Method AK101

For the Determination of Gasoline Range Organics
Version 04/08/02

1. Scope and Application

1.1 Analytes

1.1.1 This method is designed to measure the concentration of Gasoline Range Organics (GRO) in water and soil. This corresponds to an alkane range from the peak start of n-hexane (C_6) to the peak start of n-decane (C_{10}), and to a boiling point range between approximately 60°C and 170°C (see example of chromatogram in Figure 1 of this method.

1.1.2 Components with boiling points greater than or equal to C_{10} present in products such as diesel or fuel oil are detectable under the conditions of the method.

1.1.3. With the optional photo ionization detector (PID), this method can be extended for specific determination of volatile aromatics (BTEX) as specified in EPA Method SW-846 8021B. **Please be aware that any reference to 8021B is in regard to apparatus and not sample preparation. All AK101 samples must be preserved with methanol.**

1.2 Quantitation Limits

The Practical Quantitation Limit (PQL) of this method for GRO must not exceed 20 mg/kg GRO as gasoline for soils and 100 µg/L GRO as gasoline for water.

1.3 Dynamic Range

Dilutions should be performed as necessary to put the chromatographic envelope within the linear range of the method. In general, the approximate range is 50 to 2,000 µg/L of gasoline.

1.4 Experience

This method is based on a purge-and-trap, Gas Chromatography (GC) procedure. This method must be used by, or under supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs as a quantitative tool.

2. Method Summary

2.1 This method provides gas chromatographic conditions for the detection of volatile petroleum fractions such as gasoline. Other nonpetroleum compounds with similar characteristics and boiling points may also be detected with this method. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. A flame ionization detector (FID), or PID/FID in series, provides detection. Quantitation must be performed by comparing the total chromatographic area between and including C_6 (n-hexane) and C_9 (n-nonane), to the peak start time of C_{10} (n-decane), including resolved and unresolved components, based on FID response compared to a blended commercial gasoline standard (Section 3.2 of this method) and using forced baseline-baseline integration. (See Table 1 of this method for suggestions regarding purge-and-trap operating parameters.)

2.2 Water samples must be analyzed directly for GRO by purge-and-trap extraction and gas chromatography. Soil or waste samples are dispersed in methanol to dissolve and preserve the volatile organic constituents (see Table 2 of this method). A portion of the methanol solution is injected into water, and then analyzed in a manner similar to water analysis. Conversely, methanol extracts may be injected directly into the GC/PID/FID if all quality control criteria of the methods are met.

2.3 Special field sampling techniques are required to minimize the loss of volatile organic compounds from soil. Conventional sampling and sample handling techniques are not acceptable.

2.4 Benzene, toluene, ethylbenzene and total xylene isomers (BTEX) may be determined simultaneously with GRO if the gas chromatograph is outfitted with the optional PID detector, and all requirements of EPA SW-846 Method 8021B are met.

2.5 This version of the method was developed by Mary Jane F. Pilgrim, Ph.D. It is based, in part, on: U.S. EPA SW-846 [1] methods 5030, 8000, 8021B, 8015; a single laboratory method evaluation study conducted by the American Petroleum Institute (API) [2]; work by the EPA Total Petroleum Hydrocarbons Methods Committee [3]; and work by the Alaska Department of Environmental Conservation, State Chemistry Laboratory, with support from the Contaminated Sites Program.

3. Definitions

3.1 Gasoline Range Organics (GRO): All chromatographic peaks, both resolved and unresolved, eluting between the peak start time for C_6 (n-hexane) and the peak start time for C_{10} (n-decane). Quantitation is based on a direct comparison of the baseline - baseline integrated area within this range to the total area of the calibration standard over the same (C_6 - C_{10}) range, using FID response. Surrogate peak areas shall be determined by valley to valley integration.

3.2 Gasoline Calibration Standard (GCS): An equal-weight mixture of regular, plus, and premium grades of commercial gasoline, mixed and diluted to appropriate concentrations, used to prepare a standard curve.

3.3 Calibration Verification Standard (CVS): A gasoline quality control standard (Certified, or equivalent) prepared as in Section 3.2 of this method but with product from a source other than that used to prepare the GCS. This standard serves as a quality control check to verify the accuracy of calibration.

3.4 Continuing Calibration Standard (CCS): A mid-range working standard diluted from the GCS, used to verify that the analytical system is operating in a manner comparable to that at the time of calibration.

3.5 Surrogate: The recommended surrogate is either bromofluorobenzene or α,α,α-trifluorotoluene. Other compounds may be used as a surrogate if they are non-polar, purgeable from water and methanol, and do not co-elute with any significant component of the GCS and elute prior to the start of C_{11}. Surrogates may be added in the field or the laboratory or both.

3.6 Surrogate Blank: A laboratory or field blank sample spiked with the surrogate used in the sample batch. The surrogate recovery is used to evaluate method control (see Section 7.3 of this method).

3.7 Laboratory Fortified Blank (LFB): A method blank sample spiked with a commercial gasoline or blend of gasoline. The spike recovery is used to evaluate method control. The CVS may be used as the Laboratory Fortified Blank.

3.8 Retention Time Window Standard: A normal alkane standard containing n-hexane and n-decane (C_6 and C_{10}) which is analyzed once per 24 hour day or with each batch of samples, whichever is less frequent, not to exceed 20 samples per batch. This standard is used to establish the retention time window for quantitation of GRO. The compounds of BTEX can be included if all quality control criteria are met (see Section 10 of this method).

3.9 Method Detection Limit (MDL): The minimum concentration of a compound that can be measured and reported with 99 percent confidence that the value is greater than zero, determined from analysis of a sample in a given matrix containing the analyte. (See 40 C.F.R. 136, Appendix B, for method of determining method detection limit.) Each laboratory must demonstrate and periodically update method detection limits for each analyte of interest. MDL's must be updated when a significant change in instrument, method, or personnel occurs.

3.10 Practical Quantitation Limit (PQL): Five times the MDL.

3.11 Instrument blank: Reagent water known to be free of purgeable compounds within the integration window. Analyzed prior to the start of an analytical batch to demonstrate the analytical system is free of contamination.

3.12 Other terms are as defined in SW-846 [1].

4. Interferences

4.1 High levels of heavier petroleum products such as diesel or heating fuel may contain some volatile components producing a response within the retention time range for GRO. Other organic compounds, including chlorinated solvents, ketones, and ethers are also detectable by this method. As defined in the method, the GRO results include these compounds.

