

State of Alaska
**DEPARTMENT OF
ENVIRONMENTAL CONSERVATION**

DIVISION OF SPILL PREVENTION AND RESPONSE
CONTAMINATED SITES PROGRAM



Underground Storage Tanks Procedures Manual

**GUIDANCE FOR TREATMENT OF
PETROLEUM-CONTAMINATED SOIL AND WATER
AND
STANDARD SAMPLING PROCEDURES**

August 18, 2014

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CHAPTER 1

GUIDANCE FOR TREATMENT OF PETROLEUM-CONTAMINATED SOIL AND WATER AT UNDERGROUND STORAGE TANK SITES

CHAPTER 1. GUIDANCE FOR TREATMENT OF PETROLEUM-CONTAMINATED SOIL AND WATER AT UNDERGROUND STORAGE TANK SITES

For more information regarding remedial technologies that are available, refer to the document entitled *How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites, A Guide for Corrective Action Plan Reviewers*, EPA 510-B-94-003, dated October 1994, published by the United States Environmental Protection Agency, and available from that agency. A copy is available for review at the Department of Environmental Conservation's offices in Anchorage, Fairbanks, Juneau, and Soldotna.

SECTION 1. GUIDANCE FOR THE TREATMENT OF PETROLEUM-CONTAMINATED SOIL AND WATER

1.1 Purpose, Applicability, and Exclusions

The following is intended as guidance for the treatment of petroleum-contaminated soil and groundwater associated with underground storage tanks (USTs) as defined by AS 46.03.450. It may be used as guidance for other petroleum releases from other tanks such as home heating oil tanks regulated under 18 AAC 75.

Petroleum-contaminated media and debris generated by releases or spills from USTs are temporarily excluded from the Toxicity Characteristic Leaching Procedures requirements of the Resource Conservation and Recovery Act (RCRA) (see 40 C.F.R. 261.4(b)(10)).

The corrective action activities of petroleum-contaminated soils are an important part of the corrective action process at leaking underground storage tank (LUST) sites. Contaminated soils that remain in place without treatment may pose not only an environmental and public health risk, but can significantly prolong the groundwater corrective action effort, resulting in significantly higher total corrective action costs.

1.2 Introduction

Various options for managing petroleum-contaminated sites, including guidance for use in Alaska, are highlighted in this chapter. The technology for managing petroleum-contaminated soil and water is continually improving. The large number of sites that need to be addressed has created a demand for innovative, cost-effective solutions. The Alaska Department of Environmental Conservation (ADEC) intends to maintain a flexible approach toward the evaluation and approval of new treatment technologies that are protective of human health and safety and the environment. Examples of proposed remedial technologies for petroleum-contaminated soils and water include bioremediation, landspreading, vapor extraction systems, solidification, fixation, asphalt recycling, thermal desorption, soil washing, groundwater pump and treat, and air sparging.

A health and safety plan addressing important chemical and physical hazards should be prepared and used. Any handling of gasoline-contaminated soils, in particular, will result in volatilization of light fractions of petroleum. Organic vapors should be monitored and workers must be in compliance with Occupational Safety and Health Administration requirements under 29 C.F.R.1910.120 for training and personal protective gear.

Regular checks should be made at the area to ensure that no further releases occur and that all equipment and containment systems are operating properly. In particular, checks should be made immediately before, during, and after high winds and heavy rainfall. One person should be assigned the responsibility for ensuring that these checks are made and for keeping a log of the maintenance. Many well-designed storage or treatment systems operate poorly due to poor maintenance. Operation and maintenance are as important to the effectiveness of the treatment as the design.

SECTION 2. TREATMENT TECHNOLOGIES

2.1 Bioremediation

Bioremediation is a treatment method that decreases petroleum product concentrations in soil and groundwater through biological action. Bioremediation may be performed in-situ, in a specially designed treatment cell, or by landfarming. Different requirements may apply, depending on whether landfarming, in-situ, or cell bioremediation is used. If in-situ bioremediation or landfarming is used, the treatment design will require more detailed attention regarding site conditions. Cell bioremediation requires more extensive construction, but fewer monitoring and testing requirements.

2.1.1 Landfarming

Landfarming involves spreading contaminated soil in a thin layer on a liner over the ground's surface. Biological activity may be enhanced by the addition of a combination of the following amendments: nutrients, mechanical aeration, water addition, and pH adjustment. Landfarming should not be confused with landspreading. Landspreading relies mainly on aeration and unenhanced biological action to perform treatment. The design parameters for a landspreading facility, however, are similar to the design parameters for a landfarming facility. Landfarming works well for gasoline and diesel and more slowly for heavier hydrocarbons.

2.1.2 In-Situ Bioremediation

In-situ bioremediation is most often accomplished in combination with vapor extraction and bioventing. This technology uses naturally occurring microorganisms that are stimulated to biodegrade contaminated soils in place. The most developed and most feasible bioremediation method for in-situ treatment relies on optimizing environmental conditions by providing an oxygen source that is delivered to the subsurface through an injection well or infiltration system for the enhancement of microbial activity.

2.1.3 Cell Bioremediation

Cell bioremediation employs specially designed treatment cells to contain contaminated soils and enhance biodegradation of hydrocarbons. Soil moisture, temperature, oxygen, and nutrients are controlled to optimize conditions for soil bacteria.

The major difference between in-situ bioremediation and cell bioremediation is how the contaminated soil is contained. In cell bioremediation, the contaminated soil is placed in a liner, tank, pad, or other structure designed to completely contain any leachate generated from the treatment process.

2.2 Landspreading

Landspreading is a passive treatment method that decreases petroleum product concentrations in soil through biological action and aeration. Landspreading operations may require a solid waste disposal permit under 18 AAC 60. In general, a permit is not required if the soil will be removed from the landspreading site after the landspreading activity is complete.

Landspreading works well with soils contaminated with gasoline and soils lightly contaminated with diesel or other heavier chain petroleum products.

2.3 Vapor Extraction Systems

Vapor extraction involves the forced withdrawal or injection of air into subsurface soils to promote the volatilization of hydrocarbons. Contaminants move from the soil into the air stream. As the air exits the soil, it is either discharged directly to the atmosphere or treated to remove the contaminants before discharge. Vapor extraction works best with highly volatile contaminants, such as gasoline, in a uniform soil horizon with low organic content. Vapor extraction can be performed in-situ or in a prepared cell.

2.3.1 In-Situ Vapor Extraction

In-situ vapor extraction involves installing vertical or horizontal piping in the area of soil contamination. An air blower is then used to draw vapors out from the subsurface. In-situ vapor extraction should be used for volatile contaminants only in areas where soil permeability allows easy vapor movement. Permeability will affect well spacing. The amount of soil organic matter and soil moisture will also affect the ease of stripping volatiles.

In-situ vapor extraction systems can be a series of wells, some type of French drain system buried in the contaminated area, or any other mechanical structure designed to push or pull air through the contaminated area.

Use of explosion proof equipment and automatic shutoff devices that will shut down the system is recommended if the atmosphere inside the treatment building exceeds 20 percent of the lower explosive limit (LEL).

2.3.2 Prepared Cell Vapor Extraction

This technology is similar to in-situ vapor extraction. Prepared cell vapor extraction involves excavating the contaminated soil and placing it in treatment cells. Perforated pipes are placed within the treatment cells. The treatment cells are entirely enclosed with a liner and air is forced through the perforated pipes with blowers. Treatment cell venting can be effective for most of the year and can be done during periods of wet weather.

Like in-situ vapor extraction, prepared cell vapor extraction should be used for volatile contaminants. The amount of soil organic matter and soil moisture will also affect the ease of stripping volatiles.

2.4 Solidification and Fixation

Solidification and fixation are processes whereby additives are mixed into contaminated soil to immobilize the contaminants in the soil. The petroleum hydrocarbons become chemically and/or physically bound into the resulting mixture, limiting the solubility or leach ability of a contaminant.

Solidification and fixation usually refers to the use of cementing agents that transform contaminated soil into freestanding, relatively impermeable blocks. It is important that the reuse of the treated material be for a beneficial purpose. If not, the treated material must be disposed of in accordance with 18 AAC 60. Examples of beneficial reuse include aggregate for concrete, road base course, building foundation fill, and parking lot base course. Beneficial reuse must occur in an area that is at least six feet above the seasonal high water table. Examples of *nonbeneficial* use include nonstructural fill, stockpiles, and wetlands fill.

2.5 Asphalt Recycling

Cold or hot mix asphalt recycling involves blending petroleum-contaminated soil with sand and gravel aggregate for the manufacture of asphaltic concrete or lower grade asphalt mixtures for road beds. Soil particle diameter and the amount of silt and clay in the contaminated soil are limiting factors for this option.

This technology is generally used only with soils contaminated by diesel, heating oils, and heavier chain petroleum hydrocarbon fuels. This treatment is *not* recommended for soils heavily contaminated with gasoline. Soils that exhibit free flowing product or the potential of free product are not acceptable for asphalt recycling.

The asphalt produced by the cold asphalt recycling method is generally only suitable as a base coat and is not considered a finished product.

2.6 Thermal Desorption

Thermal desorption employs both permanent and mobile units. This technology uses a rotary kiln heated to 300° to 700° F to volatilize hydrocarbons from contaminated soil. Some petroleum hydrocarbons will remain in the soil depending on soil temperature, moisture content, texture, time in the unit, contaminant type and contaminant concentration. The emissions are oxidized in an afterburner to prevent discharge of large quantities of unburned hydrocarbons into the atmosphere.

This method is effective for treating most types of petroleum contaminants, although higher temperatures are needed to remove heavy hydrocarbons from soil.

Silty soil creates significant operational problems for thermal treatment systems because of dust generation and baghouse limitations. Large debris often cannot be processed in the thermal desorption unit and may need to be segregated and addressed separately.

2.7 Soil Washing

Soil washing is a technique that removes petroleum hydrocarbons from the soil by actively leaching the contaminants from the soil into a leaching medium. The extracted contaminants can then be removed from the washing fluid by conventional treatment methods. Soil washing with surfactants or solvents can achieve acceptable residual petroleum hydrocarbon levels for soil. However, the washing process results in large amounts of wastewater that must be managed. It may be difficult to treat soils with a high percentage of silts and clays or organic matter and achieve corrective action goals.

2.8 Groundwater Pump and Treat

Groundwater pump and treat is used when groundwater beneath a site is contaminated with petroleum. Contamination may be in the form of free product floating on the water table or petroleum constituents dissolved in the water. Any free product should be removed as soon as possible.

For dissolved phase contamination, groundwater is extracted, treated, and disposed. Several types of treatment could be used depending on the type and concentration of the contaminant and the site conditions. Some of the possible treatment technologies include oil/water separators, air strippers, activated carbon, and bioremediation or some combination (such as using an air stripper and activated carbon for volatile organic compounds and an oil/water separator for heavier end compounds). Disposal options for extracted groundwater include discharging to surface water, groundwater (re injection), a sewer system, and an industrial wastewater treatment facility. A permit may be required before discharge of any extracted water.

2.9 Air Sparging

Air sparging involves the injection of air into the subsurface below the groundwater surface to volatilize hydrocarbon or other constituents dissolved in the groundwater and adsorbed to the soil. The volatilized hydrocarbon constituents are then removed from the vadose zone with vapor extraction wells. In addition to volatilizing petroleum contaminants, air sparging increases groundwater dissolved oxygen levels which increases biological activity leading to in-situ destruction of contaminants.

This technology is optimized in homogenous soils with high permeability and should be used only for volatile contaminants. However, introducing oxygen enhances biodegradation of heavier chain compounds such as diesel.

It is essential that a detailed site characterization is completed and that it defines any preferential flow paths that might exist. Failure to properly characterize a site and design a treatment system could result in vapor migration to areas that can result in serious safety considerations (for example, basements or crawl spaces can collect vapors and present an explosion hazard). Special consideration should be given to areas without a significant vadose zone.

2.10 Monitored Natural Attenuation

Natural attenuation is the reduction in the concentration and mass of hazardous substances due to naturally occurring physical, chemical, and biological processes without human intervention. These processes include, but are not limited to, dispersion, diffusion, sorption, retardation, and degradation processes such as biodegradation. Other terms associated with natural attenuation in the literature include “intrinsic remediation”, “intrinsic bioremediation”, “passive bioremediation”, “natural recovery”, and “natural assimilation”.

Under appropriate field conditions, benzene, toluene, ethyl benzene, and xylenes (BTEX) may degrade through microbial activity and ultimately produce non-toxic products such as carbon dioxide and water. Where microbial activity is sufficiently rapid, the dissolved BTEX contaminant plume may stabilize (*i.e.*, stop expanding), and contaminant concentrations may eventually decrease to levels below regulatory cleanup levels.

Following degradation of a dissolved BTEX plume, a residue consisting of heavier petroleum hydrocarbons of relatively low solubility and volatility will typically be left behind in the original source (spill) area. Although this residual contamination may have a lower potential for further migration, it still may pose a threat to human health, safety, and welfare or the environment either from direct contact with soils in the source area or by continuing to slowly leach contaminants to groundwater. For these reasons, monitored natural attenuation alone is generally not sufficient to clean up a petroleum release site.

