# TPH - Gasoline Range Organics

References: **Maine 4.2.17**, Maine Health and Environmental Testing Laboratory, 09/06/1995.

**EPA 8015B (Modified),** SW-846, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, EPA SW-846, Update III, 1997.

## 1. Scope and Application

**Matrices:** This method is suitable for the analysis of waters, soils, or wastes.

**Definitions:** See Alpha Laboratories Quality Manual Appendix A

This method is designed to measure the concentration of gasoline range organics, from MTBE through naphthalene inclusive, in both water and soil. This corresponds to a boiling point range between approximately 60 ºC and 220 ºC.

The analytical procedure is based on a purge-and-trap, Gas Chromatography (GC) procedure.

With the optional PID/FID in series, the method can be extended for the specific determination of petroleum volatile organic compounds (PVOCs) as specified in the current edition of EPA Method 8020.

The data report packages present the documentation of any method modification related to the samples tested. Depending upon the nature of the modification and the extent of intended use, the laboratory may be required to demonstrate that the modifications will produce equivalent results for the matrix. Approval of all method modifications is by one of the following laboratory personnel before performing the modification: Area Supervisor, Laboratory Services Manager, Laboratory Director, or Quality Assurance Officer.

This method is restricted to use by or under the supervision of analysts experienced in the operation of the Gas Chromatograph and in the interpretation of Gas Chromatograph data. Each analyst must demonstrate the ability to generate acceptable results with this method by performing an initial demonstration of capability, analyzing a proficiency test sample and completing the record of training.

After initial demonstration, ongoing demonstration is based on acceptable laboratory performance of at least a quarterly laboratory control sample or acceptable performance from an annual proficiency test sample. A major modification to this procedure requires demonstration of performance. The identification of major method modification requiring performance demonstration is directed by the QA Officer and/or Laboratory Director on a case-by-case basis.

## 2. Summary of Method

This method provides gas chromatographic conditions for the detection of volatile petroleum fractions such as gasoline, Stoddard solvent, or mineral spirits. Samples are analyzed utilizing purge-and-trap sample concentration. The gas chromatograph is temperature programmed and utilizes a capillary column to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID) or FID with photoionization detector (PID) in series (photoionization detector first in the series). Quantitation is based on FID detector response to a gasoline component standard.

This method is suitable for the analysis of waters, soils, or wastes. Water samples can be analyzed directly for gasoline range organics by purge-and-trap extraction and gas chromatography. Soil or waste samples are dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is then analyzed by purge-and-trap GC.

This method is based in part on (1) API's Petroleum Hydrocarbon Methods (Revised August 1993); (2) work by the Wisconsin Ad-Hoc Committee on LUST Program Analytical Requirements and Wisconsin State Laboratory or Hygiene; and (3) work by the Maine Laboratory Hydrocarbon Study Committee.

### 2.1 Method Modifications from Reference

Soil samples do not have extraction surrogates or spikes added to them at the time of methanol preservation. Surrogates and spikes are added directly to the 5mL syringe containing water and the appropriate volume of the methanol extract.

# 3. Detection Limits

The laboratory follows the procedure found in 40CFR Part 136 to determine the MDL on an annual basis. The method detection limits determined by the laboratory are on file for review.

The Reported Detection Limit for water is 50 µg/L and for soil is 2.5 mg/Kg.

# 4. Interferences

**4.1** Heavier petroleum products such as diesel fuel may contain some volatile components producing a response within the retention time range for GRO. Other compounds that respond to the FID, such as chlorinated and oxygenated hydrocarbons, are detected by this method and will be included in the concentration. Spills of known specific constituents are analyzed and quantified by a method specific for those constituents. If the chromatogram exhibits the characteristics of fuel oil, the GRO is reported but flagged with a recommendation for DRO analysis.

**4.2** Samples can be contaminated by diffusion of volatile organics through the sample container septum during shipment and storage or by dissolution of volatiles into the methanol used for preservation. Trip Blanks prepared from both reagent water and methanol should be carried through sampling and subsequent storage and handling to serve as a check on such contamination.

