ALASKA LEGISLATURE COMMITTEE FILES 1997-1998 8672
9640 SENATE LABOR & COMMERCE

APPENDIX C

LABORATORY DATA REPORT CHECK SHEET (page 1 of 2)

Reviewer _____ **Date** _____

Project _____

1. Laboratory name _____, address _____ telephone number_____, fax number_____
   QA Officer Signature _____ date signed _____
2. Report date _____
3. Analyte of interest, or target analyte _____
4. Extraction method # _____ and name _____
5. Type of matrix _____
6. Field sample number_____
7. Lab sample number_____
8. Lab file ID number_____
9. Date sampled_____
10. Date received_____
11. Date extracted_____
12. Date analyzed____
13. Sample collection point_____
14. Site or project name_____
15. Concentration of analyte (mg/kg dry or mg/L)_____
    % solids analysis or explanation _____
    method detection limit or method reporting limit indicated _____
16. Identification of flags or qualifiers _____
    All corrections and strikeouts initialed and dated _____
17. Precision and accuracy value for each sample set _____
18. Ambient container temperature upon receipt of sample _____
    time/date temperature measured ___ sample refrigerated ___ temperature ___
    date/time _____
19. Sample transfer log/release/chain-of-custody form _____
20. Analyst's name on all report pages _____ with date prepared _____
    Analyst's signature/initials on all chromatograms _____
21. Dilution factor _____
22. Case narrative summary _____
23. Report securely bound _____, with sequentially numbered pages _____

LABORATORY DATA REPORT CHECK SHEET (page 2 of 2)

NOTE: All items listed below must be kept on file for at least three years after analysis:

1. Laboratory file identification number _____
2. Original data package (with analyst's initials)
   Sample queue ___ chromatograms included ___ chromatograms clearly labeled _____
   chromatograms baseline-baseline integrated ___
   integration report included (clearly labeled) ___
   integration range clearly indicated ___ date/time on all chromatograms_____

3. Calibration report (with analyst's initials)
   Date/time of initial calibration ___ concentration range clearly indicated _____
   composition of calibration standard(s)___ Lab Control Standard analyzed, date/time _____
   Continuing Calibration Standard analyzed, date/time ____

4. Surrogate used ____ surrogate properly identified _____
   % recovery for each sample ____ acceptable range indicated _____
   outliers explained _____

5. Alkane/window retention time standard analyzed _____
   components properly identified _____

6. Column performance/separation number _____ Date determined _____
   analyst's initials _____

7. Spike/spike duplicate analyzed _____ recoveries _____ relative % difference _____
   acceptable range clearly indicated _____ outliers explained _____

8. Blank data (no blank correction of field samples!)
   Reagent blank _____, Method blank _____, Bottle blank _____

9. **Optional.** Reference (library) sample included _____ Pattern match/narrative summary _____

The AK Methods in Appendix D are repealed and replaced as follows:

APPENDIX D

Alaska Series Laboratory Methods for the Analysis of

Gasoline Range Organics (AK101), Diesel Range Organics (AK102), and Residual Range Organics (AK103)

Forward for All AK Series Methods

The Alaska Department of Environmental Conservation (ADEC) has published these laboratory methods to provide ADEC-approved laboratory test methods and related information for laboratory analysts, data users, and other interested parties. The test methods may be used, without permission, for laboratory testing to provide measurements relative to regulations in ADEC programs. **Except where explicitly specified in a regulation**, the use of these test methods is not mandatory.

These test methods have been written to provide comprehensive guidance for analysts attempting to analyze samples. However, ADEC does not intend for users to follow all details of a method in a prescriptive, rote fashion. Rather, **except where specifically indicated by the words "shall," "must," or "required,"** analysts have the flexibility to modify method procedures, parameters, equipment, reagents, etc. for all method steps, if the changes do not adversely affect the method performance needed to achieve the data quality needs of the study being conducted. Examples of the types of flexibility allowed include changes in chromatographic conditions, columns, traps, sample extraction conditions, glassware and sample size.

The flexibility is intended to provide laboratories a way to improve test methods (for example, reduce the generation of laboratory wastes, use existing equipment, reduce costs) without having to undergo elaborate studies and a time-consuming approval process. In exercising this flexibility, laboratories must be able to demonstrate and document that the changes implemented can produce results that are consistent with the data quality needs of the intended application, based on the results of initial and ongoing quality control activities.

Chapter One of EPA's publication SW-846 describes a variety of quality control activities that may be used to evaluate the appropriateness of any method modification and of the sample results. Additional quality control activities are described in the individual methods.

The test methods provide information relative to the expected performance (accuracy, precision and sensitivity) of the method when applied by a well operated laboratory. These performance data should be used both to assist in the selection of a method for a given application and to evaluate whether a modification is appropriate.

In summary, the test methods included in this appendix provide comprehensive guidance which may be used by laboratories, individual analysts, and the regulated community. The results from quality control sample analyses are used to evaluate the quality of sample results relative to the intended use of the data.

Method AK101
For the Determination of Gasoline Range Organics
Revision 3.1, 1/21/97

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 C_6 to the peak start of C_{10} and a boiling point range between approximately 60°C and 170°C.

1.1.2 Components 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 methods 602 and 8020.

1.2 Quantitation Limits

1.2.1 The Practical Quantitation Limit (PQL) of this method for GRO is approximately 5 mg/kg GRO as gasoline for soils and 0.1 mg/L GRO as gasoline for water.

1.3 Dynamic Range

1.3.1 Dilutions should be performed as necessary to put the chromatographic envelope within the linear range of the method. In general, the approximate range is 0.5 to 2 mg/L of gasoline.

1.4 Experience

1.4.1 This method is based on a purge-and-trap, Gas Chromatography (GC) procedure. This method should 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. Summary of Method

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. Samples must be analyzed using purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a flame ionization detector (FID) or PID/FID in series. Quantitation must be performed by comparing the total chromatographic area between and including C_6 (hexane) and C_9 (nonane), to the peak start time of C_{10}, including resolved and unresolved components, based on FID response compared to a blended commercial gasoline standard (paragraph 3.2) and using forced baseline-baseline integration. See Table 1, for suggestions regarding purge and trap operating parameters.

2.2 Water samples can be analyzed directly for GRO by purge-and-trap extraction and gas chromatography. Soil or waste samples are dispersed in methanol to dissolve the volatile organic constituents. (See Table 2). A portion of the methanol solution is injected into water and then analyzed.

2.3 Special field sampling techniques are required to minimize the loss of volatiles from soil resulting from conventional sampling and sample handling techniques.

2.4 This version of the method was developed by Dr. Mary Jane F. Pilgrim, and is based in part on U.S. EPA SW-846 [1] methods 5030, 8000, 8020, 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 Storage Tank 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 (hexane) and the peak start time for C_{10} (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.

3.2 Gasoline Calibration Standard (GCS): An equal-weight mixture of unleaded, leaded, and premium commercial gasolines mixed and diluted to appropriate concentrations, used to prepare a standard curve. In areas where leaded gasoline is not available, a second unleaded regular gasoline may be used to prepare the calibration standard. Leaded gasoline is generally available from retailers of aviation fuels.

3.3 Calibration Verification Standard (CVS): A gasoline quality control standard (preferably ERA Certified, or equivalent) prepared as in 3.2 but with product from a source other than that used to prepare the Gasoline Calibration Standard. It is used by the laboratory 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 Gasoline Calibration Standard, used to verify that the analytical system is operating in a manner comparable to that at the time of calibration.

3.5 Surrogate Control Standard (SCS): Either bromofluorobenzene or trifluorotoluene, or a mixture of both, used as a laboratory data quality control.

3.6 Surrogate Control Sample: A method blank sample spiked with the surrogate used in the method. The surrogate recovery is used to evaluate method control (sec 7.3).

3.7 Laboratory Fortified Blank (LFB): A method blank sample spiked with a commercial gasoline other than the ones blended to prepare the GCS. The spike recovery is used to evaluate method control. The CVS is used in 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).

3.9 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 high for that compound. This is caused by the difference in response factors seen with the GCS and various solvents. An alternative detection and quantitation procedure may be more 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 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, it should be followed by analysis of a solvent blank or reagent water to check for 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 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 9.6.1).

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 the Department.

6. Apparatus and Materials

(Unless otherwise indicated, all apparatus and materials are representative, not required.)

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 which 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 Microsyringes: 1, 5, 10, 25, 100, 250, 500 and 1000 uL.

6.3 Analytical balance, capable of accurately weighing to the nearest 0.0001 g for preparation of standards and per cent moisture determinations, and a top-loading balance capable of weighing to the nearest 0.1 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.

6.5.2 Columns:

6.5.2.1 - Column 1: 105-m x 0.53 mm ID. Restek RTX 502.2, 0.3 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 Method AK 101, Table 1 for summary.

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.

6.5.3.2 - Trap: The trap must be capable of retaining GCS components at the highest concentration of the calibration curve, and concommitantly 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.

An alternate trap uses 7.6-cm Carbopack B and 1.3-cm Carbosieve S-III (Supelco Cat# 2-0321R). This trap should be desorbed at 240°C and baked to 300°C. Another useful trap is the "J" 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 purgable 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 which 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 602/8020 quantitation on the PID. Due to potential interferences, the internal standard is not recommended for GRO (FID) quantitation.

7.3.2 Recommended Surrogate: 50 ug/mL of bromofluorobenzene and /or trifluorotoluene . Add 5.0 uL of this surrogate directly into the 5 mL syringe with every water sample and reference standard analyzed. Surrogate is spiked into soil samples during the extraction step (see 8.2.1). A second surrogate may be used in addition to, but not in place of, the surrogate sent to the field (8.2.1).

7.3.3 Retention Time Window Standard: This mixture of hexane and decane serves as a retention time window defining mix for GRO. The concentration of the individual components should not be less than 500 ug/mL and not more than 1000 ug/mL. Additional standards may be added to this mix if 602 or 8020 is to be done concomitantly.

7.3.4 Calibration Standards: A mixture of equal weights of leaded, unleaded and supreme gasolines serves as the Gasoline Calibration Standard. No fewer than 3 concentrations of the GCS are diluted directly into a 5 mL syringe (linear range approximately 0.5 to 2.0 mg/L) at the time of calibration. BTEX calibration should meet the criteria specified in EPA method 602 for waters [11] and in SW846 method 8020 for soils [1]. Other than one standard concentration near the practical quantitation limit, the expected range of concentrations found in real samples should define the working range of the GC (see 9.3.2).

7.3.5 Stock Standard for Calibration Verification: From a blend of commercial gasolines other than those used to prepare the GCS, make an equal weight mixture as described in 7.3.4. Prepare a dilution of 500 ug/mL in methanol. Addition of the following amounts yields the indicated concentrations when preparing LFBs:

0.005 mL added to 5 mL water:	0.5 mg/L
0.5 mL added to 10 g soil:	25 mg/kg

When verifying the BTEX calibration curve, the criteria set forth in EPA method 602 should be met [11].

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 uL of 50% 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) must accompany all sampling kits, at a recommended ratio of 1 for every 10 samples collected, and should be stored and analyzed with the field samples.

8.2 Soils and Sediments: Soil and sediment samples require special procedures to minimize the loss of volatiles during transit from the field to laboratory.

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

8.2.2 Solid samples should be collected with minimum disturbance into tared 4 oz (or larger, if appropriate) jars with a Teflon-lined septum fused to the lid. 25 mL aliquots of methanol (includes 1.2 mL of a surrogate solution at 50 ug/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 the event of breakage.

8.2.6 Although it is not necessary to refrigerate all 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 was prepared.

8.2.8 A reagent methanol trip blank should be prepared in the same manner as the sample vials, and should contain surrogated methanol. Trip blanks must accompany all sampling kits, at a recommended ratio of 1 for every 10 samples collected, and should be stored and analyzed with the field samples.

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 Assessment Firm 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 % 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 collection.

8.3 28 days is the maximum holding time for soil and sediment samples collected into methanol.

8.4 Because the jars are pre-weighed, it is extremely important that the sampler put evidence tape on the kit ONLY 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).

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

9. Procedure

9.1 Volatile compounds are introduced into the gas chromatograph by purge-and-trap. 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. 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 9.10.

9.3.2 For best retention of volatile compounds, samples should be collected into tared, methanol and surrogate containing sample jars (see 8.2).

9.3.3 The entire volume of soil must be submerged in a methanol and 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 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 min.

9.4.5 Allow sediment to settle. Note alternate sample preparation procedure on 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 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 0.1 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 ug/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 product 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.

9.7.2 Other columns: Set GC conditions to meet the criteria in 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 less 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 syringe containing reagent water in the following manner: Using a microsyringe, add the aliquot of calibration standard directly to the reagent water in the glass syringe (refer to 9.10.7) 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 5.0-uL of the 50 ug/mL SCS. 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 ug of gasoline in 5 mL of water (2 mg/L) be purged. A calibration concentration at 0.01 mg/L (0.5 to 1.5 ug/L for individual volatiles) is recommended for additional quantitation if BTEX is to be included.