Source control measures usually need to be implemented in conjunction with natural attenuation processes. Other controls such as institutional controls may also be necessary to ensure protection of human health, safety, and welfare and the environment.

Performance monitoring is a critical element for a natural attenuation strategy to evaluate cleanup effectiveness and to ensure protection of human health, safety, and welfare and the environment. The monitoring program developed for each site should specify the location,

frequency, and type of samples and measurements necessary to evaluate remedy performance and define the anticipated performance objectives of the remedy. Performance monitoring should continue as long as contamination remains above required cleanup levels.

Typically, monitoring is continued for a specified period (*e.g.*, one to three years) after cleanup levels have been achieved to ensure that concentration levels are stable and remain below cleanup levels. The mechanisms for maintaining the monitoring program should be clearly established in the cleanup decision or other site documents, as appropriate. Details of the monitoring program should be provided to ADEC as part of any proposed natural attenuation remedy. For more information, consult the EPA guidance entitled *Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tanks Sites* (EPA, 1997b).

SECTION 3. TREATMENT CHECKLISTS

The following checklists provide the essential components needed to complete a treatment project using the specified treatment technology. Additional criteria may be required dependent upon site-specific conditions. If used, a signed copy of the checklist should be enclosed in the front of the final corrective action report submitted to ADEC. Checklists are for voluntary use and are not mandatory.

Landfarming Checklist

Project Name _____ **UST Facility #0-00** _____
Page Number in Report _____

- ___ Workplan with detailed specifications for the landfarming project (18 AAC 78.250(e)(3)).
- ___ Design plan that will provide prevention of contamination migration to previously unaffected areas unless otherwise approved by the department in a corrective action plan (18 AAC 78.250(e)(4)).
- ___ Workplan schedule for conducting field work, monitoring, corrective action performance, and submittal of interim and final corrective action reports (18 AAC 78.250(e)(1)).
- ___ Site control plan (18 AAC 78.250(e)(8)).
- ___ Wastewater discharge permit for any discharge of regulated wastewater (18 AAC 72).
- ___ Project complies with air quality standards and requirements (18 AAC 78.250(e)(9) and 18 AAC 50).
- ___ Nondomestic wastewater system plan approval for the construction, alteration, installation, modification, or operation of any nondomestic wastewater treatment works or disposal system under 18 AAC 72.600 (18 AAC 78.250(e)(11) and 18 AAC 72).
- ___ Project maintains appropriate separation distance from surface water, water supply wells, and groundwater (18 AAC 78.274(a)(2)).
- ___ If applicable, description of cultured microbes, any additives, breakdown products, and oxygen source with their rate of application and biodegradation (18 AAC 78.250(e)(12)(E)).
- ___ If a landfarm is constructed off-site, department approval before moving contaminated soil to the treatment site (18 AAC 78.274(b)).
- ___ If landfarm is constructed off-site, compliance with the treatment facility requirements (18 AAC 78.273).
- ___ Information submitted that addresses leachate (18 AAC 78.250(e)(12)(A)).
- ___ Post-treatment sampling to ensure cleanup standards have been met (18 AAC 78.605(b)).
- ___ Cleanup standards achieved (18 AAC 78.600 - 18 AAC 78.625).
- ___ Treated soils returned to original site or disposed of properly in accordance with department approval (18 AAC 78.274(b)).

I certify that I have personally reviewed the above checklist and that all information noted is contained in the attached report.

Name _____ Signature _____

Title _____ Date _____

In-Situ Bioremediation Checklist

Project Name _____ **UST Facility #0-00** _____
Page Number in Report _____

- _____ Workplan with detailed specifications for the in-situ bioremediation project (18 AAC 78.250(e)(3)).
- _____ Design plan that will provide prevention of contamination migration to previously unaffected areas unless otherwise approved by the department in a corrective action plan (18 AAC 78.250(e)(4)).
- _____ Workplan schedule for conducting field work, monitoring, corrective action performance, and submittal of interim and final corrective action reports (18 AAC 78.250(e)(1)).
- _____ Site control plan (18 AAC 78.250(e)(8)).
- _____ Wastewater discharge permit for any discharge of regulated wastewater (18 AAC 72).
- _____ Project complies with air quality standards and requirements (18 AAC 78.250(e)(9) and 18 AAC 50).
- _____ Nondomestic wastewater system plan approval for the construction, alteration, installation, modification, or operation of a nondomestic wastewater treatment works or disposal system under 18 AAC 72.600 (18 AAC 78.250(e)(11) and 18 AAC 72).
- _____ Site monitoring plan showing placement locations for monitoring wells (18 AAC 78.250(e)(13)(A)).
- _____ Hydrogeologic description of the site addressing soil and sediments present, stratigraphy, groundwater gradient, confining layers, perched water, aquifer transmissivity, percolation rates from precipitation, and other relevant factors (18 AAC 78.250(e)(13)(B)).
- _____ If required by ADEC, hydrogeologic modeling addressing capture zones, effects of hydraulic loading, and plume migration (18 AAC 78.250(e)(13)(C)).
- _____ If applicable, description of cultured microbes, any additives, and electron acceptor source with their rate of application and biodegradation (18 AAC 78.250(e)(12)(E)).
- _____ Post-treatment sampling to ensure cleanup standards have been met (18 AAC 78.605(b)).
- _____ Cleanup standards achieved (18 AAC 78.600 - 18 AAC 78.625).

I certify that I have personally reviewed the above checklist and that all information noted is contained in the attached report.

Name _____ Signature _____

Title _____ Date _____

Cell Bioremediation Checklist

Project Name _____ **UST Facility #0-00** _____
Page Number in Report _____

- _____ Workplan with detailed specifications for the cell bioremediation project (18 AAC 78.250(e)(3)).
- _____ Design plan that will provide prevention of contamination migration to previously unaffected areas unless otherwise approved by the department in a corrective action plan (18 AAC 78.250(e)(4)).
- _____ Workplan schedule for conducting field work, monitoring, corrective action performance, and submittal of interim and final corrective action reports (18 AAC 78.250(e)(1)).
- _____ Site control plan (18 AAC 78.250(e)(8)).
- _____ Wastewater discharge permit for any discharge of regulated wastewater (18 AAC 72).
- _____ Project complies with air quality standards and requirements (18 AAC 78.250(e)(9) and 18 AAC 50).
- _____ Soil placed on liner meeting long-term storage requirements (18 AAC 78.274).
- _____ Nondomestic wastewater system plan approval for the construction, alteration, installation, modification, or operation of a nondomestic wastewater treatment works or disposal system under 18 AAC 72.600 (18 AAC 78.250(e)(11) and 18 AAC 72).
- _____ Information submitted that addresses containment and handling of leachate (18 AAC 78.250(e)(12)(A)).
- _____ Project maintains appropriate separation distance from surface water, water supply wells, and groundwater (18 AAC 78.274(a)(2)).
- _____ If applicable, description of cultured microbes, any additives, and oxygen source with their rate of application and biodegradation (18 AAC 78.250(e)(12)(E)).
- _____ If treatment cell is constructed off-site, department approval before moving contaminated soil to the treatment site (18 AAC 78.274(b)).
- _____ If treatment cell is constructed off-site, compliance with the treatment facility requirements (18 AAC 78.273).
- _____ Post-treatment sampling to ensure cleanup standards have been met (18 AAC 78.605(b)).
- _____ Cleanup standards achieved (18 AAC 78.600 - 18 AAC 78.625).
- _____ Treated soils returned to original site or disposed of properly in accordance with department approval (18 AAC 78.274(b)).

I certify that I have personally reviewed the above checklist and that all information noted is contained in the attached report.

Name _____ Signature _____

Title _____ Date _____

Landspreading Checklist

Project Name _____ **UST Facility #0-00** _____
Page Number in Report _____

- ___ Workplan with detailed specifications for the landspreading project (18 AAC 78.250(e)(3)).
- ___ Design plan that will provide prevention of contamination migration to previously unaffected areas unless otherwise approved by the department in a corrective action plan (18 AAC 78.250(e)(4)).
- ___ Workplan schedule for conducting field work, monitoring, corrective action performance, and submittal of interim and final corrective action reports (18 AAC 78.250(e)(1)).
- ___ A list of additives and additive effects (18 AAC 78.250(e)(7)).
- ___ Site control plan (18 AAC 78.250(e)(8)).
- ___ Wastewater discharge permit for any discharge of regulated wastewater (18 AAC 72).
- ___ Project complies with air quality standards and requirements (18 AAC 78.250(e)(9) and 18 AAC 50).
- ___ Nondomestic wastewater system plan approval for the construction, alteration, installation, modification, or operation of a nondomestic wastewater treatment works or disposal system under 18 AAC 72.600 (18 AAC 78.250(e)(11) and 18 AAC 72).
- ___ Information submitted that addresses leachate (18 AAC 78.250(e)(12)(A)).
- ___ Project maintains appropriate separation distance from surface water, water supply wells, and groundwater (18 AAC 78.274(a)(2)).
- ___ If landspreading is constructed off-site, department approval before moving contaminated soil to the treatment site (18 AAC 78.274(b)).
- ___ If landspreading is constructed off-site, compliance with the treatment facility requirements (18 AAC 78.273).
- ___ Post-treatment sampling to ensure cleanup standards have been met (18 AAC 78.605(b)).
- ___ Cleanup standards achieved (18 AAC 78.600 - 18 AAC 78.625).
- ___ Treated soils returned to original site or disposed of properly in accordance with department approval (18 AAC 78.274(b)).

I certify that I have personally reviewed the above checklist and that all information noted is contained in the attached report.

Name _____ Signature _____

Title _____ Date _____

In-Situ Vapor Extraction Checklist

Project Name _____ **UST Facility #0-00** _____
Page Number in Report ____

- ____ Workplan with detailed specifications for the in-situ vapor extraction project (18 AAC 78.250(e)(3)).
- ____ Design plan that will provide prevention of contamination migration to previously unaffected areas unless otherwise approved by the department in a corrective action plan (18 AAC 78.250(e)(4)).
- ____ Workplan schedule for conducting field work, monitoring, corrective action performance, and submittal of interim and final corrective action reports (18 AAC 78.250(e)(1)).
- ____ Site control plan (18 AAC 78.250(e)(8)).
- ____ Wastewater discharge permit for any discharge of regulated wastewater (18 AAC 72).
- ____ Project complies with air quality standards and requirements (18 AAC 78.250(e)(9) and 18 AAC 50).
- ____ Nondomestic wastewater system plan approval for the construction, alteration, installation, modification, or operation of a nondomestic wastewater treatment works or disposal system under 18 AAC 72.600 (18 AAC 78.250(e)(11) and 18 AAC 72).
- ____ Site monitoring plan showing placement locations for monitoring wells (18 AAC 78.250(e)(13)(A)).
- ____ Hydrogeologic description of the site addressing soil and sediments present, stratigraphy, groundwater gradient, confining layers, perched water, aquifer transmissivity, percolation rates from precipitation, and other relevant factors (18 AAC 78.250(e)(13)(B)).
- ____ If required by ADEC, hydrogeologic modeling addressing capture zones, effects of hydraulic loading, and plume migration (18 AAC 78.250(e)(13)(C)).
- ____ Post-treatment sampling to ensure cleanup standards have been met (18 AAC 78.605(b)).
- ____ Cleanup standards achieved (18 AAC 78.600 - 18 AAC 78.625).

I certify that I have personally reviewed the above checklist and that all information noted is contained in the attached report.

Name _____

Signature _____

Title _____

Date _____

Prepared Cell Vapor Extraction Checklist

Project Name _____ **UST Facility #0-00** _____
Page Number in Report _____

- ___ Workplan with detailed specifications for the cell vapor extraction project (18 AAC 78.250(e)(3)).
- ___ Design plan that will provide prevention of contamination migration to previously unaffected areas unless otherwise approved by the department in a corrective action plan (18 AAC 78.250(e)(4)).
- ___ Workplan schedule for conducting field work, monitoring, corrective action performance, and submittal of interim and final corrective action reports (18 AAC 78.250(e)(1)).
- ___ A list of additives and additive effects (18 AAC 78.250(e)(7)).
- ___ Site control plan (18 AAC 78.250(e)(8)).
- ___ Wastewater discharge permit for any discharge of regulated wastewater (18 AAC 72).
- ___ Project complies with air quality standards and requirements (18 AAC 78.250(e)(9) and 18 AAC 50).
- ___ Soil placed on liner meeting long-term storage requirements (18 AAC 78.274).
- ___ Nondomestic wastewater system plan approval for the construction, alteration, installation, modification, or operation of a nondomestic wastewater treatment works or disposal system under 18 AAC 72.600 (18 AAC 78.250(e)(11) and 18 AAC 72).
- ___ Information submitted that addresses containment and handling of leachate (18 AAC 78.250(e)(12)(A)).
- ___ Project maintains appropriate separation distance from surface water, water supply wells, and groundwater (18 AAC 78.274(a)(2)).
- ___ If treatment cell is constructed off-site, department approval before moving contaminated soil to the treatment site (18 AAC 78.274(b)).
- ___ If treatment cell is constructed off-site, compliance with the treatment facility requirements (18 AAC 78.273).
- ___ Post-treatment sampling to ensure cleanup levels have been met (18 AAC 78.605(b)).
- ___ Cleanup standards achieved (18 AAC 78.600 - 18 AAC 78.625).
- ___ Treated soils returned to original site or disposed of properly in accordance with department approval (18 AAC 78.274(b)).

