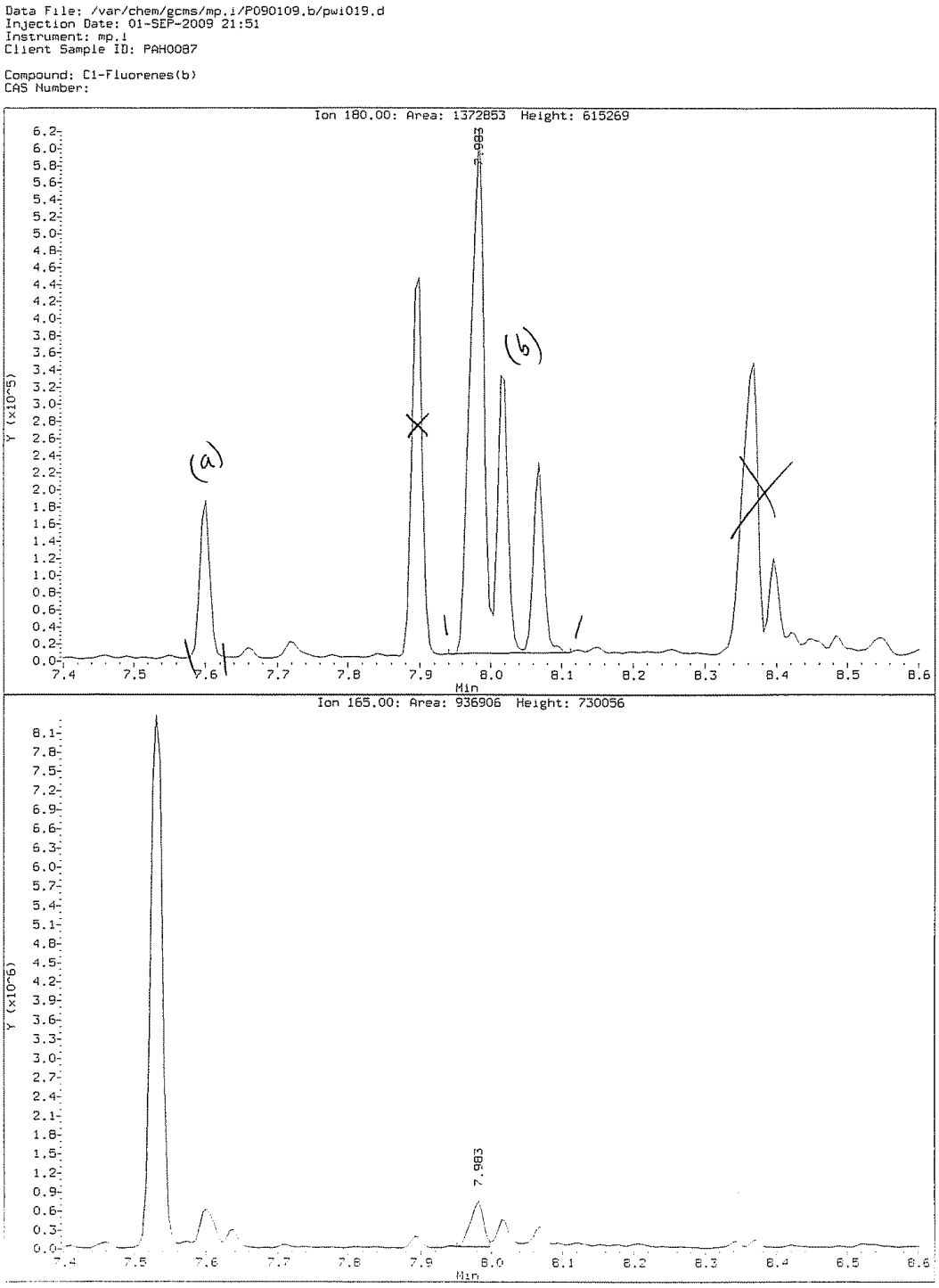

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pwi019.d
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Instrument: mp.i
Client Sample ID: PAH0087

Compound: C2-Fluorenes
CAS Number: Q2772

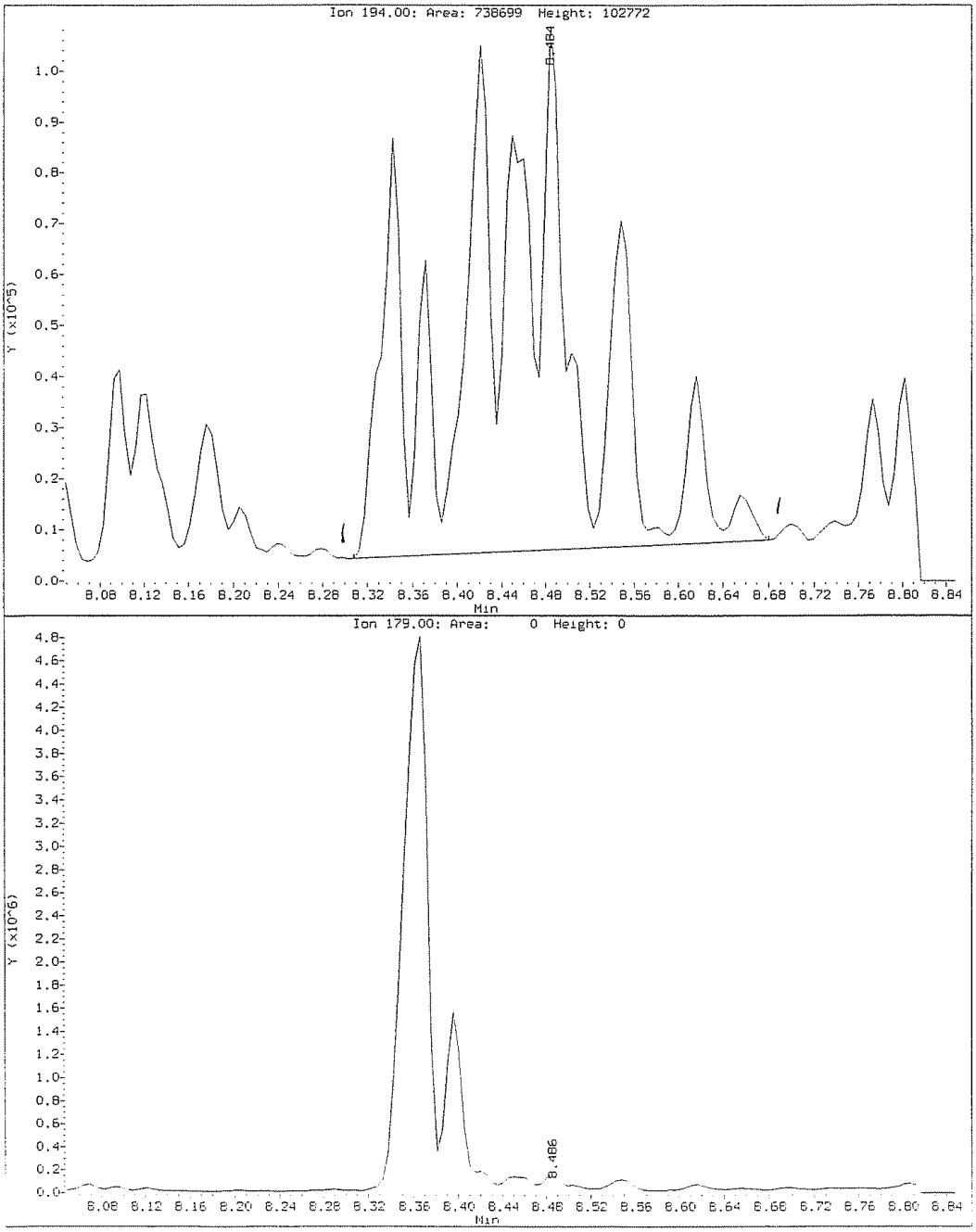

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pwi019.d
Injection Date: 01-SEP-2009 21:51
Instrument: mp.i
Client Sample ID: PAH0087