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 continuing calibration response factor can be used in place of a calibration curve. Use the average response factor from the calibration curve as reference.

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

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 (7.5.3) 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 midpoint 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 (9.8.4) by more than 25% a new calibration curve must be prepared.

$$\text{Percent difference} = \frac{R_1 - R_2 \times 100}{R_1}$$

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 (6.5). Make three injections of the Retention Time Window Standard (7.3.3) 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 plus or minus three times the standard deviation of the absolute retention time for each component.

9.9.2.2

In those cases where the standard deviation for a particular analyte is zero, the laboratory should use $\pm$0.05 min. as a retention time window.

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

9.10 Gas Chromatograph Analysis:

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 (9.8) has been performed, verify the calibration by analysis of a mid-point CCS (9.8.6). 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 and at the end of each sequence or twice in each batch, whichever is more frequent. If the result does not fall within the range specified in Table 3, corrective action must be performed. A matrix spike/matrix spike duplicate may be used in place of the LFBs if the quality control criteria specified in Table 1 for LFBs is met by the matrix spike and duplicate.

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 9.8.4). This is done for GRO as a "group" from the CCS if GRO only is to be quantitated and for each of the components in the Retention Time Window Standard if additional quantitation for BTEX is required. If the response factors have a difference greater than 25%, corrective action must be taken.

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 100 uL 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 hexane and the beginning of 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 uL 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 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 100 uL (this is used in calculating the PQL, section 1.2).

9.10.8.1 Follow directions for filling a syringe as outlined in 9.10.7.1, 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 8.2). 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 range of 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 9.10.8.1 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). 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 Paragraph 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. Continue as in 9.10.7.

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 9.10.8 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 0.001 g. Dry the sample overnight in a warm (100±5°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 0.001g. Record the weight.

9.11.4 Return the soil sample to the oven for an additional time period (not less than 2 hours), cool again in the desiccator until the sample reaches room temperature, and weigh to the nearest 0.001g.

9.11.5 If the weight of the sample has remained constant (± 4%) from the initial "dry" weight (9.11.4), use this number for the moisture determination (see 9.12.2). If the second weighing shows that the sample has lost further weight, continue drying and weighing the sample until the weight becomes constant, then proceed to 9.12.2.

9.11.6 If a sample contains a high concentration of petroleum product, constant weight may be difficult to attain. If, after several tries, the ±4% criteria cannot be reached an estimated % moisture may be reported with appropriate explanation.

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 9.8 and baseline-baseline projection. Refer to Section 9.9 (Retention Time Window.)

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

Aqueous Samples:

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

Where:

C_s =	Concentration of Gasoline Range Organics
RF =	Response factor, as described in 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):

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

Where:

Vt =	Volume of total extract (uL) (use 10000 uL for standard 10 mL extract volume).
Vi =	Volume of extract actually purged (uL)
W =	Weight of sample extracted, kg. The 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 8000A[1].

10. Quality Control (See Method AK 101, Table 3)

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 Method 8000, Section 8.0, and in this method.

10.2 After successful calibration (Section 9.3), 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), or within the limits established by the project plan (whichever is more stringent). Also, the mid-point CCS must be analyzed at the end of each sequence and once per 20 samples, and compared to the successful calibration as described in 9.8.6, and fall within established limits (see Table 3). Method detection limits (MDL) must be established as specified in 40 CFR part 136 appendix B.

10.3 With every batch, duplicate LFBs must be analyzed. The matrix for these samples should be reagent water for batches of aqueous samples or methanol/Ottawa sand (or other appropriate standard soil) for soil sample batch analyses. The accuracy and precision of the duplicates must be within established limits (see Table 3).

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 9.3, 10.2, 10.3 and 10.4 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), verify calculations, dilutions, and standard solutions. Verify instrument performance.

10.6.1 High recoveries may be due to a coeluting 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.

10.7 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 set forth 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 set forth in 9.8.4 and 9.8.5, the instrument must be recalibrated.

10.9.1.2 If the continuing calibration does not meet the criteria set forth in 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), the following assessments and/or correction actions must occur:

A) Check to be sure there are no errors in calculations and that the concentration of the surrogate and internal standard solution 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) Reprepare 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. Provided all other QC acceptance criteria are met (section 10), it is only necessary to reprepare/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 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 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), 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) Reprepare 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), 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 Single-lab method performance data for the methanol extraction method in Ottawa Sand and other 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
Ottawa Sand[1]	50	70
Ottawa Sand[1]	50	78
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, DEC Laboratory. Gasoline used = GCS.
3 All highly organic, high moisture soil matrices showed less than 30% analyte recovery.

11.3 The method detection limit calculated according to 40 CFR, Part 136, Appendix B was 0.5 mg/kg GRO as gasoline for the methanol extraction of soils and .01 mg/L GRO as gasoline for waters. The recommended Practical Quantitation Limit (PQL) is 5 mg/kg GRO as gasoline for soil and 0.1 mg/L GRO as gasoline for water. For purposes of this method, the PQL is defined as 10 times the MDL.

11.4 The PQL must be no more then 0.1 times the Maximum Contaminant Limit for the project.

12. References

12.1 USEPA "SW-846 Test Methods for Evaluating Solid Waste", 3rd Edition; Methods 5030, 8000, 8015 and 8020.

12.2. "Sampling and Analysis of Gasoline Range Organics in Soils," American Petroleum Institute Pub. #4516, October 1991.

12.3. "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.

12.4 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.

12.5. 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.

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

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

12.8. 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.

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

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

Method AK 101 - Table 1
Purge and Trap Operating Parameters
For GRO/602/8020

Parameter	Setting
Purge Gas	Nitrogen or Helium
Purge Gas Flow Rate (mL/min.)	40
Purge Time (min.)	12.0 ± 0.1
Purge Temperature (°C)	Ambient
Desorb Temperature (°C)	180
Back Flush Inert Gas Flow (mL/min.)	20-60
Desorb Time (min.)	4
Trap Bake-out Time (min.)	10

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 (uL)[b]
5-100	100
200	50
1000	10
5000	100 uL 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 100 uL of methanol for each blank, sample and control.

c Dilute an aliquot of the methanol extract and then take 100 uL for analysis.

Method AK 101 - Table 3

Acceptance Criteria for Quality Control

ANALYTE	SPIKE CONCENTRATION		CONTROL LIMITS	
	Water (mg/L)	Soil (mg/kg)	% Recovery	Relative % Difference
Lab-Fortified Blanks				
Gasoline Range Organics	0.5	25	60-120	20
Laboratory Sample Surrogate Recovery				
Trifluorotoluene or Bromofluorobenzene	0.05	2.5	60-120	
Field Sample Surrogate Recovery				
Trifluorotoluene or Bromofiuorobenzene	0.05	2.5	50-150	
Continuing Calibration/ Calibration Verification Standards				
See 7.3	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.

Method AK 102
For Determination of Diesel Range Organics
Revision 3, 1/31/96

1. Scope and Application

1.1 Objectives

1.1.1 This method is designed to measure the concentration of Diesel Range Organics (DRO) in water and soil. This corresponds to an n-alkane range from the beginning of C_{10} to the beginning of C_{25}, and a boiling point range of approximately 170° C to 400° C. (See Method AK 102, Table 1).

1.1.2 Components greater than C_{24} present in products such as motor oils or lubricating oils are detectable under the conditions of the method.

1.2 Quantitation Limits

Practical quantitation limits (PQL) for this method for analysis of DRO are based on 100 ug/mL of diesel #2 in the extract and are approximately 0.10 mg/L for waters and 4.0 mg/kg for soils.

1.3 Dynamic Range

Dilutions should be performed as necessary to put the chromatographic envelope within the linear range of the method. Linear range is dependent in part upon column type, detector sensitivity, and injection volume. Typically, the approximate range is 0.01 mg/L to 100 mg/L as diesel.

1.4 Experience

This method is based on a solvent extraction, gas chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of solvent extractions and gas chromatographs as quantitative tools.

2. Method Summary

2.1 This method provides gas chromatographic conditions for the detection of semi-volatile petroleum products such as diesels. Other, non-petroleum compounds, with similar characteristics and boiling points, may also be detected with this method. One liter of Samples must be spiked with a surrogate compound and extracted with methylene chloride. The extract is dried and concentrated. An aliquot of the extract must be injected into a capillary column gas chromatogram equipped with a flame ionization detector (FID), which has been temperature programmed to facilitate separation of organic compounds. Quantitation must be performed by comparing the total chromatographic area between and including the peak start of C_{10} to the peak start of C_{25},

including both resolved and unresolved components , based on FID response compared to a blended commercial diesel standard (see paragraph 3.2). Integration must be performed using forced baseline-baseline integration.

2.2 This version of the method was developed by Dr. Mary Jane Pilgrim, and is based, in part, on a modification of the American Petroleum Institute consensus "Method for the Determination of Diesel Range Organics," Revision 2, 2/5/92 [11], supplemented with information gathered by the State of Alaska, Department of Environmental Conservation, State Chemistry Laboratory, with support from the Storage Tank Program. It is based in part on US Environmental Protection Agency Methods 8000 and 8100, SW-846, "Test Methods for Evaluating Solid Waste," 3rd Edition [1], Method OA-2 [2] and work by the EPA Total Petroleum Hydrocarbons Method Committee [3], and the State of Oregon, "Total Petroleum Hydrocarbon Methods" QAR 340-122-350 dated December 11, 1990.

3. Definitions

3.1 Diesel Range Organics (DRO): All chromatographic peaks, both resolved and unresolved, eluting between the peak start of n-decane (C_{10}) and the peak start of n-pentacosane (C_{25}). Quantitation is based on direct comparison of the area within this range to the total area over the same (C_{10} - C_{25}) range of the calibration standard as determined by FID response, using forced baseline-baseline integration.

3.2 Diesel Calibration Standard (DCS): A blend of equal weights of arctic diesel, diesel #1 and diesel #2 (1:1:1), diluted to appropriate concentrations in methylene chloride or acetone. In those areas where arctic diesel is unavailable, kerosene-K2 may be used to prepare the calibration standard. This deviation must be noted on the final report. The DCS mixture serves as a calibration standard for DRO.

3.3 Surrogate Control Standard (SCS): Ortho-terphenyl or equivalent, used as a laboratory data quality control.

3.4 Surrogate Control Sample: A method blank sample spiked with surrogate. The surrogate recovery is used to evaluate method control (see Method AK 102. Table 2).

3.5 Calibration Verification Standard (CVS): A quality control standard (preferably Environmental Resources Association (ERA) Certified, or equivalent), prepared as in 3.2 but with products from a source other than those used to prepare the Diesel Calibration Standard. It is used by the laboratory as a quality control check to verify the accuracy of calibration.

3.6 Laboratory Fortified Blank (LFB): A method blank sample spiked with a commercial diesel fuel other than those blended to make the Diesel Calibration Standard (3.2). The spike recovery is used to evaluate method control (see Method AK 102, Table 2). The CVS may be used in the LFB.

3.7 Retention Time Window Standard: A mixture of the normal alkanes n-decane and n-pentacosane (C_{10} and C_{25}) which is analyzed once every 24 hour "day" or with each batch of samples, whichever is less frequent, not to exceed 20 samples per batch. This standard serves to define the retention time window for DRO.

3.8 Internal Standard: Alpha androstane, used to normalize DRO concentrations. Use of an internal standard is recommended, but not required.

3.9 Standard Soil: Ottawa sand, Norwood loam, Houston black clay, or other standard soil with characteristics which match the field samples as closely as possible, used in quality control standards.

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

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

4. Interferences

4.1 Other organic compounds including, but not limited to, animal and vegetable oil and grease, chlorinated hydrocarbons, phenols, phthalate esters and biogenic terpenes are measurable under the conditions of this method. Heavier petroleum products such as lubricating oil and crude oils also produce a response within the retention time range for DRO. As defined in the method, the DRO results include these compounds.

4.2 Method interferences may be reduced by washing all glassware with hot soapy water and then rinsing it with tap water, methanol, and methylene chloride. Heating the glassware to reduce contaminants should not be necessary if this cleaning method is followed. At least one blank must be analyzed with each extraction batch to demonstrate that the laboratory samples are free from method interferences.

4.3 High purity reagents such as Burdick and Jackson GC[2] methylene chloride or Baker capillary grade methylene chloride must be used to minimize interference problems.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is encountered, it should be followed by analysis of a solvent blank to check for instrument contamination.

5. Safety Issues

5.1 The toxicity or carcinogenicity of each reagent 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 Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should also be made available to all personnel involved in chemical analysis. Additional references to laboratory safety should be available and identified for use by the analyst.

5.2 A hearing protection device should be used when performing sonication.

6. Apparatus and Materials

(Unless otherwise indicated, all apparatus and materials are suggested only.)

