OA-1

METHOD FOR DETERMINATION OF VOLATILE PETROLEUM HYDROCARBONS (GASOLINE)

REVISION 7/27/93

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of volatile petroleum hydrocarbons and other individual components such as Benzene, Toluene, Ethylbenzene, Xylenes, Methyl Ethyl Ketone, and Methyl t-Butyl Ether in water and soil/solids.

2.0 SUMMARY OF METHOD

2.1 This method provides gas chromatographic conditions for the detection of certain volatile petroleum fractions such as gasoline. Samples are analyzed utilizing purge-and-trap sample concentration. A temperature program is used in conjunction with the gas chromatograph to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID) or FID with photoionization detector (PID) in series or mass spectrometer (MS). PID only is not acceptable for quantitation of the petroleum hydrocarbons. Note: Highly contaminated soil may require MS or PID for the determination of Benzene, Toluene, Ethylbenzene, and Xylenes.

2.1.1 Identification of various petroleum products is performed by comparison of the chromatograms of samples and commercial products. Quantitation is based on detector response to an external standard of commercial product.

2.2 If the preceding sample introduction techniques are not applicable due to high level contamination, a portion of the sample is dispersed in methanol to dissolve the volatile organic constituents. A portion of the methanolic solution is combined with water in a purging chamber, and analyzed by purge-and-trap GC following the standard procedure for water samples.

2.3 This method is based on USEPA SW-846 methods 5030, 8000, and 8015 and American Petroleum Institute (API) "Method for Determination of Gasoline Range Organics, Revision 4". The components standard specified in the API method may only be used to quantitate individual components.

3.0 INTERFERENCES

3.1 High levels of heavier petroleum products such as diesel fuel may contain some volatile components producing a response within the retention range for gasoline. These heavier products may also require extensive column baking between sample analyses, particularly with the packed columns (Columns 1 and 2).

3.2 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage. A trip blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.3 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. If a solvent is used then the device must be dried to remove the solvent. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of a blank of reagent water to check for cross contamination. 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 105°C oven between analyses. The trap and other parts of the system such as autosampler valves, etc. are also subject to contamination; therefore frequent bake-out and purging of the entire system may be required.

3.4 Impurities in the purge gas and organic compounds out-gassing from plumbing prior to the trap account for many contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-TFE plastic coating, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; 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. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.

5.0 APPARATUS AND MATERIALS

5.1 Gas chromatograph

5.1.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for purge-and-trap sample introduction and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system capable of determining peak height and/or areas is recommended. A gas chromatograph/mass spectrometer system may also be used.

5.1.2 Columns:
5.1.2.1 Column 1: 6-ft x 0.1-in I.D. stainless steel or glass column packed with 1% SP-1000 on Carbopack-B 60/80 mesh or equivalent.

5.1.2.2 Column 2: 6-ft x 0.1-in I.D. stainless steel or glass column packed with n-octane on Porasil-C 100/120 mesh (Durapak) or equivalent.

5.1.2.3 Column 3: 60-m x 0.75 mm VOCOL capillary column or equivalent.

5.1.2.4 Column 4: 30-m x 0.53 mm J&W DB-1 capillary column, 5 micron film thickness, or equivalent.

5.1.2.5 Column 5: 105-M x 0.53-mm I.D. Restek RTX 502.2, 3 micron film thickness, or equivalent.

5.1.3 Detector: Flame ionization (FID), or photoionization detector (PID) in series with an FID. If GC/MS is used, the total ion chromatogram may be used in place of the FID chromatogram, and quantitation of individual compounds (benzene, toluene, total xylenes, and surrogates) is performed using the customary quantitation ions as in SW-846 method 8240.

5.2 Syringes: 5-mL Luerlok glass hypodermic and a 5-mL gas-tight syringe with shutoff valve.

5.2.1 For purging large sample volumes for low detection limit analysis of aqueous samples for petroleum products, 25- or 50-mL syringes may be used. Subsequently substitute the appropriate volume in the method wherever 5-mL is stated when low detection limits are required.