Compound: C3-Fluorenes
CAS Number: Q2773

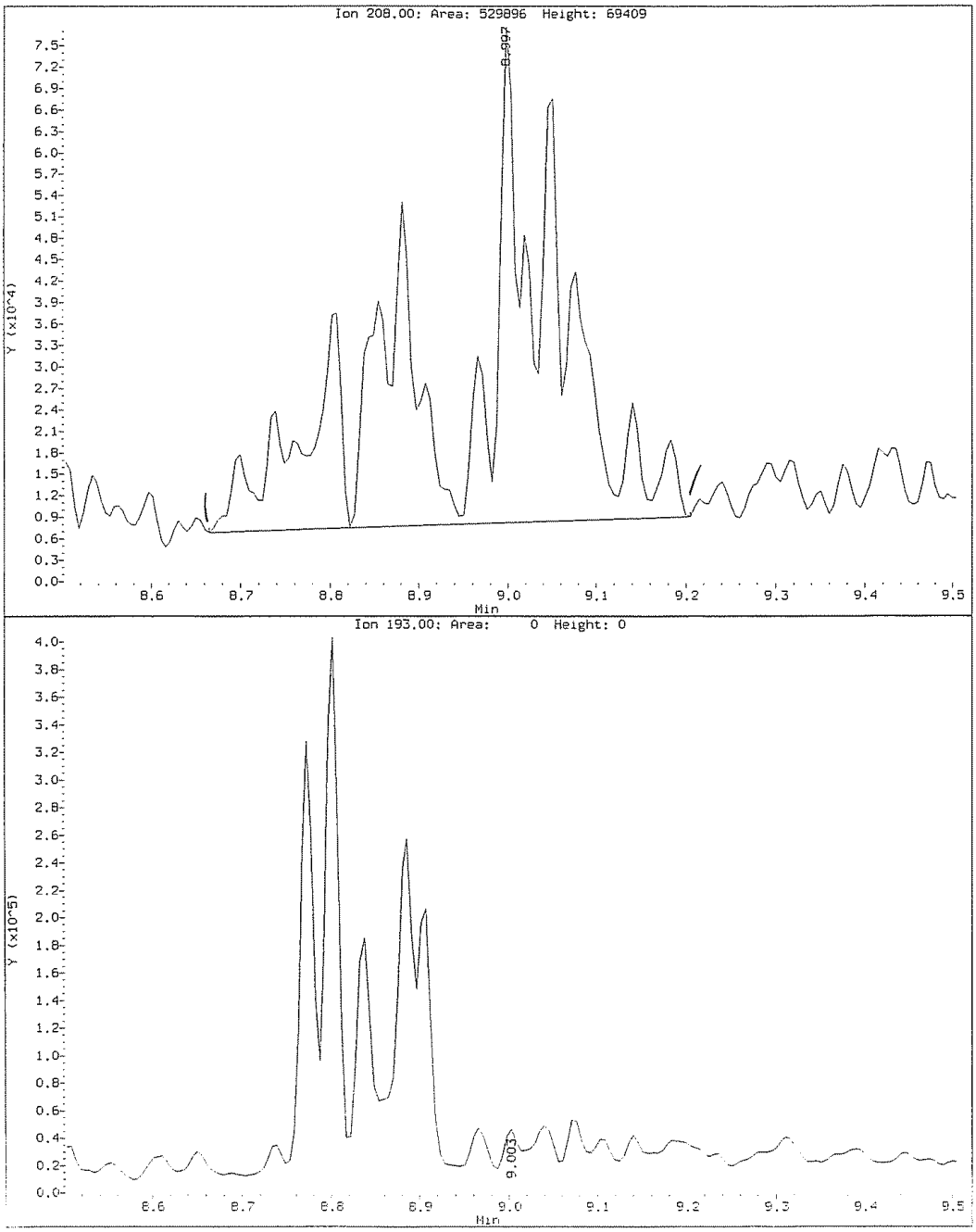

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pwi019.d
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Instrument: mp.i
Client Sample ID: PAH0087

Compound: C1-Dibenzothiophenes
CAS Number: 02768

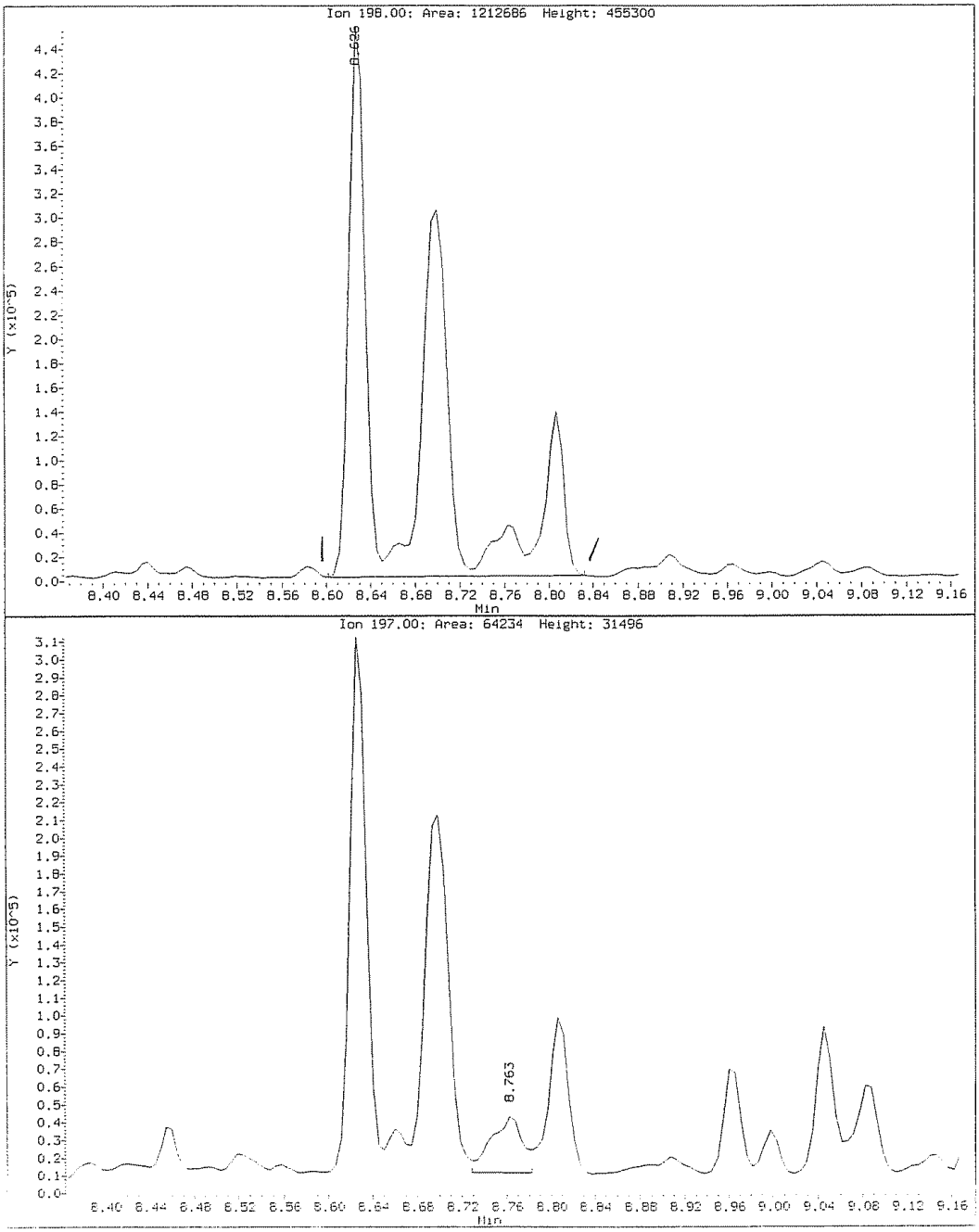

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pwi019.d
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Instrument: mp.i
Client Sample ID: PAH0087

Compound: C2-Dibenzothiophenes
CAS Number: 02769

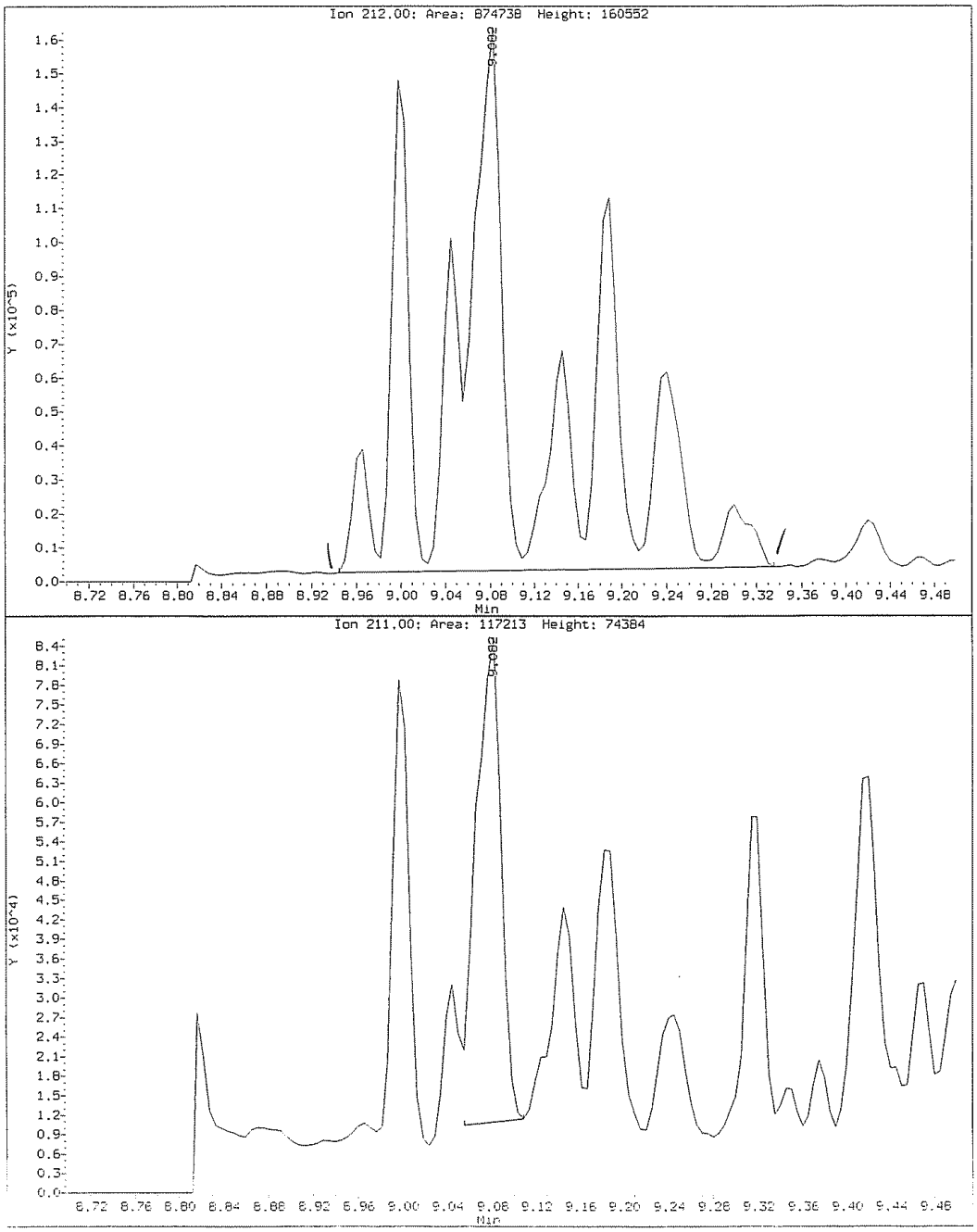

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pwi019.d
Injection Date: 01-SEP-2009 21:51
Instrument: mp.i
Client Sample ID: PAH0087