6.1 Glassware

6.1.1 4 oz. amber glass wide mouth jars with Teflon-lined screw caps

6.1.2 Separatory funnel - 2000 mL with Teflon stopcock

6.1.3 Continuous liquid-liquid extractor - equipped with Teflon or glass connecting joints and stopcocks requiring no lubrication (Hershberg-Wolf Extractor, Ace Glass Company, Vineland, New Jersey, P/N6841-10, or equivalent).

6.1.4 Concentrator tube. Kuderna-Danish 10 mL graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

6.1.5 Evaporative flask, Kuderna-Danish 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

6.1.6 Snyder column, Kuderna-Danish three ball macro (Kontes K-503000-0121 or equivalent). Rotary evaporation set-up may be used alternatively.

6.1.7 Jars: One liter amber glass, with Teflon lined screw caps.

6.18 Two mL glass vials with Teflon-lined cap (autosampler vials).

6.1.9 Disposable pipettes: Pasteur.

6.1.10 Graduated cylinders: 250 mL.

6.1.11 Glass or Teflon funnels.

6.2 Boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

6.3 Micro syringes: 1 ul, 5 ul, 10 ul, 25 ul, and 100 ul.

6.4 Water bath - Heated with concentric ring cover, capable of temperature control (+/- 2°C). The bath should be used in a hood.

6.5 An analytical balance capable of accurately weighing 0.0001 g should be used for preparing standards and % moisture determinations. A top-loading balance capable of weighing to the nearest 0.1 g should be used for sample preparation.

6.6 Stainless steel spatula.

6.7 Gas Chromatography

6.7.1 Gas Chromatograph: Analytical system including appropriate gas supply and all required accessories, including a Flame Ionization Detector (FID), column supplies, gases, and syringes. A data system capable of determining peak areas using a forced baseline - baseline projection is required. A data system capable of storing and reintegrating chromatographic data is recommended.

6.7.2 Columns

6.7.2.1 Column 1: 25 M x 0.25 mm Quadrex 007 5% methyl phenyl 0.5 micron film thickness.

6.7.2.2 Alternate column: 30 M x 0.53 mm ID Restek RTX-5, 1.5 micron film thickness

6.7.2.3 Other Columns may be used - capillary columns may be essential to achieve the necessary resolution. The column must resolve C_{10} from the solvent front in a midrange DCS or CVS and, if AK103 is to be done simultaneously, must resolve C_{24} from C_{25}.

6.8 Sonication

6.8.1 Ultrasonic cell disrupter: A horn-type sonicator equipped with a titanium tip should be used. A Heat Systems-Ultrasonics, Inc. Model W-385 (475 watt) sonicator or equivalent (power wattage must be a minimum of 375 with pulsing capability and No. 200 ½ inch Tapped Disrupter Horn) plus No. 207 3/4 inch Tapped Disrupter Horn, and No. 419 1/8 inch Standard tapered Microtip probe.

6.8.2 A Sonabox or equivalent is recommended with the above disrupter for decreasing sound (Heat Systems-Ultrasonics, Inc. Model 432 13 or equivalent).

6.9 Soxhlet extraction apparatus as described in SW-846 Method 3540 [1].

6.10 Nitrogen evaporator with high purity (grade 4.5 or equivalent) nitrogen gas source.

7. Reagents and Standards

7.1 Reagent Water: Water that has been shown to be free from DRO compounds - a Millipore system or equivalent is recommended.

7.2 Methylene Chloride, Hexane, Acetone - pesticide grade or equivalent. At a minimum, the solvents must be shown to be free from DRO.

7.3 Sodium Sulfate - (ACS grade) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray or by extracting three times with methylene chloride and drying at 100±5° C. Incomplete cleaning of sodium sulfate can result in DRO contamination of samples.

7.4 Stock Standard Solutions - Prepare the following stock standards. Unless noted, all are prepared in the methylene chloride listed in 7.2 above. Standard preparation should follow guidelines in SW846 [1]. All standards prepared by the laboratory must be stored without headspace at -10 to -20°C and protected from light. Marking of the meniscus is helpful in maintaining stock standard integrity. Standards must be replaced within 6 months of preparation. Standards should be checked regularly to assure their integrity. Standards which are purchased pre-made from commercial suppliers may be kept for the life, and under the conditions, specified by the manufacturer if different than described in this paragraph.

7.4.1 Optional Stock Internal Standard: 1000 ug/mL 5 alpha-androstane. Other internal standards may be used provided they do not interfere with the DRO components.

7.4.2 Recommended Surrogate Control Standard: 200 ug/mL ortho-terphenyl (OTP). A working solution is made at 20 ug/mL (recommended concentration) in acetone.

7.4.3 Diesel Calibration Standard: A blend of equal weights of diesel fuel, mixed together to form a composite diesel fuel (1:1:1, arctic diesel : diesel #1 : diesel #2) is used to prepare stock calibration standards in methylene chloride. No fewer than 3 concentrations of this DCS are used for instrument calibration. A five point calibration curve is recommended. Other than one standard concentration near the practical quantitation limit, the expected range of concentrations found in project samples should define the working range of the GC. If arctic diesel is not available, kerosine-K2 may be used in its place. This substitution, if used, must

be noted on the final data reports. A mid-range dilution of this blend serves as the Continuing Calibration Standard.

7.4.4 Retention Time Window Standard: A stock solution of C_{10} and C_{25} each at a level of at least 2000 ug/mL. This blend of alkanes serves as a retention time window defining mix for DRO.

7.4.5 Stock Calibration Verification Standard (CVS): From a blend of commercial diesels other than those used to prepare the DCS, make an equal weight mixture as described in 7.4.3. A working solution is made at a recommended concentration of 5000 ug/mL in acetone.

8.0 Sample Collection, Preservation, Containers, and Holding Times

8.1 Water samples are collected, in duplicate, in one liter amber glass containers with Teflon-lined screw caps and acidified to pH 2 or less with HCl.

8.2 Soils are collected in a core tube, or 4 or 8 oz amber glass jar with Teflon-lined lid. The samples are stored at 4° ± 2° C from the time of collection until extraction. Extraction must be performed on waters within 7 days and soils within 14 days [1]. All analyses of extracts must take place within 40 days.

8.3 Soil samples to be analyzed for both volatiles and DRO may be collected in the same, methanol preserved container and stored as for GRO (AK101). If this option is selected, the mechanics of the collection, preservation and container should be discussed with the client before sampling kit preparation. DRO extraction and analysis must still meet the requirements of 8.2, above.

9. Procedure

9.1 Sample Preparation

The preferred method for water extraction is SW-846 Method 3510 (Separatory Funnel Liquid-Liquid Extraction), and for soil samples Method 3540 (Soxhlet Extraction). However, any sample extraction technique which meets the quality assurance requirements specified in Section 10 and Table 1 of this method may be used.

9.1.1 Water extraction - Separatory Funnel.

9.1.1.1 Measure a 1 L portion of the sample and transfer to a 2 L separatory funnel. If the sample is in a 1 L or smaller bottle, mark the water meniscus on the side of the sample bottle. Measure the exact volume by adding tap water to the bottle to the marked level, and then transferring the volume of tap water to a 1 L graduated cylinder. Use no more than 1 L of

sample per 2 L separatory funnel. For blanks and quality control standards, pour 1 L of reagent water (7.1) into the separatory funnel.

9.1.1.2 Check and note the pH of the sample. If the field samples have been preserved with HCl, it is recommended that the quality control samples and blanks be preserved in the same way.

9.1.1.3 Add 1 mL of surrogate standard (7.4.2, recommended level of 20 ug/mL if o-terphenyl is used).

9.1.1.4 For every batch or 20 samples extracted (whichever is more frequent), prepare duplicate LFBs by adding 1 mL of 5000 ug/mL CVS (7.4.5) to each of two 1 L volumes of reagent water. Daily or for every 20 samples (whichever is more frequent), prepare a method blank using 1 L of reagent water. Surrogate must be added to both the LFBs and the method blank.

9.1.1.5 For samples, add 60 mL methylene chloride to the sample bottle to rinse the inner walls after the sample has been transferred to the separatory funnel. **Do Not** cap and shake the bottle, rinse the glass only; then transfer the solvent to the separatory funnel. Extract the sample by shaking it for no less than two minutes with frequent ventilation.

9.1.1.6 Allow the layers to separate (approx 10 minutes rest after shaking). If there is an emulsion, break it. If the emulsion cannot be broken (recovery of <80% of the methylene chloride, corrected for water solubility of methylene chloride), transfer the sample, solvent, and emulsion into the extraction chamber of a continuous extractor and proceed as described in SW846 Method 3520 (Continuous Liquid-Liquid Extraction). Alternative physical techniques for breaking up emulsions may be acceptable.

9.1.1.7 Drain the bottom layer (methylene chloride) into a 250 mL graduated cylinder or other calibrated glassware.

9.1.1.8 Repeat the extraction twice more, using a 60 mL aliquot of methylene chloride each time. Collect the solvent in the same graduated cylinder (or equivalent) as described in 9.1.1.7. Record the volume recovered (recommended) and other prep information as an indication of extraction efficiency.

9.1.1.9 Put a plug of glass wool in a glass or Teflon funnel and fill about 2/3 full with anhydrous sodium sulfate. Rinse the funnel and sodium sulfate with 30-40 mL of methylene chloride, discard rinsate. Pour the extract through the rinsed sodium sulfate into a 500 mL Kuderna-Danish (K-D) evaporative concentrator. Rinse the graduated cylinder, then the sodium

sulfate, with small amounts of methylene chloride. Add these rinses to the K-D.

9.1.1.10 Add a few boiling chips (6.2) to the K-D and attach a 3-ball Snyder to the top. Pre-wet the column by adding about 1 mL of methylene chloride to the inverted column before attaching it to the K-D.

Note: The concentration step is critical; losses of target compounds can occur if care is not taken.

9.1.1.11 Place the K-D in a heated water bath set at 95°C so that the receiver tube is immersed in hot water and the entire lower rounded surface is bathed in steam. At a proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume is less than or equal to 10 mL, remove the K-D from the bath and allow it to cool completely.

Note: The extraction and concentration steps must be performed under a hood. Not only is the methylene chloride a potential health hazard (see MSDS), ***if the heated water bath is not properly temperature-controlled, the concentration apparatus can explode.***

9.1.1.12 After the K-D has cooled, rinse the Snyder column and middle flask with a small amount of methylene chloride. Transfer the extract to a calibrated 15 mL centrifuge tube, rinsing with a small amount of methylene chloride. Rinse all of the ground glass joints well, as compounds collect on the ground glass.

9.1.1.13 If further concentration is desired, carefully concentrate the extract to no less than 1.0 mL under a gentle stream of nitrogen using the evaporation apparatus. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher (5-10 mL). Transfer to a labeled vial of appropriate size with Teflon-lined cap, mark the meniscus. Extracts should be stored in a non-frost free freezer.

9.1.1.14 Record information for the extraction and concentration steps.

9.1.2 Soil Preparation - Soxhlet Extraction

9.1.2.1 Decant any water layer that may accompany the solid layer in the sample. Note what percent of the sample the water represents and, if sufficient volume exists, extract and analyze the water for DRO. Also note the apparent condition of the sample (presence of foreign materials, variable particle size, presence of oil sheen, multiple phases, etc).

9.1.2.2 Weigh 10 g to 30 g of the original sample into an extraction thimble. Add an equal weight of anhydrous sodium sulfate and stir the mixture well with a wooden tongue depressor. The sample should have a grainy texture - if the sample clumps, add more sodium sulfate until a grainy texture is achieved and note the addition. (Do this for all samples and standards.)

9.1.2.3 Place loaded thimbles in extractors and add surrogate to both field and quality control samples.

9.1.2.4 Add CVS to the duplicate LFBs. These quality control samples should contain 10 g of methylene chloride rinsed Ottawa Sand or alternative standard soil. In addition, prepare a method blank.

9.1.2.5 Add 300 mL of methylene chloride to the 500 mL extraction flask. Less extraction solvent may be used if the quality control criteria specified in Section 10 and Table 1 are met. Also add a few methylene chloride washed carborundum boiling chips to the flask. Connect the extractor to the flask and the condenser to the extractor. Allow samples to extract for 18-24 hours, or as long as necessary to achieve optimum surrogate recovery. Be sure that coolant is flowing around the condensers.

9.1.2.6 Recommendation: After extraction, disassemble extractor and add about 3 g anhydrous sodium sulfate to the extract and allow to incubate for 2 hours. (This assures that the extract is water-free before concentration.)

9.1.2.7 Transfer extract into a clean 500 mL K-D and proceed from 9.1.1.9.

9.1.3 Moisture Determination for Solids

9.1.3.1 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 petroleum compound

concentrations in the soil, all drying should be done under a functioning hood.

9.1.3.2 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 0.001 g. Dry the sample overnight in a warm (100±5°C) oven.

9.1.3.3 Remove the sample from the oven and cool in a desiccator until the sample reaches room temperature, and weigh to the nearest 0.001g. Record the weight.

9.1.3.4 Return the soil sample to the oven for an additional time period (not less than 2 hours), cool again in the desiccator until the sample reaches room temperature, and weigh to the nearest 0.001g.