5.3 Volumetric flask: 10-,50-,100-, 500, and 1,000-mL with a ground-glass stopper.

5.4 Microsyringes: 1-µL, 5-µL, 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL.

5.5 Syringe valve: Two-way, with Luer ends (three each), if applicable to the purging device.

5.6 Balance: Analytical, capable of accurately weighing to the nearest 0.0001-g, and a top-loading balance capable of weighing to the nearest 0.1-g.

5.7 Glass scintillation vials: 20-mL, with screw-caps/crimp caps and Teflon liners or glass culture tubes with a screw-cap and Teflon liner.

5.8 Spatula: Stainless Steel.

5.9 Disposable pipets: Pasteur.

5.10 Purge-and-trap device: The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

5.10.1 The recommended purging chamber is designed to accept 5-mL samples with a water column at least 3-cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15-mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3-mm at the origin. The purge gas must be introduced no more than 5-mm from the base of the water column. For soil samples, a needle sparger with detachable purge vessel suitable for 5-gram soil sample and reagent addition (including 5-mL of reagent water) is required. Alternate sample purge devices may be used, provided equivalent performance is demonstrated.

5.10.2 The trap must be at least 25-cm long and have an inside diameter of at least 0.105-in. Starting from the inlet, the trap may be packed with the following adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0-cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap. If the determination of dichlorodifluoromethane or other fluorocarbons of similar volatility is not

required, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Prior to initial use, the trap should be conditioned according to manufacturer instructions. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. 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 samples.

5.10.3 The desorber should be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake-out mode.

5.10.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph.

5.10.5 Trap Packing Materials. Prepared traps are also available commercially.

5.10.5.1 2,6-Diphenylene oxide polymer: 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

5.10.5.2 Methyl silicone packing: OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

5.10.5.3 Silica gel: 35/60 mesh, Davison, grade 15 or equivalent.

5.10.5.4 Coconut charcoal: Prepare from Barnebey Cheney, CA-580-26 lot #M-2649, by crushing through 26 mesh screen.

5.11 Heater or heated oil bath: Should be capable of maintaining the purging chamber to within 1°C over a temperature range from ambient to 40°C.

6.0 REAGENTS

6.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit (MDL) of the analytes of interest.

6.2 Stock standards: Stock solutions may be prepared from commercial alcohol-free gasoline. A different stock solution is prepared for the individual components benzene, toluene, ethylbenzene, and xylenes. Prepare stock standards in methanol.

6.2.1 Place about 9.8-mL of methanol in a 10-mL tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1-mg.

6.2.2 Using a 100-µL syringe, immediately add two or more drops of commercial product or standard to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

6.2.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in micrograms per microliter (µg/µL) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.2.4 Transfer the stock standard solution into a Teflon-sealed screw-cap/crimp-cap bottle. Store, with minimal headspace, at approximately -10°C to -20°C and protect from light.

6.2.5 Standards must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

6.3 Secondary dilution standards: Using stock standard solutions, prepare secondary dilution standards in methanol, as needed. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Section 6.4 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.4 Calibration standards: Calibration standards at a minimum of three concentration levels are prepared in reagent water from the secondary dilution of the stock standards. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. One set of standards must include the appropriate commercial material(s) for identification and quantitation while another set would include individual compounds. In order to prepare accurate aqueous standard solutions, the following precautions must be observed.

6.4.1 The volume of alcoholic standards injected into reagent water must be monitored to prevent methanol from obscuring the gasoline chromatograms.

6.4.2 Use a microsyringe such as a 25-µL Hamilton 702N or equivalent (variations in needle geometry may adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

6.4.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

6.4.4 Mix aqueous standards by inverting the flask three times only.

6.4.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

6.4.6 Aqueous standards are not stable and should be discarded after 1 hr, unless properly sealed and stored. The aqueous standards can be stored up to 24 hr, if held in sealed vials with zero headspace.