I certify that I have personally reviewed the above checklist and that all information noted is contained in the attached report.

Name _____ Signature _____

Title _____ Date _____

Solidification and Fixation Checklist

Project Name _____ **UST Facility #0-00** _____
Page Number in Report ____

- ___ Workplan with detailed specifications for the solidification or fixation project (18 AAC 78.250(e)(9)).
- ___ Design plan that will provide prevention of contamination migration to previously unaffected areas unless otherwise approved by the department in a corrective action plan (18 AAC 78.250(e)(4)).
- ___ Workplan schedule for conducting field work, monitoring, corrective action performance, and submittal of interim and final corrective action reports (18 AAC 78.250(e)(1)).
- ___ A list of additives and additive effects (18 AAC 78.250(e)(7)).
- ___ Site control plan (18 AAC 78.250(e)(8)).
- ___ Wastewater discharge permit for discharge of regulated wastewater (18 AAC 72).
- ___ Project complies with air quality standards and requirements (18 AAC 78.250(e)(9) and 18 AAC 50).
- ___ Soil placed on liner meeting long-term storage requirements (18 AAC 78.274).
- ___ Nondomestic wastewater system plan approval for the construction, alteration, installation, modification, or operation of a nondomestic wastewater treatment works or disposal system under 18 AAC 72.600 (18 AAC 78.250(e)(11) and 18 AAC 72).
- ___ Information submitted that addresses containment and handling of leachate (18 AAC 78.250(e)(12)(A)).
- ___ Project maintains appropriate separation distance from surface water, water supply wells, and groundwater (18 AAC 78.274(a)(2)).
- ___ If solidification or fixation project is off-site, department approval before moving contaminated soil to the treatment site (18 AAC 78.274(b)).
- ___ If solidification or fixation is off-site, compliance with the treatment facility requirements (18 AAC 78.273).
- ___ Post-treatment sampling to ensure cleanup standards have been met (18 AAC 78.605(b)).
- ___ Cleanup standards achieved (18 AAC 78.600 - 18 AAC 78.625)
- ___ Treated soils returned to original site or disposed of properly in accordance with department approval (18 AAC 78.274(b)).

I certify that I have personally reviewed the above checklist and that all information noted is contained in the attached report.

Name _____ Signature _____

Title _____ Date _____

Asphalt Recycling Checklist

Project Name _____

UST Facility #0-00 _____

Page Number in Report _____

- _____ Workplan with detailed specifications for the asphalt recycling project (18 AAC 78.250(e)(3)).
- _____ Design plan that will provide prevention of contamination migration to previously unaffected areas unless otherwise approved by the department in a corrective action plan (18 AAC 78.250(e)(4)).
- _____ Workplan schedule for conducting field work, monitoring, corrective action performance, and submittal of interim and final corrective action reports (18 AAC 78.250(e)(1))
- _____ A list of additives and additive effects (18 AAC 78.250(e)(7)).
- _____ Site control plan (18 AAC 78.250(e)(8)).
- _____ Wastewater discharge permit for discharge of regulated wastewater (18 AAC 72).
- _____ Project complies with air quality standards and requirements (18 AAC 78.250(e)(9) and 18 AAC 50).
- _____ Soil placed temporarily on liner meets appropriate storage requirements (18 AAC 78.274).
- _____ Nondomestic wastewater system plan approval for the construction, alteration, installation, modification, or operation of a nondomestic wastewater treatment works or disposal system under 18 AAC 72.600 (18 AAC 78.250(e)(11) and 18 AAC 72).
- _____ Information submitted that addresses leachate (18 AAC 78.250(e)(12)(A)).
- _____ Project maintains appropriate separation distance from surface water, water supply wells, and groundwater (18 AAC 78.274(a)(2)).
- _____ If using a hot asphalt batch plant, certify that processes incorporating contaminated soils meet all current industry standards for asphalt paving (18 AAC 78.250(e)(12)(C)).
- _____ If required by ADEC, results of a leaching assessment (18 AAC 78.250(e)(12)(D)(iii)).
- _____ If required by ADEC, a pavement structure design study certified by a registered engineer (18 AAC 78.250(e)(12)(D)(i)).
- _____ If asphalt recycling is completed off-site, department approval before moving contaminated soil to the treatment site (18 AAC 78.274(b)).
- _____ If asphalt recycling is completed off-site, compliance with the treatment facility requirements (18 AAC 78.273).
- _____ Post-treatment sampling to ensure cleanup standards have been met (18 AAC 78.605(b)).
- _____ Cleanup standards achieved (18 AAC 78.600 - 18 AAC 78.625).
- _____ Treated soils returned to original site or disposed of properly in accordance with department approval (18 AAC 78.274(b)).

I certify I personally reviewed the above checklist and that all information noted is contained in the attached report.

Name _____ Signature _____

Title _____ Date _____

Thermal Desorption Checklist

Project Name _____ **UST Facility #0-00** _____
Page Number in report _____

- ___ Workplan with detailed specifications for the thermal desorption project (18 AAC 78.250(e)(3)).
- ___ Design plan that will provide prevention of contamination migration to previously unaffected areas unless otherwise approved by the department in a corrective action plan (18 AAC 78.250(e)(4)).
- ___ Workplan schedule for conducting field work, monitoring, corrective action performance, and submittal of interim and final corrective action reports (18 AAC 78.250(e)(1)).
- ___ A list of additives and additive effects (18 AAC 78.250(e)(7)).
- ___ Site control plan (18 AAC 78.250(e)(8)).
- ___ Wastewater discharge permit for discharge of regulated wastewater (18 AAC 72).
- ___ Project complies with air quality standards and requirements (18 AAC 78.250(e)(9) and 18 AAC 50).
- ___ Contaminated soil placed on liner meets appropriate storage requirements until final confirmation samples confirm they meet appropriate cleanup standards (18 AAC 78.274).
- ___ Nondomestic wastewater system plan approval for the construction, alteration, installation, modification, or operation of a nondomestic wastewater treatment works or disposal system under 18 AAC 72.600 (18 AAC 78.250(e)(11) and 18 AAC 72).
- ___ Information submitted that addresses containment and handling of leachate (18 AAC 78.250(e)(12)(A)).
- ___ Project maintains appropriate separation distance from surface water, water supply wells, and groundwater (18 AAC 78.274). ___ If thermal desorption is completed off-site, department approval before moving contaminated soil to the treatment site (18 AAC 78.274(c)).
- ___ If thermal desorption is completed off-site, compliance with the treatment facility requirements (18 AAC 78.273).
- ___ Post-treatment sampling to ensure cleanup standards have been met (18 AAC 78.605(b)).
- ___ Cleanup standards achieved (18 AAC 78.600 - 18 AAC 78.625).
- ___ Treated soils returned to original site or disposed of properly in accordance with department approval (18 AAC 78.274(b)).

I certify that I have personally reviewed the above checklist and that all information noted is contained in the attached report.

Name _____ Signature _____

Title _____ Date _____

Soil Washing Checklist

Project Name _____ **UST Facility #0-00** _____
Page Number in Report _____

- ___ Workplan with detailed specifications for the soil washing project (18 AAC 78.250(e)(3)).
- ___ Design plan that will provide prevention of contamination migration to previously unaffected areas unless otherwise approved by the department in a corrective action plan (18 AAC 78.250(e)(4)).
- ___ Workplan schedule for conducting field work, monitoring, corrective action performance and submittal of interim and final corrective action reports (18 AAC 78.250(e)(1)).
- ___ A list of additives and additive effects (18 AAC 78.250(e)(7)).
- ___ Site control plan (18 AAC 78.250(e)(8)).
- ___ Wastewater discharge permit for discharge of regulated wastewater (18 AAC 72).
- ___ Project complies with air quality standards and requirements (18 AAC 78.250(e)(9) and 18 AAC 50).
- ___ Soil placed temporarily on liner meets appropriate storage requirements (18 AAC 78.274).
- ___ Nondomestic wastewater system plan approval for the construction, alteration, installation, modification, or operation of a nondomestic wastewater treatment works or disposal system under 18 AAC 72.600 (18 AAC 78.250(e)(11) and 18 AAC 72).
- ___ Information submitted that addresses containment and handling of leachate (18 AAC 78.250(e)(12)(A)).
- ___ Project maintains appropriate separation distance from surface water, water supply wells, and groundwater (18 AAC 78.274(a)(2)).
- ___ If soil washing is completed off-site, department approval before moving contaminated soil to the treatment site (18 AAC 78.274(b)).
- ___ If soil washing is completed off-site, compliance with the treatment facility requirements (18 AAC 78.273).
- ___ Post-treatment sampling to ensure cleanup standards have been met (18 AAC 78.605(b)).
- ___ Cleanup standards achieved (18 AAC 78.600 - 18 AAC 78.625).
- ___ Treated soils returned to original site or disposed of properly in accordance with department approval (18 AAC 78.274(b)).

I certify that I have personally reviewed the above checklist and that all information noted is contained in the attached report.

Name _____ Signature _____

Title _____ Date _____

Groundwater Pump and Treat Checklist

Project Name _____ **UST Facility #0-00** _____
Page Number in Report ____

- ____ Workplan with detailed specifications for the groundwater pump and treat project (18 AAC 78.250(e)(3)).
- ____ Design plan that will provide prevention of contamination migration to previously unaffected areas unless otherwise approved by the department in a corrective action plan (18 AAC 78.250(e)(4)).
- ____ Workplan schedule for conducting field work, monitoring, corrective action performance, and submittal of interim and final corrective action reports (18 AAC 78.250(e)(1)).
- ____ A list of additives and additive effects (18 AAC 78.250(e)(7)).
- ____ Site control plan (18 AAC 78.250(e)(8)).
- ____ Wastewater discharge permit for discharge of regulated wastewater (18 AAC 72).
- ____ Project complies with air quality standards and requirements (18 AAC 78.250(e)(9) and 18 AAC 50).
- ____ Nondomestic wastewater system plan approval for the construction, alteration, installation, modification, or operation of a nondomestic wastewater treatment works or disposal system under 18 AAC 72.600 (18 AAC 78.250(e)(11) and 18 AAC 72).
- ____ Site monitoring plan showing placement locations for monitoring wells (18 AAC 78.250(e)(13)(A)).
- ____ Hydrogeologic description of the site addressing soil and sediments present, stratigraphy, groundwater gradient, confining layers, perched water, aquifer transmissivity, percolation rates from precipitation, and other relevant factors (18 AAC 78.250(e)(13)(B)).
- ____ If required by ADEC, hydrogeologic modeling addressing capture zones, effects of hydraulic loading, and plume migration (18 AAC 78.250(e)(13)(C)).
- ____ Post-treatment sampling to ensure cleanup standards have been met (18 AAC 78.605(b)).
- ____ Cleanup standards achieved (18 AAC 78.600 - 18 AAC 78.625).

I certify that I have personally reviewed the above checklist and that all information noted is contained in the attached report.

Name _____ Title _____

Signature _____ Date _____

Air Sparging Checklist

Project Name _____ **UST Facility #0-00** _____
Page Number in Report _____

- _____ Workplan with detailed specifications for the air sparging project (18 AAC 78.250(e)(3)).
- _____ Design plan that will provide prevention of contamination migration to previously unaffected areas unless otherwise approved by the department in a corrective action plan (18 AAC 78.250(e)(4)).
- _____ Workplan schedule for conducting field work, monitoring, corrective action performance, and submittal of interim and final corrective action reports (18 AAC 78.250(e)(1)).
- _____ A list of additives and additive effects (18 AAC 78.250(e)(7)).
- _____ Site control plan (18 AAC 78.250(e)(8)).
- _____ Wastewater discharge permit for discharge of regulated wastewater (18 AAC 72).
- _____ Project complies with air quality standards and requirements (18 AAC 78.250(e)(9) and 18 AAC 50).
- _____ Nondomestic wastewater system plan approval for the construction, alteration, installation, modification, or operation of a nondomestic wastewater treatment works or disposal system under 18 AAC 72.600 (18 AAC 78.272(a)(9) and 18 AAC 72).
- _____ Site monitoring plan showing placement locations for monitoring wells (18 AAC 78.250(e)(13)(A)).
- _____ Hydrogeologic description of the site addressing soil and sediments present, stratigraphy, groundwater gradient, confining layers, perched water, aquifer transmissivity, percolation rates from precipitation, and other relevant factors (18 AAC 78.250(e)(13)(B)).
- _____ If required by ADEC, hydrogeologic modeling addressing capture zones, effects of hydraulic loading, and plume migration (18 AAC 78.250(e)(13)(C)).
- _____ Post-treatment sampling to ensure cleanup standards have been met (18 AAC 78.605(b)).
- _____ Cleanup standards achieved (18 AAC 78.600 - 18 AAC 78.625).