9.1.3.5 If the weight of the sample has remained constant (± 4%) from the initial "dry" weight (9.1.3.4), use this number for the moisture determination (see 9.6.1). If the second weighing shows that the sample has lost further weight, continue drying and weighing the sample until the weight becomes constant, then proceed to 9.6.1.

9.1.3.6 If a sample contains a high concentration of petroleum product, constant weight may be difficult to attain. If, after several tries, the ±4% criteria cannot be reached an estimated % moisture may be reported with appropriate explanation.

9.1.4 Dilution Technique

9.1.4.1 This is used for product or waste samples for which extraction is not appropriate and which are soluble in methylene chloride.

9.1.4.2 Weigh 1 g of sample into a 10 mL volumetric flask. Dilute to 10 mL with methylene chloride. Transfer to a 12 mL vial with a Teflon lined lid. Mark meniscus and store at ≤4°C.

9.2 Gas Chromatography

9.2.1 Conditions (Recommended):

Set helium column pressure to 20#. Set column temperature to 40° C for 2 minutes, then ramp at a rate of 12° C/min to 320° C and hold for 15 min. (run time = 36 minutes). Set FID Detector to 320° C and injector to 280° C. The reference book High Resolution Chromatography by Hewlett-Packard is a good source of information on how to optimize flow rates, etc.

9.2.2 Performance Criteria: GC run conditions and columns must be chosen to meet the following criteria:

9.2.2.1 Resolution of the methylene chloride solvent front from C_{10}.

9.2.2.2 The separation number, TZ, should be greater than 15 for C_{24} and C_{25}, if RRO is to be analyzed concomitantly.

$$TZ = \frac{\text{retention time } C_{25} - \text{retention time } C_{24}}{W_{½} \text{ of } C_{25t} + W_{½} \text{ of } C_{24}} - 1$$

Where "$W_{½}$" = peak width at half-height

9.2.2.3 The column must be capable of separating typical diesel components from the surrogate and internal standards. In particular, there are potential problems with the resolution of n-C_{19}/ortho-terphenyl and n-C_{21}/5 alpha-androstane at varying relative concentrations.

9.3 Calibration

9.3.1 Calibrate the GC, set up as in 9.2, with an initial five point (recommended) calibration using DCS (7.4.3). The final calibration curve must be represented by no less than 3 concentrations of DCS.

9.3.2 Choose DCS concentrations to cover the DRO range expected in the samples, or the linear range of the instrument, whichever is less. One of the concentrations must be at or near the practical quantitation limit.

9.3.3 Tabulate the area response of the calibration standard against mass injected. The ratio of the response to the amount injected, defined as the response factor (RF), can be calculated for the standard at each concentration. If the average percent relative standard deviation (%RSD) is less than 25% over the working range, linearity through the origin can be assumed, and the continuing calibration response factor can be used in place of a calibration curve.

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

Where: Ax = Peak area of analyte
Ais = Peak area of internal standard
Qis = Amount of internal standard
Qx = Amount of analyte

Alternately, external standard calibration may be used (See Method 8000 [1]).

Then,

$$\text{External Standard Response Factor (RF)} = \frac{\text{Total peak area of standard}}{\text{Mass injected}}$$

9.3.4 The calibration curve must be confirmed using the CVS (7.4.5). This standard verifies the accuracy of the calibration. The concentration of the CVS should be within the expected concentration range of the samples to be analyzed.

9.3.5 The working RF or calibration curve must be verified on each working day (24 hours) by the injection of a CCS (7.4.3) at a concentration mid-point on the calibration curve. The CCS is a diluted aliquot of the same standard used to initially calibrate the instrument. If the response for the CCS varies from the predicted response by more than 25%, a new calibration curve must be prepared.

$$\text{Percent Difference} = \frac{R_1 - R_2 \times 100}{R_1}$$

where:
R1 = Average RF from the calibration curve
R2 = Response Factor from CCS

9.4 Retention Time Window Definition:

9.4.1 Before establishing windows, be certain that the GC system is within optimum operating conditions (6.6). Make three injections of the Retention Time Window Standard (7.4.3) 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.

9.4.2 Calculate the standard deviation of the three absolute retention times for decane and pentacosane and the surrogate.

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

9.4.2.2 In those cases where the standard deviation for a particular analyte is zero, the laboratory should use $\pm$ 0.05 min. as a retention time window.

9.4.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed or instrument conditions changed. The data must be retained by the laboratory for at least a year.

9.4.4 Retention time windows must be verified regularly and updated no less frequently than once a year.

9.5 Gas Chromatograph Analysis

9.5.1 Samples are analyzed by GC/FID. Optimum injection volumes (2 uL using the conditions established in 9.2) must be established for specific instrument conditions.

9.5.2 For internal standard calibration, the internal standard is spiked into each sample and standard at a concentration of 200 ug/mL of sample extract. Twenty uL of 5-alpha androstane stock at 1000 ug/mL may be spiked into the 1 mL final volume or a corresponding amount may be added to an aliquot of the final extract. (Note: DRO values >2000 ug/mL may lead to measurement bias due to coelution with the internal standard.)

9.5.3 If initial calibration (9.3) has been performed, verify the calibration by analysis of a mid-point CCS. With each day's run, open a 24 hour analysis window. This is done by running the Retention Time Window Standard (7.4.4).

9.5.4 Calculate the percent difference of the response factor from the mean response factor as in 9.3.2. This is done for DRO as a group from the CCS. If the response factor has a percent difference greater than 25%, corrective action must be taken.

9.5.5 A methylene chloride blank must be analyzed each day to determine the area generated from normal baseline noise under the conditions prevailing in the 24 hour period. This area is generated by projecting a horizontal baseline between the retention times observed for the peak start of C_{10} and the peak start of C_{25}. This methylene chloride blank is integrated over the DRO area in the same manner as for the field samples and is reported as the solvent blank. (Refer to reference 4.) **Do not baseline subtract. This information is for data interpretation purposes only.**

9.5.6 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 column must be baked out and subsequent blanks analyzed until the system is shown to retain contaminant at concentrations less than the PQL.

9.5.7 If the DRO concentration exceeds the linear range of the method (as defined by the range of the calibration curve) in the final extract, corrective action must be taken. The response of the major peaks should be kept in the upper half of the linear range of the calibration curve. Due to potential measurement bias, internal standard calibration should not be used when DRO exceeds 5000 ug/mL in the final extract (ref. 9.5.2). The sample should be diluted or external standard calibration should be used.

9.6 Calculations:

9.6.1 % Moisture Calculation for Soils

$$\% \text{ Moisture} = (A-C)/(A-B) \times 100$$

Where:

A= weight of boat + wet sample
B= weight of boat
C= weight of boat + dry sample

Note: Make sure drying oven is placed under a hood. Heavily contaminated soils will produce strong organic vapors.

9.6.2 Internal Standard Calibration: The concentration of DRO in the sample must be determined by calculating the absolute weight of analyte chromatographed from a summation of peak response for all chromatographic peaks eluting between the peak start of n-decane and the peak start of n-pentacosane, using the calibration curve or the response factor determined in section 9.3. Also refer to Section 9.4 (Retention Time Window Definition). The concentration of DRO is calculated as follows:

Aqueous/Soil samples:

$$C_s = \frac{(Ax)(Cis)(D)(Vt)}{(Ais)(RF)(Vs)}$$

Where:

Cs = Concentration of DRO (mg/L or mg/kg).
Ax = Response for the DRO in the sample, units in area.
RF = Response Factor from CCS (see 9.3.3).
Ais = Response for the internal standard, units same as for Ax.
Cis = Internal standard concentration (mg/mL).
Vt = Volume of final extract in mL.
D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.
Vs = Amount of sample extracted in L or kg.

9.6.3 To calculate mg/dry kg for soil samples,

$$\text{mg/dry kg DRO} = \frac{Cs}{1-(\%\ \text{moisture}/100)}$$

The % moisture calculation must be included in the data package (see *9.6.1*).

9.6.4 External Standard Calibration:

Aqueous/Soil samples:

$$C_s = \frac{(Ax)\,(A)\,(Vt)\,(D)}{(As)\,(Vs)}$$

Where:

Cs = Concentration of DRO (mg/L or mg/kg).
Ax = Response for the DRO in the sample, units in area.
As = Response for the external standard, units same as for Ax.
A = External standard concentration (mg/mL).
Vt = Volume of Final extract in mL.
D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.
Vs = Amount of sample extracted in L or kg.

9.6.5 Some software programs are capable of performing 9.6.1 and 9.6.3 with minimal analyst intervention. Additionally, some software programs can "update" a calibration curve based on the response of the CCS. If a calibration curve is updated in this manner, a valid CVS must be analyzed and results must fall within the Quality Control Criteria specified in Section 10 and Table 1 before field samples can be analyzed.

10. Quality Control (See Table 1 of this method).

10.1 The laboratory must establish and maintain the ability to generate acceptable accuracy and precision and to 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 recovery as outlined in Method 8000, section 8.0 [1], and in this method.

10.2 After successful calibration (Section 9.8), analyze the reagent blank. The reagent blank must be analyzed with every extraction batch. The surrogate recovery must be within established limits (see Method AK 102, Table 1), or within the limits established by the project plan (whichever is more stringent) and the control sample must not have DROs above the practical quantitation limit.

10.3 With every batch or 20 samples, duplicate LFBs must be analyzed (reagent water or Ottawa sand matrix, as is appropriate to the samples being analyzed). The accuracy and precision of the duplicate standards must be within established limits (Table 1). Also, the mid-point CCS must be analyzed at the end of each sequence and once per 20 samples, and compared to the successful calibration as described in 9.8.6, and fall within established limits (Table 1).

10.4 Every batch of samples extracted must be accompanied by a method blank to demonstrate that samples are free from method interference. The method blank must have DROs less than the PQL.

10.5 Each laboratory should generate control limits based on the average recovery, with ± 2 standard deviations as a warning limit and ± 3 standard deviations the action limit. Method Detection Limits (MDL) must be established using 40 CFR Part 136, Appendix B.

10.6 If any of the criteria in 9.3, 10.2, 10.3 and 10.4 are not met, corrective action must be taken before samples are analyzed.

10.7 Calculate the surrogate standard recovery in each sample. If recoveries are outside established limits, (Table 1), verify calculations, dilutions, and standard solutions. Verify instrument performance.

10.7.1 High recoveries may be due to a coeluting matrix interference or the presence of high molecular weight contaminants; examine the sample chromatogram.

10.7.2 High recoveries may also be due to memory effects caused by poor sample volatility, backflash, or carryover; check instrument conditions, injection volume, and injector temperature.

10.7.3 Low recoveries may be due to adsorption by the sample matrix (muskeg, tundra, forest loam, etc).

10.7.4 Low recoveries may also be caused by incorrect integration. The chromatographic profile of DROs may not give baseline resolution of all components, resulting in a characteristic rise in baseline underneath the resolved hydrocarbon components. Do not use peak-to-peak integration, use forced baseline integration.

10.7.5 If internal calibration has been used, DRO results must be normalized using the internal standard response. If surrogate recovery is still outside of established limits, corrective action must be taken.

10.7.6 If external calibration has been used, and surrogate recovery is outside of established limits, offered corrective action must be taken.

10.8 If field samples show low surrogate recovery due to suspected matrix effects, DRO results must be flagged. If the surrogate recovery is <50% and the calculated DRO concentration falls within a factor of 2 of the action level, the laboratory should recommend that the client resubmit the sample for matrix spike/matrix spike duplicate analysis. (To perform matrix spike analyses, follow 9.1, except use a field sample instead of a standard matrix.) 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.

10.9 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.

10.10 Minimum quality control acceptance criteria are set forth in this section. More stringent quality control criteria may be required by specific project plans.

10.11 Corrective Action

10.11.1 Calibration

10.11.1.1 If the initial calibration does not meet the criteria set forth in 9.3.3 and 9.3.4, the instrument must be recalibrated.

10.11.1.2 If the continuing calibration does not meet the criteria set forth in 9.3.5 and Table 1, the instrument must be recalibrated.

10.11.2 Surrogates

10.9.2.1 If surrogates are outside established control limits (Table 1), the following assessments and/or correction actions must occur:

A) Check to be sure there are no errors in calculations and that the concentration of the surrogate and internal standard solution 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) Reprepare and reanalyze the sample if none of the above resolves the problem.

10.11.2.2 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. Provided all other QC acceptance criteria are met (section 10), it is only necessary to reprepare/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.

10.11.3 Blanks:Additional blanks may be necessary for certain projects to meet the goals of Chapter 2, section 9 of the UST Procedures Manual.

10.11.3.1 Instrument Blanks:
Instruments must be evaluated with each 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.

10.11.3.2 Method Blank:
Method Blanks must be analyzed with each extraction batch IF the results of the field samples show contamination above the MCL. The Method Blank for AK102 can also serve as the Reagent Blank if DRO is less than the PQL.