6.4.7 An alternative is to prepare calibration standards directly into the 5-mL or 25-mL syringe.

6.5 Surrogate standards: The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two surrogate compounds, chlorobenzene, trifluorotoluene, and/or bromofluorobenzene. From stock standard solutions prepared as in Section 6.2, prepare a secondary dilution in methanol resulting in a final concentration of 300- to 600-ng/µL of each surrogate (or an appropriate level to achieve peak determination). Add 0.5- to 1.0-µL of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed; the smaller quantity is generally appropriate for capillary columns, the larger for packed columns.

6.6 Methanol: pesticide quality or better. Store away from other solvents.

7.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

7.1 A representative sample with minimal opportunity for loss of volatiles must be taken. Aqueous samples should be collected in duplicate or triplicate without agitation and without headspace in contaminant-free glass 40-mL vials with Teflon-lined septa in the caps. Aqueous samples to be analyzed for aromatic hydrocarbons should be preserved with 1:1 Hydrochloric acid. The Teflon layer must contact the sample. Soils may be collected in the same type of containers or in 4 oz. wide-mouth soil bottles with Teflon-lined lids; the latter container may be more easily filled, depending on soil consistency, but it may not provide the hermetic seal desired for optimal preservation of volatiles. Soils should be disturbed as little as possible and containers filled as full as possible. Refrigerate samples after collection and transport to the laboratory as quickly as possible.

7.2 Volatile samples, especially those to be analyzed for the aromatics (benzene, toluene, and total xylenes) should be analyzed as soon after collection as possible. Extensive holding time studies are not currently available for volatile petroleum products, but a typical volatile holding time of 14 days is suggested.

8.0 PROCEDURE

8.1 Volatile compounds are introduced into the gas chromatograph by purge-and-trap. Purge-and-trap may be used directly on ground water samples or low-level contaminated soils and sediments. For high-level soils or sediments, methanolic extraction may be necessary prior to purge-and-trap analysis.

8.2 Gas chromatography conditions (Recommended):

8.2.1 Column 1: Set helium gas flow at 40-mL/min flow rate. Set column temperature at 50°C for 3 min; then program an 8°C/min temperature rise to 220°C and hold for 15 min or longer as necessary to elute late peaks.

8.2.2 Column 2: Set helium gas flow at 40-mL/min flow rate. Set column temperature at 50°C for 3 min; then program a 6°C/min temperature rise to 170°C and hold for 4 min or longer as necessary to elute late peaks.

8.2.3 Column 3: Set helium gas pressure to column appropriately to obtain good resolution and separation of commercial gasoline for identification of product. Set column temperature at 50°C for 4 min; then program at 5°C/min. to 250°C and hold for 15 min., or longer as necessary to elute late peaks.

8.2.4 Column 4: Set helium gas pressure to column appropriately to obtain good resolution and separation of commercial gasoline for identification of product. Set column temperature at 40°C for 6 min; then program at 5°C/min to 260°C and hold for 5 min., or longer as necessary to elute late peaks.

8.2.5 Column 5: Set column pressure to 20 # or appropriately to obtain good resolution and separation of commercial gasoline for identification of product. Set column temperature at 40°C for 1 min; then program at 5°C/min. to 100°C; then 8°C/min. to 260°C and hold for 7.5 min. Conditions may be altered to improve resolution.

8.3 Calibration:

8.3.1 Prepare final solutions containing required concentrations of calibration standards, including surrogate standards, as indicated in Section 6.4. Proceed with purge-and-trap analysis procedure.

8.3.2 Run identification standards of commercial materials at a minimum of three concentration levels above detection limits and covering the expected range of samples or the linear range of the instrument.

8.3.3 External standard calibration procedure:

8.3.3.1 For quantitation utilizing the commercial material most nearly matching the sample and appropriate individual compounds (benzene, toluene, total xylenes, and surrogates), prepare calibration standards as indicated in Section 6.4. One of the external standards should be at a concentration near, but above, the method detection limit. The other concentrations should correspond to the expected range of concentrations found in samples or should define the working range of the detector.