I certify that I have personally reviewed the above checklist and that all information noted is contained in the attached report.

Name _____ Title _____

Signature _____ Date _____

CHAPTER 2

STANDARD SAMPLING PROCEDURES

CHAPTER 2. STANDARD SAMPLING PROCEDURES

SECTION 1. PROGRAM DESCRIPTION

1.1 Program Objectives

This manual outlines the standard operating procedures, quality control procedures, and data quality objectives for regulated underground storage tank (UST) site characterizations, site assessments, release investigations, and corrective actions. It directs the collection, interpretation, and reporting of data. This data will enable tank owners and operators and ADEC to evaluate the presence, degree, and extent of any groundwater, surface water, and soil contamination and to determine if further action is necessary.

1.2 Program Approach

To meet program objectives, this manual outlines a systematic approach to conducting UST site assessments and investigations. This approach is based on scientific studies, United States Environmental Protection Agency (EPA) guidance and methods, Alaska's UST regulations in 18 AAC 78, guidelines, input from the Alaska UST regulations workgroup, and assessment strategies used in Alaska and other states. This manual details sampling, laboratory analysis, and data reporting procedures, along with all required quality control functions. It also lists persons responsible for the major tasks required by 18 AAC 78. The manual covers activities in the following areas:

- personnel and responsibilities
- data quality objectives
- sampling procedures
- sample transfer log
- laboratory analytical procedures
- equipment maintenance and calibration
- data reduction, validation, and reporting
- quality control checks
- precision, accuracy, and completeness assessment
- corrective action scenarios
- internal audits
- reporting to management

Information about site sampling locations and site history, with reference to any existing documents for historical information and data available, must be included in the site-specific project plan or report submitted for each project undertaken for which a plan is required.

SECTION 2. PROGRAM ORGANIZATION AND RESPONSIBILITIES

2.1 Personnel and Responsibilities

All activities under this chapter, including the collection, interpretation, and reporting of data, shall be conducted or supervised by a qualified environmental professional as defined in 18 AAC 78. When a qualified environmental professional is not available, a qualified sampler as defined in 18 AAC 78 may conduct sampling of soil stockpiles, bioremediation systems, surface water, or groundwater monitoring wells if described and approved in the sampling and analysis plan. A qualified environmental professional is responsible for performing principal investigation and quality assurance officer tasks. The responsibilities for these tasks under this chapter are as follows:

(1) The qualified environmental professional is responsible for overall management of the UST site assessment and site investigation, including adherence to the procedures outlined in this chapter.

(2) The QA officer, which may also be the qualified environmental professional, is responsible for overall quality assurance of assessment and investigation of UST sites and facilities. The QA officer is responsible for conducting scheduled field audits and providing ongoing review, monitoring, and evaluation of the field and laboratory activities. The QA officer shall validate or supervise validation of all reports to ADEC.

2.2 Accountability

While a laboratory must assure satisfactory levels of quality control within the laboratory to maintain its status with ADEC, the owner or operator shall ensure that the qualified environmental professional

(1) verifies the status of the laboratory being used; a list of certified and provisionally approved laboratories is available from ADEC;

(2) ensures that analytical testing meets the objectives of this chapter that refer to laboratories and the applicable requirements of 18 AAC 78;

(3) reports in any project report connected with this chapter any deviation from standard laboratory procedures of which it becomes aware;

(4) takes appropriate corrective actions as outlined in Section 10 of this manual if questions or problems arise with the laboratory analysis.

SECTION 3. QUALITY ASSURANCE

3.1 Responsibility and Definitions

Quality assurance (QA) objectives are quantitative and qualitative criteria needed to support specific regulatory action and describe the acceptability of data. The qualified environmental professional has primary responsibility for field QA and is accountable for the overall QA of the samples.

Quantitative QA criteria are precision, accuracy, and completeness. Qualitative QA criteria are representativeness and comparability. QA is determined on a site-specific basis for each project based on the following:

(1) **Precision:** Precision is a measure of the variability or random error in sampling, sample handling, preservation, and laboratory analysis.

(2) **Accuracy:** Accuracy is a measure of the closeness of an individual measurement or an average of a number of measurements to the true value.

(3) **Completeness:** Completeness is a measure of the amount of valid data obtained compared to the amount expected. For purposes of this chapter, completeness is calculated as the amount of usable samples divided by the minimum number of required samples, expressed as a percentage. A minimum confidence level of 85 percent is required. The formula to be used follows:

$$\%C = (V/N) \times 100$$

Where %C = Completeness

V = Number of valid samples, as determined by above calculations and by procedures outlined Section 8.3.3 of this manual (Determining the final validity of samples)

N = Total number of measurements necessary to achieve a specified statistical level of confidence in decision making.

(4) **Representativeness:** Representativeness describes the degree to which data characterize the actual conditions at a site.

(5) **Comparability:** Comparability expresses the confidence with which one data set can be compared with another. Data must be reported in the same units of quantitation and in accordance with the reporting requirements of 18 AAC 78. Sampling and laboratory reports and procedures might be audited to assure that they follow standard procedures and reporting formats.

SECTION 4. SAMPLING PROCEDURES

4.1 Overview of Sampling Approach

The systematic sampling approach outlined below must be used to assure that data collection activities provide usable data.

(1) Sampling must begin with an evaluation of background information, historical data, and site conditions. This evaluation is used to prepare a site-specific sampling strategy.

(2) In combination with the requirements of 18 AAC 78 and the results of the pre-sampling investigation, field screening results must be used to determine where samples will be collected. Field screening results may also be used to segregate soils, based on apparent levels of contamination, to help monitor potential exposures, and for health and safety monitoring. However, field screening may not take the place of laboratory samples required as discussed in Section 4.5 of this chapter (Determining sample locations).

(3) Samples must be collected with appropriate, clean tools. Decontamination of sampling equipment must follow the practices described in this section.

(4) Stockpiles must be sampled in accordance with Section 4.5.1 of this chapter (Sample locations for contaminated untreated stockpiles).

(5) If necessary, sufficient monitoring and observation wells must be properly installed to determine the presence, degree, or extent of groundwater contamination. Sampling of groundwater must follow the standard procedures outlined in Section 4.7.2 of this chapter (Sampling groundwater monitoring wells).

(6) Samples must be collected and preserved in appropriate sample containers, as listed in Table 1.

**Table 1: Reference Guide to Sample Collection and Laboratory Analysis
Part A: Soils, Sediments, Sludges, and Fill Materials**

Parameter	Preparation/ Analytical Method ¹	Method Detection Limit ²	Practical Quantitation Limit ³	Container Description (Minimum) [Clear glass may be substituted for amber if samples are protected from exposure to light, this exception does not apply to metals]	Preservation/ Holding Time
Gasoline range organics	AK101*	2 mg/kg	20 mg/kg	4 oz. amber glass, TLS	Methanol preservative, Cool 4° ± 2°C / 28 days
Diesel range organics	AK102*	2 mg/kg	20 mg/kg	4 oz. amber glass, TLC	Cool 4° ± 2°C / 14 days to extraction, less than 40 days to analysis of extract
Residual range organics	AK103*	10 mg/kg	100 mg/kg	4 oz. amber glass, TLC	Cool 4° ± 2°C / 14 days to extraction, less than 40 days to analysis of extract
Aliphatic gasoline range organics	AK101AA*	2 mg/kg	20 mg/kg	4 oz. wide-mouth amber glass jar with Teflon lined silicon rubber septum seal	Methanol preservative / 28 days from sampling
Aromatic gasoline range organics	AK101AA*	2 mg/kg	20 mg/kg	4 oz. wide-mouth amber glass jar with Teflon lined silicon rubber septum seal	Methanol preservative / 28 days from sampling
Aliphatic diesel range organics	AK102AA*	2 mg/kg	20 mg/kg	4 oz. wide-mouth amber glass jar, TLC	Cool 4° ± 2°C / 14 days to extraction, less than 40 days to analysis of extract
Aromatic diesel range organics	AK102AA*	2 mg/kg	20 mg/kg	4 oz. wide-mouth amber glass jar, TLC	Cool 4° ± 2°C / 14 days to extraction, less than 40 days to analysis of extract
Aliphatic residual range organics	AK103AA*	10 mg/kg	100 mg/kg	4 oz. wide-mouth amber glass jar, TLC	Cool 4° ± 2°C / 14 days to extraction, less than 40 days to analysis of extract
Aromatic residual range organics	AK103AA*	10 mg/kg	100 mg/kg	4 oz. wide-mouth amber glass jar, TLC	Cool 4° ± 2°C / 14 days to extraction of sample, less than 40 days to analysis of extract
Benzene	AK101**, 8021B or 8260B	0.007 mg/kg	0.05 mg/kg	4 oz. amber glass, TLS	Methanol preservative, Cool 4° ± 2°C / 28 days
Toluene	AK101**, 8021B or 8260B	0.007 mg/kg	0.05 mg/kg	4 oz. amber glass, TLS	Methanol preservative, Cool 4° ± 2°C / 28 days
Ethylbenzene	AK101**, 8021B or 8260B	0.007 mg/kg	0.05 mg/kg	4 oz. amber glass, TLS	Methanol preservative, Cool 4° ± 2°C / 28 days
Total xylenes	AK101**, 8021B or 8260B	0.007 mg/kg	0.05 mg/kg	4 oz. amber glass, TLS	Methanol preservative, Cool 4° ± 2°C / 28 days
Total BTEX	AK101**, 8021B or 8260B	0.007 mg/kg	0.05 mg/kg	4 oz. amber glass, TLS	Methanol preservative, Cool 4° ± 2°C / 28 days
Polynuclear Aromatic Hydrocarbons (PAH) ⁴	8270C or 8310	0.1 mg/kg	1 mg/kg	4 oz. amber glass, TLS	Cool 4° ± 2°C / 14 days to extraction, less than 40 days to analysis of extract
Total Volatile Chlorinated Solvents ⁶	8260B or 8021B	0.008 mg/kg	0.08 mg/kg	4 oz. amber glass, TLS	Methanol preservative, Cool 4° ± 2°C / 28 days
Polychlorinated biphenyls (PCBs)	8082	0.01 mg/kg	0.05 mg/kg	4 oz amber glass, TLC	Cool 4° ± 2°C / 14 days to extraction, less than 40 days to analysis of extract
Total Arsenic	6010B, 6020, 7060A, or 7061A	0.3 mg/kg	3 mg/kg	100mL Widemouth HDPE jar ⁵ , TLC	6 months
Total Barium	6010B, 6020, 7080A, or 7081	20 mg/kg	200 mg/kg	100mL Widemouth HDPE jar ⁵ , TLC	6 months
Total Cadmium	6010B, 6020,	0.8 mg/kg	8.0 mg/kg	100mL Widemouth HDPE jar ⁵ , TLC	6 months

Table 1: Reference Guide to Sample Collection and Laboratory Analysis
Part A: Soils, Sediments, Sludges, and Fill Materials

Parameter	Preparation/ Analytical Method ¹	Method Detection Limit ²	Practical Quantitation Limit ³	Container Description (Minimum) [Clear glass may be substituted for amber if samples are protected from exposure to light, this exception does not apply to metals]	Preservation/ Holding Time
	7130, or 7131A				
Total Chromium	6010B, 6020, 7190, or 7191	2 mg/kg	20 mg/kg	100mL Widemouth HDPE jar ⁵ , TLC	6 months
Total Lead	6010B, 6020, 7420, 7421	2 mg/kg	20 mg/kg	100mL Widemouth HDPE jar ⁵ , TLC	6 months
Total Nickel	6010B, 6020, 7520, or 7521	2 mg/kg	20 mg/kg	100mL Widemouth HDPE jar ⁵ , TLC	6 months
Total Vanadium	6010B, 7911, 6020, or 7910	20 mg/kg	200 mg/kg	100mL Widemouth HDPE jar ⁵ , TLC	6 months

Legend to follow Part B

Notes to Table 1, Part A:

- ¹ Unless otherwise noted, all preparation and analytical methods refer to those contained in EPA's *Test Methods for the Evaluating Solid Waste, Physical/Chemical Methods*.
- ² Method detection limits (MDL), specified in 40 C.F.R. Part 136, Appendix B, revised as of July 1, 1996, adopted by reference, are determined at the department's chemistry laboratory and participating department-approved laboratories.
- ³ Practical quantitation limits (PQL), like method detection limits, are instrument specific. PQLs must be established by each laboratory and must equal or have a value lower than the PQL in the table. For purposes of this chapter, PQL = 10 x MDL, except for PCB which is PQL = 5x MDL.
- ⁴ Naphthalene can be analyzed by AK101.
- ⁵ HDPE, High Density Polyethylene sample collection bottles, critically cleaned for trace metals analysis.
- ⁶ May be analyzed out of AK101 methanol preserved sample, if not used, then sample must be preserved with methanol in the field.
- * ADEC Analytical Methods AK101, AK102, and AK103 are included in Appendix C. ADEC Analytical Methods AK101AA, AK102AA, and AK103AA are included in Appendix D.
- ** The AK101 method can be extended for specific determination of volatile aromatics (BTEX) as specified in EPA Method 8021B for solids utilizing methanol preservation option only. All AK101 samples must be preserved with methanol.