4.2 Samples contaminated with a single compound which is detectable using this method (e.g., some solvents,) and which are quantitated against the GCS, may result in a value which is biased for that compound. This is caused by the difference in response factors for the GCS and various solvents. An alternative calibration, detection or quantitation procedure may be appropriate if the identity and quantity of the compound are specific project concerns.

4.3 Samples can become contaminated by diffusion of volatile organics during shipment and storage. A trip blank prepared from reagent water (for water samples) or methanol (for soil and sediment samples) and carried through sampling and subsequent storage and handling is highly recommended to serve as a check for such contamination.

4.4 Contamination by carryover can occur when high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and purging device should be rinsed between samples with reagent water and methanol. If an unusually concentrated sample is encountered, analysis of a solvent blank or reagent water to check for contamination should follow it. 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 methanol, and then dry in a 105° C oven between analyses. The

trap and other parts of the system are also subject to contamination. Therefore, frequent bake-out and purge of the entire system may be necessary. A screening of all samples prior to analysis is recommended to protect analytical instrumentation (see Section 9.6.1 of this method).

4.5 High moisture content in soil samples may cause moisture dilution resulting in results biased low. Moisture dilution is dilution of methanol preservative by moisture contained in the sample.

5. Safety Issues

5.1 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. 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. A reference file of material safety data sheets should also be made available to all personnel involved in chemical analyses. Additional references to laboratory safety should be made available and identified for the information of the analyst. Some data (i.e., on methanol) is available from ADEC.

6. Apparatus and Materials

Unless otherwise indicated, apparatus and materials are representative, not required. Except for soil sample preservation, refer to EPA Methods 5030, 602 and 8021B for remaining equipment and reagent. For soil sample preservation, see Section 8.2 of this method.

6.1 Glassware

6.1.1 40-mL glass vials with Teflon-lined septa and screw caps (a.k.a., VOA or VOC vials).

6.1.2 4-oz. amber glass wide mouth jars with Teflon-lined septa that are fused to the screw caps.

6.1.3 Volumetric flasks, class A: 10-mL, 50-mL, 100-mL, 500-mL, and 1000-mL with ground glass stoppers.

6.1.4 Disposable pipettes: Pasteur.

6.2 Syringes

6.2.1 5-mL Luerlock glass syringe and 5-mL gas-tight syringe with shutoff valve.

6.2.2 For purging large sample volumes for low detection limit analysis, 25- or 50-mL syringes may be used. Remember to adjust other volumes as necessary throughout the method.

6.2.3 Micro-syringes: 1-, 5-, 10-, 25-, 100-, 250-, 500-, and 1000-µL.

6.3 Analytical balance, capable of accurately weighing to the nearest 0.0001 g for preparation of standards and percent moisture determinations and a top-loading balance capable of weighing to the nearest 0.01 g for samples.

6.4 Stainless steel spatula

6.5 Gas Chromatography

6.5.1 Gas Chromatograph: Analytical system complete with gas chromatograph suitable for purge-and-trap sample introduction and all required accessories, including detectors (FID required, additional PID optional), column supplies, gases and syringes. A data system capable of determining peak areas using a forced baseline and baseline projection is required. A data system capable of storing and reintegrating chromatographic data is recommended. Disclaimer: Suggestions for columns and traps, necessary for the proper completion of this procedure, are the recommendations at the time of the published revision. As new advancements are developed it is acceptable to replace dated technology as long as it can be demonstrated that the quality control criteria of the method is intact.

6.5.2 Columns:

6.5.2.1 Column 1: HP5MS. 30-m x 0.32 mm ID. 100 micron film thickness or equivalent.

6.5.2.2 Capillary columns may be essential to achieve necessary resolution. The column must resolve C_6 from the methanol solvent front in a mid-range LCS standard and, if BTEX is to be done simultaneously, must resolve ethylbenzene from m/p-xylene.

6.5.2.3 The column must be capable of separating typical gasoline components from the surrogate and (optional) internal standard.

6.5.3 Purge-and trap device: The purge-and-trap device consists of three separate items: the sample purger (sparging device), the trap, and the desorber (furnace). Several complete assemblies are commercially available. (See Table 1 of this method for summary of operating parameters.)

6.5.3.1 Purging chamber: 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 should have a

total volume of less than or equal to 15 mL. In any case, the purge chamber must be configured so that the quality assurance requirements specified in Section 10 of this method are met. A 25-mL chamber may be necessary to meet project specific detection limit requirements.

6.5.3.2 Trap: The trap must be capable of retaining GCS components at the highest concentration of the calibration curve, and concomitantly meet the quality assurance requirements specified in Section 10 of this method. Before initial use, the trap should be conditioned as specified by the manufacturer. Vent the trap effluent to the hood, not to the analytical column. Before daily use, the trap should be conditioned, according to manufacturer's specifications, with back flushing. The trap may be vented to the analytical column during daily conditioning; however, the column should be run through the temperature program before analysis of samples to assure that any contamination from trap conditioning has been removed.

Suggested traps are the "J" trap or BTEX trap and should be conditioned and used according to manufacturer's specifications.

6.5.3.3 - Desorber (Furnace): The desorber should be capable of rapidly heating the trap to the required temperature for desorption. The trap should not be heated higher than the manufacturer specified tolerances.

6.5.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as long as complete transfer of the sample is assured.

7. Reagents and Standards

7.1 Reagent Water: Carbon-filtered, purged water which has been shown to be free from purgeable compounds (this has also been called organic-free water). Nitrogen or helium may serve as purge gas.

7.2 Methanol: Pesticide grade or equivalent. Store away from other solvents. At a minimum, the methanol must not show GRO contamination above the PQL.

7.3 Stock Standard Solutions - Prepare the following stock standards. Unless otherwise noted, all are prepared using the methanol listed in 7.2 as solvent. Standard preparation should follow guidelines in SW-846 [1]. All standards prepared by the laboratory must be stored without headspace at -10° to -20°C and protected from light. Standards must be replaced within 6 months of preparation. Standards should be checked regularly to assure their integrity. Standards that are purchased pre-made from commercial suppliers may be kept for the life, and under conditions, specified by the manufacturer if different than described in this paragraph.

7.3.1 Internal Standard: An internal standard (1-chloro-4-fluorobenzene) is

recommended for 8021B quantitation on the PID. Due to potential interferences, the internal standard is not recommended for GRO (FID) quantitation.