8.3.3.2 Inject each calibration standard utilizing the purge-and-trap. Tabulate peak height and/or area response against mass injected. The results can be used to prepare a calibration curve for the detector. A correlation coefficient of 0.995 or higher should be obtained. Alternatively, the ratio of the response to the amount injected, defined as the response factor (RF), can be calculated for each analyte at each standard concentration. If the percent relative standard deviation (%RSD) of the response factor is less than 20% over the working range, linearity through the origin can be assumed, and the average response factor can be used in place of a calibration curve.

$$\text{Response Factor} = \frac{\text{Mass injected(in nanograms)}}{\text{Total area of peak}}$$

8.3.3.3 The working calibration curve or response factor must be verified on each working day by the injection of one or more calibration standards. If the response for the standard varies from

the predicted response by more than +/- 20%, a new calibration curve must be prepared for that analyte.

$$\text{Percent Difference} = \frac{R1 - R2}{R1} \times 100$$

where:

R1 = Response Factor from average response factor of the current calibration curve.
R2 = Response Factor from daily standard.

8.4 Retention Time Windows:

8.4.1 Before establishing windows, be certain that the GC system is within optimum operating conditions. Make three injections of all single component standard mixtures (surrogate standards and appropriate individual compounds such as benzene, toluene, and total xylenes) and multiresponse products throughout the course of a 72 hr period. Serial injections over less than a 72 hr period may result in retention time windows that are too tight.

8.4.2 Calculate the standard deviation of the three absolute retention times for each single component standard. For multiresponse products, choose one or more major peak(s) from the envelope and calculate the standard deviation of the three retention times for that peak.

8.4.2.1 The retention time window is defined as plus or minus three times the standard deviation of the absolute retention times for each standard; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. For multiresponse petroleum products, the analyst should use the retention time window but should primarily rely on pattern recognition.

8.4.2.2 In those cases where the standard deviation for a particular standard is zero, the laboratory must substitute the standard deviation of a close eluting, similar compound to develop a valid retention time window.

8.4.3 The laboratory should calculate retention time windows for each standard on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

8.5 Gas chromatographic analysis:

8.5.1 Aqueous samples: Introduce volatile compounds into the gas chromatograph using the purge-and-trap method. Add 0.5- to 1.0-µL of surrogate standard to the sample prior to purging.

8.5.1.1 Adjust the purge gas flow rate (nitrogen or helium) to 25-40-mL/min on the purge-and-trap device.

8.5.1.2 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0-mL. This process of taking an aliquot destroys the validity of the liquid

sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe or a smaller VOA vial at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hr. Care must be taken to prevent air from leaking into the syringe.

8.5.1.3 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

8.5.1.4 Dilutions may be made in volumetric flasks (10-mL to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

8.5.1.5 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this volume of reagent water to the flask.

8.5.1.6 Inject the proper aliquot of samples from the syringe prepared in Paragraph 8.5.1.2 into the flask. Dilute the sample to the mark with reagent water. Cap the flask, and invert three times. Repeat the above procedure for additional dilutions. Alternatively the dilutions can be made directly in the glass syringe to avoid further manipulation of the sample and loss of volatiles.

8.5.1.7 Fill a 5-mL syringe with diluted sample as in Paragraph 8.5.1.2.

8.5.1.8 Add 0.5- to 1.0-µL of surrogate spiking solution through the valve bore of the syringe; then close the valve.

8.5.1.9 Attach the syringe-syringe valve assembly to syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

8.5.1.10 Close both valves and purge the sample for 9-12 min.

8.5.1.11 At the conclusion of the purge time, attach the trap to the chromatograph, adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly heating the trap to 180°C and backflushing the trap with inert gas for 4 minutes.

8.5.1.12 While the trap is desorbing into the gas chromatograph, empty the purging chamber. Purge vessels should be cleaned prior to subsequent analyses to avoid carryover of pollutant compounds.

8.5.1.13 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 sec; then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C. Trap temperatures up to 220°C may be employed; however, the higher temperature will shorten the useful life of the trap. After approximately 7-35 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

8.5.1.14 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 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.