**4.3** Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. For volatile samples containing high concentrations of water-soluble materials, suspended solids, high boiling compounds or organohalides, it may be necessary to wash the syringe or purging device with a detergent solution, rinse with distilled water, and then dry in a 105ºC oven between analyses. The trap and other parts of the system are also subject to contamination, therefore frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation. Whenever an unusually concentrated sample is encountered, it should be followed by analysis of a water blank to check for cross-contamination.

**4.4** The retention time window definition (methyl-tertiary-butylether through naphthalene inclusive) introduces a negative bias, however, it improves comparability between laboratory data. Note that gasoline blends often contain 10% ethanol, which could be responsible for a portion of this negative bias.

# 5. Safety

The toxicity or carcinogenicity of each reagent and standard used in this method is not fully established; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. A reference file of material data handling sheets is available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available in the Chemical Hygiene Plan.

All personnel handling environmental samples known to contain or to have been in contact with municipal waste must follow safety practices for handling known disease causative agents.

# 6. Sample Collection, Preservation, and Handling

## 6.1 Sample Collection and Preservation

### 6.1.1 Aqueous Samples

Aqueous samples are collected in duplicate, without agitation and without headspace in VOA vials with Teflon-lined septa screw caps. The Teflon liner must contact the sample.

Samples are acidified to a pH of 2.0 or less at the time of collection. This is typically accomplished by adding 3 or 4 drops (0.1 to 0.2mL) of 1:1 HCL (1 part reagent water and one part concentrated hydrochloric acid) to a 40mL sample. Samples must be cooled to 4 ± 2 ºC immediately after collection.

The laboratory must determine the pH of all water samples at the time of analysis and if the pH is found to be greater than 2.0, it must be noted.

A reagent water trip blank accompanies each batch of water samples.

### 6.1.2 Soil Samples

Methanol (purge and trap grade) must be added to the sample vial before or immediately after sample collection. In lieu of the in-field preservation of samples with methanol, soil samples may be collected in specially designed, air tight sampling devices. Samples that have not been preserved in the field are preserved in the lab as soon as possible after arrival in the lab. Date and time of preservation is noted on the Chain of Custody or final report.

Samples must be cooled to 4 ± 2 ºC immediately after collection.

A methanol trip blank accompanies each batch of soil samples.

## 6.2 Sample Handling

Water and soil samples must be analyzed within 14 days of collection.

# 7. Equipment and Supplies

**7.1 Gas Chromatograph:** Agilent 6890 or equivalent, Data system Enviroquant Software in conjunction with Nelson Intelligent 900 Series Interface.

**7.1.1 Column:** Restek RTX-502.2 Capillary Column, 105m X .53mm I.D., 3.0 micron film thickness or equivalent. The column must be capable of achieving a 60% resolution of all 10 components, with the exception of m/p-xylene. It must also be capable of separating methyl tert butyl ether from methanol solvent peak. The Resolution is defined as:

$$\frac{(\text{Height of smallest peak} - \text{Height of valley}) \times 100\%}{(\text{Height of smallest peak})}$$

**7.1.2 Detector:** FID (in series with a PID detector, optional)

**7.1.3 Purge-and-trap Device:** The purge and trap device consists of two separate pieces of equipment: a purging device coupled to a desorber (Autosamplers: Tekmar 2016, Archon, Centurion. Concentrators: Tekmar 2000/3000 or equivalent, or Encon evolution).

**7.1.3.1** Purge/carrier gas = Helium, analytical grade, (99.999% pure).

**7.1.3.2** Traps are conditioned, desorbed, and baked according to manufacturer's guidelines. The trap may be vented to the analytical column during daily conditioning, however, the column must be run through the temperature program prior to analysis of the samples.

**7.1.3.3** The desorber must be capable of rapidly heating the trap to 260ºC.

**7.2 Analytical Balance:** A top-loading balance capable of weighing to the nearest 0.01 g (for weighing soil samples).

**7.3 Ultrasonic Bath**

**7.4 VOA Vials:** 40mL amber VOC vials with Teflon/silicone septa.

**7.5 Syringes:** 5mL gas-tight syringe with shutoff valve.

**7.6 Volumetric Flask (class A):** 10mL, 50mL, 100mL, 500mL, 1000mL with a ground-glass or screw-top stopper.

**7.7 Microsyringes:** 1µL, 5µL, 10µL, 25µL, 100µL, 250µL, 500µL, and 1000µL.

**7.8 Spatula:** Stainless steel.

# 8. Standards and Reagents

**8.1 Reagent Water:** Organic-free water; municipal tap water filtered through carbon.

**8.2 Methanol:** Purge-and-trap grade or equivalent. Store away from other solvents.

**8.3 Gasoline Component Stock Standard:** Purchased from Ultra Scientific UST-100, GRO PVOC/WISC mix. Refer to Table 1 for concentrations. Store with minimal headspace at -10°C to -20°C. Expires 6 months from the date of opening or upon signs of degradation or evaporation.