7.3.2 Recommended Surrogates: 50 μg/mL of bromofluorobenzene and / or α,α,α-trifluorotoluene. Add 5.0 μL of this surrogate directly into the 5-mL syringe with every sample and standard analyzed. Surrogate is spiked into soil samples during the extraction step (see Section 8.2.1 of this method). A second surrogate may be used in addition to, but not in place of, the surrogate sent to the field (Section 8.2.1). The use of alternate surrogates is optional. Surrogate compounds must be non-polar, purgeable from water, elute prior to the start of C_{11} and must not co-elute with any significant component of gasoline. Surrogated methanol is prepared at a ratio of 2.5 mL of methanol to 0.5 mL of surrogate spiking solution at 50 μg/mL.

7.3.3 Retention Time Window Standard: This mixture of n-hexane and n-decane serves as a retention time window defining mix for GRO. The concentration of the individual components should not be less than 500 μg/mL and not more than 1000 μg/mL. Additional analytes may be added to this mix if 8021B is to be done concomitantly.

7.3.4 Calibration Standards: A mixture of equal weights of regular, plus, and premium grades of unleaded gasoline serves as the Gasoline Calibration Standard. Gasoline standards must be certified as non-oxygenate gasoline or the gasoline concentration must be adjusted to reflect the contribution from oxygenates. No fewer than 3 concentrations of the GCS are diluted directly into a 5-mL Luerlock syringe (linear range approximately 50 to 2,000 μg/L) at the time of calibration. BTEX calibration should meet the criteria specified in EPA SW-846 Method 8021B for waters and soils [1]. Other than one standard concentration near the practical quantitation limit, the expected range of concentrations found in the field samples should define the working range of the GC (see Section 9.3.2 of this method).

7.3.5 Stock Standard for Calibration Verification: From a blend of oxygenate free commercial gasoline other than those used to prepare the GCS, make an equal weight mixture as described in Section 7.3.4 of this method. Prepare a dilution of 500 ug/mL in methanol.

Note: When verifying the BTEX calibration curve, the criteria in the appropriate EPA method should be met [1, 12].

8. Sample Collection, Preservation, Handling, and Holding Times

8.1 Aqueous Samples:

8.1.1 Aqueous samples should be collected without agitation and without headspace in contaminant-free, amber glass 40-mL vials with Teflon-lined septa in the caps. A sufficient number of samples should be collected to provide for quality control criteria and for back-up in the event of breakage. If amber glass vials are not available, clear glass may be substituted if the samples are protected from light. The Teflon layer must contact the sample (zero headspace). Sample vials should contain 200 µL of 50% hydrochloric acid (HCl) as a preservation for volatile analytes. Refrigerated samples (4 ± 2° C) must be analyzed within 14 days of collection.

8.1.2 A trip blank (contaminant-free amber glass 40-mL vial with Teflon-lined septum, filled to zero headspace with purged, organic free water preserved with the same acid as the samples, if possible) must accompany each shipping container and should be stored and analyzed with the field samples. Trip blank analysis is not required if all samples in a shipping container are less than the project specific cleanup level.

8.2 Soils and Sediments: Soil and sediment samples require special procedures to minimize the loss of volatile organic compounds during transit from the field to laboratory. **Please note that this sample preservation is different from SW-846 Method 8021B. The use of sodium bisulfate as a preservative is not acceptable.**

8.2.1 Soil or sediment samples must be collected into appropriately sized containers and submerged in surrogated methanol.

8.2.2 Solid samples must be collected with minimum disturbance into tared jars with a Teflon-lined septum fused to the lid. Jars should be 4-oz or larger, if appropriate. 25-mL aliquots of methanol (includes 1.2 mL of a surrogate solution at 50 µg/mL) should be carefully added to the undisturbed soil until the sample is submerged.

8.2.3 It is extremely important that the weight of the jar, the weight of the methanol/surrogate solution, and the weight of the sample collected be known. These must either be measured directly, or sufficient information documented so that these weights can be calculated.

8.2.4 The ratio of soil to methanol used to calculate the MDL and PQL offered in this method was 1:1 (w:w). However, absorbent, organic soils such as muskeg and tundra will require a higher methanol-to-sample ratio, while beach sand may tolerate a lower ratio.

8.2.5 Soil for volatiles analysis can be collected using any coring device that minimizes soil disturbance. Any scraping, stirring, or similar activity will result in a loss of volatiles during sampling. A sufficient number of samples should be collected to provide for backup in case of breakage.

8.2.6 Although it is not necessary to refrigerate all methanol preserved samples at 4° ± 2° C after collection and until analysis is complete, collected samples must be kept below 25° C.

8.2.7 A second surrogate, added to the methanol and soil mixture after sample collection, may be used in addition to, but not in place of, the surrogate with which the field methanol preservative was prepared.

8.2.8 A reagent methanol trip blank must be prepared in the same manner as the sample vials, and must contain surrogated methanol. One trip blank must be included with each shipping container and must be stored and analyzed with the field samples. Trip blank analysis is not required if all samples in a shipping container are less than the project specific cleanup level.

8.2.9 Field blanks may be added to the sampling protocol and are prepared in the field by addition of surrogated methanol to the prepared container, as required by the qualified environmental professional or the Project Manager.

8.2.10 A sample of the same soil to be analyzed for GRO should be collected into a moisture-proof container for per cent moisture determination. This sample should be processed as soon as possible upon arrival at the laboratory to assure that the resulting moisture determination is representative of the preserved sample as surveyed.

8.2.11 Trip blanks, field blanks, method blanks, etc. should be prepared from the same batch of solvent, reagents and vials as are used for sample preservation.

8.3 Twenty-eight days is the maximum holding time for soil and sediment samples collected under this section.

8.4 Because the jars are pre-weighed, it is extremely important that the sampler put evidence tape on the kit ONLY, or the bubble bags in which the sample bottles are shipped, and not on the individual bottles. Removal of evidence tape is extremely difficult and the additional weight biases final results. Also, the glue on the evidence tape can contribute to the volatiles concentration in the sample (per Rocky Mountain Analytical, direct communication).

8.5 Trip blanks, field blanks, and bottle blanks should be prepared as appropriate to meet the quality assurance goals of the project plan.

8.6 Performance Evaluation (PE) Samples must be obtained from a supplier approved by The NELAC Institute (TNI) or a supplier approved to ISO 17043 standards.