Table 1: Reference Guide to Sample Collection and Laboratory Analysis (cont.)**Part B: Ground, Surface, Waste, and Marine Waters⁴**

Parameter	Preparation/ Analytical Method ¹	Method Detection Limit ²	Practical Quantitation Limit ³	Container Description	Preservation/ Holding Time
Gasoline range organics	AK101*	10 µg/L	100 µg/L	40 mL VOA, TLS	HCL to pH less than 2, 4° ± 2°C /14 days from sampling
Diesel range organics	AK102*	80 µg/L	800 µg/L	1 L amber glass, TLC	HCL to pH less than 2, 4° ± 2°C /14 days to extraction, 40 days to analysis of extract
Residual range organics	AK103*	50 µg/L	500 µg/L	1 L amber glass, TLC	Acidify to a pH of 2 using HCL, H ₂ SO ₄ or HNO ₃ / 7 days to extraction, 40 days to analysis of extract
Aliphatic gasoline range organics	AK101AA**	2 µg/L	20 µg/L	40 ml VOA with Teflon lined silicon rubber septum seal	HCL to a pH of 2 / 14 days from sampling
Aromatic gasoline range organics	AK101AA**	0.2 µg/L	2 µg/L	40 ml VOA with Teflon lined silicon rubber septum seal	HCL to a pH of 2 / 14 days from sampling
Aliphatic diesel range organics	AK102AA**	20 µg/L	200 µg/L	1 L amber glass, TLC	Acidify to a pH of 2 using HCL, H ₂ SO ₄ or HNO ₃ / 7 days to extraction, 40 days to analysis of extract
Aromatic diesel range organics	AK102AA**	20 µg/L	200 µg/L	1 L amber glass, TLC	Acidify to a pH of 2 using HCL, H ₂ SO ₄ or HNO ₃ / 7 days to extraction, 40 days to analysis of extract
Aliphatic residual range organics	--	--	--	--	--
Aromatic residual range organics	AK103AA**	50 µg/L	500µg/L	1 L amber glass, TLC	Acidify to a pH of 2 using HCL, H ₂ SO ₄ or HNO ₃ / 7 days to extraction, 40 days to analysis of extract
Benzene	AK101, 8021B, or 8260B	0.7 µg/L	5 µg/L	duplicate 40 mL vials/sample, TLS	HCL to pH less than 2, 4° ± 2°C /14 days
Toluene	AK101, 8021B, or 8260B	0.7 µg/L	5 µg/L	duplicate 40 mL vials/sample, TLS	HCL to pH less than 2, 4° ± 2°C /14 days
Ethylbenzene	AK101, 8021B, or 8260B	0.7 µg/L	5 µg/L	duplicate 40 mL vials/sample, TLS	HCL to pH less than 2, 4° ± 2°C /14 days
Total xylenes	AK101, 8021B, or 8260B	0.7 µg/L	5 µg/L	duplicate 40 mL vials/sample, TLS	HCL to pH less than 2, 4° ± 2°C /14 days
Total BTEX	AK101, 8021B, or 8260B	0.7 µg/L	5 µg/L	duplicate 40 mL vials/sample, TLS	HCL to pH less than 2, 4° ± 2°C /14 days
Polynuclear Aromatic Hydrocarbons (PAH) ⁶	8270C or 8310	1 µg/L	10 µg/L	1 L amber glass, TLS	4° ± 2°C, Ascorbic acid, dark / 7 days to extraction, 40 days to analysis of extract
Total Volatile Chlorinated Solvents	8021B or 8260B	0.8 µg/L	8 µg/L	duplicate 40 mL vials/sample, TLS	HCL to pH less than 2, 4° ± 2°C Na ₂ S ₂ O ₃ / 14 days
Polychlorinated biphenyls (PCBs)	8081A or 8082	1 µg/L	5 µg/L	1 L amber glass, TLC	4° ± 2°C / 7 days to extraction / 40 days to analysis of extract
Total Arsenic †	6010B, 6020, 7060, or 7061	8 µg/L	80 µg/L	min. 100 mL HDPE ⁵	HNO ₃ to pH less than 2 / 6 months max. total holding time
Total Barium	6010B, 6020, 7080A, or 7081	10 µg/L	100 µg/L	min. 100 mL HDPE ⁵	HNO ₃ to pH less than 2 / 6 months max. total holding time
Total Cadmium †	6010B, 6020, 7130, or 7131A	0.6 µg/L	6 µg/L	min. 100 mL HDPE ⁵	HNO ₃ to pH less than 2 / 6 months max. total holding time
Total Chromium †	6010B, 6020, 7190, or 7191	10 µg/L	100 µg/L	min. 100 mL HDPE ⁵	HNO ₃ to pH less than 2 / 6 months max. total holding time
Total Lead †	6010B, 6020, 7420, or 7421	2.0 µg/L	20 µg/L	min. 100 mL HDPE ⁵	HNO ₃ to pH less than 2 / 6 months max. total holding time

Table 1: Reference Guide to Sample Collection and Laboratory Analysis (cont.)					
Part B: Ground, Surface, Waste, and Marine Waters ⁴					
Parameter	Preparation/ Analytical Method ¹	Method Detection Limit ²	Practical Quantitation Limit ³	Container Description	Preservation/ Holding Time
Total Nickel	6010B, 6020, 7520, or 7521	10 µg/L	100 µg/L	min. 100 mL HDPE ⁵	HNO ₃ to pH less than 2 / 6 months max. total holding time
Total Vanadium	6010B, 6020, 7910, or 7911	20 µg/L	200 µg/L	min. 100 mL HDPE ⁵	HNO ₃ to pH less than 2 / 6 months max. total holding time

Notes to Table 1, Part B:

¹ Unless otherwise noted, all preparation and analytical methods refer to those contained in EPA's *Test Methods for the Evaluating Solid Waste, Physical/Chemical Methods*, SW-846.

² Method detection limits (MDL), specified in 40 C.F.R. Part 136, Appendix B, revised as of July 1, 1996, adopted by reference, are determined at the department's chemistry laboratory and participating department-approved laboratories.

³ Practical quantitation limits (PQL), like method detection limits, are instrument specific. PQLs must be established by each laboratory and must equal or have a value lower than the PQL in the table. For purposes of this chapter, PQL = 10 x MDL, except for PCBs which is PQL = 5 x MDL.

⁴ Sample collection and laboratory analyses for water collected from drinking water sources must be done in accordance with 18 AAC 80.

⁵ HDPE, High Density Polyethylene sample collection bottles, critically cleaned for trace metals analysis.

⁶ Naphthalene can be analyzed by 8021B or 8260B.

* ADEC Analytical Methods AK101, AK102, and AK103 are included in Appendix C. ADEC Analytical Methods AK101AA, AK102AA, and AK103AA are included in Appendix D.

† Analytical methods 6010B, 7080A, 7130, 7420, 7520, and 7910 are for high contaminant level screening only. These can be used for closure only if site specific MDL criteria are met. Analytical methods 6020, 7031A, 7060, 7061, 7081A, 7190, 7191, 7421, 7521, and 7911 are acceptable for closure.

Legend to Table 1:

PAH = acenaphthene, anthracene, benzo-a-anthracene, benzo-a-pyrene, benzo-b-fluoranthene, benzo-k-fluoranthene, chrysene, dibenzo-a,h-anthracene, fluorene ideno-123-cd-pyrene, naphthalene, and pyrene

VOA = Volatile Organic Analysis;

TLC = Teflon lined screw caps;

TLS = Teflon lined septa sonically bonded to screw caps

4.2 Documentation of Sampling Procedures

A field log book or another type of field record must be used to document the collection of samples and site data. This record must include:

- (1) the name of each qualified environmental professional on site supervising or conducting a characterization, assessment, or investigation;
- (2) the date and time of sampling;
- (3) weather conditions, including temperature, wind speed, humidity, and precipitation;
- (4) the name of each person who physically collected the samples;
- (5) clear photographs of the site, bottom of excavation, and removed tanks;
- (6) the results of an inspection of the tank and piping for corrosion;
- (7) a site sketch that, at a minimum, shows
 - (A) locations of all known present and past USTs, piping and pump islands, including UST identification numbers assigned by ADEC;
 - (B) distances from tanks to nearby structures;
 - (C) property line locations;
 - (D) sampling locations and depths and corresponding sample ID numbers;
 - (E) any release sites;
 - (F) any free product sites;
 - (G) scale; and
 - (H) a north arrow.

When appropriate, the site sketch should include the following relevant features:

- (1) a description of the size of the excavation;
- (2) field instrument readings;
- (3) location of stockpiled soils;
- (4) depth, width, and type of backfill material used to surround tanks and piping;

- (5) soil types;
- (6) utility trenches;
- (7) wells within 100 feet;
- (8) depth to groundwater or seasonal high groundwater level; and
- (9) surface drainages, including potential hydraulic connections with groundwater.

4.3 Pre-Sampling Activities

Before conducting field sampling activities, the site background information must be collected and recorded, the site conditions must be compiled as provided in Sections 4.3.1 and 4.3.2 of this chapter, and the necessary notifications must be made to agencies as provided in Section 4.3.3 of this chapter.

4.3.1 Site Background

Before beginning field work, the following information must be collected and recorded:

- (1) the names, addresses, and telephone numbers of the owner, operator, and businesses on the site;
- (2) for rural areas, the quarter section, township, and range of the site;
- (3) locations of all present and past USTs, piping, and pump islands;
- (4) a description of known UST systems, including capacity, dimension, age, and material of construction and location and types of fill and vent pipes, valves, and connectors;
- (5) history of types of products stored in the tanks;
- (6) history of known releases and available data from previous soil or groundwater sampling at the site;
- (7) type and classification of native soil;
- (8) location of wells within 100 feet of the site;
- (9) surface waters and wetlands in the immediate vicinity of site;
- (10) depth to groundwater or seasonally high groundwater level;
- (11) property line locations;
- (12) distances from tanks to nearby structures; and

(13) type and location of below ground utility lines that could create pathways for contaminant migration.

In addition, where relevant and practical, the following information on the site must be collected and recorded:

- (1) location of each hold-down pad or anchoring system, if any;
- (2) the name of the contractor who installed the tank, if known;
- (3) dates of each installation and upgrade;
- (4) performance history, including repair records, inventory records, tightness testing records, leak detection system records, or records of water pullouts;
- (5) depth and width of backfill area and type of backfill material used to surround tanks and piping;
- (6) surface drainage characteristics, including potential hydraulic connections with groundwater;
- (7) location of other nearby USTs, either active or inactive, or other potential sources of contamination; and
- (8) previous site uses, including historical waste handling procedures.

4.3.2 Surface Observation of Site Conditions

An observation of the site's surface must be conducted before sample collection to assist in determining field sampling approaches and locations. Activities that must be completed during this observation include:

- (1) locating the aboveground components of each UST;
- (2) confirmation of the amount of fuel currently in each tank;
- (3) determination of tank size;
- (4) observation for aboveground utilities;
- (5) underground utility locations (contact utility location centers where available);
- (6) visual inspection for surface indications of releases;
- (7) if practical and no safety hazard exists, check for odor of petroleum in nearby structures (basements); and
- (8) check sumps and access manholes for evidence of pump leakage.

Key areas that must be observed for surface indications of a release include:

- (1) vent pipes and fill holes;
- (2) pavement depressions, buckling, cracks, or patches that could indicate that subsurface problems have historically occurred;
- (3) cracks or stains at base of pumps; and
- (4) evidence of stressed vegetation that may have resulted from a release or spill.

The results of the site observations must be recorded in a field log book or other appropriate document.

4.3.3 Notification to Agencies

Notification to ADEC, local governments, and fire departments is required before any site assessment work is performed for closure or change-in-service and is subject to the requirements of 18 AAC 78.085.

4.4 Field Screening

Field screening is the use of portable devices capable of detecting petroleum contaminants on a real-time basis or by rapid field analytical technique. Field screening must be used to help assess the following locations where contamination is most likely to be present:

Tank Area

- areas of suspected or obvious contamination;
- adjacent to and below all fill and vent pipes;
- excavation sidewalls below the tank midline;
- one representative sample for at least every 100 square feet of excavation bottom

Piping Run

- areas of suspected or obvious contamination;
- below piping joints, elbows, connections, and damaged piping components; if these locations are unknown then screening must occur below original level of piping at 10 foot-intervals; the 10-foot interval is chosen because pipe sections commonly used are 10-foot lengths and because of limits of detection of soil gas vapors from the release source;

- adjacent to and below all dispensers.