Compound: C3-Dibenzothiophenes
CAS Number: Q2770

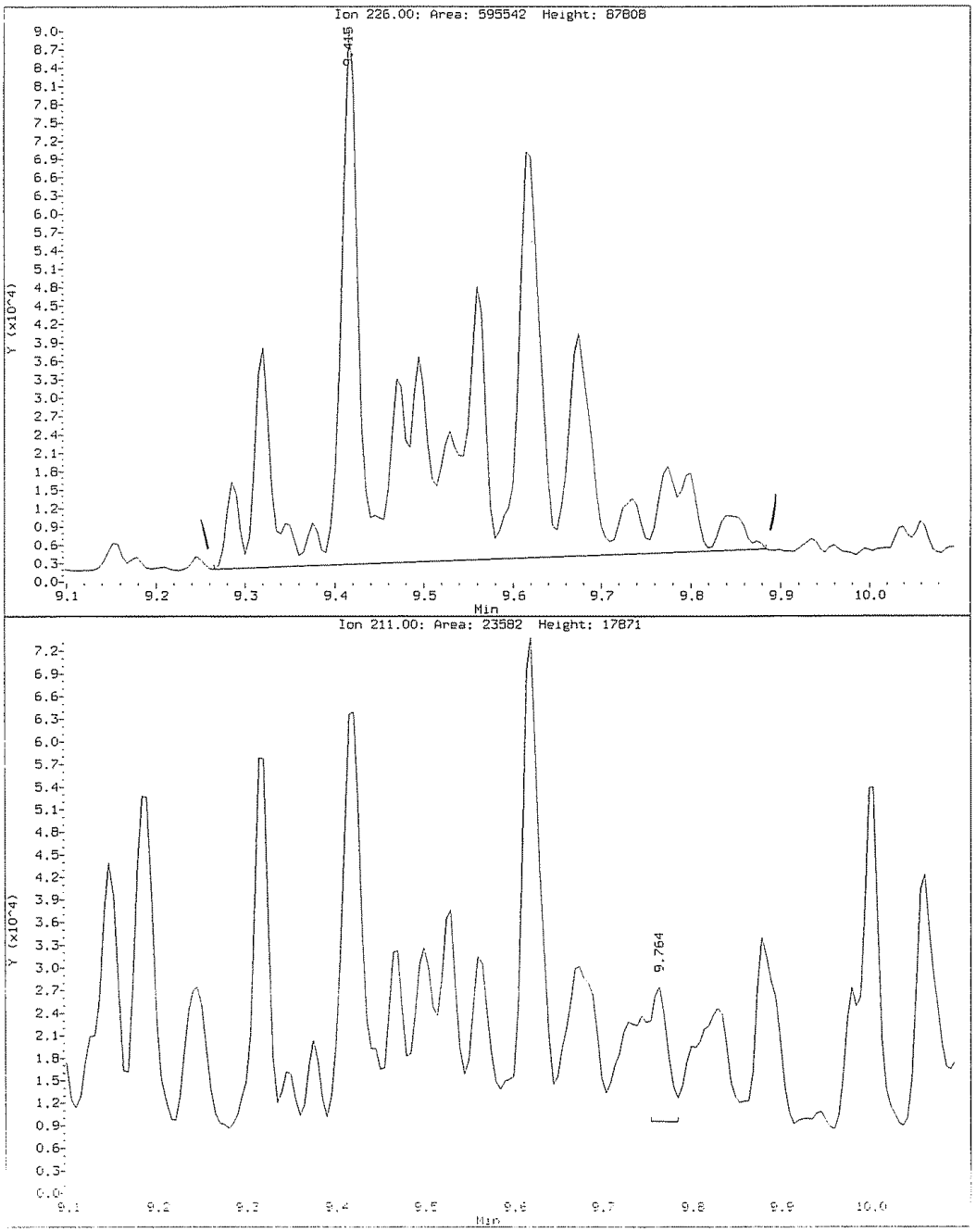

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pwi019.d
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Instrument: mp.i
Client Sample ID: PAH0087

Compound: C4-Dibenzothiophenes
CAS Number: 02842

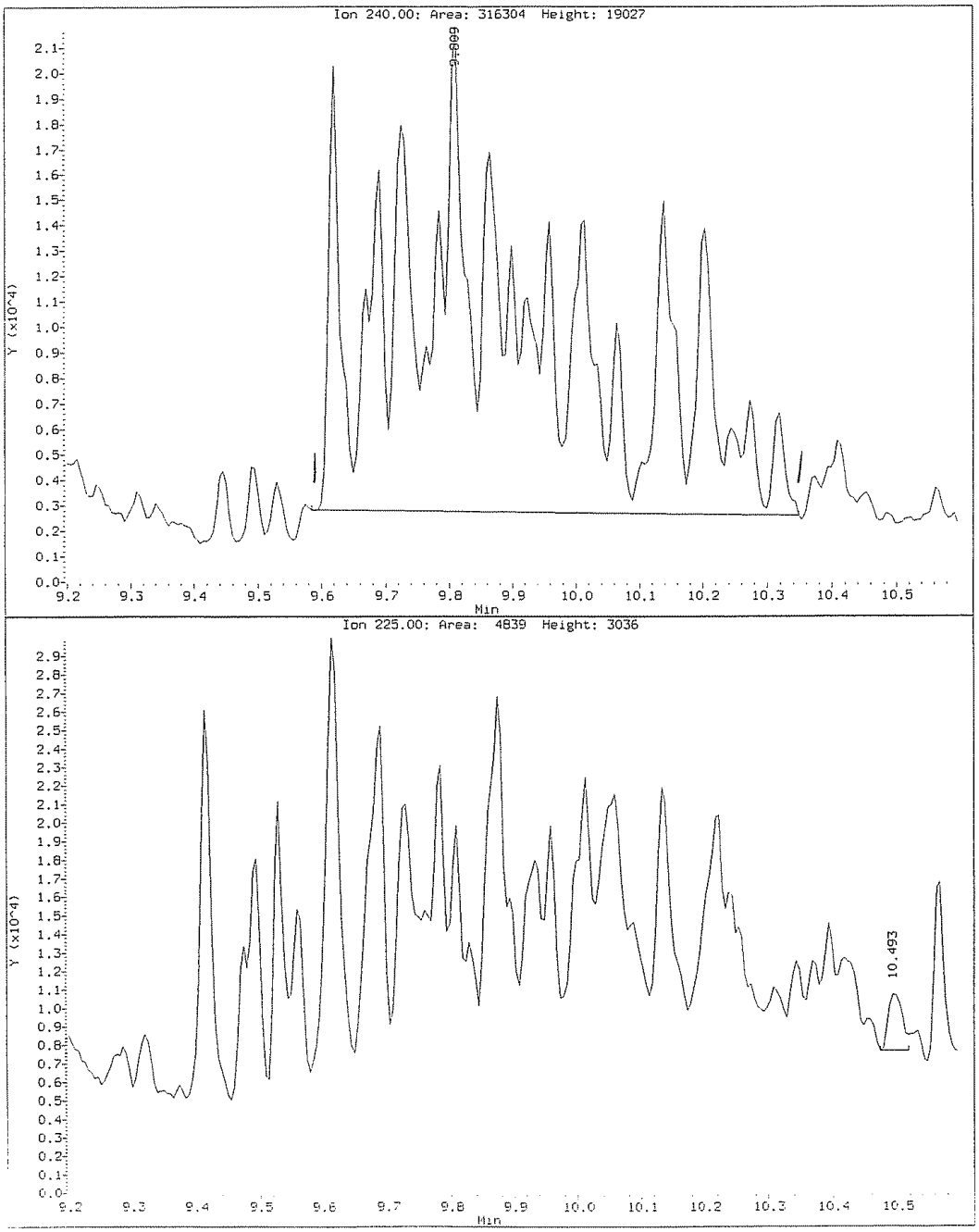

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pwi019.d
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Instrument: mp.i
Client Sample ID: PAH0087