**8.3.1 GRO Calibration Stock Standard:** To a 10mL volumetric flask, add 1mL of Gasoline Component Stock Standard (Section 8.3), Add 500µL of 4-bromofluorobenzene (Section 8.5.2) and 500µL of a,a,a-trifluorotoluene (Section 8.5.1). Bring to volume with Methanol. Store with minimal headspace at -10°C to -20°C. Expires 6 months from the date of preparation or upon signs of degradation or evaporation.

**8.3.1.1 GRO Working Calibration Standards**

Store standards with minimal headspace at -10°C to -20°C. Standards expire 6 months from the date of preparation or upon signs of degradation or evaporation.

**8.3.1.1.1 Level 1, 50ng ranges, 5ng surrogates:** To a 100mL volumetric flask, add 1µL of GRO Calibration Stock Standard (Section 8.3.1). Bring to volume with Methanol.

**8.3.1.1.2 Level 2, 100ng ranges, 10ng surrogates:** To a 100mL volumetric flask, add 2µL of GRO Calibration Stock Standard (Section 8.3.1). Bring to volume with Methanol.

**8.3.1.1.3 Level 3, 500ng ranges, 50ng surrogates:** To a 100mL volumetric flask, add 10µL of GRO Calibration Stock Standard (Section 8.3.1). Bring to volume with Methanol.

**8.3.1.1.4 Level 4, 2000 ng ranges, 200ng surrogates:** To a 5mL syringe, add 5mL reagent water and 2µL of GRO Calibration Stock Standard (Section 8.3.1).

**8.3.1.1.5 Level 5, 5000ng ranges, 500ng surrogates:** To a 5mL syringe, add 5mL reagent water and 5µL of GRO Calibration Stock Standard (Section 8.3.1).

**8.3.1.1.6 Level 6, 10000ng ranges, 1000ng surrogates:** To a 5mL syringe, add 5mL reagent water and 10µL of GRO Calibration Stock Standard (Section 8.3.1).

**8.3.1.1.7 Level 7, 20000ng ranges, 2000ng surrogates:** To a 5mL syringe, add 5mL reagent water and 20µL of GRO Calibration Stock Standard (Section 8.3.1).

**8.4 Gasoline Component Stock Standard (second source for LCS, MS):** Purchased from Accustandard GRH-003S-Pak. Store with minimal headspace at -10°C to -20°C. Standard expires 6 months from the date of preparation or upon signs of degradation or evaporation.

**8.4.1 Continuing Calibration Standard, LCS, MS:** To a 10mL volumetric flask, add 200µL of second source Gasoline Component Stock Standard (Section 8.4). Add 200µL 4-BFB (Section 8.5.2) and 200µL aaa-trichfluorotoluene (Section 8.5.1). Bring to volume with Methanol.

**CCV/LCS:** Spike 5µL of this solution into 5mL of reagent water.

**MS:** Spike 5µL of this solution into 5mL of a second aliquot of sample.

### 8.5 Surrogate Control Stock Standards

Standards expire 6 months from the date of opening or upon signs of degradation or evaporation. These standards are stored with minimal headspace at -10°C to -20°C.

**8.5.1** **a,a,a-trifluorotoluene:** 2000µg/mL, purchased from Ultra Scientific, Cat # STS-220N

**8.5.2** **4-bromofluorobenzene**: 2000µg/mL, purchased from Ultra Scientific, Cat # STS-110N.

**8.6 Working Surrogate Standard Solution:** To a 10mL volumetric flask, add 200µL 4-BFB (Section 8.5.2) and 200µL aaa-trichfluorotoluene (Section 8.5.1). Bring to final volume with MeOH for a final concentration of 40ug/L. Standard expires 6 months from the date of preparation or upon signs of degradation or evaporation. Store with minimal headspace at -10°C to -20°C.