9. Procedure

9.1 Volatile compounds are introduced into the gas chromatograph by purge-and-trap (see exception, Section 2.2 of this method). Purge gas should be set at a flow rate of 25 - 40 mL/min. and purge time at 12 min., or conditions necessary to optimize the resulting chromatography.

9.2 Waters:

9.2.1 Purge-and-trap may be used directly on most water samples.

9.2.2 Water samples high in dispersed sediments (non-settling or slow settling solids) must NOT be filtered before analysis, as this results in loss of volatiles. Centrifugation also forces the gases out of the water matrix. In most cases, a muddy water sample can be left undisturbed until the solids settle out. An aliquot of the sample can then be taken with a 5-mL gas tight syringe, being careful not to disturb the sediment layer. Introduction of sediment into the purge device can result in occlusion of the frit, leading to incomplete purging of the sample and low-biased results. In any case, sample preparation should be noted, and an approximate volume given for the solids, if present.

9.3 Soils and Sediments:

9.3.1 Soils and solids are methanol extracted. An aliquot of the extract is added to reagent water and analyzed as in Section 9.10 of this method.

9.3.2 For best retention of volatile compounds, samples should be collected into tared, sample jars containing the methanol-surrogate solution (see Section 8.2 of this method).

9.3.3 The entire volume of soil must be submerged in the methanol-surrogate solution.

9.3.4 Weigh the sample jar upon receipt and record the total filled weight. Swirl the jar gently for 2 minutes to be sure that the soil sample is dispersed into the methanol, and allow the sediment to settle. It is recommended that the meniscus of the methanol be marked and dated on the outside of the jar.

9.3.5 Best results are obtained by allowing the sample volatiles to equilibrate with the methanol for at least 48 hours before continuing with the analysis. However, this is not always possible. In any case, note the time difference between when the

methanol was delivered into the soil sample and when analysis was initiated.

9.4 Soils and Sediments Collected without Methanol Preservation:

9.4.1 When solids are collected by the sampling techniques described in SW-846 [1], volatile results are biased low. Therefore, data from these samples (collected without methanol preservative) must be reported as "greater than or equal to" the calculated mg/kg GRO as gasoline and may not be accepted as valid by state project managers.

9.4.2 To prepare extracts from these types of collection containers, gently mix the contents of the sample container with a narrow metal spatula. Do not discard any supernatant liquids, as the entire contents of the sample container must be represented.

9.4.3 For sediment/soil and waste that are insoluble in methanol, weigh 10 g (wet weight) of sample into a tared 20-mL vial, using a top loading balance. Note and record the actual weight to 0.1 g.

9.4.4 Quickly add 9.5 mL of methanol and 0.5 mL of the 50 ug/mL surrogate spiking solution to the vial (or, after adding spiking solution, fill to the line on the volumetric flask), cap and swirl (do not shake) for 2 minutes.

9.4.5 Allow sediment to settle. The alternate sample preparation procedure must be noted on the data transmittal.

Note: To avoid loss of volatile organics or cross contamination, these steps must be performed rapidly and without interruption, in a laboratory free from gasoline or solvent fumes.

9.5 Methanol Soluble Solids:

9.5.1 For waste that is soluble in methanol weigh 1 g (wet weight), to the nearest 0.01 g into a tared 10-mL volumetric flask.

9.5.2 Quickly add 9.5 mL of methanol and 0.5 mL of the 50 μg/mL surrogate spiking solution to the vial (or, after adding spiking solution, fill to the line on the volumetric flask), cap and swirl for 2 minutes, to disburse the waste into the methanol.

9.5.3 Allow sediment to settle, pipette an aliquot to an amber glass vial for storage at 4° ± 2°C (zero headspace).

9.6 Sample Screening:

9.6.1 It is highly recommended that all samples be screened prior to analysis, as these samples may contain enough petroleum to overload the column and/or detector(s). This screening step may be analysis of a solid sample's methanol extract (diluted) using AK101, the headspace method (SW-846 Method 3810 [1]) or the hexadecane extraction and screening method (SW-846 Method 3820 [1]).

9.7 Gas Chromatography Conditions (recommended)

9.7.1 Column 1: Set helium column pressure to 20#. Set column temperature to 30° C for 1 min., then ramp at a rate of 5° C/min. to 100° C, then 8° C/min. to 240° C and hold for 7.5 min. Conditions may be altered to improve the resolution of GRO. H_2 may be used as carrier gas, N_2 as purge gas. Conditions may be altered to accommodate the optional gases.

9.7.2 Other columns: Set GC conditions to meet the criteria in Section 6.5.2.2.

9.8 Calibration:

9.8.1 The GC system should be set up as in Section 6.5. This should be performed prior to calibration or to final preparation of the samples or sample extracts for analysis.

9.8.2 The GRO calibration curve must be represented by no fewer than 3 concentrations of GCS (a 5 point calibration curve is recommended). Prepare final solutions of GCS and surrogate directly in a 5-mL glass Luerlock syringe containing reagent water. Using a microsyringe, add the aliquot of calibration standard directly to the reagent water in the glass syringe (refer to Section 9.10.7 of this method) by inserting the needle through the syringe opening. When discharging the contents of the microsyringe, be sure that the tip of the needle is well beneath the surface of the reagent water to prevent escape of calibration standard components. Similarly, add the SCS. The concentration of the surrogate can increase with increasing GCS concentration, or remain at a fixed value for all calibration standards and samples. Inject the prepared dilution(s) into the purge vessel(s) through the two-way valve, and proceed with calibration.

9.8.3 Choose GCS concentrations to cover the GRO range expected in the samples or the linear range of the instrument, whichever is less. One of the concentrations must be near the practical quantitation limit. Due to potential carry over, it is recommended that not more than 10 μg of gasoline in 5 mL of water (2 mg/L) be purged.

9.8.4 Tabulate the area response of the gasoline against mass injected. The ratio of the amount injected to the response, the response factor (RF), can be calculated for the standard at each concentration. If the percent relative standard deviation (%RSD) is less than 25% 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.

External Standard Response Factor = $\frac{\text{Total area of Standard}}{\text{Standard amount injected}}$

Internal Standard Response Factor = $\frac{(Ax)\,(Qis)}{(Qx)\,(Ais)}$

Where: Ax = Area response of analyte
Ais = Area response of internal standard
Qis = Amount of internal standard
Qx = Amount of analyte

9.8.5 The calibration curve must be confirmed using the CVS. This second source standard (Section 3.3 of this method) verifies the accuracy of the calibration. The concentration of the CVS should be within the expected concentration range of the samples to be analyzed.

