OKLAHOMA DEPARTMENT OF ENVIRONMENTAL QUALITY

METHODS 8020/8015 (MODIFIED)

GASOLINE RANGE ORGANICS (GRO)

1. SCOPE AND APPLICATION:

1.1. This method is designed to measure the concentration of gasoline range organics in water and soil. This corresponds to a hydrocarbon range of C_6-C_{10} and a boiling range between approximately 60^{o}C and 220^{o}C.

1.2. The Practical Quantitation Limit (PQL) of this method for total gasoline range organics is approximately 20 ug/l for waters and 100 ug/kg for soils, with the PQL for individual components being 2 ug/l for waters and 10 ug/kg for soils.

1.3. This method is based on a purge-and-trap gas chromatography procedure. This method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographic data. The analysts should be skilled in the interpretation of gas chromatographs and their use as a quantitative tool.

1.4. Through the use of PID/FID in series, this method can be used for the specific determination of petroleum volatile organic compounds (PVOC) as specified in EPA Method 8020. The Gasoline Component Standard may be used as the PID calibration standard for the determination of PVOCs.

2. SUMMARY OF METHOD:

2.1. This method provides the gas chromatographic conditions for the detection of volatile petroleum fractions such as gasoline. Samples are analyzed using purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID) with photoionization detector (PID) in series. Quantitation of total gasoline range organics (TGRO) is based on the FID response to the GRO calibration standard while quantitation of the petroleum volatile organic compounds (PVOC) is based on the PID response to that standard.

2.2. This method is suitable for the analysis of waters, soil, and wastes. Samples can be analyzed directly for GRO by purge-and-trap extraction and gas chromatography. Soils or waste samples may be dispersed in methanol to

dissolve the volatile organic constituents. A portion of the methanolic solution is then analyzed by purge-and-trap gas chromatograph.

2.3. This method is based in part on: 1) USEPA SW-846: Methods 5030, 8000, 8015, and 8020; 2) a single laboratory method evaluation study conducted by the American Petroleum Institute; 3) work by the EPA Total Petroleum Hydrocarbons Committee; and 4) work by the Wisconsin Ad-Hoc Committee on LUST Program Analytical Requirements and Wisconsin State Laboratory of Hygiene.

3. DEFINITIONS:

3.1. Gasoline Range Organics (GRO): All chromatographic peaks eluting between methyl-tertiary-butylether and naphthalene. Quantitation is based on a direct comparison of the area within this range to the total area of the ten components of the Gasoline Component Standard.

3.2. Gasoline Component Standard: A ten component blend of typical gasoline compounds (see Table 1). This standard serves as the quantitation standard and retention time windows for GRO and PVOCs.

3.3. Gasoline Component Spike: A duplicate reagent water, method blank, or matrix sample spiked with the Gasoline Component Standard and analyzed along with samples as a quality control check

3.4. Trip Blank: A vial of water supplied by the laboratory, treated in the same manner as sample vials, and carried along with samples to ensure that any contamination found in the samples is in fact in those samples

3.5. Other terms as defined in SW-846.

4. INTERFERENCES:

4.1. High levels of heavier petroleum products such as diesel fuel may contain some volatile components producing a response within the retention time range for GRO. Other organic compounds, such as chlorinated solvents, ketones and ethers are measurable. As defined in this method, the GRO results include these compounds. Neat products should be quantified by specific analysis for the product in question. (The term "neat product" is defined as a product containing only a single compound.) An example of this is a storage tank or a spill of benzene.

4.2. Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and/or storage. Trip blanks should be

carried through sampling and subsequent storage and handling to serve as a check on such contamination.

4.3. Contamination can occur by carryover whenever high-level and low-level samples are analyzed sequentially. To prevent such carryover, the syringe and sparging tube must be thoroughly washed with detergent and reagent water and then dried in a 105^{o}C oven between analyses. The trap and other parts of the system may also be contaminated, therefore, a frequent bake-out and purging of the entire system is highly recommended. A screening step is recommended to protect the analytical instrumentation. A method blank of organic-free water is run through this method before processing any samples in order to demonstrate that the system is free of interferences. Additional method blanks must be analyzed after every ten samples, at a minimum, to demonstrate that the system is free of carryover. If, in the professional judgement of the analyst, carryover may have occurred, the sample must be reanalyzed. If a blank exceeds the minimum threshold (PQL) for the analysis, the samples in the preceding set must be reanalyzed.

4.4. It is highly desireable that moisture control equipment be installed as part of the purge-and-trap system, as some users have experienced difficulties in obtaining proper separation of the MTBE solvent peak from the FID solvent front without such equipment.

5. SAFETY ISSUES:

The toxicity or carcinogenity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

6. APPARATUS

6.1. Gas Chromatograph: Analytical system complete with a programmable gas chromatograph suitable for purge-and-trap sample introduction, a data system to measure peak areas, and all required accessories (detector, column, supplies, etc.).