Spike 5µL of this solution into 5mL of each sample and Blank.

## 9. Procedure

### 9.1 Set-up

**9.1.1** Gas Chromatography Conditions: Agilent 6890 or equivalent.

| | |
|---|---|
| PID Temperature | 250 ºC |
| FID Temperature | 250 ºC |
| Column | 12.5 mL/min |
| Carrier /Makeup Gas | Helium, 99.999 grade @ 12.5 mL/min |
| | Air @ 350 mL/min |
| | Hydrogen @ 30 mL/min |
| Injection Port | 250 ºC |

**9.1.2** **Oven Conditions:** 45 ºC for 2 minutes to 100 ºC at 3 ºC/min, to 160 ºC at 8 ºC/min, to 230 ºC at 20 ºC/min for 11.6 minutes.

**9.1.3** **Typical Purge and Trap Conditions:**

| | |
|---|---|
| Purge Gas: | Helium |
| Purge Gas Flow Rate: | 40 mL/min |
| Purge Temperature: | 35 ºC or less |
| Purge Time: | 11.0 ± 0.1minutes |
| Dry purge: | 4 minutes |
| Desorb Preheat: | 220 $^{o}$C |
| Desorb temp: | 225 $^{o}$C |
| Desorb Time: | 6 minutes |
| Bake temp: | 260 $^{o}$C |
| Bake time: | 15 minutes |

## 9.2 Initial Calibration

**9.2.1** Per Section 9.4 and under the conditions listed in Section 9.1, analyze the Gasoline Component Standard at the seven concentration levels (1 µg/L, 2µg/L, 10µg/L, 40µg/L, 100µg/L, 200µg/L and 400µg/L) listed in Section 8.3.1.1. Whenever a calibration curve is analyzed, an independent check standard (Section 8.4.1) is also analyzed to validate the curve (the LCS serves as a second source verification).

**9.2.2 Relative Response Factors**

The external standard calibration technique is used.

A collective calibration factor must be established for the GRO hydrocarbon range. The GRO marker compounds that determine the GRO range are MTBE through naphthalene, inclusive.

**9.2.3 Initial Calibration Criteria**

If the RSD for an individual analyte is ≤ 20%, then the response for this compound is considered linear over the range and the mean calibration factor is used to quantitate sample results. If the RSD criterion is not met for an analyte, linearity through the origin cannot be assumed. The calibration is repeated for any compounds that fail, or a calibration curve is generated for this compound and used for sample quantitation. If the linear calibration curve is used, the correlation coefficient must be at least 0.99.

**9.2.4 Retention Time Windows and Quantitation**

**9.2.4.1** All chromatographic peaks eluting from methyl-tertiary-butylether through naphthalene, inclusive are used to calculate the retention time window. Quantitation is based on a direct comparison of the area within this range to the total area of the 10 components in the Gasoline Component Standard. (Using a "baseline to baseline" integration as opposed to a "valley to valley" integration.)

**9.2.4.2** The retention time window is defined as beginning approximately 0.1 minutes before the retention time of methyl-tertiary-butylether and ending 0.1 minutes after the retention time of naphthalene in the calibration run.

**9.2.4.3** The laboratory must determine retention time windows for the first and last standard on each GC column and whenever a new GC column is installed. This data must be retained by the laboratory.

**9.2.4.4** Quantify by summing all peak areas eluting from methyl-tertiary-butylether through naphthalene, inclusive.

## 9.3 Standardization (Continuing Calibration Verification)

The working calibration curve must be verified on each working day, by the injection of a midpoint Gasoline Component Standard (or an LCS). If the response for the Gasoline Component Standard varies from the predicted response by more than 20%, the analytical system is examined to determine the cause and corrective action is performed and/or a new continuing calibration standard is prepared and analyzed. If the 20% criteria is still not met, the system must be recalibrated. Any samples that were analyzed following the standards that did not meet calibration criteria must be reanalyzed. If reanalysis is not possible, the data must be flagged and a narrative submitted for inclusion on the Client report.