9.8.6 The working calibration curve or response factor must be verified on each working day by the injection of a mid-point CCS. The CCS is a diluted aliquot of the same standard used to initially calibrate the instrument. If the response factor for the CCS varies from the average response factor from the calibration curve (Section 9.8.4 of this method) by more than 25% a new calibration curve must be prepared.

Percent difference = $((R_1 - R_2) / R_1) \times 100$

where: R_1 = Average RF from the calibration curve.
R_2 = Response factor from CCS.

9.9 Retention Time Window

9.9.1 Before establishing windows, be certain that the GC system is within optimum operating conditions (see Section 6.5 of this method). Make three injections of the Retention Time (RT) Window Standard (see Section 7.3.3 of this method) throughout the course of a 72 hour period. Serial injections over less than a 72 hour period result in retention time windows that are too tight.

9.9.2 Calculate the standard deviation of the three absolute retention times for each component and for the surrogate.

9.9.2.1 The retention time window for individual peaks is defined as the average RT plus or minus three times the standard deviation of the absolute retention times for each component.

9.9.2.2 In those cases where the standard deviation for a particular analyte is zero, the laboratory should use ±0.05 min. in place of the standard deviation.

9.9.3 The laboratory must calculate retention time windows for each standard on each GC column and when a new GC column type is installed or instrument conditions changed. The laboratory must retain the data for at least five years and update it at least once a year.

9.10 Gas Chromatograph Analysis: Generally, the analytical batch on a pre-calibrated instrument will follow this flow: Reagent Blank, Retention Time Window Standard, opening CCS, Method Blank, Field Samples, spikes, reps, etc. (20), LFB. Repeat sequence, then end with closing CCS.

9.10.1 Samples are analyzed by GC/FID. Water, with or without methanol extract, to be analyzed for GRO is introduced into the programmed gas chromatograph (Section 9.2) using purge-and-trap sample concentration.

9.10.2 If initial calibration (see Section 9.8 of this method) has been performed, verify the calibration by analysis of a mid-point CCS (see Section 9.8.6 of this method). After the last sample has been analyzed, the same CCS must be analyzed to demonstrate that the analytical system is still in control. With each day's run, open a 24 hour analysis window. This is done by running the Retention Time Window Standard.

9.10.3 An LFB at a concentration representative of the field samples being analyzed must also be run once every 20 samples. If the result does not fall within the range specified in Table 3 of this method, corrective action must be performed and all affected samples re-analyzed.

9.10.4 Calculate the percent difference of the response factor from the mid-point CCS from the mean response factor for each analyte to be quantitated (as in Section 9.8.4 of this method). This is done for GRO as a "group" from the CCS if GRO is to be quantitated (FID) and for each of the components in the Retention Time Window Standard if additional quantitation for BTEX is required (PID). If the response factors have a difference greater than 25%, corrective action must be taken and all samples re-analyzed.

9.10.5 A reagent water blank must be analyzed each day to determine the area generated from normal baseline noise under the conditions prevailing within the 24 hour period. Add up to 300 µL of methanol to the blank when soil or sediment extracts are to be analyzed. The noise area is generated by projecting a horizontal baseline between the retention times observed between the beginning of n-hexane and the beginning of n-decane. This lab control sample is integrated over the GRO area in the same manner as for the field samples and is reported as the reagent blank.

Do not blank subtract. This information is for data interpretation purposes only.

9.10.6 Blanks should also be run after samples suspected of being highly concentrated, to prevent carryover. If the blank analysis shows contamination above the practical quantitation limit, the trap and column must be baked out and subsequent blanks analyzed until the system is shown to retain contaminants at concentrations less than the PQL.

9.10.7 Water samples may be introduced into the system in the following manner:

9.10.7.1 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 pour the sample into the syringe using caution not to agitate the sample which would result in loss of volatiles. Replace the plunger and compress the sample. Invert the syringe so that the air bubble rises to the top (valve end) of the syringe. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Add 5 µL surrogate spiking solution through the valve bore of the syringe and proceed with analysis.

9.10.7.2 This process of taking an aliquot destroys the validity of the liquid sample for future analysis. Therefore, if there is only one 40-mL vial of sample, the analyst should fill a second syringe at the same time the first one is prepared, in the same manner, to protect against possible loss of sample integrity. This second sample is maintained at 4±2° C with valve closed only until such time as the analyst has determined that the first sample has been analyzed successfully. If a second analysis is needed, it must be from the second syringe and must be analyzed within 24 hours of the opening of the original sample vial. Care must be taken to prevent air from leaking into (and to prevent volatiles from leaking out of) the syringe containing the backup aliquot.

9.10.8 Methanol extracts from soils or sediments must be diluted into reagent water for analysis, as are methanol soluble dilutions. Table 2 of this method is provided at the end of the method to help determine the volume of methanol extract to add to the 5 mL volume of regent water, in order to keep the response of the major constituents in the upper half of the linear range of the curve. The maximum volume of methanol extract usable per 5 mL purge volume is usually 300 µL (this is used in calculating the PQL, Section 3.10 of this method).

9.10.8.1 Follow directions for filling a syringe as outlined in Section 9.10.7.1 of this method, except use reagent water instead of sample. Introduce desired volume of methanol extract by inserting the needle of a microsyringe through the valve opening of the reagent water filled 5-mL

syringe and depressing the micropipette plunger when the needle is well below the surface of the reagent water. The surrogate has already been added (see Section 8.2 of this method). Proceed with analysis.

9.10.9. Dilutions:

9.10.9.1 If the product concentration exceeds the linear range of the method as defined by the calibration curve, the sample (or extract or dilution) must be diluted and reanalyzed. The response of the major peaks should be kept in the upper half of the linear range of the calibration curve.

9.10.9.2 It is most desirable to adjust the volume of extract introduced into the reagent water as in Section 9.10.8.1 of this method to compensate for concentrated sample extracts. However, if that is not possible, the following procedure is appropriate for diluting samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe:

9.10.9.3 Dilutions may be made in class A volumetric flasks (10-mL to 100-mL seem most useful), or other quantitative glassware with similar accuracy. Select the volumetric flask that will allow for the necessary dilution. Although intermediate dilutions may be necessary for highly concentrated samples, remember that the more transfers the sample makes, the greater the chance components will be lost.

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

9.10.9.5 Inject the proper aliquot of sample from the syringe prepared in Section 9.10.7.2 into the flask. Aliquots of less than 1-mL are not recommended for dilution of water samples using this method. Make sure aliquot is introduced well below the surface of the reagent water in the volumetric flask to minimize sample loss.