6.1.1. GC Column: A capillary column such as a 30 m x 0.53 mm I.D., 3.0 µ film DB-5, or any other column capable of resolving typical gasoline components. It must also resolve methyl-tertiary-butylether from the methanol solvent peak and ethylbenzene from m/p-xylene. Although a suitable packed column may be found, it is recommended that a capillary column be used to attain the

required resolution. Typical chromatograms are attached at the end of this document.

6.1.2. Detector: Flame ionization detector and photoionization detector in series.

6.1.3. Purge-and trap device: The purge-and-trap device consists of three major components: the sample purger, the trap, and the desorber. Several complete devices are available commercially.

6.1.3.1. A 5-ml capacity needle sparge tube is recommended for use with water samples. A 25-ml capacity needle sparge tube may be used for soil analysis. Commercially-available products include: Tekmar needle sparge glassware, 5 ml, 1/2", #14-2052-024 and Tekmar Test tube soil sampler, 3/4", #12-0507-024. Alternate purge devices may be used if equivalent performance can be demonstrated.

6.1.3.2. The recommended trap should be at least 25 cm long and have an inside diameter of at least 0.105 in., such as the Tekmar Trap I. The trap length and packing may be varied as long as equivalent performance is verified. Prior to initial use, the trap should be conditioned overnight at 180^{o}C by backflushing with an inert gas flow of at least 20 ml/min. The trap effluent should be vented to the hood, not the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 180^{o}C with backflushing. Traps other than the recommended trap should be desorbed 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 sample analysis.

6.1.3.3. The desorber should be capable of rapidly heating the trap to 180^{o}C for desorption.

6.2. Balances: A balance capable of accurately weighing 0.0001 g should be used for the preparation of standards. A top-loading balance capable of weighing to the nearest 0.1 g is suitable for sample weights.

6.3. Sample vials: Waters: 40 ml glass vials with teflon/silicone septa; soils: any glass container with teflon or aluminum foil lined lid.

6.4. Syringes: 5 ml glass hypodermic syringe with Luerlock tip, such as Hamilton 1005TEFLL, and a 5 ml gas-tight syringe with shut-off valve. Gas-tight microsyringes in the appropriate sizes in the range of 1 ul to 500 ul.

6.5. Volumetric Flasks: Appropriate sizes with ground-glass stoppers.

6.6. Disposable pipets: Pasteur-type, 5.75 in, or equivalent.

6.7. Spatula/scoop: Stainless steel.

7. REAGENTS

7.1. Reagent water: Organic-free water.

7.2. GRO-free sand.

7.3. Methanol: Any grade is acceptable provided it is proven to be interference-free.

7.4. Stock Standard Solutions: Preparation of stock standard solutions should be performed using appropriate volumetric glassware. Solutions should be stored in Teflon-sealed screw-cap bottles, with minimal headspace, at -10^{o}C to -20^{o}C, protected from light.

7.4.1. Stock GRO Standard : An acceptable stock standard for GRO components is the commercially-available standard as described in Table 1. The following procedure is provided as an alternative to commercially-available and certified solutions. Standards should be replaced after six months, or sooner if comparison with check standards indicates a problem.

7.4.1.1. Place about 8 ml of methanol in a 10 ml tared, ground-glass stoppered volumetric flask. Allow the flask to stand unstoppered for about 10 minutes, or until all methanol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.4.1.2. Using a 500-ul syringe, immediately add 200 ul to 300 ul of the gasoline standard to the flask. [The liquid must fall directly into the methanol without contacting the neck of the flask.] Reweigh the flask.

7.4.1.3. Dilute to volume, stopper, and mix by inverting the flask three times. Calculate the concentration in ug/ml from the net gain in weight. (When compound purity is assayed at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard.)

7.4.2. Calibration Standards: Prepare calibration standards at a minimum of three concentration levels in organic-free water from the stock GRO standard. One of the concentration levels should be at the PQL of the individual components, while the remaining levels should correspond to the working range of the GC.

8. SAMPLE COLLECTION, PRESERVATION, AND HANDLING:

8.1. Water samples should be collected in triplicate without agitation and without headspace in contaminant-free, glass, 40 ml vials with Teflon-lined septa in the caps. The teflon liner must contact the sample. Cool samples to 4° C immediately after collection, and hold a 4° C

8.1.1. Samples must be collected in such a way that no air bubbles pass through the sample as the container is filled and that no air is trapped in the sample after it is sealed. The seal must be maintained until the time of analysis.

8.1.2. Water samples must be preserved with HCl at the time of collection. A few drops of concentrated acid should be sufficient to bring the pH below 2. [Sample bottles containing the preservative acid may be supplied by the laboratory in lieu of this field preservation, and should be so noted on the sample collection document].