Compound: C1-Phenan/Anthracenes
CAS Number: 02777

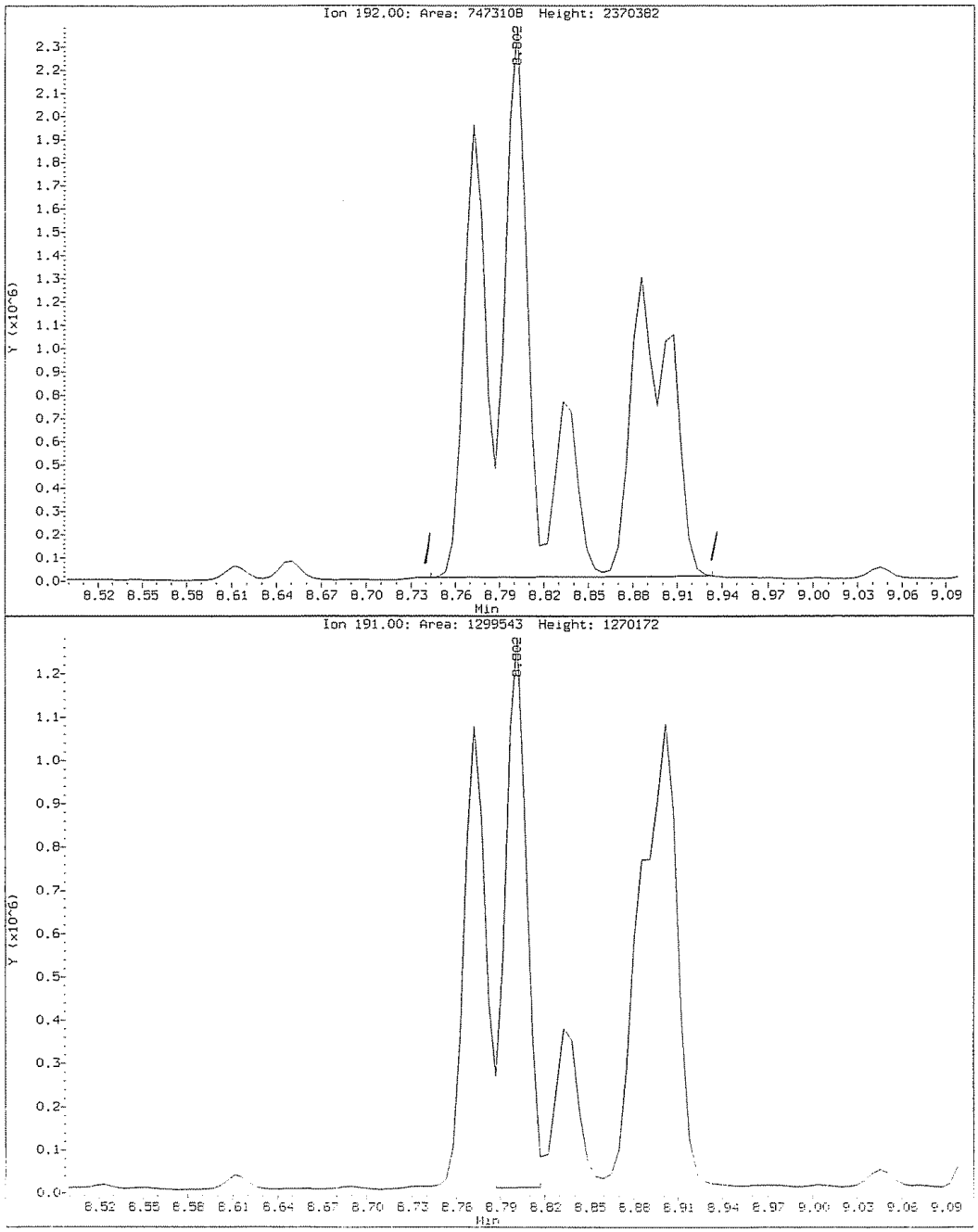

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pwi019.d
Injection Date: 01-SEP-2009 21:51
Instrument: mp.i
Client Sample ID: PAH0087

Compound: C2-Phenan/Anthracenes
CAS Number: Q2778

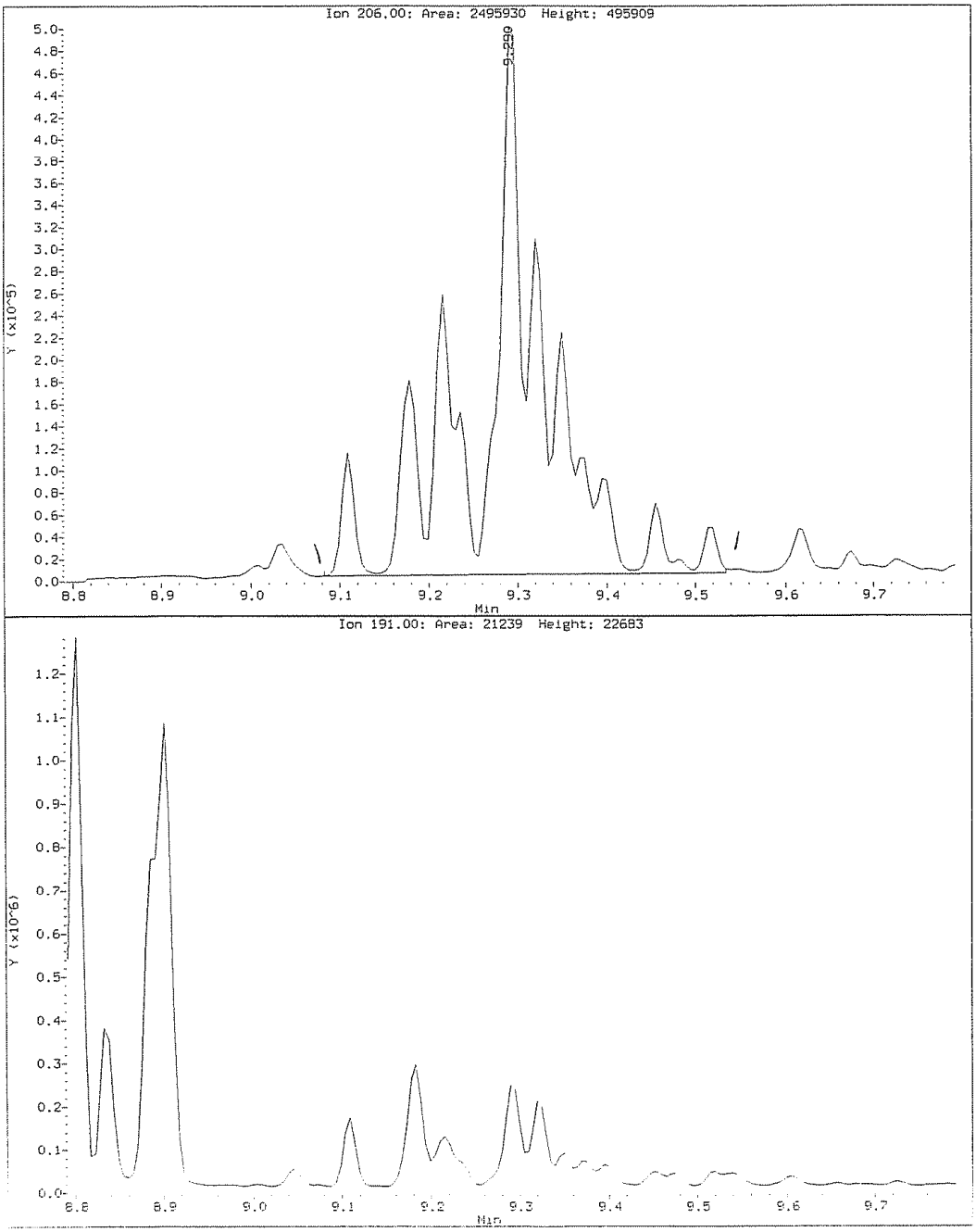

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pw1019.d
Injection Date: 01-SEP-2009 21:51
Instrument: mp.i
Client Sample ID: PAH0087