10.11.3.3 Field Blank:
If the field samples yield DROs above the MCL, and contamination is found below the PQL in the Reagent Blank, a Field Blank should be analyzed to identify whether the source of contamination originated in the field sample collection procedure, during trip 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.)

10.11.4 Laboratory Fortified Blanks

10.11.4.1 If the analyte recovery from the LFBs is outside the established recovery limits (Table 1), 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) Reprepare and reanalyze the samples if none of the above resolves the problem.

10.11.4.2 If there relative percent difference between the LFB results exceeds the control limits, but meets the percent recovery criteria (Table 1), 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 Single lab method performance data for the DROs method in Ottawa sand and other soil types is presented below.

11.2 Results for diesel spikes (methylene chloride extraction direct injection, soils)

Matrix	Diesel Spike Amount mg/kg	Percent Recovery
Ottawa Sand	70	97
Ottawa Sand	70	98
Glacial Blue Clay	70	70
Glacial Blue Clay	70	76
Forest Loam	70	136
Forest Loam	70	163
River Sediment	70	142
River Sediment	70	167
Marine Sand	70	95
Marine Sand	70	88

Notes: Analyses performed by State of Alaska, DEC Laboratory. Diesel used = DCS.
All highly organic soil matrices showed high analyte recovery due to naturally occurring DROs.

11.3 The method detection limit for soil calculated according to 40 C.F.R., Part 136, Appendix B (1994) was 1.6 mg/kg (external standard calibration, Ottawa sand).

12. References

1. USEPA "SW-846 Test Methods for Evaluating Solid Waste", 3rd Edition; Methods 8000, 8100, 3510, 3520, 3540, and 3550.

2. "Method OA-2: Extractable Petroleum in Products," Revision January 10, 1990", University Hygienic Laboratory, Iowa City, Iowa.

3. "Method for Determination of Extractable Petroleum Hydrocarbons (EPH) in Soil and Water," Draft-February 28, 1990, prepared for Total Petroleum Hydrocarbons Method Committee by Midwest Research Institute.

4. Zilis, K., M. McDevitt, and J. Parr, "A Reliable Technique for Measuring Petroleum Hydrocarbons in the Environment," presented at the conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater, NWWA, Houston, Texas, November 1988.

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10. ASTM "Standard Methods for Comparison of Waterborne Petroleum Oils by Gas Chromatography," pp. 3328-78.

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12. Research done by the State of Alaska, Department of Environmental Conservation, Division of Environmental Quality, Juneau Environmental Analysis Laboratory.

Method AK 102, Table 1
ACCEPTANCE CRITERIA FOR QUALITY CONTROL

ANALYTE	SPIKE CONCENTRATION Water (mg/L)	Soil (mg/kg)	CONTROL LIMITS % Recovery	Relative % Difference
Lab Fortified Blanks				
Diesel Range Organics	0.5	20	60 - 120	20
Continuing Calibration/ Calibration Verification				
Diesel Range Organics			75 - 125	
Laboratory Sample Surrogate Recovery				
Ortho-terphenyl	0.02	0.8	60 - 120	
Field Sample Surrogate Recovery				
Ortho-terphenyl	0.02	0.8	50 - 150	

Method AK 103
For Determination of Residual Range Organics
Revision 2.0, 1/31/96

1. Scope and Application

1.1 Objectives

1.1.1 This method is designed to measure the concentration of Residual Range Organics (RRO) in soil. This corresponds to an n-alkane range from the beginning of C_{25} to the end of C_{36}, and a boiling point range of approximately 400° C to 500° C.

1.1.2 The method is primarily designed to measure lubricating or motor oils or other heavy petroleum products. Components greater than C_{36} present in products such as asphalts, and mid-range petroleum products such as diesel and bunker C, are also detectable under the conditions of the method.

1.1.3 This method can be an extension of the Method for Determination of Diesel Range Organics as specified in AK102. All quality assurance requirements of both methods (Section 10) must be met. Reasonable modification in order to accommodate the concurrent analysis of DRO and RRO is within the scope of this method.

1.2 Quantitation Limits: The practical quantitation limit (PQL) for this method of analysis of RROs is based on studies done by laboratories other than the State of Alaska, Department of Environmental Conservation, State Chemistry Laboratory and is approximately 100 mg/kg for soils using motor oil as a standard.

1.3 Dynamic Range: Dilutions should be performed as necessary to put the chromatographic envelope within the linear range of the method. Linear range is dependent in part upon column type, detector sensitivity, and injection volume. Typically, the approximate range is 10 mg/L to 200 mg/L.

1.4 Experience: This method is based on a solvent extraction, gas chromatography (GC) procedure. This method should be used by, or under the supervision of, analysts experienced in the use of solvent extractions and gas chromatographs and skilled in interpreting gas chromatograms and their use as a quantitative tool.

2. Method Summary

2.1 This method provides gas chromatographic conditions for the detection of high molecular weight semi-volatile petroleum products such as motor oils. Other non-petroleum products, with similar characteristics and boiling points, may also be detected with this method. The sample is spiked with a surrogate compound and extracted with methylene chloride. The extract is dried and concentrated to a known volume. A portion of the dried, concentrated extract is injected into a capillary column gas chromatograph equipped with a flame ionization detector (FID), which has been temperature programmed to facilitate separation of organic compounds. Quantitation must be performed by comparing the total chromatographic area between the peak start of C_{25} and the peak end of C_{36}, both resolved and unresolved components, based on FID response, and using forced baseline-baseline intergation, compared to a blended commercial standard called the Residuals Calibration Standard (see paragraph 3.2).

2.2 This version of the method was developed by Dr. Mary Jane Pilgrim, and is based in part on US EPA Methods 8000 and 8100, SW-846, "Test Methods for Evaluating Solid Waste," 3rd Edition [1], Method OA-2 [2], the API consensus method "Method for the Determination of Petroleum Hydrocarbons", Original version, 2/3/92 [3] and work by the EPA Total Petroleum Hydrocarbons Method Committee [4], the State of Oregon, "Total Petroleum Hydrocarbon Methods" QAR 340-122-350 dated December 11, 1990 and the State of Washington, "Hydrocarbon Identification Method" WTPH-HCID from Guidance for Remediation of Releases from Underground Storage Tanks, document 91-30 dated July 1991, and data from Alaska's State Chemistry Laboratory, with support from the Storage Tank Program .

3. Definitions

3.1 Residual Range Organics (RRO): All chromatographic peaks both resolved and unresolved, eluting between the peak start of n-pentacosane (C_{25}) and the peak end of. n-hextriacontane (C_{36}). Quantitation is based on direct comparison of the area within this range to the total area of the motor oil standard within the same (C_{25} - C_{36}) range as determined from FID response using baseline-baseline integration.

3.2 Residuals Calibration Standard (RCS): A blend of equal weights of 30 weight and 40 weight motor oils (1:1) and diluted to appropriate concentrations in methylene chloride. This standard serves as a calibration standard for RRO. It is recommended that the RCS components be combined with the DCS components if DRO (AK102) is to be done simultaneously.

3.3 Surrogate Control Standard (SCS): n-Triacontane-d62 or equivalent, used as a laboratory data quality control. Any variance from this surrogate must be approved by the ADEC Approval Authority, and a demonstration of suitability must be performed. This surrogate may be combined with the surrogate for DRO (AK102) if the methods are to be done simultaneously.

3.4 Surrogate Control Sample : A method blank sample spiked with surrogate . The surrogate recovery is used as a laboratory control (see Method AK 103, Table 1.

3.5 Calibration Verification Standard (CVS): A commercial motor oil blend, prepared as in 3.2 but with products from a source other than those used to prepare the RCS . It is used by the laboratory as a quality control check to verify the accuracy of the calibration.

3.6 Laboratory Fortified Blank (LFB): A method blank sample spiked with CVS (3.5). The spike recovery is used to evaluate method control (see Method AK 103, Table 1).

3.7 Retention Time Window Standard: A mixture of the normal alkanes n-pentacosane (C_{25}) and n-hextriacontane (C_{36}) which is analyzed once every 24 hour "day" or with each batch of samples, whichever is less frequent, not to exceed 20 samples per batch. This standard serves to define the retention time window for RRO.

3.8 Internal Standard: No internal standard has been used in development of this method. Any internal standard which mimics the chemical characteristics of heavy petroleum products may be used, with prior ADEC approval.

3.9 Standard Soil: Ottawa sand or other standard soil with characteristics which match the field samples as closely as possible, used in quality control standards.

3.10 Continuing Calibration Standard (CCS): A mid-range working standard diluted from the RCS (3.2), used to verify that the analytical system is operating in a manner comparable to that at the time of calibration.

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

4. Interferences

4.1 Other organic compounds including, but not limited to, animal and vegetable oil and grease, chlorinated hydrocarbons, phenols, phthalate esters, and biogenic terpenes are measurable under the conditions of this method. Some lighter petroleum products such as bunker C and diesels, as well as crude oils, may produce a response within the retention time range for RRO. As defined in the method, the RRO results include these compounds.

4.2 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing it with tap water, methanol, and methylene chloride. Heating the glassware to reduce contaminants should not be necessary if this cleaning method is followed. At least one blank must be analyzed with each extraction batch to demonstrate that the samples are free from method interferences.

4.3 High purity reagents such as Burdick and Jackson GC[2] methylene chloride or Baker capillary grade methylene chloride must be used to minimize interference problems.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. When an unusually concentrated sample is encountered, it should be followed by a solvent blank to check for instrument contamination.

5. Safety Issues

5.1 The toxicity or carcinogenicity of each reagent 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 Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Date Sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety should be available and should be identified for use by the analyst.

5.2 A hearing protection device should be used when performing sonication.

6. Apparatus and Materials

(Unless otherwise indicated, all apparatus and materials are suggested.)

6.1 Glassware

6.1.1 4 oz. amber glass wide mouth jars with Teflon-lined screw caps

6.1.2 250 mL glass centrifuge tubes (if using sonication extraction).

6.1.3 Two mL glass vials with Teflon-lined cap (autosampler vials).

6.1.4 Disposable pipettes: Pasteur.

6.1.5 Graduated cylinders: 250 mL.

6.1.6 Glass or Teflon funnels.

6.2 Boiling chips - Approximately 10/40 mesh. Heat to 400°C for 30 minutes or Soxhlet extract with methylene chloride.

6.3 Micro syringes: One ul, 5 ul, 10 ul, 25 ul, and 100 ul or as needed.

6.4 Water bath - Heated with concentric ring cover, capable of temperature control (+/- 2°C). The bath should be used in a hood.

6.5 An analytical balance capable of accurately weighing 0.0001 g should be used for preparing standards and % moisture determinations. A top-loading balance capable of weighing to the nearest 0.1 g should be used for sample preparation.

6.6 Stainless steel spatula.

6.7 Gas Chromatography

6.7.1 Gas Chromatograph: Analytical system including appropriate gas supply and all required accessories, including a Flame Ionization Detector (FID), column supplies, gases, and syringes. A data system capable of determining peak areas using a forced baseline - baseline projection is required. A data system capable of storing and reintegrating chromatographic data is recommended.

6.7.2 Columns

6.7.2.1 Column 1: 5 M x 0.53 mm SGE HT-5, 0.1 micron film thickness.

6.7.2.2 Alternate columns: 30 M x 0.32 mm ID J&W DB-1 or DB-5, 0.25 micron film thickness.

6.7.2.3 Other Columns may be used - capillary columns may be required to achieve the necessary resolution. The column must resolve C_{25} from C_{24} in a midrange RCS or CVS if AK102 is to be done simultaneously. See 9.2.2 for additional column performance criteria.

6.8 Sonication

6.8.1 Ultrasonic cell disrupter: A horn-type sonicator equipped with a titanium tip should be used. A Heat Systems-Ultrasonics, Inc. Model W-385 (475 watt) sonicator or equivalent (power wattage must be a minimum of 375 with pulsing capability and No. 200 ½ inch Tapped Disrupter Horn) plus No. 207 3/4 inch Tapped Disrupter Horn, and No. 419 1/8 inch Standard tapered Microtip probe.

6.8.2 A Sonabox or equivalent is recommended with the above disrupter for decreasing sound (Heat Systems-Ultrasonics, Inc. Model 432 13 or equivalent).

6.9 Soxhlet extraction apparatus as described in SW-846 Method 3540 [1].

6.10 Nitrogen evaporator with high purity (grade 4.5 or equivalent) nitrogen gas source.

7. Reagents and Standards

7.1 Reagent Water: Water that has been shown to be free from RRO compounds - a Millipore system or equivalent is recommended.

7.2 Methylene Chloride, Hexane, Acetone - pesticide grade or equivalent. At a minimum, the solvents must be shown to be free from RRO.

7.3 Sodium Sulfate - (American Chemical Society (ACS) grade) granular, anhydrous. Purify by heating at 400°C for 4 hours in a shallow tray, or by extracting three times with methylene chloride and drying at 100° 5° C. Incomplete cleaning of sodium sulfate can result in contamination.