8.2 Soil samples may be collected and stored on ice in ENCORE samplers, or other equivalent sampling devices. Any clean glass container may suffice provided the lid is lined with aluminum foil or teflon and the container is filled as full as possible. These should be collected in sufficient number to provide for backup analysis in the event of breakage and to allow screening. Every effort should be made to minimize handling and avoid excessive disturbance of the soil sample.

8.3. A trip blank must be included with each sample set. If one is not provided, the laboratory must include a note to this effect on the final analytical report for each sample within that set.

8.4. All samples must be analyzed within 14 days of collection.

9. ANALYTICAL PROCEDURE:

9.1. Volatile compounds are introduced into the gas chromatograph through a purge-and-trap apparatus. Samples emitting a noticeable odor will need to be diluted prior to initial analysis. Professional judgement should be used by the analysts in the need for, or extent of, dilution priorto initial analysis. Concentrations noted will be reported in ug/l for water samples and ug/kg for soil samples (on a wet-weight basis).

9.2. Gas Chromatography: Chromatographic conditions for the recommended column are set forth in Table 2. Conditions may be altered as necessary to improve resolution of the gasoline range organics. If a column other than the recommended column is used, set the GC conditions to meet the criteria set forth in 6.1.1.

9.3. Retention Time Window and Quantitation:

9.3.1. The retention time window for total GRO is defined as beginning approximately 0.1 min before the retention time of methyl-tertiary-butylether and ending 0.1 min after the retention time of naphthalene in the calibration run. Retention time windows for the individual components are similarly established as ± 0.1 min of the retention times in the calibration run.

9.3.2. Quantitation is based on a direct comparison of the area within the range to the total area of the components in the gasoline component standard, using a "baseline -to-baseline" integration, as opposed to a "valley-to-valley" integration.

9. 4. Sample Screening and Analysis

9.4.1. Samples should be initially screened by the analyst to determine the probability of contamination. Indicators such as odor, appearance, and source will be considered by the analyst in the determination of whether, and to what extent, the samples should be diluted prior to initial analysis on the GC.

9.4.1.1. Water samples are to be analyzed as follows: Place 5 ml of sample into a sparge tube using a 5 ml Luerlock syringe and initiate the analysis program.

9.4.1.2. Soil samples are to be analyzed as follows: Place a known weight of sample into a sparge tube containing 5 ml of organic-free water and initiate the analysis program.

9.4.2. If the screening process indicates GRO contamination that is beyond the calibration range of the instrument, proceed as follows:

9.4.2.1. Water samples are diluted as follows: Dilute a known volume of the sample, not to exceed 5 ml, in 10 ml of methanol , then inject a known volume of this mixture into 5 ml of organic-free water within a sparge tube and initiate the analysis program. Either or both the sample amount and/or the mixture amount injected into

the sparge tube may vary according to the analyst's assessment of the sample in question.

9.4.2.2. Soil samples are diluted as follows: Place a known weight of the sample, not to exceed 5 g, into 10 ml of methanol;, then, inject a known volume of this mixture into 5 ml of organic-free water within a sparge tube and initiate the analysis program. Either or both the sample amount and/or the mixture amount injected into the sparge tube may vary according to the analyst's assessment of the sample in question.

NOTE:The amount of methanol injected into the sparge tube will, if continuously increased, eventually mask the benzene peak.

9.4.3. If the initial analysis of a sample or a dilution of a sample is found to have a concentration of analytes that exceeds the initial calibration range, that sample must be reanalyzed at a higher dilution. The degree of dilution will be considered adequate when response to all analytes in question are within the calibration range.

9.5. Calculations: From linear regression of the GC responses to the calibration standard (R) against their known concentrations (C in ug/l) derive the following linear equation:

$$C = mR + b$$

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

Water Samples: $C_S = (mR_S + b)(D)$

Soil Samples: $C_S = [(mR_S + b)(D)(V_t)(K)] / [(V_p)(W)]$

Where:

C_S =Concentration of the sample in ug/l for waters and ug/kg on a wet-weight basis for soils;

m = Slope of the calibration curve;

R_S = GC response of the sample within the GRO retention time window;

b = Intercept of the calibration curve;

D = Dilution factor if sample was diluted;

V_t = Total volume of soil extract;

V_p = Volume of soil extract purged;

K = 0.005 l. This constant adjusts for conversion from the dilution of the volume of extract purged up to the 5 mls used for purging.

W = Wet weight of soil sample in kg.

10. CALIBRATION:

10.1. Two multi-level calibrations are required. In each instance, one level at the PQL and a minimum of two other levels represent the working range of the GC. [Total gasoline range organics (TGRO) are calibrated on the flame ionization detector (FID), while the petroleum volatile organic compounds are calibrated on the photoionization detector (PID) using the retention time windows discussed in 9 above.]