Compound: C3-Phenan/Anthracenes
CAS Number: 02779

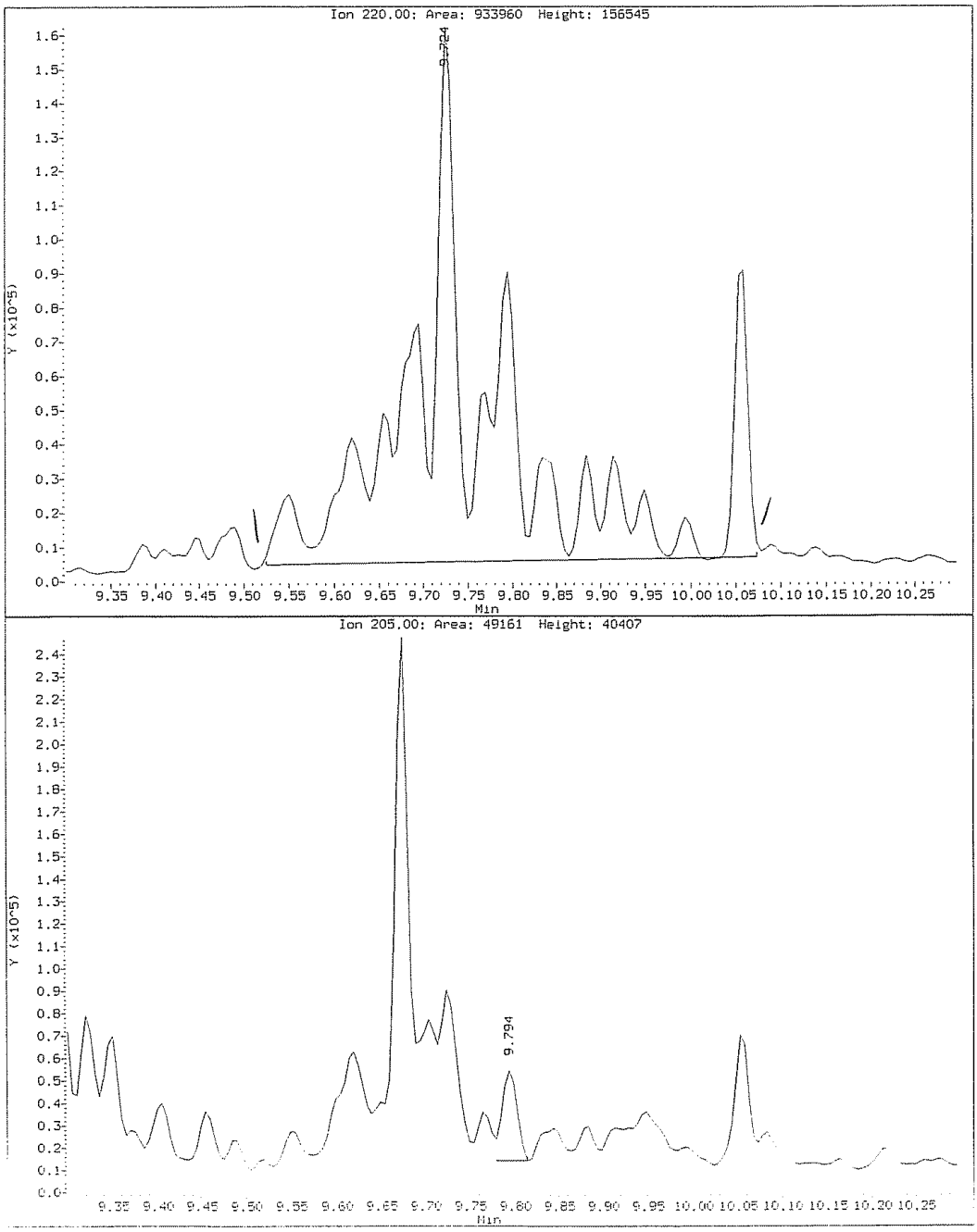

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pwi019.d
Injection Date: 01-SEP-2009 21:51
Instrument: mp.i
Client Sample ID: PAH0087

Compound: C4-Phenan/Anthracenes
CAS Number: Q2780

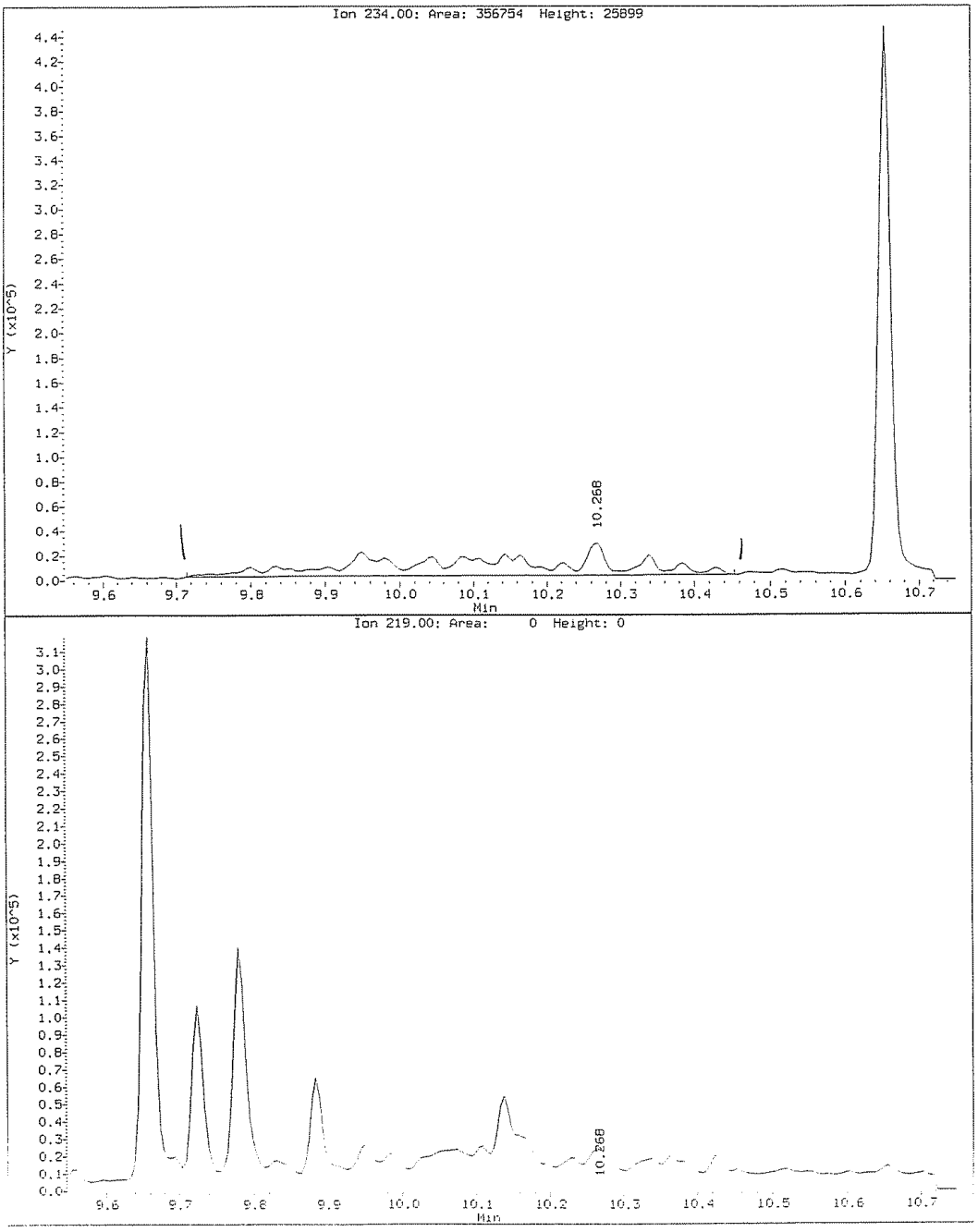

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pwi019.d
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Instrument: mp.i
Client Sample ID: PAH0087

Compound: C1-Fluoran/Pyrenes
CAS Number: Q2774

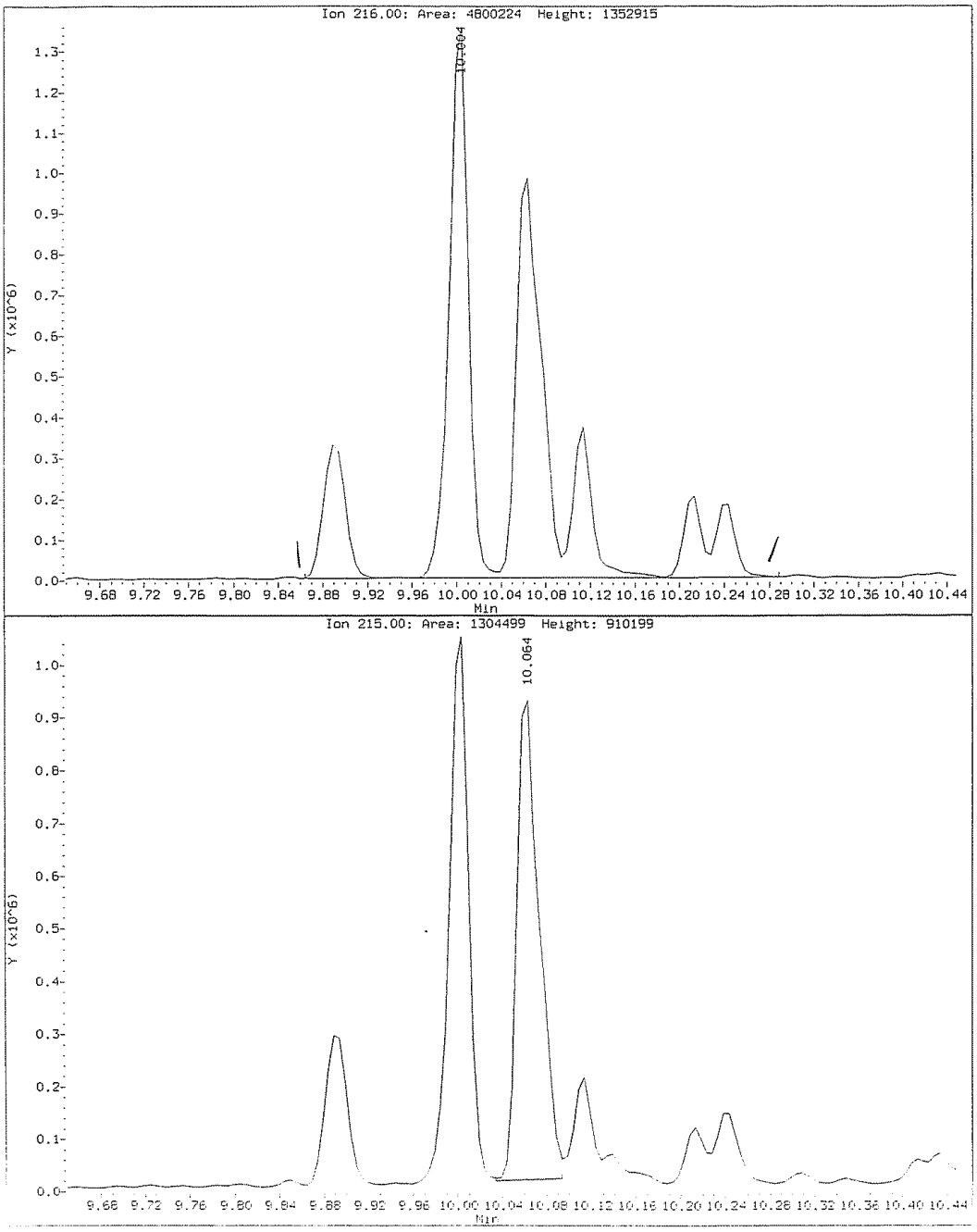

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pwi019.d
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Instrument: mp.i
Client Sample ID: PAH0087