8.5.1.15 All dilutions should keep the response of the major constituents (previously saturated peaks) in the linear range of the curve.

8.5.2 Low-level method for soils/sediments: This is designed for samples containing individual purgeable compounds of <1-mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-level method is based on purging a heated sediment/soil sample mixed with reagent water containing surrogate standard. Analyze all reagent blanks and standards under the same conditions as samples.

8.5.2.1 Recommended sample weights are 5-g. If quantitation limits needed (per data quality objectives in the sampling and analysis plan) can be met, 1-g sample weights or the high level protocol (see section 8.5.3) may be used.

8.5.2.2 The GC system should be set up prior to preparation of the sample to avoid loss of volatiles from standards and samples. A heated purge calibration curve should be prepared and used for the quantitation of all samples analyzed following the low-level soil/sediment procedure. Follow the initial and daily calibration instructions, except for the addition of a 40°C purge temperature.

8.5.2.3 Remove the plunger from a 5-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0-mL. Add 0.5- to 1.0-µL of the surrogate spiking solution to the syringe through the valve.

8.5.2.4 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount determined in Paragraph 8.5.2.1 into a tared purge device. Note and record the actual weight to the nearest 0.1-g.

8.5.2.5 Add the spiked reagent water to the purge vessel, which contains the weighed sample, and connect the vessel to the purge-and-trap system. NOTE: Prior to the attachment of the purge device, steps 8.5.2.4 and 8.5.2.5 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free of solvent fumes.

8.5.2.6 Heat sample to 40°C +/- 1°C and purge sample.

8.5.2.7 Proceed with analysis as outlined in Paragraphs 8.5.1.10-8.5.1.15. If saturated peaks occur or would occur if a 1-g sample were analyzed, the high-level method must be followed.

8.5.2.8 For the reagent blank use 5-mL of the reagent water with surrogate.

8.5.3 High-level method for soil/sediment: Method is based on extracting the sediment/soil with methanol. Waste samples are either extracted or diluted, depending on solubility in methanol. An aliquot of the extract is added to reagent water containing surrogate standard. This is purged at ambient temperature for 9-12 minutes. All samples with a predicted concentration of >1.0-mg/kg should be analyzed by this method.

8.5.3.1 The sample (for volatile organics) consists of the entire contents of the sample container. Do not discard any supernatant liquids. Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and waste that are insoluble in methanol, weigh 5-g (wet weight) into a tared 20-mL vial, using a top loading balance. Note and record the actual weight to 0.1-gram. For waste that is soluble in methanol, weigh 1-g (wet weight) into a tared scintillation vial or culture tube or a 10-mL volumetric flask. (If a vial or tube is used, it must be calibrated prior to use. Calibrate by pipeting 10.0-mL of methanol into the vial and marking the bottom of the meniscus. Discard this solvent.)

8.5.3.2 Quickly add 10-mL of methanol to the vial. For methanol soluble waste dilute to 10-mL with methanol. Cap and shake for 2 min or sonicate for 15 min.

Note: Steps 8.5.3.1 and 8.5.3.2 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in laboratory free from solvent fumes.

8.5.3.3 Pipet approximately 1-mL of the extract to a GC vial for storage, using a disposable pipet. The remainder may be disposed. Transfer approximately 1 - mL of reagent methanol to a separate GC vial for use as method blank for each set of samples. These extracts should be stored at 4 °C in the dark, prior to analysis.

8.5.3.4 The GC system should be set up as in Section 5.0. This should be performed prior to the addition of the methanol extract to reagent water.

8.5.3.5 If a screening procedure was followed, use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-level analysis to determine the appropriate volume. If the sample was submitted as a high-level sample, start with 10-µL for analysis on capillary columns or 25- 50-µL for analysis on packed columns. All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

8.5.3.6 Remove the plunger from a 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to allow for additional amount to be added. Pull the plunger to 5.0-mL to allow volume for the addition of the sample extract and of surrogate standard. Add the volume of methanol extract determined in Paragraph 8.5.3.5, the volume must be carefully monitored to prevent the amount of methanol from obscuring the gasoline. The maximum number of µL of extract to be injected varies with column capacity and instrumentation.