## 9.4 Equipment Operation and Sample Analysis

### 9.4.1 Gas Chromatographic Analysis of Water Samples and Soil Samples

**9.4.1.1** Retrieve sample VOA vials from the sample bank refrigerator just prior to loading onto the Purge and Trap. Soil samples preserved with methanol must be shaken for 1 – 2 minutes to extract the volatile components into the methanol. Let sample settle prior to taking methanol aliquot.

**9.4.1.2** Rinse a 5mL Luerlock syringe with reagent water. For aqueous samples, add appropriate amount of sample (typically 5mL) to the syringe after pouring off approximately 2 – 3 mL of sample to waste. For soil samples, fill the syringe with 5mL of reagent water. Add the appropriate amount of the methanol extract (typically 100µL) to the syringe containing the reagent water. Less sample (water or methanol) may be used if sample history or screening information indicates high concentrations of target or non-target analytes. Add 5 µL of surrogate standard solution (Section 8.5) to the sample. Load the sample into a purge tube on the Autosamplers: Tekmar 2016, Archon or Centurion. Concentrators: Tekmar 2000/3000 or equivalent, or Encon evolution.

**9.4.1.3** If sample dilutions are necessary, they may be made in volumetric flasks (10mL to 100mL). Dilutions are made without delay. If aliquots of sample less than 1mL are required, use microliter syringes to transfer the sample aliquot to the flask. Dilute to the mark with reagent water.

Alternatively, the dilutions may be made directly in a gas tight syringe to avoid further loss of volatiles.

All dilutions must ensure that the response of the major constituents is within the linear range of the curve.

**9.4.1.4** If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has a saturated response from a compound, this analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can be analyzed that is free of interferences at less than the reporting limit.

## 9.5 Instrument Maintenance

If the response of the PID detector decreases significantly, perform a cleaning of the PID lamp per the manufacturer's instructions. If the response is still low, the PID lamp is replaced with a new one (PID lamp life is typically 30 – 90 days).

Additional maintenance is performed to maintain GC system performance. This includes periodic replacement of injector septa, replacement of injector liner(s), and clipping several inches off of the injector end of the capillary column. The trap used in the Purge and Trap equipment will also need periodic replacement, when system performance degrades.

All maintenance and repair is recorded in the appropriate Instrument Maintenance Log.

## 9.6 Calculations

**9.6.1** The concentration of Gasoline Range Organics in the sample is determined from a summation of the total peak area of all chromatographic peaks eluting from methyl-tertiary-butylether through naphthalene, inclusive, and comparing to the calibration curve. (Using a "baseline to baseline" integration as opposed to a "valley to valley" integration.) Refer to Section 9.2.4.

Quantification is based on the average response from the calibration curve. The %RSD of the RF's must not exceed 20%

Linear regression: From the calibration standards GC responses, R, and their known concentrations, Cin µg/L, the following linear equation is derived [R is plotted on the y-axis; C is plotted on the x-axis]:

$R = mC + b$; which can be rearranged to $C = (R – b) /(m)$

Using the slope (m) and the intercept (b) from this equation, the concentration of sample can be calculated from the following equations:

**Water Samples:**

$Cx = (Rs – b) (D) / (m)$

**Soil Samples:**

$Cs = [(Rs-b) (D) (Vt) (K)] / [(Vp) (W) (m)]$

Where:

**Cs** = Concentration of sample in µg/L for waters and mg/Kg on a dry weight basis for soils. (Note: Wet weight basis can be used upon Client request.)

**m** = slope of the calibration curve

**Rs** = GC response of sample in the GRO retention time window

**b** = intercept of calibration curve

**D** = dilution factor if water sample or soil extract was diluted

**Vp** = volume of soil extract purged (units must be the same as those used for Vt)

**K** = $5 \times 10^{-6}$ L mg/µg (this constant adjusts for both conversion from µg/Kg to mg/Kg and for the dilution of the volume of extract purged up to the 5mL used for purging).

**W** = total dry weight of soil sample in Kg. (This weight can be the wet weight if requested by the Client.)

**9.6.2** Blank areas cannot be subtracted from the sample areas. Chromatographic baseline rises due to temperature programming are corrected for by using baseline correction. The baseline correction is performed by the most convenient method that the data handling system allows.