Compound: C1-Benz(a)anthraceneChrysenes
CAS Number: Q2764

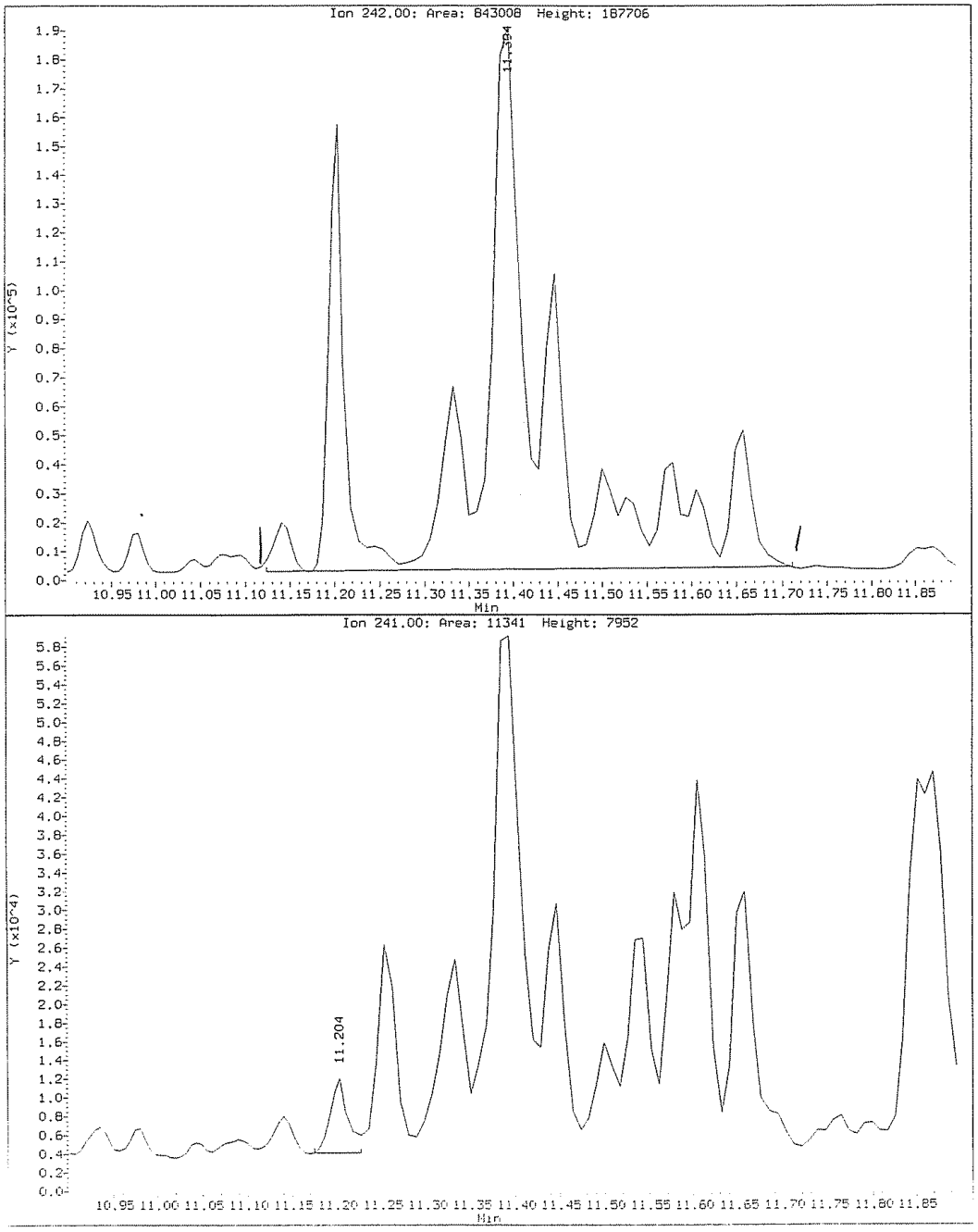

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pwi019.d
Injection Date: 01-SEP-2009 21:51
Instrument: mp.i
Client Sample ID: PAH0087

Compound: C2-Benz(a)anthraceneChrysenes
CAS Number: 02765

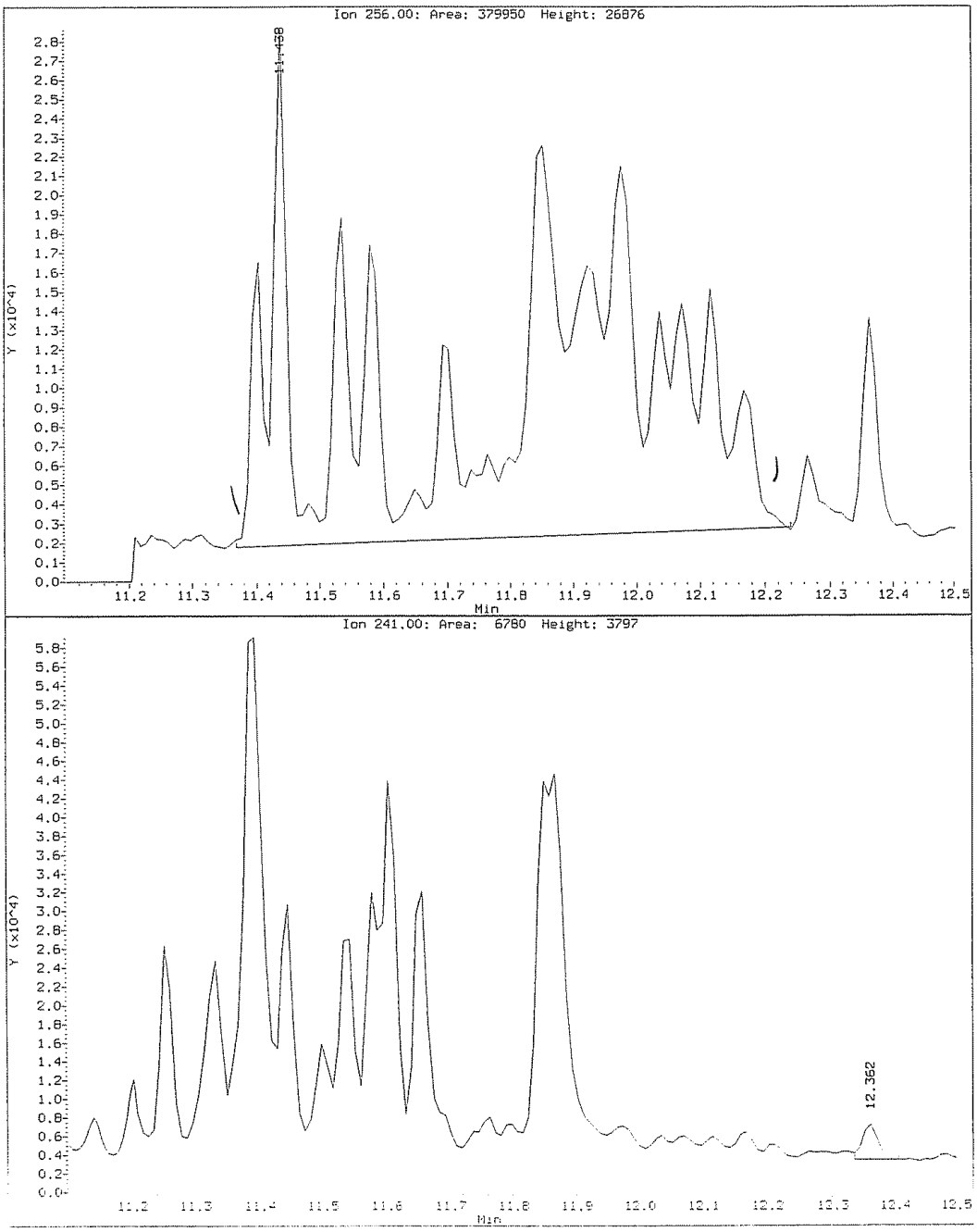

Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pwi019.d
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Instrument: mp.i
Client Sample ID: PAH0087