8.5.3.7 Attach syringe-syringe valve assembly to syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

8.5.4 Samples are analyzed in a set referred to as an analysis sequence. The sequence begins with instrument calibration followed by sample extracts interspersed with multilevel calibration standards. The sequence ends when the set of samples has been injected or when qualitative and/or quantitative QC criteria are exceeded.

8.5.5 If the responses exceed the linear range of the system, use a smaller amount of sample or use the high-level procedure for soils, as appropriate.

8.5.6 The response factor for each analyte to be quantitated must not exceed +/- 20% difference when compared to the initial standard of the analysis sequence. When this criterion is exceeded, inspect the GC system to determine the cause and perform whatever maintenance is necessary prior to recalibration and proceeding with sample analysis. All samples that were injected following the standard exceeding QC criteria must be reanalyzed.

8.6 Calculations:

8.6.1 External standard calibration: The concentration of each analyte in the sample may be determined by calculating the absolute weight of analyte purged, from the peak response for individual analytes or a summation of peak response for mixtures such as gasoline, using the calibration curve or the calibration factor determined in Paragraph 8.3.3.2. The concentration of a specific analyte is calculated as follows:

Aqueous samples:

Concentration (µg/L) = [(Ax)(A)(D)]/[(As)(Vs)]

where:

Ax = Response for the analyte in the sample, units in area or height.

A = Absolute weight of standard purged, ng.

As = Response for the external standard, units same as for Ax.

D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

Vs = Volume of sample extracted or purged, mL.

Nonaqueous samples:

Concentration (ng/g) = [(Ax)(A)(D)]/[(As)(W)]

where:

W = Weight of sample extracted or purged, g. The wet weight is used.

Ax, As, A, and D have the same definition as for aqueous samples.

9.0 QUALITY CONTROL

9.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of spiked samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data generated. Ongoing data quality checks are compared with established performance criteria to determine if results of analyses meet the performance characteristics of the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the measurements were performed in an in-control mode of operation.

9.2 Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of sample preparation and measurement steps.

9.3 For each analytical batch (up to 20 samples), a reagent blank, duplicate and spike must be analyzed (frequency of the spikes may be different for different monitoring programs). The blank, duplicate and spike must be carried through all stages of the sample preparation and measurement steps.

9.4 The experience of the analyst performing gas chromatography is invaluable to the success of the methods. Each day that analysis is performed, the daily calibration sample should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still good, the injector is leaking, etc. If any changes are made to the system (e.g. column changed), recalibration of the system must take place.

9.5 Check surrogate standard recovery in all samples, blanks, and spikes. Determine if recovery is within limits (limits established by performing QC procedure outlined in Method 8000, Section 8.10 of SW-846).

9.5.1 If recovery is not within limits, the following is required.

- Check to be certain there are no errors in calculations, surrogate solutions, etc. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

10.0 METHOD PERFORMANCE

10.1 The accuracy and precision obtained will be determined by the sample matrix, sample introduction technique, and calibration procedures used.

10.2 Specific method performance information will be provided as it becomes available. Typical chromatograms of gasoline product with surrogate standards added and purged from water are included at the end of the method; column 1 and column 4 were used. Each laboratory performing this method will need to analyze materials for identification of products using the columns, instruments, data systems, etc. specific to that laboratory.

11.0 REFERENCES

1. United States Environmental Protection Agency, "SW-846 Test Methods for Evaluating Solid Waste", 3rd Ed., Methods 5030, 8000, 8015.

2. American Society for Testing and Materials, "Standard Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography", ASTM 3328-78 (Reapproved 1982).

3. University Hygienic Laboratory, Iowa City, IA, Method 0A-1, previous revisions 7/1/91, 1/10/90.

4. American Petroleum Institute, "Method For Determination of Gasoline Range Organics", Revision 4.