When possible, field screening samples should be collected directly from the excavation or from the excavation equipment's bucket. If field screening is conducted only from the equipment's bucket, then a minimum of one field screening sample must be collected from each 10 cubic yards of excavated soil. If instruments or other observations indicate contamination, soil must be separated into stockpiles based on apparent degrees of contamination. At a minimum, soil suspected of contamination must be segregated from soil observed to be free of contamination. Two levels of field screening procedures are:

(1) use of field screening devices to perform synoptic surveys of potentially contaminated areas to determine the approximate locations containing contaminants (qualitative screening); and

(2) use of field screening devices to provide a semi-quantitative estimate of the amount of contaminant present at a specific location (semi-quantitative screening).

4.4.1 Field Screening Devices

Many field screening instruments are available for detecting petroleum contaminants in the field on a rapid or real-time basis. Acceptable field screening instruments must be suitable for the contaminant being screened. The procedure for field screening using photoionization detectors (PIDs) and flame ionization detectors (FIDs) is described in Section 4.4.2 of this chapter. If other instruments are used, a description of the instrument or method and its intended use must be provided to ADEC. Whichever field screening method is chosen, the accuracy of the method must be verified throughout the sampling process through use of appropriate standards to match the use intended for the data. Unless ADEC indicates otherwise, wherever the requirement for field screening is stated in this chapter, instrumental or analytical methods of detection must be used, not olfactory or visual screening methods.

4.4.2 Headspace Analytical Screening Procedure for Field Screening (Semi-Quantitative Field Screening)

The most commonly used field instruments for UST site assessments in Alaska are FIDs and PIDs. The following headspace screening procedure to obtain and analyze field screening samples must be adhered to when using FIDs and PIDs:

(1) partially fill (one-third to one-half) a clean jar or clean Ziploc bag with the sample to be analyzed; total capacity of the jar or bag may not be less than eight ounces (app. 250 ml), but the container should not be so large as to allow vapor diffusion and stratification effects to significantly affect the sample;

(2) if the sample is collected from a split spoon, it must be transferred to the jar or bag for headspace analysis immediately after opening the split-spoon; if the sample is collected from an excavation or soil pile, it must be collected from freshly uncovered soil;

(3) if a jar is used, its top must be quickly covered with clean aluminum foil or a jar lid; screw tops or thick rubber bands must be used to tightly seal the jar; if a ziplock bag is used, it must be quickly sealed shut;

(4) headspace vapors must be allowed to develop in the container for at least 10 minutes but no longer than one hour; containers must be shaken or agitated for 15 seconds at the beginning and end of the headspace development period to assist volatilization; temperatures of the headspace must be warmed to at least 40° F (approximately 5° C), with instruments calibrated for the temperature used;

(5) after headspace development, the instrument sampling probe must be inserted to a point about one-half the headspace depth; the container opening must be minimized and care must be taken to avoid uptake of water droplets and soil particulates;

(6) after probe insertion, the highest meter reading must be taken and recorded, which normally will occur between two and five seconds after probe insertion; if erratic meter response occurs at high organic vapor concentrations or conditions of elevated headspace moisture, a note to that effect must accompany headspace data;

(7) calibration of PID and FID field instruments must follow the procedures outlined in Section 7.1 of this chapter (Calibration and maintenance of field instruments); and

(8) all field screening results must be documented in the field record or log book.

4.5 Determining Sample Locations

The locations and numbers of laboratory samples to be taken depend on the requirements of 18 AAC 78 for the specific type of sampling activity. The results of field screening must be used to determine the location from which to obtain samples. Samples must be obtained from locations that field screening and observations indicate are most heavily contaminated. A positive field screening result is one in which any deflection in the meter reading occurs at locations where samples are required. Samples analyzed with field screening devices may not be substituted for required laboratory samples. Specific types of sampling activity are as follows:

- (1) site assessment for a UST closed in place (18 AAC 78.090);
- (2) site assessment for a UST that has been removed (18 AAC 78.090);
- (3) site assessment for temporary closure, or change in service, of a UST (18 AAC 78.090);
- (4) investigating a suspected release (18 AAC 78.200 - 18 AAC 78.235);
- (5) release investigation (18 AAC 78.235); and
- (6) documentation that corrective actions have met applicable cleanup standards for soil (18 AAC 78.610) and water (18 AAC 78.620) through final verification sampling.

Within the constraints for sampling locations listed above, laboratory samples must be taken where contamination is most likely to be present.

4.5.1 Sample Locations for Contaminated Untreated Stockpiles

As noted in Section 4.4 of this chapter (Field screening), soils must be segregated during excavation based on apparent degrees of contamination. Soils must be stockpiled in accordance with 18 AAC 78.274.

Characterizing stockpiled soil is necessary to determine whether treatment or disposal of the soil is needed, to assist with selection of treatment or disposal methods, and to establish baseline data for use in evaluating the effectiveness of treatment.

To determine if untreated stockpiled soils can be disposed or considered not contaminated, stockpiled soils must be characterized by using

- (1) field screening; at least one soil sample must be obtained from each 10 cubic yards of stockpiled soil for field screening purposes; samples must be obtained from various depths in the pile, but none less than 18 inches beneath the exposed surface of the pile; field screening must follow the procedures outlined in this section and results must be documented in a site log book; and

(2) the number of grab samples collected from each stockpile as required by 18 AAC 78.605(c).

4.5.2 Alternative Sample Collection Procedures

Alternative sampling collection procedures, such as Cone Penetrometer Testing, HydroPunch, and Borehole Geophysical Logging may be used to determine soil hydrogeologic characteristics, contaminant distribution, and contaminant concentration.

These procedures may be useful, with proper evaluation, in providing essential data to assess and delineate the extent of contamination during site characterizations, release investigations, and corrective actions. These alternative procedures may not be used in collecting samples for final verification during site assessment or corrective action.

4.5.3 Sample Locations for Treated Excavated Soils

To determine if excavated soil has been treated, final corrective action verification samples must be from the location and depth of areas showing the highest levels of contamination during field screening.

Unless otherwise approved by the ADEC project manager, at least one field screening sample must be obtained from each 10 cubic yards of treated soil. Field screening samples must be obtained from various depths, but not less than 18 inches beneath the exposed surface of the soil. Field screening must follow the procedures outlined in this section and the results must be documented in a site log book.

The number of grab samples collected from the treated soil must be as required by 18 AAC 78.605(b).

4.6 Collecting Soil Samples

As required by 18 AAC 78, the following procedures must be used to collect soil samples for laboratory analysis:

(1) unless otherwise approved by ADEC, all laboratory soil samples must be grab samples and may not be composited before analysis, except that soil samples for total arsenic, cadmium, chromium, and lead that are for screening purposes may be composited in the field or in the laboratory before analysis;

(2) soil samples taken directly from the surface of excavations must be obtained from freshly uncovered soil; a minimum of six inches of soil must be removed immediately before collection, and the sample must be obtained from the newly uncovered soil; if the excavation has been open for longer than one hour, at least 18 inches of soil must be removed immediately before collection;

(3) soil samples collected from excavation equipment buckets must be obtained from the center of the bucket and away from the bucket sides; at least six inches of soil must be removed immediately before collection;

(4) if soil samples are collected from a soil boring, samples should be collected using a hollow stem auger and split spoon sampler or Shelby tube; using an auger, the drill hole must be advanced to the desired depth; then the center rods of the auger must be withdrawn from the drill hole and the plug and pilot bit removed from the center rods; the sampler must be attached to the correct length of drill rod and must be driven ahead of the auger flights in order to collect a relatively undisturbed sample; after the split spoon or Shelby tube has been retrieved back out of the boring, the desired sample section must be immediately removed from the sampling device; only soil from the middle portion of the spoon may be used for samples; soil from the very ends of the spoon must be discarded as they often contain disturbed soils; a clean sampling tool must be used to quickly collect the sample from the undisturbed portion with a minimum of disturbance and the sample container must be quickly capped, sealed, and labeled; and

(5) soil samples for all parameters listed in Table 1 must be collected in accordance with method specifications.

Alternative methods to obtain soil samples may be used only if the methods have been approved by ADEC before sampling.

The following steps must be taken to minimize collection errors:

(1) all samples must be collected with disposable or clean tools that have been decontaminated as outlined in Section 4.8 of this chapter (Decontamination of field equipment);

(2) disposable gloves must be worn and changed between sample collections;

(3) sample containers must be filled quickly;

(4) soil samples must be placed in containers in the order of volatility; for example, volatile organic aromatic samples must be taken first, gasoline range organics next, heavier range organics next, and soil classification samples last;

(5) containers must be quickly and adequately sealed, and rims must be cleaned before tightening lids; tape may be used only if known not to affect sample analysis;

(6) sample containers must be labeled as outlined in Section 4.9.2 of this chapter (Labeling sample containers);

(7) containers must immediately be preserved according to procedures in Section 4.9.1 of this chapter (Sample containers); unless specified otherwise, at a minimum, the samples must be immediately cooled to $4\pm 2^{\circ}\text{C}$ and this temperature must be maintained through delivery to laboratory until samples are analyzed.

If groundwater is encountered while soil sampling, the provisions of 18 AAC 78.090 must be followed concerning sampling of the groundwater interface.

4.7 Obtaining Groundwater Samples from Borings/Wells

Groundwater samples might be required if contamination of the groundwater is suspected. Water sampled directly from an excavation is not necessarily representative of normal groundwater conditions and will not be evaluated as a representative groundwater sample. In such cases, installation and sampling of a groundwater monitoring well might be required, as determined by ADEC under 18 AAC 78.615.

4.7.1 Installing Groundwater Monitoring Wells

Unless otherwise directed by ADEC, if groundwater monitoring wells are required, the installation must be as required by 18 AAC 78.615(b), and the following procedures must be used:

- (1) if the direction of groundwater flow is known, at least three monitoring wells must be installed and sampled, one upgradient and two downgradient of the potential contamination source;
- (2) if the direction of groundwater flow is unknown, it is recommended that the number of wells installed be sufficient to characterize the groundwater flow using horizontal and vertical control measures; at least three monitoring wells must be installed and sampled;
- (3) well drilling equipment must be decontaminated as outlined in Section 4.8 of this chapter (Decontamination of field equipment) before drilling at each new location; and
- (4) wells should be driven with a hollow stem auger or cable drill; if other methods are used, ADEC approval must be obtained before the well is installed.

The following details of well construction must be recorded in the field record:

- (1) well location, determined by reference to site bench mark;
- (2) total depth of boring;
- (3) depth to groundwater at time of drilling;
- (4) diameter of boring;
- (5) depth to top and bottom of screened interval;
- (6) diameter of screened interval;
- (7) diameter of casing;
- (8) well construction material;
- (9) depth of packed filter interval;
- (10) depth and thickness of seals;
- (11) type of surface cap;
- (12) names of drilling firm and drilling personnel; and
- (13) soil log completed using the Unified Soil Classification System, U. S. Soil Conservation Service classification system, or another similar soil classification system.

Under 11 AAC 93.140, a log of the well must be submitted to the Alaska Department of Natural Resources (ADNR) within 45 days after installing a well. The log must include the location and depth of the well, an accurate log of the type and depths of soil and rock formations encountered, the depth and diameter of the casing, screened intervals, well completion materials, and the static water level in the well. Well logs should be submitted to ADNR/Mining and Water Management, P.O. Box 107005, Anchorage, AK 99510; (907) 762-2165. Well logs for sites within the northern region should be sent to ADNR/Division of Water, 3700 Airport Way, Fairbanks, AK 99706; (907) 451-2772. Well log reporting forms are available from the ADNR/Alaska Hydrologic Survey at the above addresses.

4.7.2 Sampling Groundwater Monitoring Wells

If multiple wells are sampled, the wells upgradient of the site should be sampled first to minimize cross-contamination. Before sampling wells, the depth to groundwater must be determined by manual or electronic means. Measurement devices must be calibrated before use to an accuracy of at least 0.02 foot.

4.7.2.1 Determining Well Depth and Presence of Non-Aqueous Phase Liquids

Before sampling a monitoring well, the column of water in the well casing must be checked for the presence of nonaqueous phase liquids, including free petroleum products that might be floating on top of the water or in a separate layer at the bottom of the casing. Nonaqueous phase liquids are identified by:

- (1) carefully lowering a clean bailer, in a manner that will create minimum disturbance, into the well before purging and observing the liquids removed from the top and the bottom of the water column;
- (2) using a paste type of detector with ingredients that will not lead to cross-contamination; or
- (3) using an electronic device designed to detect nonaqueous liquids and to measure the thickness of the nonaqueous layer.

If free product is present, the well must be bailed or pumped to remove the product and must be monitored to evaluate the recharge rate.

4.7.2.2 Well Purging

Monitoring wells must be purged before sampling unless otherwise approved by ADEC, using the following procedure (or an equivalent):

(1) at least three casing volumes of water must be removed from the well before sample collection or, for low yield wells, until the well bore is evacuated; or instead of purging three casing volumes, measure the purge water temperature, pH, and conductivity until these parameters are stable to within 10 percent variability between measurements;

(2) all purged water must be carefully collected, containerized, and stored for proper disposal pending evaluation of groundwater sample analyses; the results of the analyses and the applicable federal, state, and local water quality criteria must determine the acceptable method for disposal of the purge water; and

(3) upgradient wells should be purged before downgradient wells to help minimize possible cross contamination.