Compound: C3-Benz(a)anthraceneChrysenes
CAS Number: 02766

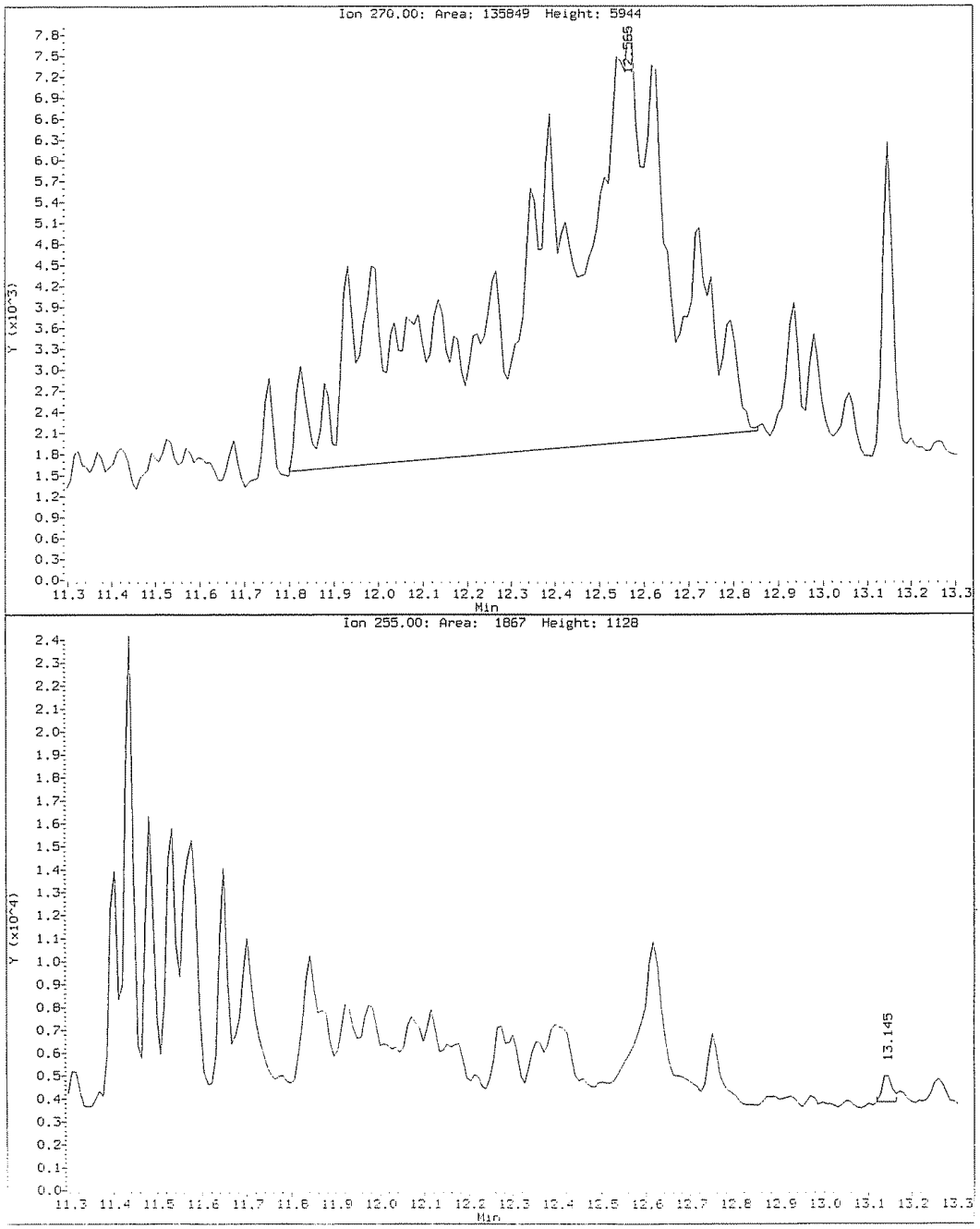
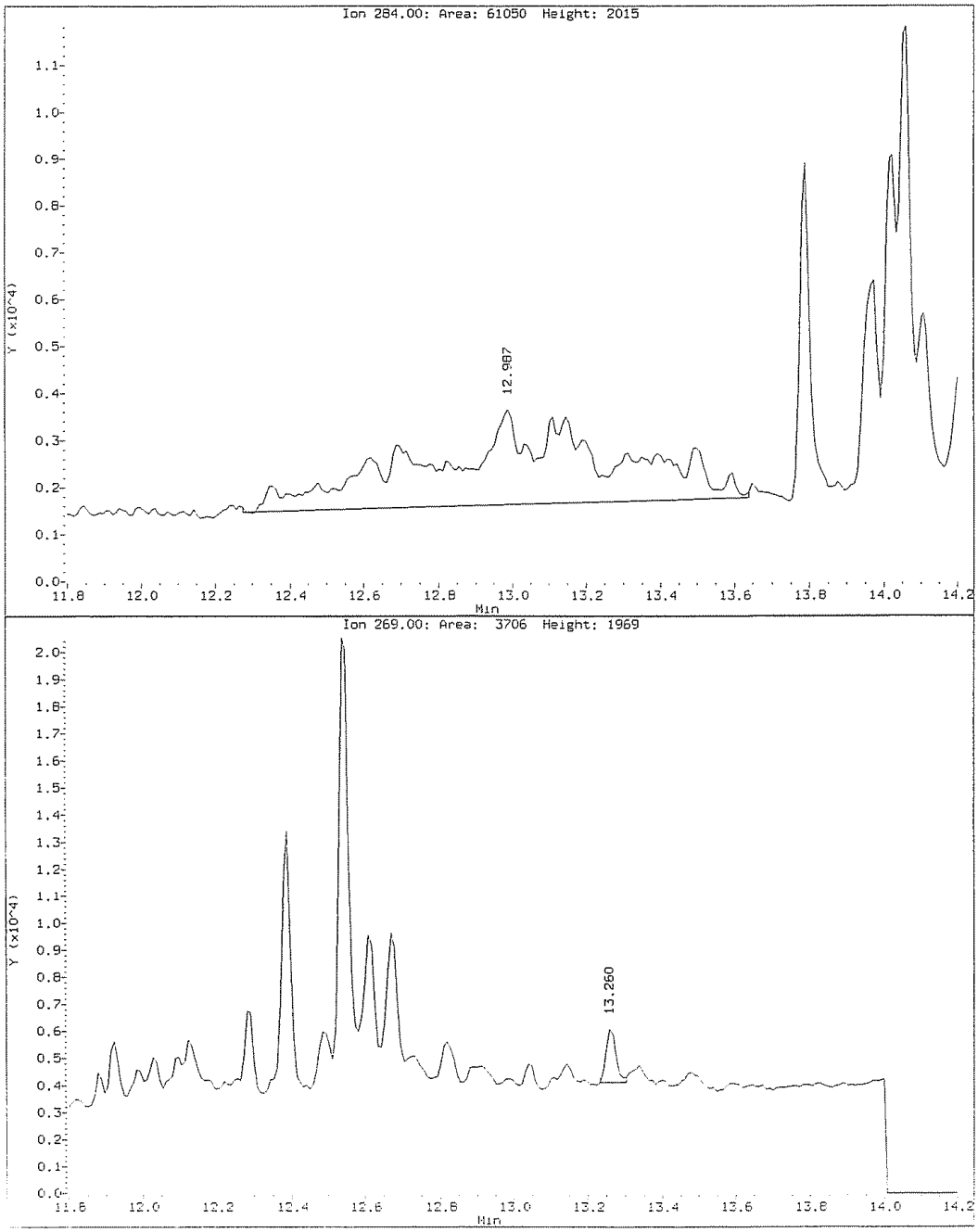


Figure 3: C1-C4 Alkyl Homologue Peak Patterns (continued)

Data File: /var/chem/gcms/mp.i/P090109.b/pw1019.d
Injection Date: 01-SEP-2009 21:51
Instrument: mp.i
Client Sample ID: PAH0087

Compound: C4-Benz(a)anthraceneChrysenes
CAS Number: Q2767



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. 10)

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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. Refer to SOPs KNOX-OP-0001, current revision and KNOX-ID-0012, current revision for the procedures used for sample extraction and cleanup.

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 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.

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 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.

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 prior to analysis. The results are used to measure the recovery of the internal standards and the cleanup standard.

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.

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.
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.

Material	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
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.

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.

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.

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.

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 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 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

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
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

1 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 10% 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.

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 established control limits. In the situation where method blank internal standard recoveries are below acceptance limits, method blank results can be used if the following criteria are met:

- All internal standards peaks must exhibit a 10:1 signal to noise ratio or greater
- The estimated detection limit (EDL) is at or above the minimum level (ML)

9.3.5.1 The application of the above criteria must be noted in the case narrative.

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.

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 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:

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).

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;

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

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;

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

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

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.

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

Where:
C_{Exp} = The expected concentration of the Standard.
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 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 method 1613B, 8290/8290A or in Table 8 for methods 23, 00231A 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) $\geq$ 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 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
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.

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.

$$Qrs = \frac{Crs \times Vrs}{S}$$

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

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

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.

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

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

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

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:

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

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)

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 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:

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

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

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

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:

$$\mathrm{M}axL = \frac{C\max \times Vfe}{W\mathrm{s}}$$

Where:

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

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 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 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.

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/OCDF and non-2378s exceed the calibration range. Although this allowance is not made by method 1613B, this procedure does not require dilution for OCDD/OCDF and non-2378s 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 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

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

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

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.

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.

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

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	-	-	-

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	-	-

Table 7

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

		1613B			8290/8290A	
Analyte	**VER (ng/mL)**	**All Isomers (ng/mL)**	**Tetra only (ng/mL)**		**Shift Open %D**	**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.

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.

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.

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.

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.

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.