7.4 Stock Standard Solutions - Prepare the following stock standards. Unless noted, all are prepared in the methylene chloride listed in 7.2 above. Standards preparation should follow guidelines in SW846 [1]. All standards prepared by the laboratory must be stored without headspace at -10 to -20° C and protected from light. Marking of the meniscus is helpful in maintaining stock standard integrity. Standards must be replaced within 6 months of preparation. Standards should be checked regularly to assure their integrity. Standards which are purchased pre-made from commercial suppliers may be kept for the life, and under the conditions, specified by the manufacturer if different than described in this paragraph.

7.4.1 Recommended Surrogate: 5000 ug/mL n-Triacontane-d62 (dTC). A working solution is made at 500 ug/mL (recommended concentration) in acetone.

7.4.2 Residuals Calibration Standard (RCS): A blend of equal weights of motor oil, mixed together to form a composite motor oil (1:1, 30 weight: 40 weight :) is used to prepare stock calibration standards in methylene chloride. No fewer than 3 concentrations of this Residuals Calibration Standard are used for instrument calibration. A five point calibration curve is recommended. Other than one standard concentration near the practical quantitation limit, the expected range of concentrations found in project samples should define the working range of the calibration.

7.4.3 Retention Time Window Standard : A stock solution of C_{25} and C_{36} n-alkanes with each component at a level of at least 10,000 ug/mL (recommended). This blend of alkanes serves as a retention time window defining mix for RRO.

7.4.4 Stock CVS: From a blend of commercial motor oils other than those used to prepare the RCS, make an equal weight mixture as described above (7.4.2). Prepare a stock solution of 25,000 Ug/mL in methylene chloride. A working solution is made at a recommended concentration of 5,000 ug/mL in acetone.

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

8.1 Soils are collected in a core tube or 4 or 8 oz amber glass jar with Teflon lined lid. The samples are stored at 4 ± 2° C from the time of collection until extraction. Extraction must be performed on soils within 14 days.[1]. All analyses of extracts must take place within 40 days.

8.2 Soil samples to be analyzed for volatiles, DRO and RRO may be collected in the same, methanol preserved container and stored as for GRO (AK101). If this option is selected, the mechanics of the collection, preservation and container should be discussed with the client before sampling kit preparation. RRO extraction and analysis must still meet the requirements of 8.1, above.

9. Procedure

9.1 Sample Preparation: The preferred procedure for extraction is Method 3540 (Soxhlet Extraction). However, any sample extraction technique which meets the quality assurance requirements specified in Section 10 and Table 1 of this method may be used.

9.1.1 Soil Preparation - Soxhlet Extraction

9.1.1.1 Decant any water layered on the sample. Refer to method AK102, section 9.1.2 if DRO is to be done simultaneously. Mix the sample well and note any foreign objects or anomalies (variably particle size, presence of oil sheen, multiple phases, etc.).

9.1.1.2 Weigh 10 g to 30 g of the original sample into an extraction thimble. Add an equal weight of anhydrous sodium sulfate and stir the mixture well with a wooden tongue depressor, taking care to not rupture the thimble. The sample should have a grainy texture - if the sample clumps, add more sodium sulfate until a grainy texture is achieved and note the addition. (Do this for all samples and standards.)

9.1.1.3 Place loaded thimbles in extractors and add surrogate to all samples, both field and quality control.

9.1.1.4 Add CVS to the duplicate LFBs. These standards should contain 10 g of methylene chloride rinsed standard soil. In addition, prepare a method blank

9.1.1.5 Add 300 mL of methylene chloride to the 500 mL extraction flask. More or less extraction solvent may be used if the quality control criteria specified in Section 10 and Table 1 are met. Also add a few methylene chloride washed carborundum boiling chips to the flask. Connect the extractor to the flask and the condenser to the extractor. Allow samples to extract for 18-24 hours, or as long as necessary to achieve optimum surrogate recovery. Be sure that coolant is flowing around the condensers.

9.1.1.6 Recommendation: After extraction, disassemble extractor and add about 3 g anhydrous sodium sulfate to the extract and allow to incubate for 2 hours. (This assures that the extract is water-free before concentration.)

9.1.1.7 Put a plug of glass wool in a glass or Teflon funnel and fill about 2/3 full with anhydrous sodium sulfate. Rinse the funnel and sodium sulfate with 30-40 mL of methylene chloride, discard rinsate. Pour the extract through the rinsed sodium sulfate into a 500 mL Kuderna-Danish (K-D) evaporative concentrator. Rinse the graduated cylinder, then the sodium sulfate, with small amounts of methylene chloride. Add these rinses to the K-D.

9.1.1.8 Add a few boiling chips (6.2) to the K-D and attach a 3-ball Snyder to the top. Pre-wet the column by adding about 1 mL of methylene chloride to the inverted column before attaching it to the K-D.

Note: The concentration step is critical; losses of target compounds can occur if care is not taken.

9.1.1.9 Place the K-D in a heated water bath set at 95°C so that the receiver tube is immersed in hot water and the entire lower rounded surface is bathed in steam. At a proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume is less than or equal to 10 mL, remove the K-D from the bath and allow it to cool completely.

Note: The extraction and concentration steps must be performed under a hood. Not only is the methylene chloride a potential health hazard (see MSDS), ***if the heated water bath is not properly temperature-controlled, the concentration apparatus can explode.***

9.1.1.10 After the K-D has cooled, rinse the Snyder column and middle flask with a small amount of methylene chloride. Transfer the extract to a calibrated 15 mL centrifuge tube, rinsing with a small amount of methylene chloride. Rinse all of the ground glass joints well, as compounds collect on the ground glass.

9.1.1.11 If further concentration is desired, carefully concentrate the extract to no less than 1.0 mL under a gentle stream of nitrogen using the evaporation apparatus. If the extract is highly colored, forms a precipitate, or stops evaporating, the final volume should be higher (5-10 mL). Transfer to a labeled vial of appropriate size with Teflon-lined cap, mark the meniscus. Extracts should be stored in a non-frost free freezer.

9.1.1.12 Record information for the extraction and concentration steps.

9.1.2 Moisture Determination for Solids

9.1.2.1 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 petroleum compound concentrations in the soil, all drying should be done under a functioning hood.

9.1.2.2 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 0.001 g. Dry the sample overnight in a warm (100±5 °C) oven.

9.1.2.3 Remove the sample from the oven and cool in a desiccator until the sample reaches room temperature, and weigh to the nearest 0.001g. Record the weight.

9.1.2.4 Return the soil sample to the oven for an additional time period (not less than 2 hours), cool again in the desiccator until the sample reaches room temperature, and weigh to the nearest 0.001g.

9.1.2.5 If the weight of the sample has remained constant (± 4%) from the initial "dry" weight (9.1.2.3), use this number for the moisture determination (see 9.6.1). If the second weighing shows that the sample has lost further weight, continue drying and weighing the sample until the weight becomes constant, then proceed to 9.6.1.

9.1.2.6 If a sample contains a high concentration of petroleum product, constant weight may be difficult to attain. If, after several tries, the ±4% criteria cannot be reached an estimated % moisture may be reported with appropriate explanation.

9.1.3 Dilution Technique

9.1.3.1 This is used for product or waste samples for which extraction is not appropriate and which are soluble in methylene chloride.

9.1.3.2 Weigh 1 g of sample into a 10 mL volumetric flask. Dilute to 10 mL with methylene chloride. Transfer to a 12 mL vial with a Teflon-lined lid. Mark meniscus and store at ≤4 °C.

9.2 Gas Chromatography

9.2.1 Conditions (Recommended): Set helium column pressure to 20#. Set column temperature to 40° C for 2 minutes, then ramp at a rate of 12° C/min to 380° C and hold for 15 min. (run time = 49 minutes). Set FID Detector to 380° C and injector to 280° C. The reference book High Resolution Chromatography by Hewlett-Packard is a good source of information on how to optimize flow rates, etc.

9.2.2 Performance Criteria: GC run conditions and columns must be chosen to meet the following criteria:

9.2.2.1 Resolution of the methylene chloride solvent front from C_{10}, and C_{24} from C_{25}, if DRO (AK102) is to be done simultaneously.

9.2.2.2 The separation number, TZ, should be greater than 15 for C_{24} and C_{25} if DRO is to be analyzed concomitantly.

$$TZ = \frac{\text{retention time } C_{25} - \text{retention time } C_{24}}{W_{1/2} \text{ of } C_{25} + W_{1/2} \text{ of } C_{24}} - 1$$

Where "$W_{1/2}$" = peak width at half-height

9.2.2.3 The column must be capable of separating typical motor oil components from surrogate and internal standards.

9.3 Calibration

9.3.1 Calibrate the GC, set up as in 9.2, with an initial five point (recommended) calibration using RCS (7.4.2). The final calibration curve must be represented by no less than 3 concentrations of RCS.

9.3.2 Choose Residual Calibration Standard concentrations to cover the DRO range expected in the samples, or the liner range of the instrument, whichever is less. One of the concentrations must be at or near the practical quantitation limit.

9.3.3 Tabulate the area response of the calibration standard against mass injected. The ratio of the response to the amount injected, defined as the response factor (RF), can be calculated for the standard at each concentration. If the average percent relative standard deviation (%RSD) is less than 25% over the working range, linearity through the origin can be assumed, and the continuing calibration response factor can be used in place of a calibration curve.

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

Where: Ax = Peak area of analyte
Ais = Peak area of internal standard
Qis = Amount of internal standard
Qx = Amount of analyte

Alternately, external standard calibration may be used (See Method 8000 [1]). Then,

External Standard Response Factor = $\frac{\text{Total peak area of standard}}{\text{Mass injected}}$

9.3.2 The calibration curve must be confirmed using the CVS (7.4.5). This standard verifies the accuracy of the calibration. The concentration of the CVS should be within the expected concentration range of the samples to be analyzed.

9.3.3 The working response factor or calibration curve must be verified on each working day (24 hours) by the injection of a CCS (7.4.3)) at a concentration mid-point on the calibration curve. If the response for this standard varies from the predicted response by more than 25%, a new calibration curve must be prepared.

$$\text{Percent Difference} = \frac{R_1 - R_2}{R_{avg}} \times 100$$

where:

R_1 = Average RF from the calibration curve
R_2 = Response Factor from CCS
$R_{avg} = (R_1 + R_2)/2$

9.4 Retention Time Window Definition

9.4.1 Before establishing windows, be certain that the GC system is within optimum operating conditions (9.2). Make three injections of the Retention Time Window Standard (7.4.3) 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.

9.4.2 Calculate the standard deviation of the three absolute retention times for C_{25}, C_{36} and the surrogate.

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

9.4.2.2 In those cases where the standard deviation for a particular analyte is zero, the laboratory should use $\pm$ 0.05 min. as a retention time window.

9.4.3 The laboratory must calculate retention time windows for each standard on each GC column and whenever a new GC column is installed or instrument conditions changed. The data must be retained by the laboratory.

9.4.4 Retention time windows must be verified regularly and updated no less frequently than once a year.

9.5 Gas Chromatograph Analysis

9.5.1 Samples are analyzed by GC/FID. Optimum injection volumes (2 uL using the conditions established in 9.2) must be established for specific instrument conditions.

9.5.2 For internal standard calibration, the internal standard is spiked into each sample and standard at a specified concentration. (Note: High RRO values may lead to measurement bias due to coelution with the internal standard.)

9.5.3 If initial calibration (9.3) has been performed, verify the calibration by analysis of a mid-point CCS (9.3.2). With each day's run, open a 24 hour analysis window. This is done by running the Retention Time Window Standard (7.4.3).

9.5.4 Calculate the percent difference of the response factor from the mean response factor as in 9.3.3. This is done for RRO as a group from the CCS. If the average response factor has a difference greater than 25%, corrective action must be taken.

9.5.5 A methylene chloride blank must be analyzed each day to determine the area generated on normal baseline noise under the conditions prevailing in the 24 hour period. This area is generated by projecting a horizontal baseline between the retention times observed for the peak start of C_{25} and the peak end of C_{36}. This blank is integrated over the RRO area in the same manner as for the field samples and is reported as the solvent blank [Refer to reference 4]. **Do not baseline subtract. This information is for data interpretation purposes only.**

9.5.6 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 column must be baked out and subsequent blanks analyzed until the system is shown to retain contaminants at concentrations less than the PQL.

9.5.7 If the RRO concentration exceeds the linear range of the method (as defined by the range of the calibration curve) in the final extract, corrective action must be taken. The response of the major peaks should be kept in the upper half of the linear range of the calibration curve. Due to potential measurement bias, internal standard calibration should not be used when RRO exceeds 5000 ug/mL in the final extract. The sample should be diluted or external standard calibration should be used.

9.6 Calculations:

9.6.1 % Moisture Calculation

$$\% \text{ Moisture} = (A-C)/(A-B) \times 100$$

Where:

A= weight of boat + wet sample
B= weight of boat
C= weight of boat + dry sample

Note: Make sure drying oven is placed under a hood. Heavily contaminated soils will produce strong organic vapors.