9.10.9.6 Dilute the sample to the mark with reagent water, disturbing the surface as little as possible. Cap the flask and invert three times. Repeat the above procedure for additional dilutions. Analyze the diluted sample as in Section 9.10.7 of this method.

9.10.10 Alternative Dilution Technique:

9.10.10.1 Alternatively, the dilutions can be made directly in the glass syringe to avoid loss of volatiles. If diluting methanol extracts, follow Section 9.10.8 of this method using a smaller volume of extract in the 5 mL purge volume or the procedure outlined for the dilution of water

samples.

9.10.10.2 Attach a syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject sample into the purging chamber. Proceed with the analysis. For more information, refer to purge-and-trap methods in SW-846 [1].

9.11 Moisture Determination for Solids

9.11.1 Moisture determinations must accompany all soils data (reported in mg/dry kg) so the client can, at will, determine the results in the original soil condition. Reporting in mg/dry kg can best be done if an unpreserved portion of the sample (collected without methanol) is provided. Because of the potential for high gasoline or related compound concentrations in the soil, all drying should be done under a functioning hood.

9.11.2 To determine percentage of moisture, pre-weigh an aluminum weighing boat. Weigh 5-10 g of the sample into the boat and record both weights to the nearest 0.01 g. Dry the sample overnight in a warm (105° C) oven.

9.11.3 Remove the sample from the oven and cool in a desiccator until the sample reaches room temperature, and weigh to the nearest 0.01 g. Record the weight.

9.12 Calculations:

9.12.1 External Standard Calibration:

The concentration of Gasoline Range Organics in the sample is determined by calculating the absolute weight of analyte purged, from a summation of peak response for all chromatographic peaks, resolved and unresolved, eluting between the peak start time for C_6 (hexane) and the peak start time for C_{10} (decane), using the calibration curve or the calibration factor determined in Section 9.8 of this method and baseline-baseline projection. Refer to Section 9.9 (Retention Time Window.)

The concentration of GRO may be calculated as follows [Method 8000B, 1]:

Aqueous Samples*:*

$$C_s \text{ (mg/L)} = \frac{(A_x)(D)}{(RF)(Vs)}$$

Where: **C_s** = Concentration of Gasoline Range Organics
RF = Response factor, as described in Section 9.8.4
Ax = Response for the Gasoline Range Organics in the sample, units in

area

Vs = Volume of sample purged, in liters.

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

Solid samples (methanol extraction):

$$C_s \text{ (mg/kg)} = \frac{(A_x)(Vt)(D)}{(RF)(W)(V_i)}$$

Where: Vt = Volume of total extract (μL) (use 10000 μL for standard 10 mL extract volume).

Vi = Volume of extract actually purged (μL)

W = Weight of sample extracted, kg. The dry wet weight is used.

Ax, RF, and D have the same definition as above.

Note: Some chromatographic software programs are capable of performing these calculations with minimal analyst intervention.

9.12.2 Moisture Determination (%)

Moisture (%) = [(A-C)/(A-B)] x 100

Where: A = weight of aluminum boat + wet sample

B = weight of boat

C = weight of boat + dry sample

9.12.3 Internal Standard Calibration.

If internal standard calibration is used, please refer to SW-846 Method 8000B[1].

10. Quality Control (See Table 3 of this method)

10.1 The laboratory must demonstrate, through the analysis of quality control check standards, that the operation of the measurement system is in control. This must include the analysis of QC check samples plus the calculation of average recovery and the standard deviation of the recovery as outlined in this method and in Method 8000B, Section 8.0.

10.2 After successful calibration (Section 9.8 of this method), analyze a reagent blank sample. The reagent blank must be analyzed with every analytical batch. The surrogate recovery must be within established limits (see Table 3 of this method), or within the limits established by the project plan (whichever is more stringent). Also, the mid-point CCS must be analyzed at the beginning and end of each sequence, and compared to the successful calibration as described in Section 9.8.6 of this method, and fall within established limits (see Table 3 of this method). Method detection limits (MDL) must be established as specified in 40 C.F.R. 136, Appendix B, and renewed as specified in Section 3.9 of this method.

10.3 An LFB must be analyzed with every analytical batch, and also run once every 20 samples. The matrix for these samples should be reagent water for batches of aqueous samples or methanol for soil sample batch analyses. The accuracy and precision of the duplicates must be within established limits (see Table 3 of this method).

10.4 With every batch of samples extracted, the reagent blank must be analyzed. The reagent blank must have GRO less than the practical quantitation limit.

10.5 If any of the criteria in Sections 9.8, 10.2, 10.3, and 10.4 of this method are not met, corrective action must be taken before samples are analyzed.

10.6 Calculate the surrogate recovery in each sample. If recoveries are outside established limits (Table 3 of this method), verify calculations, dilutions, and standard solutions. Verify instrument performance.

10.6.1 High recoveries may be due to a co-eluting matrix interference -examine the sample chromatogram.

10.6.2 Low recoveries may be due to adsorption by the sample matrix (i.e., high humus soils).

10.6.3 Low recoveries may be due to a poor purge (clogged purge tube or frit). If this is suspected, check the purge tube with a blank before reanalyzing the sample.

10.6.4 If the surrogate recovery is outside established limits due to suspected matrix effects, GRO results must be flagged. If the surrogate recovery is less than 50%, and the calculated GRO results are within a factor of 2 of the action limit, the laboratory should recommend that the client resubmit the sample for matrix spike and matrix spike duplicate analysis. This is a recommendation, not a requirement of the method, and therefore, the onus is not on the analytical laboratory to absorb the cost of the additional analyses.

10.6.5 If surrogate recovery is low due to moisture dilution, results should be recalculated using a dilution factor determined by the following calculation:

$$\frac{C_1 \times V_1}{[V_1 + [A \times (B/100)]]} = C_2$$

Where: C_1 = concentration of surrogate as measured
C_2 = adjusted value of surrogate
V_1 = volume of methanol preservative
A = total wet weight of sample
B = percent moisture of sample

10.7 Bottle blanks and matrix spikes are recommended for specific sampling programs. Field blanks, trip blanks, field duplicates are required as stated in Chapter 2, Section 9 of the *UST Procedures Manual*.

10.8 Minimum quality control acceptance criteria are in Section 10 of this method. More stringent quality control criteria may be required by specific project plans.