**9.6.3** If the water blank concentration (this does not include trip blanks) exceeds 50µg/L, (or the minimum reporting level if lower) all water samples associated with this blank (samples run since the last blank that was below 50 µg/L) must be rerun.

**9.6.4** If a methanol blank concentration (this does not include trip blanks) exceeds 2.5mg/L, all soil samples associated with this blank (samples that have concentrations greater than 2.5mg/Kg since the last blank that was below 2.5mg/L) must be rerun.

**NOTE:** The blank level is equivalent to 50µg/L in the water sample prepared by spiking 100µL of the methanol blank into 5mL of water. This is also equivalent to 2.5mg/Kg in soil.

**9.6.5** To ensure that peaks outside the GRO window are not missed, run the chromatogram out 5 minutes past the last component in the GRO component standard. All significant peaks (and baseline rises) outside the window should be qualitatively assessed and reported.

**9.6.6** Soil concentration is reported on a dry-weight basis unless specified by the Client. The report indicates whether results are on a wet or dry weight basis.

# 10. Quality Control and Data Assessment

The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a calibration verification standard is used to confirm the measurements were performed in an in-control mode of operation.

## 10.1 Demonstration of Capability

The analyst must make an initial, one-time, demonstration of the ability to generate acceptable accuracy and precision with this method. Each time a method modification is made, the analyst is required to repeat the procedure.

Repeated failure confirms a general problem with the measurement system or analytical technique of the analyst. If the failure repeats, locate and correct the source of the problem and repeat the test for all parameters listed in the method.

**Water:** To demonstrate initial laboratory capability, analyze a minimum of four Commercial Gasoline Spikes in water, at a concentration of 50 µg/L. The accuracy must be within 80 – 120% of the known concentration, with a %RSD of 20% or less. When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must locate and correct the source of the problem and repeat the test for failed parameters of the method.

**Soil:** To demonstrate initial laboratory capability, analyze a minimum of four Commercial Gasoline Spikes in soil, at a concentration of 5 mg/Kg. The accuracy must be within 80 – 120% of the known concentration, with a %RSD of 20% or less. When one or more of the parameters tested fail at least one of the acceptance criteria, the analyst must locate and correct the source of the problem and repeat the test for failed parameters of the method.

## 10.2 Blank

**10.2.1** A water Blank must be run with every analytical sequence containing water samples, utilizing the same water used to prepare standards and make dilutions. The concentration of the blank must not exceed the laboratory reporting level.

Water Blanks are analyzed after samples suspected of being highly concentrated, to prevent carryover.

**10.2.2** A reagent Methanol Blank must be run with each analytical sequence containing soil samples, utilizing the same water used to prepare standards and dilute extracts and a methanol spike of 100µL. The amount of material in the blank must not exceed the laboratory reporting level.

## 10.3 Calibration Verification Standard / Laboratory Control Sample (LCS)

The calibration curve must be verified with each analytical sequence by running a mid-level calibration standard.

**NOTE:** For soil batches the LCS is also injected with 100 µL methanol.

The response must fall within 20% of the expected response. If the response for the standard varies from the predicted response by more than 20%, the analytical system is examined to determine the cause and corrective action is performed and/or a new continuing calibration standard is prepared and analyzed. If the 20% criteria is still not met, the system must be recalibrated.

Any samples that were analyzed following the standard that did not meet calibration criteria must be reanalyzed. If reanalysis is not possible, the data must be flagged and a narrative submitted for inclusion on the Client report.

## 10.4 Duplicate

A duplicate sample is analyzed once for every 10 samples. The duplicate aliquot is taken from the same sample container and analyzed separately under the same conditions. The %RPD between the sample and duplicate results is calculated, and must be $\leq$ 20%. If this criterion cannot be met, the duplicate is reanalyzed. If failure continues, the data is reported and the nonconformance is narrated.

## 10.5 Matrix Spike

For every 10 water samples analyzed, the lab will analyze a Gasoline Component Spike. The spike must be run through the method in the same manner as samples. The accuracy must be within ± 20% of the known concentration. If the accuracy is outside of acceptance criteria, and the LCS is acceptable, the data is reported and the MS failure is narrated.

## 10.6 Matrix Spike Duplicates

A Matrix Spike Duplicate is performed only upon Client request.