9.6.2 Internal Standard Calibration: The concentration of RROs in the sample must be determined by calculating the absolute weight of analyte chromatographed from a summation of peak response for all chromatographic peaks eluting between the peak start of n-pentacosane and the peak start of n-pentetracontane, using the calibration curve or the response factor determined in section 9.3. Also refer to Section 9.4 (Retention Time Window Definition).

The concentration of RRO is calculated as follows:

Aqueous/Soil samples:

$$C_s = \frac{(Ax)(Cis)(D)(Vt)}{(Ais)(RF)(Vs)}$$

Where:

Cs = Concentration of RROs (mg/L or mg/kg).
Ax = Response for the RROs in the sample, units in area.
RF = Response Factor from CCS (see 9.3.1).
Ais = Response for the internal standard, units same as for Ax.
Cis = Internal standard concentration (mg/mL).
Vt = Volume of final extract in mL.
D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.
Vs = Amount of sample extracted in L or kg.

9.6.3 To calculate mg/dry kg for soil samples,

$$\text{mg/dry kg RRO} = \frac{Cs}{1-(\%\ \text{moisture}/100)}$$

The % moisture calculation must be included in the data package (see 9.1.2).

9.6.4 External Standard Calibration:

Aqueous/Soil samples:

$$C_s = \frac{(Ax)(A)(Vt)(D)}{(As)(Vs)}$$

Where:

Cs = Concentration of RROs (mg/L or mg/kg).
Ax = Response for the RROs in the sample, units in area.
As = Response for the external standard, units same as for Ax.
A = External standard concentration (mg/mL).
Vt = Volume of Final extract in mL.
D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.
Vs = Amount of sample extracted in L or kg.

9.6.5 Some software programs are capable of performing 9.6.1 and 9.6.3 with minimal analyst intervention. Additionally, some software programs can "update" a calibration curve based on the response of the CCS. If a calibration curve is updated in this manner, a valid CVS must be analyzed and results must fall within the Quality Control Criteria specified in Section 10 and Table 1 before samples can be analyzed.

10. Quality Control (See Table 1)

10.1 The laboratory must establish and maintain the ability to generate acceptable accuracy and precision and to 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 recovery as outlined in method 8000, section 8.0 [1], and this method.

10.2 After successful calibration (Section 9.3), analyze the reagent blank sample. The reagent blank must be analyzed with every extraction batch. The surrogate recovery must be within established limits (see Method AK 103, Table 1), or within the limits established by the project plan (whichever is more stringent) and the control sample should not have R R O above the practical quantitation limit.

10.3 With every batch, duplicate LFBs must be analyzed (employing the standard soil matrix appropriate to the samples being analyzed). The accuracy and precision of the duplicate standards must be within established limits. Also, the mid-point CCS must be analyzed at the end of each sequence and once per 20 samples, and compared to the successful calibration as described in 9.8.6, and fall within established limits (Table 1). Method Detection Limits (MDLs) must be established as specified in 40CFR Part 136, Apendix B.

10.4 Every batch of samples extracted must be accompanied by a method blank to demonstrate that samples are free from method interference. The method blank must have RRO less than the Practical Quantitation Limit.

10.5 Each laboratory should generate control limits based on the average recovery, with ± 2 standard deviations as a warning limit and ± 3 standard deviations the action limit.

10.6 If any of the criteria in 9.3, 10.2, 10.3 and 10.4 are not met, corrective action must be taken before samples are analyzed.

10.7 Calculate the surrogate standard recovery in each sample. If recoveries are outside established limits (Table 1) verify calculations, dilutions, and standard solutions. Verify instrument performance.

10.7.1 High recoveries may be due to a coeluting matrix interference or the presence of high molecular weight contaminants; examine the sample chromatogram.

10.7.2 High recoveries may also be due to memory effects caused by poor sample volatility, backflash, or carryover. Check instrument conditions, injection volume, and injector temperature.

10.7.3 Low recoveries may be due to adsorption by the sample matrix (muskeg, tundra, forest loam, etc).

10.7.4 Low recoveries may also be caused by incorrect integration. The chromatographic profile of RRO may not give baseline resolution of all components, resulting in a characteristic rise in baseline underneath the resolved hydrocarbon components known as the "unresolved complex mixture", or UCM. Do not use peak to peak integration; use forced baseline integration.

10.7.5 If internal calibration has been used, RRO results must be normalized using the internal standard response. If surrogate recovery is still outside of established limits, corrective action must be taken.

10.7.6 If external calibration has been used and surrogate recovery is outside of established limits, corrective action must be taken.

10.8 When field samples show surrogate recovery outside of acceptable limits due to suspected matrix effects and the calculated RROs concentration falls within a factor of 2 of the action level, the laboratory should recommend that the client resubmit the sample for matrix spike/matrix spike duplicate analysis. (To perform matrix spike analyses, follow 9.1, except use a field sample instead of a standard matrix.) 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.

10.9 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.

10.10 Minimum quality control acceptance criteria are set forth in section 10 of this method. More stringent quality control criteria may be required by specific project plans.

10.11 Corrective Action

10.11.1 Calibration

10.11.1.1 If the initial calibration does not meet the criteria set forth in 9.3.3 and 9.3.4, the instrument must be recalibrated.

10.11.1.2 If the continuing calibration does not meet the criteria set forth in 9 3.5 and Table 1, the instrument must be recalibrated.

10.11.2 Surrogates

10.11.2.1 If surrogates are outside established control limits (Table 1), the following assessments and/or correction actions must occur:

A) Check to be sure there are no errors in calculations and that the concentration of the surrogate and internal standard solution 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) Reprepare and reanalyze the sample if none of the above resolves the problem.

10.11.2.2 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. Provided all other QC acceptance criteria are met (section 10), it is only necessary to reprepare/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.

10.11.3 Blanks: Additional laboratory or field blanks may be necessary for certain projects to meet the goals of Chapter 2, section 9 of the UST Procedures Manual.

10.11.3.1 Instrument Blanks: Instruments must be evaluated with each 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.

10.11.3.2 Method Blank: Method Blanks must be analyzed with each extraction batch IF the results of the field samples show contamination above the MCL. The Method Blank for AK102 can also serve as the Reagent Blank if RRO is less than the PQL.

10.11.3.3 Field Blank: If the field samples yield DRO above the MCL, and contamination is found below the PQL in the Reagent Blank, a Field Blank should be analyzed to identify whether the source of contamination originated in the field sample collection procedure, during trip or during storage in the laboratory. This applies to AK102 and AK103 analyzed in concomitantly.

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

10.11.4 Laboratory Fortified Blanks

10.11.4.1 If the analyte recovery from the LFBs is outside the established recovery limits (Table 1), 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) Reprepare and reanalyze the samples if none of the above resolves the problem.

10.11.4.2 If the relative percent difference between the LFB results exceeds the control limits, but meets the percent recovery criteria (Table 1), 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 Specific method performance data for Revision 3.0 of AK103, Residual Range Organics, is not available at this time. Information on method performance for the C25 - C44 range (Revision 2.1) follows.

11.2 The method performance data presented is based on single lab work (State of Alaska, Department of Environmental Conservation, State Chemistry Laboratory). Performance data for the RROs method in Ottawa sand and other soil types is presented below.

CORRECTION

THE FOLLOWING DOCUMENT(S)
HAVE BEEN REFILMED TO
ASSURE LEGIBILITY OR PAGINATION

10.11.4.2 If the relative percent difference between the LFB results exceeds the control limits, but meets the percent recovery criteria (Table 1), 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 Specific method performance data for Revision 3.0 of AK103, Residual Range Organics, is not available at this time. Information on method performance for the C25 - C44 range (Revision 2.1) follows.

11.2 The method performance data presented is based on single lab work (State of Alaska, Department of Environmental Conservation, State Chemistry Laboratory). Performance data for the RROs method in Ottawa sand and other soil types is presented below.

11.3 Results for motor oil spikes (methylene chloride extraction direct injection, soils) is from duplicate analyses of matrix spikes on field projects. Biases due to naturally occurring materials and existence of mixed products in the samples may exist.

Matrix	RCS Spike Amount mg/kg	Percent Recovery
Ottawa Sand (1993-1995)	500	91 ± 12
1993 Composite	250	77 ± 13
(S.E. Alaska Soils)	500	107 ± 15
1994 Composite	250	103 ± 10
(S.E. Alaska Soils)	500	103 ± 9
1995 Single Project (S. E. Alaska Soils)	500	116 ± 9

11.4 The method detection limit for soil calculated according to 40 C.F.R., Part 136, Appendix B (1994) was 51 mg/kg (external standard calibration).

12. References

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2. "Method OA-2: Extractable Petroleum in Products," Revision January 10, 1990", University Hygienic Laboratory, Iowa City, Iowa.

3. "Method for Determination of Extractable Petroleum Hydrocarbons (EPH) in Soil and Water," Draft-February 28, 1990, prepared for Total Petroleum Hydrocarbons Method Committee by Midwest Research Institute.

4. Zilis, K., M. McDevitt, and J. Parr, "A Reliable Technique for Measuring Petroleum Hydrocarbons in the Environment," presented at the conference on Petroleum Hydrocarbons and Organic Chemicals in Groundwater, NWWA, Houston, Texas, November 1988.

5. American Petroleum Institute "Method for the Determination of Diesel Range Organics," Draft Revision 2-February 5, 1992, prepared for Total Petroleum Hydrocarbons Method Committee.

6. "Leaking Underground Fuel Tank (LUFT) Field Manual," State Water Resources Control Board, State of California, Sacramento, CA, May 1988.

7. Fitzgerald, John, "Onsite Analytical Screening of Gasoline Contaminated Media Using a Jar Headspace Procedure" in Petroleum Contaminated Soils, Vol. 2, 1989.

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

9. Hughes, B.M., and D.E. McKenzie, C.K. Trang, L.S.R. Minor, "Examples of the Use of an Advanced Mass Spectrometric Data Processing Environment for the Determination of Sources of Wastes" presented at 5th Annual Waste Testing and Quality Assurance Symposium, July 1989.

10. American Petroleum Institute, "Method for Determination of Petroleum Hydrocarbons," Draft Revision Original, 3 February 1992, prepared for the Total Petroleum Hydrocarbons Methods Committee.

11. State of Washington, Department of Ecology, "Total Petroleum Hydrocarbons Analytical Method WTPH-HCID."

12. Research done by the State of Alaska, Department of Environmental Conservation, Division of Environmental Quality, State Chemistry Laboratory.

Method AK 103, Table 1
ACCEPTANCE CRITERIA FOR QUALITY CONTROL

ANALYTE	SPIKE CONCENTRATION Soil (mg/kg)	CONTROL LIMITS % Recovery	Relative % Difference
Lab Control Samples			
Residual Range Organics	500 mg/kg	60 - 100	20
LCS/CCS			
Residual Range Organics	2000 mg/L	75 - 105	
Surrogate Control Samples			
n-Triacontane-d62	50 mg/kg	60 - 100	
Surrogate Recovery (field samples)			
n-Triacontane-d62	50 mg/kg	50 - 150	

STORAGE TANK ASSISTANCE FUND ANNUAL REPORT

FISCAL YEAR 1996

Department of Environmental Conservation
Spill Prevention and Response Division

Presented to the **First Session of the Twentieth Alaska Legislature**

February 12, 1997 • Tony Knowles, Governor • Michele Brown, Commissioner

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APPENDIX

I. INTRODUCTION

A. Statement of Purpose

On June 7, 1990, the Governor of Alaska signed into law House Bill 220 which amends Alaska Statutes Title 46, Chapter 3. This new law became effective on September 5, 1990, and is commonly referred to as the Underground Storage Tank statute. The statute provides for (1) the establishment of technical and financial assistance mechanisms to assist the owners and operators of underground storage tank systems (USTs) to comply with federal and state law; and (2) the cleanup of existing leaks and prevention of future leaks associated with USTs in order to protect the public from contamination of drinking water and to protect the environment.

The Underground Storage Tank statute established the Storage Tank Assistance Fund and mandated that the Department of Environmental Conservation submit an annual report to the legislature on the status of the fund. The purpose of the following report is to satisfy the requirements of the statute by providing information listed in Alaska Statutes Section 46.03.410.

B. Federal Law

Congress passed the Hazardous and Solid Waste Amendments of 1984 to the Resource Conservation and Recovery Act (RCRA). These amendments, in part, require the U.S. Environmental Protection Agency (EPA) to regulate USTs containing petroleum and hazardous substances. According to EPA estimates, nationwide there are several million USTs that contain petroleum or hazardous substances--tens of thousands of which, together with their associated piping, are leaking and contaminating groundwater, a major source of drinking water for a large portion of the country.

Congress directed the EPA to develop regulations for the design, construction, and installation of new tanks as well as the addition of leak detection, corrosion prevention, and spill and overflow protection to existing tanks. The EPA regulations went into effect on December 22, 1988 and USTs installed on or before that date are considered "existing tanks," while those tanks installed after that date are considered "new installations." New installations are to meet the performance standards set out in the regulations at the time of tank installation. Existing tanks are allowed to phase in these standards over a period of 10 years.