10.9 Corrective Action

10.9.1 Calibration

10.9.1.1 If the initial calibration does not meet the criteria in Sections 9.8.4, 9.8.5, and Table 3 of this method, the instrument must be recalibrated.

10.9.1.2 If the continuing calibration does not meet the criteria in Section 9.8.6 and Table 3, the instrument must be recalibrated.

10.9.2 Surrogates

10.9.2.1 If surrogates are outside established control limits (Table 3 of this method), and are not due to matrix effects, the following assessments and/or correction actions must occur:

A) Check to be sure there are no errors in calculations and that the concentrations of the surrogate and internal standard solutions are correct.
B) Check instrument performance to determine if it is within acceptable guidelines.
C) Recalculate the data and/or reanalyze the extract if any of the above checks reveals a problem.

D) Re-prepare and reanalyze the sample if none of the above resolves the problem.

10.9.2.2 If the surrogate recoveries that are outside the control limits cannot be attributed to lab error, the decision to reanalyze or flag the data should be made in consultation with the client. If all other QC acceptance criteria are met (Section 10 of this method), it is only necessary to re-prepare/reanalyze a sample one time to demonstrate that a poor surrogate recovery is due to matrix effects. A relationship can be established between surrogate recovery and moisture content of organic soils, which may help in diagnosing the cause of poor surrogate recoveries.

10.9.3 Blanks: Additional laboratory and field quality control blanks may be necessary for certain projects to meet the goals of Chapter 2, Section 9 of the *UST*

Procedures Manual.

10.9.3.1 Instrument Blanks:
Instruments must be evaluated with each analytical batch (or daily, whichever is more frequent) and must demonstrate that the analytical system is free from contamination. This is best accomplished by analyzing an Instrument Blank.

10.9.3.2 Trip Blank:
Trip Blanks must be analyzed with each sampling batch IF the results of the field samples show contamination above the maximum contaminant level (MCL). The Trip Blank for AK101 may also serve as the Method Blank and Reagent Blank in some cases.

10.9.3.3 Field Blank:
If the field samples yield GRO above the MCL, and contamination is found above the PQL in the Trip Blank, a Field Blank should be analyzed to identify whether the source of contamination originated in the field sample collection procedure, during travel or during storage in the laboratory.

Note: Blanks are reported by value. DO NOT BLANK SUBTRACT. This information is for data quality assessment purposes only.

10.9.4 Laboratory Fortified Blanks

10.9.4.1 If the analyte recovery from the LFBs is outside the established recovery limits (Table 3 of this method), the following assessments and/or corrective actions must occur:

A) Check to be sure there are no errors in calculations and that the concentration of the analyte solution is correct.
B) Check instrument performance to determine if it is within acceptable guidelines.
C) Recalculate the data and/or reanalyze the extract if any of the above checks reveals a problem.
D) Re-prepare and reanalyze the samples if none of the above resolves the problem.

10.9.4.2 If the relative percent difference between the LFB results exceeds the control limits, but meets the percent recovery criteria (Table 3 of this method), the following assessments and/or corrective actions must occur:

A) Check to be sure that there are no errors in calculations, and that the same amount and source of analyte solution, solvent and water were used for both samples in the set.
B) Check to determine if instrument performance is still within acceptable

guidelines, and that conditions did not change during the course of the batch analysis.

C) Recalculate the data if calculation error is suspected.

D) Repeat the LFB duplicate extraction and analysis, along with a representative number of samples (10% of the samples from the batch OR 1 sample, whichever is more) from the analytical batch with the failed LFB RPD. The re-analysis of the field samples is to demonstrate comparability of the extraction/analysis conditions at the time of re-extraction and analysis to those at the time of the failed QC.

11. Method Performance

11.1 Performance evaluation data and single-lab method performance data for the methanol extraction method in various soil types is presented below. Additional method performance data is available through the State of Alaska, Department of Environmental Conservation.

11.2 Results for gasoline spikes (Methanol extraction purge and trap, soils)

Matrix	Gasoline Spike Amount mg/kg	Percent Recovery
PE Samples	1190	89
Houston Black Clay[1]	50	68
Houston Black Clay[1]	50	66
Norwood Loam[1]	50	60
Norwood Loam[1]	50	57
Ottawa Sand[2]	50	97
Ottawa Sand[2]	50	96
Marine Sand[2]	50	94
Glacial Clay[2]	50	68
River Sediment[2]	50	53
Marine Sediment[2]	50	132
Forest Loam, muskeg, tundra[2,3]	50	28

1. Analyses performed by Rocky Mountain Analytical. Gasoline used = API PS6.
2. Analyses performed by State of Alaska, ADEC Laboratory. Gasoline used = GCS.
3. All highly organic, high moisture soils matrices showed less than 30% analyte recovery.

11.3 The method detection limit calculated according to 40 C.F.R. 136, Appendix B, was 0.5 mg/kg GRO as gasoline for the methanol extraction of soils and 0.01 mg/L GRO as gasoline for waters.

12.References

1. USEPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, 3d Edition; Methods 5030, 8000, 8015, 8020, and 8021B.

2. USEPA, *Sampling and Analysis of Gasoline Range Organics in Soils*, American Petroleum Institute Pub. #4516, October 1991.

3. USEPA, *Evaluation of Proposed Analytical Methods to Determine Total Petroleum Hydrocarbons in Soil and Groundwater*, prepared by Midwest Research Institute for USEPA Office of Underground Storage Tanks, August 14, 1990.

4. Urban, M.J., J.S. Smith, E.K. Schultz, R.K. Dickson, *Volatile Organic Analysis for a Soil, Sediment or Waste Sample* in Fifth Annual Waste Testing and Quality Assurance Symposium, USEPA, July 24-28, 1989.

5. Siegrist, R.L., and P.D. Jenssen, *Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils*, Environmental Science and Technology, Vol. 24, November 1990.

6. Fitzgerald, John, *On-site Analytical Screening of Gasoline Contaminated Media Using a Jar Headspace Procedure* in Petroleum Contaminated Soils, Vol. 2, 1989.

7. Senn, R.B., and M.S. Johnson, *Interpretation of Gas Chromatographic Data in Subsurface Hydrocarbon Investigations*, Ground Water Monitoring Review, 1987.

8. Hughes, B.M., D.E. McKenzie, C.K. Trang, L.S.R. Minor, *Examples of the Use of and Advanced Mass Spectrometric Data Processing Environment for the Determination of Sources of Wastes* in Fifth Annual Waste Testing and Quality Assurance Symposium; USEPA, July 24-28, 1989.