If so requested, for every 10 water samples analyzed, the lab will analyze a set of Duplicate Gasoline Component Spikes in water. The duplicate spikes must be run through the method in the same manner as samples. The accuracy of the 2 water spikes must be within 20% of the known concentration and the %RPD must be 20% or less. If these criteria cannot are not met, and the LCS is acceptable, the data is reported and the MS failure is narrated.

## 10.7 Laboratory Control Sample Duplicates

LCS Duplicates are run at a frequency of 10%. Alternatively, duplicate samples and spike samples can be substituted for the laboratory spiked duplicates at a frequency of 10%. Care must be taken to ensure that the samples are homogenous before analyzing duplicates and spikes.

### 10.8 Surrogates

If surrogate recovery is outside of the established limits of 70 – 130%, verify calculations, dilutions, and standard solutions. Verify instrument performance, including checking for leaks and purge problems if the recovery is low. Low recovery may be due to the sample matrix. The analysis is repeated. If the recovery is less than 70% or, if the analyses cannot be repeated, the data is flagged and a narrative submitted for inclusion on the Client report.

High recoveries may be due to coeluting matrix interference. Surrogate recoveries may be reported as “masked” in high-level samples exhibiting matrix interference. Additionally, the extraction surrogate may be reported as “diluted out” in high-level soil samples that must be diluted for analysis. These samples do not need to be rerun solely to try to bring surrogate recovery into acceptance limits.

### 10.9 Control Limits

The laboratory maintains performance records to document the quality of data that is generated. Method accuracy for samples is assessed and records maintained.

Control limits for the method parameters are generated by the QC staff. The control limits are calculated based on in-house performance data. The limits are compared to the control limits found in the reference method.

### 10.10 Analytical Sequence

The analytical sequence is:

- Calibration Standards (initial) or mid-range Calibration Check Standard (LCS)
- LCS Duplicate (as needed)
- Laboratory Method Blank
- Samples
- Duplicate sample (as needed)
- Matrix Spike (as needed)
- Matrix Spike Duplicate (as requested)

## 11. Method Performance

The Method Detection Limit study for waters is prepared using a commercial gasoline mixture spiked into blank water and calculated against the ten component standard.

The MDL study for soil is prepared using a commercial gasoline mixture spiked into blank sand, methanol extracted and calculated against the ten component GRO standard.

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

Method performance data is on file in the laboratory QC department. Comparison of method performance data for the laboratory to the reference method criteria occurs when laboratory in-house acceptance limits are generated. In-house generated data must be within the specifications of the reference method or the analysis is not continued until corrective action is completed.

# 12. Corrective Actions

Holding time exceedence, improper preservation and observed sample headspace are noted on the nonconformance report form.

Perform routine preventative maintenance following manufacturer's specification. Record all maintenance in the instrument logbook.

Review of standards, blanks and standard response for acceptable performance occurs for each batch of samples. Record any trends or unusual performance on a nonconformance action form.

If the CV or LCS recovery of any parameter falls outside the designated acceptance range, the laboratory performance for that parameter is judged to be out of control, and the problem must be immediately identified and corrected. The analytical result for that parameter in the unspiked samples is suspect and is only reported for regulatory compliance purposes with the appropriate nonconformance action form. Immediate corrective action includes reanalyzing all affected samples by using any retained sample before the expiration of the holding time.

# 13. Pollution Prevention

See Chemical Hygiene Plan for pollution prevention operations.

# 14. Waste Management

See Chemical Hygiene Plan for waste handling and disposal.

# 15. Attachments

**Table 1:** Gasoline Component Standards and Concentrations

# Table 1

## Gasoline Component Standards and Concentrations

| COMPONENT | CONCENTRATION, µg/mL |
|---|---|
| Methyl-t-butylether | 1000 |
| Benzene | 1000 |
| Toluene | 1000 |
| Ethylbenzene | 1000 |
| m-Xylene | 1000 |
| p-Xylene | 1000 |
| o-Xylene | 1000 |
| 1,2,4-Trimethylbenzene | 1000 |
| 1,3,5-Trimethylbenzene | 1000 |
| Naphthalene | 1000 |
| | TOTAL 10,000 |