4.7.2.3 Collecting Groundwater Samples with Bailers

If a bailer is used to collect samples, the following procedure must be used:

(1) after purging the well, sufficient time must be allowed for the well to equilibrate and fines to settle; if full recovery exceeds two hours, samples must be extracted as soon as sufficient volume is available;

(2) the water level must be remeasured after purging has occurred and water level has returned to the static level;

(3) if decontaminated equipment is used to collect the water sample, the sampler must be rinsed with analyte-free distilled or deionized water; a portion of this rinsate must be collected into a container appropriate for the most volatile analyte suspected (typically BTEX); this equipment blank (also termed decontamination blank) must be contained, preserved, and analyzed according to the procedures outlined in this chapter for that analyte;

(4) bailers must be made of glass, Teflon, stainless steel, other suitable materials, or of disposable materials such as Teflon or polyethylene; polyvinyl chloride (PVC) bailers are not acceptable for sampling volatile organic compounds; all bailers must be decontaminated as outlined in Section 4.8 of this chapter (Decontamination of field equipment);

(5) the bailer must be fitted with a new bailer line for each well sampled; the bailer and line may be handled only by personnel wearing decontaminated or disposable gloves;

(6) the bailer should be slowly lowered to minimize disturbance of the well and water column; the bailing line should be prevented from contact with the outside of the well, equipment, and clothing; special care must be taken to minimize disturbance of the water table interface when inserting the bailer;

(7) samples must be obtained as close as possible to the water level/air interface, unless analysis indicates that contamination is at a different depth;

(8) grab samples must be obtained;

(9) the bailer must be slowly lifted and the contents transferred to a clean sample container with a minimum of disturbance and agitation to prevent loss of volatile compounds; if different analytes are sampled, samples must be transferred to containers in the order of their volatility; headspace in the sample container must be minimized by filling the sample jar until a positive meniscus is present;

(10) containers must be quickly and adequately sealed; container rims and threads must be cleaned before tightening lids; unless otherwise specified, Teflon-lined screw caps must be used to seal the jar;

(11) sample containers must be labeled as outlined in Section 4.9.2 of this chapter (Labeling sample containers); and

(12) containers must be preserved immediately according to procedures in Section 4.9.1 of this chapter (Sample containers). Unless specified otherwise, at minimum the samples must be immediately cooled to $4\pm 2^{\circ}\text{C}$ and this temperature must be maintained through delivery to the laboratory until the samples are analyzed.

4.7.2.4 Alternative Methods of Collecting Groundwater Samples

If a positive displacement pumping system or another system is used instead of a bailer, it must be clean or decontaminated as described in Section 4.8 of this chapter (Decontamination of field equipment). Disturbance of the well, water column, and samples must be minimized. Only grab samples may be obtained, not composite samples. Samples must be obtained as close as possible to the water level/air interface unless analysis indicates that contamination is at a different depth. If different analytes will be sampled, samples must be transferred to containers in the order of volatility. Volatiles must be collected first, followed, in order, by gasoline range organics, heavier range organics, and metals. Container headspace must be minimized by filling the sample jar until a positive meniscus is present. Containers must be quickly and adequately sealed. Rims must be cleaned before tightening lids. Sample containers must be labeled as outlined in Section 4.9.2 of this chapter (Labeling sample containers). Containers must be preserved immediately according to procedures in Section 4.9.1 of this chapter (Sample containers). Unless specified otherwise, at a minimum the samples must be immediately cooled to $4\pm 2^{\circ}\text{C}$ and this temperature must be maintained through delivery to laboratory until the samples are analyzed.

4.8 Decontamination of Field Equipment

Decontamination of personnel, sampling equipment, and containers before and after sampling must be used to ensure collection of representative samples and to prevent the potential spread of contamination. Decontamination of personnel prevents ingestion and absorption of contaminants and must be done with a soap and water wash and deionized or distilled water rinse.

All previously used sampling equipment must be properly decontaminated before sampling and between sampling locations to prevent introduction of contamination into uncontaminated samples and to avoid cross-contamination of samples. Cross-contamination can be a significant problem when attempting to characterize extremely low concentrations of organic compounds or when working with soils that are highly contaminated.

Clean, solvent-resistant gloves and appropriate protective equipment must be worn by persons decontaminating tools and equipment.

4.8.1 Decontamination of Soil Sampling Tools

At a minimum, soil sampling tools must be cleaned and decontaminated by the following three-step procedure:

- (1) tools must be scrubbed with a stiff brush in a solution of hot water and laboratory-grade, critical cleaning detergent such as Alconox or a similar product;
- (2) tools must be rinsed twice in clean water; and
- (3) tools must be thoroughly rinsed with distilled or deionized water.

If concentrated petroleum products or highly contaminated soils are encountered during sampling, an appropriate solvent should be used to remove heavy petroleum residues from the sampling tools. This must be followed by the minimum cleaning procedure outlined above. If a solvent is used, it must be properly collected, stored, and disposed of according to acceptable hazardous waste disposal guidelines.

4.8.2 Decontamination of Water Sampling Tools

Drill auger sections, split spoons, and drive hammers that come in contact with bore holes must be cleaned before use and between borings using the following three-step procedure:

- (1) tools must either be
 - (A) scrubbed with a stiff brush in a solution of water and laboratory grade, critical cleaning detergent such as Alconox or a similar product; or
 - (B) cleaned with high pressure hot water or steam and a laboratory grade, critical cleaning detergent;
- (2) tools must be rinsed twice in clean water; and

(3) tools must be thoroughly rinsed with distilled or deionized water.

Steel tapes, well sounders, transducers, and water quality probes must be rinsed with clean water and then with deionized water.

Reusable bailers must be washed in Alconox or another laboratory grade, critical cleaning detergent solution, rinsed twice in clean water, and then rinsed with distilled or deionized water.

4.8.3 Excavation Equipment

Excavation equipment must be clean before each site excavation begins.

4.8.4 Cleaning Sample Containers

Sample containers must be cleaned and prepared by an analytical laboratory. The exterior of sample containers must be cleaned after the samples are collected and the container lids are tightly sealed. Solvents may not be used for this procedure because of the potential to contaminate the sample.

4.8.5 Disposal of Washwater, Rinsate, and Disposable Sampling Tools

Washwater and rinsate solutions must be collected in appropriate containers and disposed of properly in accordance with federal, state, and local regulations. Bailing strings and wires and other disposable sampling tools must be properly discarded after use at each well.

4.9 Sample Containers and Holding Conditions

Containers used to collect samples must be chosen based on their suitability for the analyte of interest and may vary according to the laboratory contracted to perform the analysis. Preservation methods and maximum holding conditions are method-specific and must be adhered to.

4.9.1 Sample Containers

Most containers should be glass jars with Teflon-lined lids. Sample jars of the acceptable type of material, size, and type of lid are shown in Table 1. Use of sample containers must conform to these specifications. Also shown in that table are the preservation methods and maximum holding times for each analyte of interest.

All sample containers must be inspected before transit to the site to ensure that they have undamaged lids and are tightly sealed. Jars must be placed into containers that are secured to prevent damage or tampering in transit to the site. Containers and lids must be re-inspected at the job site; containers that have lost lids or that have been damaged may not be used for sample containment.

4.9.2 Labeling Sample Containers

Indelible, waterproof ink must be used to label sample containers. Labels, if used, must be securely fastened to the container. All information entered onto the label or container must be duplicated in the field record or log book. Information on the containers or labels must include:

- (1) unique identifying number assigned to the sample for laboratory analysis;
- (2) date and time of collection;
- (3) name of person collecting the sample;
- (4) each intended laboratory analysis for the sample;
- (5) preservation method.

If possible, the following information should also be included on the container or label:

- (1) project name and location of sample;
- (2) maximum holding time (or date by which sample must be extracted and analyzed).

4.9.3 Holding Times, Conditions, and Methods of Preservation

Sample handling, transport, and analysis must be arranged so that the holding times and conditions shown in Table 1 are met. Also, volatile compounds must be extracted and analyzed as quickly as practical after collection.

Appropriate acidic preservation of samples must be provided if required in Table 1.

4.9.4 Site Safety Plan

The qualified environmental professional is responsible for a site safety plan for construction activities and activities within a confined space.

SECTION 5. SAMPLE TRANSFER LOG

5.1 Sample Transfer Log

The requirements in this section apply to all sampling associated with a site assessment, from initial investigation through all final verification samples.

A transfer log is required for each sample taken, including all associated field quality control (QC) samples. A transfer log consists of a document or label that physically accompanies each sample bottle and sample, or each batch of bottles and samples, and that provides for the name of each person assigned control of the sample and the period covered by each person's assignment. Sufficient space must be provided on the form to accommodate several different control persons, the name of their respective organization or agency, and specific spaces for commercial carriers.

The laboratory receiving samples must process the samples using control procedures documented in its approved Quality Assurance (QA) Manual and Standard Operating Procedures. This section does not apply to internal laboratory procedures.

SECTION 6. ANALYTICAL PROCEDURES

6.1 Field Screening Procedures

Use of field screening analyses with Photo Ionization Detectors (PIDs) and Flame Ionization Detectors (FIDs) must follow the relevant procedures outlined in Section 4 of this manual (Sampling Procedures) and Section 7 of this manual (Calibration and Maintenance of Field Equipment). If other instruments are used, a written description of that use must be provided to ADEC by the qualified environmental professional.

6.2 Identification of Laboratory Conducting Analyses

Only results from a laboratory certified by ADEC will be accepted by ADEC for use in reports prepared under this chapter. ADEC will not accept laboratory results unless the laboratory's current state laboratory UST identification number accompanies those results.

6.3 Determination of Analyses for Petroleum Hydrocarbons

Unless approval to deviate from these specifications is obtained in advance from ADEC, selection and use of all laboratory analyses must conform to the provisions of Table 2A and appropriate sections of this chapter. Table 2A indicates which product is to be tested for each petroleum range using Alaska Series Methods, AK 101, AK 102, AK103, AK101AA, AK102AA, and AK103AA and for the various indicator compounds listed in Table 2B, using methods from EPA's *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846. Methods are specified for each analyte in Table 1, Part A and B of this Manual. The

identity of a released refined petroleum product is assumed to be unknown unless a laboratory analysis shows that a contaminant is only a gasoline or only a nongasoline refined product, unless this requirement is waived by ADEC.

The soil cleanup standards for petroleum in 18 AAC 75.340 are based on gas chromatographic analytical measurements corresponding to a specific measured range of petroleum hydrocarbons as follows:

(1) gasoline-range organics: light-range petroleum products such as gasoline, with petroleum hydrocarbon compounds corresponding to an alkane range from the beginning of n-hexane (C₆) to the beginning of n-decane (C₁₀) and with a boiling point range between approximately 60 - 170 degrees Centigrade;

(2) diesel-range organics: mid-range petroleum products such as diesel fuel, with petroleum hydrocarbon compounds corresponding to an alkane range from the beginning of n-decane (C₁₀) to the beginning of n-pentacosane (C₂₅) and with a boiling point range between approximately 170 - 400 degrees Centigrade; and

(3) residual-range organics: heavy-range petroleum products such as lubricating oils, with petroleum hydrocarbon compounds corresponding to an alkane range from the beginning of n-pentacosane (C₂₅) to the beginning of n-hexatriacontane (C₃₆) and with a boiling point range between approximately 400 - 550 degrees Centigrade.

If it can be documented that only one type of product was stored or distributed during the operational life of a facility, a waiver may be requested from ADEC for the requirement to determine the identity of the product, in accordance with 18 AAC 78.600(d). The information collected in the examination of the site background (Section 4.3.1 of this chapter) will be used to determine if a waiver should be sought.

If leaded gasoline is a potential contaminant at the site, a preliminary laboratory analysis for lead might be required. The ADEC project manager must be contacted for this determination.

Table 2A
Determination of Sampling and Laboratory Analysis for Soil(s) and Groundwater (GW)

Petroleum Product	C6-C10 GRO	C10-C25 DRO	C25-C36 RRO ⁶	BTEX Constituents	PAH ^{1, 2, 7}	Metals and Solvents
Leaded Gasoline	S & GW			S & GW	S & GW	(S & GW) ⁵
Aviation Gasoline	S & GW			S & GW	S & GW	(S & GW) ⁵
Gasoline	S & GW			S & GW	S & GW	
JP-4	S & GW	S & GW		S & GW	S & GW	
Diesel #1/Arctic Diesel	S & GW	S & GW		S & GW	S & GW	
#2 Diesel		S & GW		S & GW	S & GW	
#3 - #6 Fuel Oils		S & GW	S & GW	S & GW	S & GW	
JP-5, JP-8, Jet A	S&GW	S & GW		S & GW	S & GW	
Waste Oil/Used oil	S & GW	S & GW	S & GW	S & GW	S & GW	(S & GW) ^{3,4}
Kerosene	S & GW	S & GW		S & GW	S & GW	
Unknown	S & GW	S & GW	S & GW	S & GW	S & GW	(S & GW) ^{3,4}

Legend:

GRO = Gasoline Range Organics {using AK 101 or AK 101AA}

DRO = Diesel Range Organics {using AK 102 or AK 102AA}

RRO = Residual Range Organics {using AK 103 (for soil) or AK 103AA (for soil and groundwater)}

BTEX = refers to individual indicator compounds to be analyzed: benzene, toluene, ethylbenzene, and total xylenes.