Congress also mandated that all UST owners, except state and federally owned or operated tanks, be able to demonstrate specific levels of financial responsibility for corrective action and cleanup associated with releases from their USTs, including third party loss and bodily injury. Commercial pollution liability insurance is the most common type of financial responsibility. The financial responsibility requirements were phased in according to the type of owner and the number of tanks owned. The final date for most tank owners to meet this requirement was December 31, 1993. Indian tribes who own USTs on Indian lands have until December, 1998 to comply. Most tank owners are required to demonstrate $1 million of financial responsibility per occurrence and $2 million aggregate. Failure to meet the requirements may result in fines of up to $10,000 per day.

C. State Law

Primarily due to EPA's pending financial responsibility requirements and the fact that it would be virtually impossible for an owner or operator of an UST

to show financial responsibility if they had a leaking tank or if the tanks needed to be upgraded, the Alaska legislature introduced the Alaska UST legislation--a portion of which included the financial assistance legislation. It was evident to lawmakers that most Alaska businesses covered by the EPA's UST regulations would be unable to meet the financial responsibility requirements or pay the resulting fines. During the legislative process, the EPA told Alaska lawmakers that federal budget cutbacks would prevent the agency from providing owners with technical assistance for complying with the new performance requirements. As a result, the EPA program would consist of enforcement only. Failure to meet performance standards could also result in $10,000 daily fines. The EPA may authorize states to implement their own UST program in place of the federal requirements if the state's requirements are "no less stringent" than EPA's and provide for adequate regulatory enforcement.

Recognizing the potential obstacles facing Alaska's UST owners and operators, the legislature passed HB 220. It was the intent of the legislation that the state

Table I
Summary of UST Financial Assistance Programs

PROGRAM	DESCRIPTION	ELIGIBLE COSTS	ASSISTANCE PROVIDED
Tank Tightness Testing & Site Assessment Incentive Program	Program sunset in FY92. Applications/Intents had to be submitted by March 5, 1992. No funds have been allocated to this program since FY92.	Provides funds directly to the owner/operator specifically to reimburse costs for tank tightness tests or site assessments to determine if there had been a release of petroleum.	50% of actual costs, not to exceed $300 per tank for tank tightness tests up to a maximum of $1200 per facility and $800 per tank for site assessments up to $3200 per facility.
Tank Cleanup Grant & Loan Program	Program active. Application period sunset June 30, 1994. * Funds currently allocated to the program through FY97. Applications for FY98 have been received.	Provides funds directly to the owner/operator specifically to cover costs of risk assessment, containment, corrective action, and cleanup.	Up to $1 million per occurrence, and owner/operator is responsible for 10% of total cleanup costs (not to exceed $25,000), which is excluded from the grant.
Tank Upgrade & Closure Grant Program	Program active. Application period sunset December 30, 1994. Funds currently allocated to the program through FY97.	Provides funds directly to the owner/operator specifically to cover costs of removal, upgrade, or replacement of UST system	Grants for upgrade, replacement or closure of an UST comprising up to sixty percent of the total eligible costs up to $60,000
Reimbursement Program	Program inactive, funding given lower priority by statute. Applications had to be submitted by March 5, 1991. To date, although $3.4 million has been applied for, no funds have been allocated for the program.	Provides reimbursement for the costs of risk assessment, containment, cleanup, corrective action, upgrading or closure activities on or after December 22, 1988 and before September 5, 1990	Total costs for reimbursement to an owner/operator under this program not to exceed $200,000. The owner/operator must have applied for this program before March 5, 1991.

*Cleanup applications were accepted through June 30, 1996 for those applicants that had an upgrade and closure application on file on or before December 30, 1994 and discovered and reported contamination before July 1, 1996 and can prove that contamination occurred before December 22, 1993.

program ensure that owners and operators receive educational, technical, and financial assistance, and be provided with incentives for compliance with federal and state requirements rather than relying solely on an enforcement program after problems develop.

D. Storage Tank Assistance Fund

A portion of the Alaska UST legislation established the Storage Tank Assistance Fund to make funds available for program implementation and staffing, and to administer the following financial assistance program: reimbursement incentives for tank tightness testing or site assessments (AS 46.03.415); grants and loans for risk assessment, containment, corrective action, and cleanup costs (AS 46.03.420); and grants for tank system upgrading and closure (AS 46.03.430). Table 1 (Summary of UST Financial Assistance), briefly describes the eligible costs and the assistance provided in each of the programs.

The Alaska Underground Storage Tank legislation required the development of an UST program through the adoption of regulations which set performance standards for both new and existing UST systems; provided for corrective action activities and cleanup standards for leaking USTs; mandated that the Department provide educational assistance to UST owners and operators; required the certification of UST workers; required the owners or operators to register all USTs; established a Board of Storage Tank Assistance; and provided guidelines for the administration of the Storage Tank Assistance Fund. Pursuant to this legislation, the Department promulgated regulations on the general requirements for eligibility for financial assistance, ineligible costs, project priority ranking procedures, application requirements, conditions of financial assistance, and grant payment procedures.

On June 9, 1994, former Governor Hickel signed House Bill 513 into law. The Bill modified the existing Underground Storage Tank law by establishing a December 30, 1994 application deadline for the closure and upgrade program, and extended the application period for cleanup assistance for those applicants who have met the closure upgrade deadline or those who are already on the closure upgrade waiting list. To be eligible for this extension, the spill must be reported by July 1, 1996 and must have occurred before December 22, 1993.

The Storage Tank Assistance fund received an initial capitalization of $6 million in fiscal year 1991. In fiscal year 1992, no new monies were appropriated to the fund.

For fiscal years 1993, 1994, 1995, and 1996 the legislature appropriated to the fund $5 million, $4.9 million, $3.5, and $3.1 million respectively, while for fiscal year 1997, $2.9 million was appropriated to the fund.

II. ABSTRACT

Funding sources for the Storage Tank Assistance Fund for Fiscal Year 1996 included a fund transfer from the Mitigation Account Fund of $2,791,300 and FY 96 tank registration receipts of $293,540. New appropriations from the Storage Tank Assistnace Fund went to the Storage Tank Assistance Program for $664,000 to pay for program operations, to the Division of Information and Administration Services for $70,500 to pay for fiscal services, to the Board of Storage Tank Assistance for $87,900 and $1,976,200 to Storage Tank Grants. In addition, encumbrance balances of $1.37 million for FY 93, FY 94, and FY 95 projects were extended to complete those projects in FY 96.

On June 30, 1996, all available funds, except $264,895 reserved for contingencies, for grants and loans from the FY 96 appropriations, had been expended or encumbered. Funds encumbered in prior fiscal years were also expended so that a total of $4,922,667 had been expended or encumbered to fund tank cleanup, upgrade or closure.

For FY 96, 700 applicants requested over $37 million. From the amount requested, the greatest amount of funds granted were used for the tank cleanup program, with a total of $4,050,733 expended or encumbered for grants, and a total of $3,296 issued for loans. Tank upgrade was the second largest assistance category, with $610,423 encumbered or expended. This category is followed by tank closures at $261,509.

This report summarizes:

(1) the amount and source of money received by the fund during fiscal year 96 (FY 96);

(2) the amount of money expended during FY 96 for each type of expense authorized under AS46.03.410(b), including tank tightness testing or site assessments, costs of risk assessment, containment, corrective action, cleanup, tank system upgrading, and closure;

(3) department activities paid for from the fund during FY 96, including the number of requests for assistance which have been made to the department to use the fund (for grants or loans for risk assessment, upgrading, closure, containment, corrective action, cleanup costs) and the number of requests funded in each activity area;

(4) the priority list of tank system sites for which the department expects to provide financial assistance in FY 97;

(5) the projected costs for the next fiscal year (FY 97) of monitoring, operating, and maintaining sites where department activities have been completed or are expected to start or be continued during the fiscal year; and

(6) the financial assistance program from inception through December 31, 1996.

III. FY 96 FUND SUMMARY

A. Funding

Table 2 lists the amount and source of money received by the Fund during FY 96. Funding sources included a fund transfer of $2,791,300 from the Mitigation Account and $293,540 from FY 96 tank registration receipts for a total amount of $3,084,840. New appropriations from the fund went to the Storage Tank Assistance Program for $1,056,700 to pay for program operations administration, to the Division of Information and Administration Services for $70,500 to pay for fiscal services, to the Board of Storage Tank Assistance for $87,900 and to Storage Tank Grants for $1,976,200. In addition, encumbrance balances totalling $1.37 million for FY 93, FY 94, and FY 95 projects were extended to complete those projects during FY 96.

B. Expenditures

As shown below on Table 2, as of June 30, 1996, the unspent balance for FY 96 grants and loans was $259,589. This balance may be expended in FY 97 since the appropriation was extended by HB 468. As can be seen from Table 2, the majority of available funds for grants was fully expended, with the balance of $264,895 available for grant amendment and other contingencies for FY 97. Table 2 also reflects $3,296 in restricted funds in the grant account for outstanding loan payments.

Table 2
Storage Tank Assistance Fund Activity for FY 96*

	Budgeted	Actual
FY 96 State Funding Sources To Storage Tank Assistance Fund		
Fiscal Year 96 Registration Receipts	380,000	293,540
Fund Transfer from Prevention Mitigation Account Fund	2,791,300	2,791,300
Total State Fund Sources	$ 3,171,300	$ 3,084,840
FY 96 Storage Tank Assistance Funds Appropriated for State Programs		
Storage Tank Assistance Program	3,120,800	2,802,800
Division of Administrative Services	70,500	70,500
	$ 3,191,300	$ 2,873,300

Financial Activity for Storage Tank Grant/Loan Program - FY96 State Funds

	Authorized	Restricted/ Revised	Expended	Encumbered	Balance
Administration					
Personal Services	544,800	0	501,143		43,657
Travel	34,700	0	15,979		18,721
Contractual	341,286	0	325,368	18,450	(2,532)
Supplies	17,000	0	9,638	852	6,510
Equipment	4,700	0	15,940		(11,240)
Lust/Ust Match	114,214	0	114,115	99	
Subtotal for Administration:	$ 1,056,700	$ -	$ 982,183	$ 19,401	$ 55,116
Grants/Loans	1,976,200	**(3,296)	632,085	1,075,023	264,895
Board	87,900		93,206		(5,306)
Administrative Services	70,500		70,500		
Subtotal for Grants, Board, Loan	$ 2,134,600	$ (3,296)	$ 796,691	$ 1,075,023	$ 259,589
Total	$ 3,191,300	$ (3,296)	$ 1,778,874	$ 1,094,424	$ 314,705

* Federal receipts and expenditures to the Storage Tank Assistance Fund are not reflected in this table.
** Loan

C. Program Activities Summary

1. Grant Activities

Table 3 summarizes each type of assistance program authorized by statute for which funds were expended or encumbered for FY 96. Table 3, and the discussion in Section D, "Assistance Requested and Funded for FY 96", also show in detail the funds expended and encumbered from both the FY 96 appropriation and the term extensions of the previously encumbered FY 93, FY 94, and FY 95 appropriations. In summary, as of June 30, 1996, a total of $4,922,667 had been expended or encumbered to fund tank cleanup, upgrade or closure.

TABLE 3
Funds Expended or Encumbered by Grant Program Activity

	June 30, 1996		
	Expended	Encumbered	Total
Cleanup			
FY 96 48006 ext 48340-93	8,669.38	9,012.40	17,681.78
FY 96 48007 ext 48700-93	90,340.71	294,807.15	385,147.86
FY 96 48008 ext 48550-94	650,659.80	247,214.33	897,874.13
FY 96 48010 ext 48550-95	737,624.95	761,073.89	1,498,698.84
FY 96 Appn. 48550-96	274,666.87	976,664.77	1,251,331.64
	$1,761,961.71	$2,288,772.54	$4,050,734.25
Upgrade			
FY 96 48006 ext 48340-93	33,540.00	7,543.50	41,083.50
FY 96 48007 ext 48700-93	19,843.85	0.00	19,843.85
FY 96 48008 ext 48550-94	10,376.88	18,270.53	28,647.41
FY 96 48010 ext 48550-95	218,873.21	368.70	219,241.91
FY 96 Appn. 48550-96	217,450.98	84,155.46	301,606.44
	$500,084.92	$110,338.19	$610,423.11
Closure			
FY 96 48006 ext 48340-93	6,705.00	14,548.70	21,253.70
FY 96 48008 ext 48550-94	10,084.78	6,242.76	16,327.54
FY 96 48010 ext 48550-95	57,214.37	11,643.31	68,857.68
FY 96 Appn. 48550-96	140,867.05	14,203.20	155,070.25
	$214,871.20	$46,637.97	$261,509.17
Program Total	**$2,476,917.83**	**$2,445,748.70**	**$4,922,666.53**

"Appn." = Appropriation

Loans for Cleanup: One loan in the amount of $3,296.40 was processed in fiscal year 1996.