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

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

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

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

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	

Table 22

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

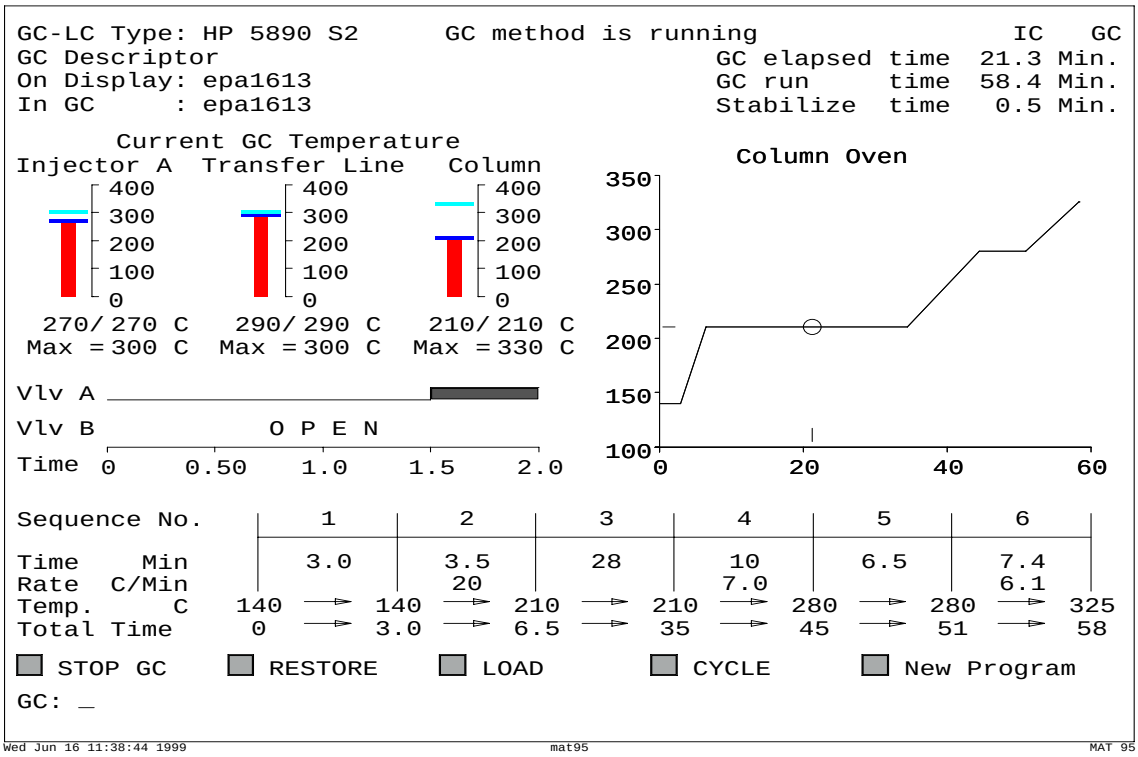
Number of Chlorine Atoms	Ion Type	Theoretical Ratio	Control Limits Lower	Control Limits Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6 [1]	M/M+2	0.51	0.43	0.59
7	M+2/M+4	1.04/1.05[3]	0.88	1.20
7 [2]	M/M+2	0.44	0.37	0.51
8	M+2/M+4	0.89	0.76	1.02

Notes:

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

Figure 1

Rtx-5 Recommended GC Operating Conditions



DB-225 Recommended GC Operating Conditions

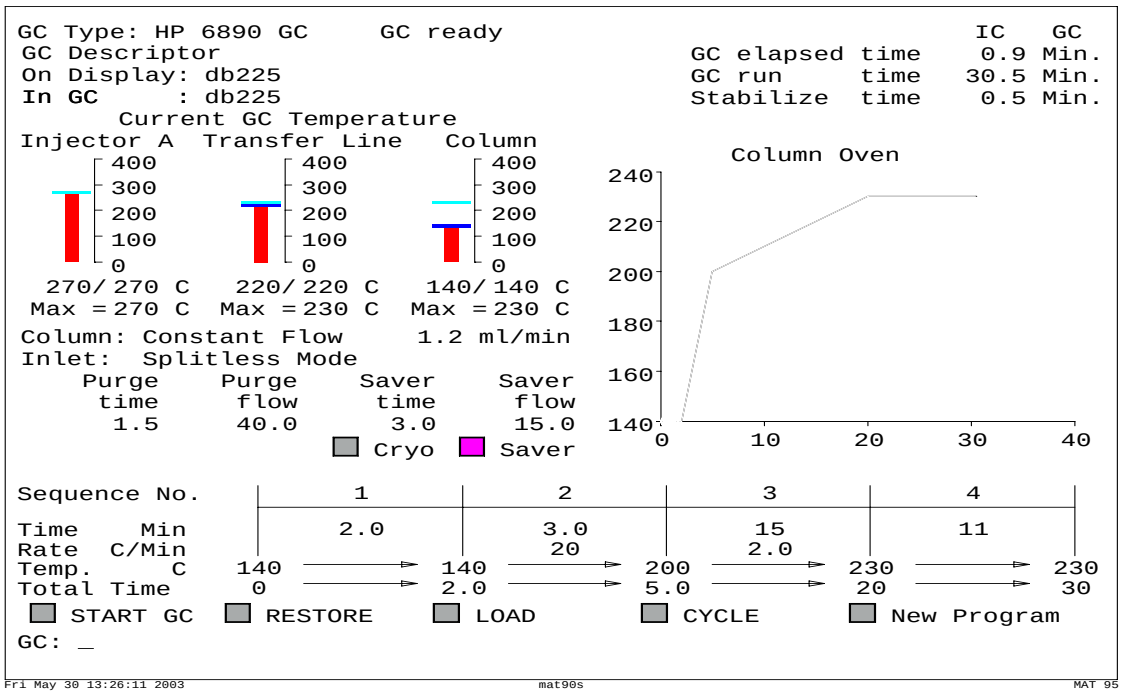


Figure 2

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
```

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

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

Fri May 30 13:22:09 2003        mat90s        MAT 95
```

Figure 3

Example Sample Data Review Checklist

TestAmerica Knoxville Dioxin GC/MS Initial Calibration Data Review / Narrative Checklist
Method: 8290/8290A - KNOX-ID-0004-R11

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:	

ID022R16.doc, 031212

Figure 3 (Continued)

Example Data Review Checklist

TestAmerica Knoxville Dioxin GC/MS Continuing Calibration Review / Narrative Checklist
Method: 8290/8290A - KNOX-ID-0004-R11

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:**	

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Figure 3 (Continued)

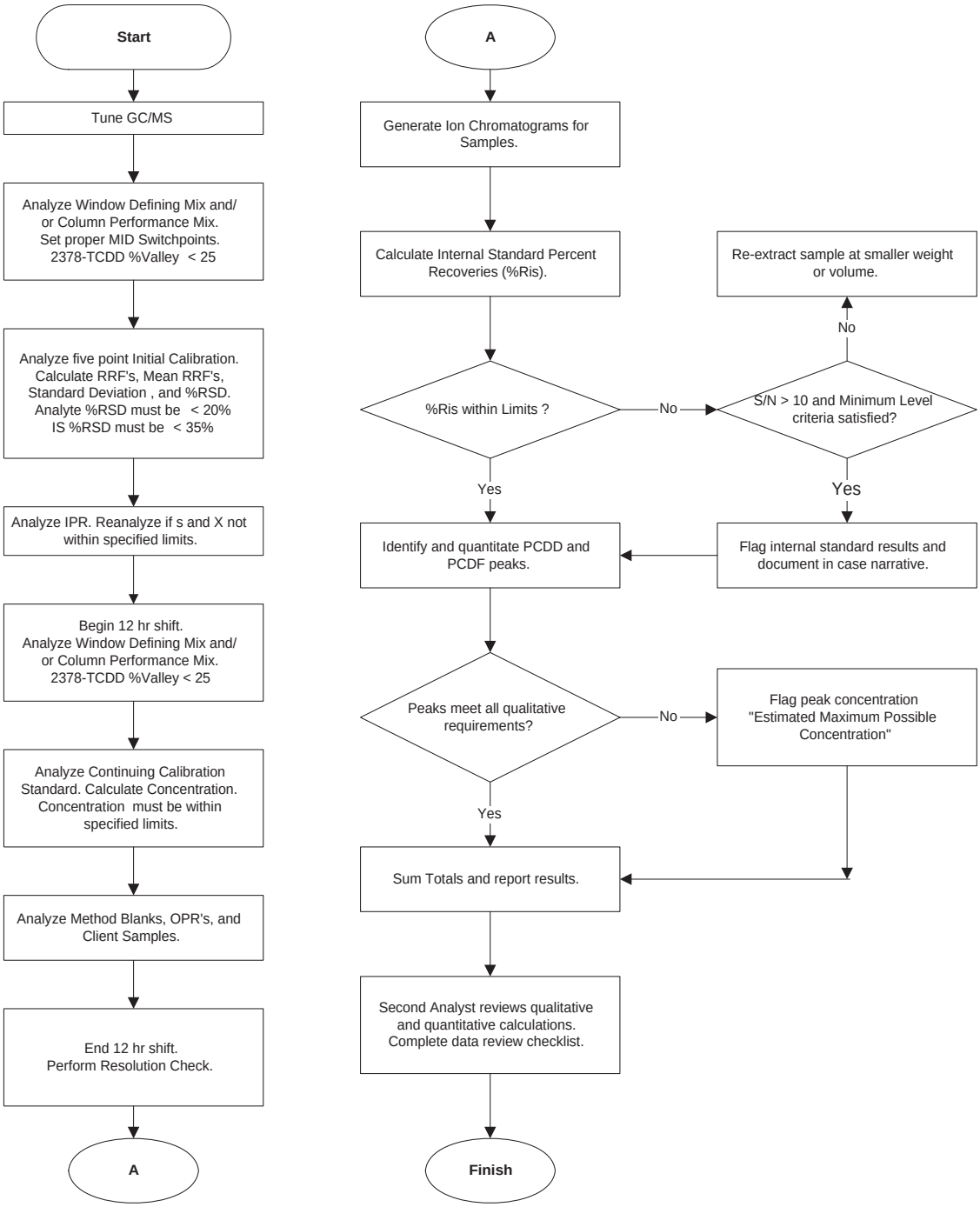
Example Data Review Checklist

TestAmerica Knoxville Dioxin GC/MS Data Review / Narrative Checklist LOT #_____
Method: 8290/8290A- KNOX-ID-0004-R11 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/LCSD done per prep batch and all analytes within the limits specified in QuantIMS reference data?				☐* Reanalysis not possible-insufficient sample. ☐LCS/LCSD %R high and affected analyte(s) were <ML in associated samples. ☐ See comment/narrative	
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 > 10x 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.

Figure 4

Analysis of PCDDs and PCDFs by HRGC/HRMS