10.2. Each day that samples are run, a calibration standard must be analyzed. If the results of that analysis fall within ± 20% of the expected analysis, the system may be considered to be in control and sample analysis may proceed. If that analysis does not meet these criteria, prepare a new working standard and run a full recalibration before proceeding with the sample analysis.

10.3. The correlation coefficient of the calibration curve used to quantitate samples must be at least 0.99. Other criteria may be used to monitor the calibration curve as long as the correlation coefficient is at least 0.99.

11. QUALITY ASSURANCE/QUALITY CONTROL:

11.1. The analyst must make an initial demonstration of the ability to generate acceptable accuracy and precision with this method by successful analysis of the following:

11.1.1. Analysis of 7 replicates of organic-free water spiked with the gasoline component standard at a concentration of 2 ug/l for each individual component with recoveries for all components within ± 30% of the known concentration and precision of all replicates within ± 20%.

11.1.2. Analysis of 7 replicates of GRO-free sand spiked with the gasoline component standard at a concentration of 10 ug/kg for each individual component with recoveries for all components within ± 40% of the known concentration and precision of all replicates within ± 20%.

11.2. A method blank of organic-free water is run through this method before processing any samples in order to demonstrate that the system is free of interferences. Additional method blanks must be analyzed after every ten samples, as a minimum, to demonstrate that the system is free of carryover. If, in the professional judgement of the analyst, carryover may have occurred, the sample must be reanalyzed. If a blank exceeds the minimum threshold (PQL) for the analysis, the samples in the preceding set must be reanalyzed.

11.3. Duplicate gasoline component spikes must be run with every batch of 10 samples or less, regardless of whether the samples are waters or soils. The laboratory must analyze these spikes in the same manner as samples. Accuracy and precision of the duplicate water spikes must be within 20% of the known individual component concentration, whereas that of duplicate soil spikes must be within 40% of the known indvidual component concentration.

11.4. A reagent methanol blank should be analyzed. If contamination is noted it is the responsibility of the laboratory to determine the source of contamination.

11.5. The correlation coefficient of the calibration curve used to quantitate samples must be at least 0.99. Other criteria may be used to monitor the calibration curve as long as the correlation coefficient is at least 0.99.

11.6. If any of the above criteria are not met, the problem must be identified and corrected before further sample analysis may proceed. Any samples run between the last QC samples that meet the criteria and those that fail to do so must be rerun. If this is not possible, the data must be flagged as suspect and so noted in the final report of the analysis.

11.7. The laboratory will maintain appropriate quality control charts of the accuracy and precision of each component of the duplicate spikes in order to identify possible trends before the system goes out of the acceptable limits on accuracy and precision.

12. METHOD PERFORMANCE:

The recommended practical quantitation limits (PQL) are as listed in Table 3.

TABLE 1

GASOLINE COMPONENT STANDARD

Commercially available from Supelco Inc as the UST Modified Gasoline Range Organics, Supelco Part # 4-8187, in a concentration of 1000 ug/ml of each component in methanol:

Benzene	1,2,4-Trimethylbenzene

Ethylbenzene
Methyl-tert-Butyl Ether
Naphthalene
Toluene
1,3,5-Trimethylbenzene
m-Xylene
o-Xylene
p-Xylene

TABLE 2

RECOMMENDED CHROMATOGRAPHIC CONDITIONS

Initial Settings:

Inlet A: 200°C
Detector A: 250°C
Inlet B: 250°C
Oven Equilibrium Time = 1.00 min.
Maximum Oven Temperature: 260°C

Oven Program Set Points:

Initial Temperature: 50°C; Initial Time: 4.00 min.

Level	Rate (°C/min)	Final Temp (°C)	Final Time (min)
1	5.0	150	0.00
2(A)	10.0	200	2.00
3(B)	20.0	250	2.50

Purge-And-Trap Parameters:
Purge Gas: Nitrogen or Helium
Purge gas flow rate: 40 ml/min @ 20 psi
Purge time: 11.0 ± 1.0 min
Purge temperature: Ambient
Desorb Temperature: 200°C for 6 min.
Bake Temperature: 250°C for 8 min.

TABLE 3

RECOMMENDED PRACTICAL QUANTITATION LIMITS

PARAMETER	WATER (ug/l)	SOIL (ug/kg)
Total Gasoline Range Organics	20	100
Benzene	2	10
Toluene	2	10

Ethylbenzene	2	10
m-Xylene	2	10
o-Xylene	2	10
p-Xylene	2	10
1,2,4-Trimethylbenzene	2	10
1,3,5-Trimethylbenzene	2	10
Naphthalene	2	10
Methyl-tert-Butylether	2	10