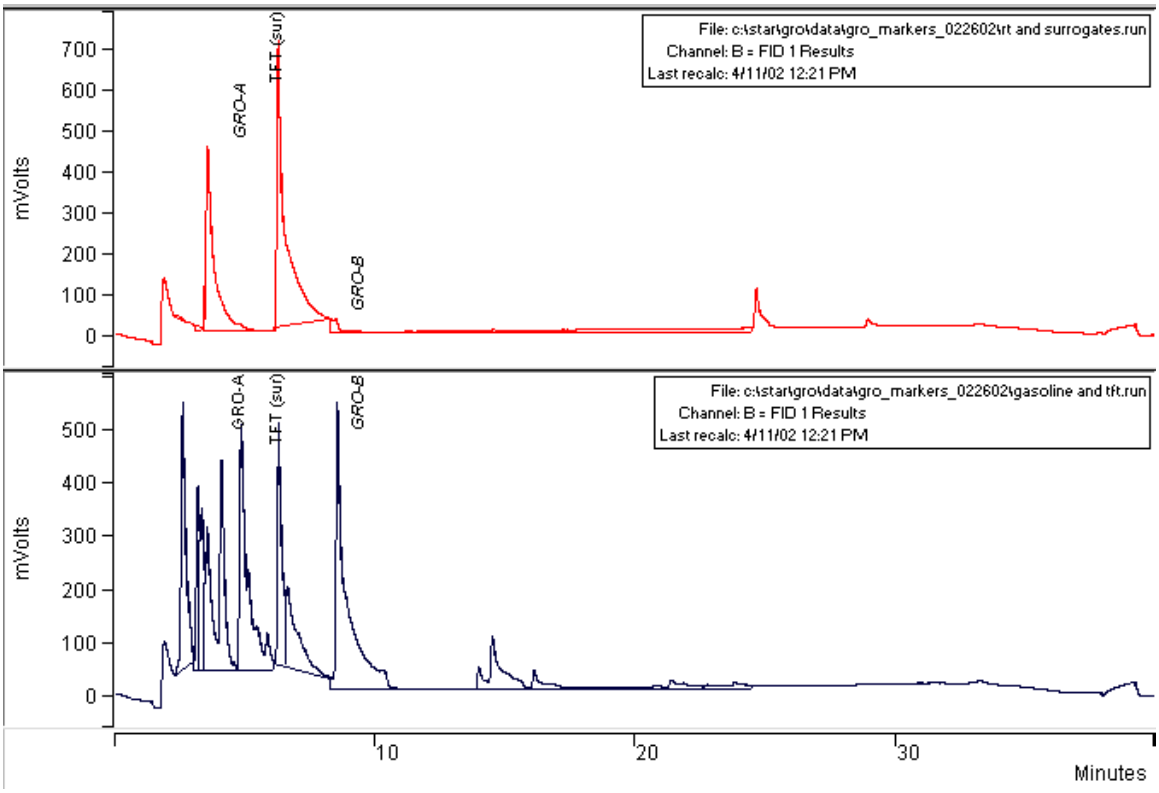
9. *Laboratory Study on Solubilities of Petroleum Hydrocarbons in Groundwater*, American Petroleum Institute Pub #4395, August 1985.

10. *Volatile Organic Analysis for a Soil, Sediment or Waste Sample (The Methanol Method)*, a symposium prepared by James S. Smith, Ph.D. for the State of Alaska, Department of Environmental Conservation, Underground Storage Tank/Leaking Underground Storage Tank program, August 16, 1993.

11. Carrell, Bob, *NWTPH-Gx, Volatile Petroleum Products Method for Soil and Water*, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington, December 1996.

12. USEPA, Guidelines for Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act (40 C.F.R.136), Part VIII, October 26, 1984.

Figure 1. Gasoline Range Organics



Hexane, a,a,a-TFT, and Decane (above)
Gasoline and a,a,a-TFT (below)

Column:
HP-5MS, 30 meters, 32 microns ID
Carrier Gas Hydrogen
Program: 1. Hold at 30 deg C for 4.42 minutes.
2. 2 deg/min to 77 deg C
3. 50 deg/min to 230 deg.
4. Hold at 230 deg 1 minute.

Purge and desorb conditions as recommended in the method

Method AK 101 - Table 1
Recommended Purge and Trap Operating Parameters[a]
For GRO/8021B

Parameter	**Setting**
Purge Gas	Nitrogen or Helium
Purge Gas Flow Rate (mL/min.)	40
Purge Time (min.)	11-12
Purge Temperature (°C)	Ambient
Desorb Temperature (°C)	140-180
Back Flush Inert Gas Flow (mL/min.)	20-60
Desorb Time (min.)	3-6
Trap Bake-out Time (min.)	8-12

[a] These parameter are recommendations. Use the settings that are proper for the trap used and which yield optimal results.

Method AK 101 - Table 2
Quantity of Methanol Extract Needed for
Analysis of Soils and Sediments

Approximate Concentration, GRO (mg/kg)[a]	Volume of Methanol Extract (µL)[b]
5-100	300
200	50
1000	10
5000	100 µL of 1/50 dilution[c]

Calculate appropriate dilution factor for concentrations exceeding this table.

a. This number is determined by sample pre-screening.

b. The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a total volume of 300 µL of methanol for each blank, sample and control.

c. Dilute an aliquot of the methanol extract and then take 300 µL for analysis.

Method AK 101 - Table 3
Acceptance Criteria for Quality Control
Based on Approved Laboratory PE Performance, 1996.

ANALYTE	SPIKE CONCENTRATION		CONTROL LIMITS	
	Water (mg/L)	Soil (mg/kg)	% Recovery	Relative % Difference
Lab-Fortified Blanks				
Gasoline Range Organics	0.1 – 1.	5 - 100	60-120	20
Laboratory Sample Surrogate Recovery				
α,α,α-Trifluorotoluene or Bromofluorobenzene	0.05	2.5	60-120	
Field Sample (based on Approved Laboratory data packages, 1996) **Surrogate Recovery**				
α,α,α-Trifluorotoluene or Bromofluorobenzene	0.05	2.5	50-150	
Continuing Calibration/ Calibration Verification Standards				
See Section 9.8.6	1.0		75 - 125	

The quality control criteria listed in this table represent the minimum acceptable levels, using highly organic soil matrices. Higher performance may be required on some projects