PAH = acenaphthene, anthracene, benzo-a-anthracene, benzo-a-pyrene, benzo-b-fluoranthene, benzo-k-fluoranthene, chrysene, dibenzo-a,h-anthracene, fluorene ideno-123-cd-pyrene, naphthalene, and pyrene

¹ PAH analysis for soils would be required for all petroleum releases, unless the sum of the applicable soil cleanup concentrations based on laboratory results in accordance with Table 2, for individual petroleum hydrocarbon fractions or ranges determined for the site by applying the corresponding Method 2 – 4 referenced in 18 AAC 75.340 is equal or less than 500 mg/kg. PAH analysis is not required for Method 1 referenced in 18 AAC 75.340.

² All of the PAH indicator compounds listed in Table 2A would be required for all petroleum products except gasoline and JP-4 fuel spill analysis which would be limited to the naphthalene only, unless the project manager requires otherwise.

³ Metals analysis, except where noted, would include: arsenic, barium, cadmium, chromium, lead, nickel, and vanadium.

⁴ Volatile chlorinated solvents and other additives listed in Table 2A must be performed if required by the project manager.

⁵ Metal analysis for lead only must be performed if required by the project manager.

⁶ For sampling groundwater for RRO use the “aromatic residual range organics” fraction parameter method listed in Table 1, Part B, of this manual.

⁷ PAH analysis for groundwater is required if there is a requirement for PAH analysis in soil.

TABLE 2B
Indicator Compounds
For Petroleum Contaminated Sites

<p><i>Volatiles (BTEX)</i></p> <ul style="list-style-type: none"> benzene toluene ethyl benzene total xylene <p><i>Polynuclear Aromatic Hydrocarbons (PAHs)* - Carcinogens*</i></p> <ul style="list-style-type: none"> benzo(a)pyrene chrysene indeno(1.,2,3-cd)pyrene benzo(k)fluoranthene benzo(b)fluoranthene benzo(a)anthracene dibenzo(a, h)anthracene <p><i>Polynuclear Aromatic Hydrocarbons (PAHs)* - Noncarcinogens</i></p> <ul style="list-style-type: none"> anthracene acenaphthene pyrene naphthalene fluorene 	<p><i>Metals as required on a case by case basis</i></p> <ul style="list-style-type: none"> Arsenic Barium Cadmium Chromium Lead Nickel Vanadium <p><i>Others as needed on a case by case basis</i></p> <ul style="list-style-type: none"> ethylene dibromide (EDB) 1,2 dichloroethane (EDC) methyl 1 tert-butylether (MTBE) volatile chlorinated solvents
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SECTION 7. CALIBRATION AND MAINTENANCE OF FIELD EQUIPMENT

Calibration and proper maintenance of field instruments is critical to obtaining acceptable data. Improper calibration or failure of an instrument in the field might result in improper choice of sample locations, failure to detect contamination, and inefficient and inadequate segregation of clean soils from contaminated soils and, thus, potentially much higher disposal or treatment costs.

7.1 Calibration and Maintenance of Field Instruments

To ensure that field instruments will be properly calibrated and remain operable in the field, the procedures set out in this section must be used.

7.1.1 Calibration

(1) If PID and FID field instruments are used, instruments must be calibrated before each testing session to yield "total organic vapors" in parts per million to a benzene equivalent. The PID instrument must be operated with a lamp source that is able to detect the contaminants of concern, operates at a minimum of 10.6 eV, and is capable of ionizing those contaminants of concern.

(2) Field instruments must be calibrated onsite.

(3) All standards used to calibrate field instruments must meet the minimum requirements for source and purity recommended in the instrument's operation manual.

(4) If the instrument's operation manual recommends specific calibration requirements for other criteria in calibrating the instrument (such as pH, conductivity, temperature, etc.), those criteria must be adhered to.

(5) Acceptance criteria for calibration must be determined depending on the potential contaminant(s) and must be within the limits set in the manufacturer's operations manual.

(6) The dates, times, and results of all calibrations and repairs to field instruments must be recorded in the field record and in the instrument's log.

(7) All users of the instrument must be trained in the proper calibration and operation of the instrument and must be required to read the operation manual before initial use.

7.1.2 Maintenance

- (1) At a minimum, operation, maintenance, and calibration must be performed in accordance with the instrument manufacturer's specifications.
- (2) All users of the instrument must be trained in routine maintenance, including battery and lamp replacement, lamp and sensor cleaning, and battery charging.
- (3) Each instrument's operation and maintenance manual must be present at the site.
- (4) Field instruments must be inspected before departure for the site and on site.
- (5) Instrument battery charge must be inspected far enough ahead of time to bring the instrument up to full charge before departure for the site.
- (6) At a minimum, a source of extra batteries and lamps (if applicable) must be readily available.

SECTION 8. DATA REDUCTION, VALIDATION, AND REPORTING

Data reduction describes the handling of standard, sample, and blank results; how blank analysis results must be used in calculating final results; examples of data sheets; and positions of persons responsible for data reduction.

Data validation is the systematic process of reviewing the data against criteria to assure the adequacy of the data.

Data reporting details how reports will be generated and what must be included in them.

8.1 Responsibility for Laboratory Data

The laboratory must conduct these activities on, and be responsible for, data that is processed within the laboratory. The owner or operator shall ensure that the qualified environmental professional reviews final laboratory data reduction, validation, and reporting and

- (1) selects a laboratory based on demonstrated ability to properly reduce, validate, and report data;
- (2) verifies laboratory approval status; a list of approved laboratories is available from ADEC; and
- (3) reviews all laboratory results and performance to ensure that the objectives of this chapter are met; if questions or problems arise with the laboratory analysis, the owner or operator shall ensure that the qualified environmental professional takes appropriate corrective actions as outlined in Section 10 of this chapter (Corrective actions); significant problems must be reported to ADEC.

8.2 Final Data Reduction

Data reduction is the compilation, condensation, and simplifying of information into a more easily understood product. The owner or operator shall ensure that the product furnished by the laboratory is examined, using standard statistical methods, by a qualified environmental professional or QA officer with the education, professional experience, and training necessary to meet a project's technical and regulatory requirements, and that this professional conducts or supervises any further reduction of field and laboratory data into the final report.

8.3 Final Data Validation

The owner or operator shall ensure that validation of field data by the qualified environmental professional occurs before the data are inserted into a report. The results of the evaluations discussed in this subsection must be documented in the report, must be used in data interpretation, and may be used to initiate corrective actions outlined in Section 10 of this chapter (Corrective actions).

8.3.1 Validation of Field Reports

The owner or operator shall ensure that the qualified environmental professional or QA officer examines all information collected through the field documentation process (Section 4.2 of this chapter). This information must be checked for

- (1) completeness;
- (2) accuracy (for example, transcription errors, internal consistency);
- (3) unexpected results, with accompanying possible explanations;
- (4) adherence to sampling procedures outlined in Section 4 of this chapter;
- (5) comparison of field instrument results with laboratory results.

8.3.2 Review of Laboratory Data

The owner or operator shall ensure that the qualified environmental professional pays special attention to the establishment of detection and control limits and deviations from them; if deviations are identified, they must be flagged for discussion in final reports and possible corrective action. Examples of limits and deviations include

- (1) any limits outside of the acceptable range;
- (2) lack of documentation showing the establishment of necessary controls; and
- (3) unexplainable trends.

8.3.3 Determining the Final Validity of Samples

Samples collected in accordance with this chapter are considered valid unless otherwise indicated. Samples that are not collected in accordance with this chapter will be considered invalid; in particular, a sample will be considered invalid if

(1) the sample collection was not conducted by a qualified sampler or qualified environmental professional or supervised by a qualified environmental professional as required by 18 AAC 78;

(2) the sample was collected with previously-used tools that were not decontaminated as outlined in this chapter;

(3) the sample was not taken at the location or depth specified by this chapter;

(4) the sample was not taken at a location determined by a correctly calibrated and operated field instrument or by other documented observation to be representative of the most likely areas of contamination;

(5) the sample was collected using a method not listed in this chapter or a method that is inappropriate for the analyte;

(6) the sample was composited before analysis, unless compositing of the sample is explicitly specified by this chapter or approved by ADEC in the workplan required under 18 AAC 78;

(7) the sample jar was not clean before soils or water were deposited into it;

(8) the sample was incorrectly labeled (or not labeled) and field records do not show the location where the sample was collected;

(9) a water sample from a boring or well was not collected in accordance with Section 4.7 of this chapter;

(10) an improper analysis method was performed on the sample;

(11) the analysis of the sample was conducted by a laboratory that was not approved by ADEC at the time of analysis.

8.4 Data Reporting

8.4.1 Information to Be Included in Reports

Reports prepared under this chapter must, at a minimum, contain the following:

- (1) the laboratory's data summary as required by Section 8.4.2 of this chapter (Laboratory data reports for samples) for each sample analyzed;
- (2) an interpretation of data and sampling results, as required by the tasks discussed in Section 8.3 of this chapter (Final data validation);
- (3) a table that contrasts the required field quality control data (discussed in Section 9.1.1 of this chapter) with the limits specified by this chapter (Section 8.4.2, below);
- (4) a case narrative for the project;
- (5) a separate section or attachment that discusses all deviations from procedures outlined in this chapter and any relevant information compiled from field records or other information required by 18 AAC 78 including a discussion of any deviations from this chapter for any sampling or analytical methods and procedures, whether used by the qualified environmental professional or by the laboratory;
- (6) for corrective action sampling activities, a separate section or attachment that discusses all corrective actions taken as required by Section 10 of this chapter, and any other corrective action for other deviations from this chapter including corrective action (such as resubmission of the sample) for sample results that fall within a factor of 2 of the action level after having had corrections for matrix interferences applied (see discussion in Section 10.4 of this chapter-- Corrective actions with laboratory);
- (7) a summary of the site assessment or release investigation information, provided to the owner or operator on a form available from ADEC (Site Assessment and Release Investigation Summary Form, see Appendix A), or similar format containing the same information; and
- (8) other items required for reports by 18 AAC 78.

8.4.2 Laboratory Data Reports for Samples

(a) For each project conducted under this chapter, the owner or operator shall ensure that the qualified environmental professional provides a data transmittal summary for each sample analyzed by the laboratory, including all field and laboratory QC samples, whether the samples are rejected or not. The following items must be submitted in the report:

- (1) laboratory name, address, telephone number, fax number (if available), UST Lab ID number, and the name of the person authorizing release of laboratory data;
- (2) report date;
- (3) type of analysis (gasoline, diesel, etc.);
- (4) the analytical and extraction method used and method number (see Tables 1 and 2);
- (5) the type of matrix;
- (6) the field sample number;
- (7) the laboratory sample number;
- (8) the UST laboratory identification number assigned by ADEC;
- (9) the date sampled;
- (10) the date received;
- (11) the date extracted and digested;
- (12) the date analyzed;
- (13) the location of the sample collection point;
- (14) the site or project name;
- (15) the concentrations of analyte (reported in micrograms per liter for liquids, milligrams per kilogram, dry weight basis for solids);
- (16) definitions of any characters used to qualify data;
- (17) precision and accuracy values for each sample set, with at least one precision and accuracy evaluation for each set of 20 samples;
- (18) the ambient temperature of the interior of the shipping container adjacent to the sample container when received by the laboratory;
- (19) a copy of the sample transfer logs for each sample or group of samples;
- (20) the analyst's name, signature or initials, and date signed;

(21) the dilution factor;

(22) a narrative summary report for each set of samples (not to exceed 20 samples per set), including a discussion of any significant matrix interferences, low surrogate recoveries, or analyte identifications as appropriate; and

(23) Laboratory Data Report Check Sheet (Appendix B).

(b) The following items must be retained on file by the laboratory for at least ten years after the analysis. They are not required in the report, but must be made available to ADEC upon request:

(1) the UST laboratory identification number assigned by ADEC;

(2) copies of all sample gas chromatogram traces with the attached integration report; copies of the reconstructed ion chromatograms (RIC's) must be provided if performing the analysis by mass spectroscopy; chromatograms must be provided for all samples, method blanks, and daily calibration standard; chromatograms must be identified with a sample identification and the time and date of analysis;

(3) a document containing the date and time for the initial calibration and the standards used to verify instrument settings for the data reported; include the composition and concentration range of standards used to establish and verify maintenance of instrument calibration; and

(4) a document explaining laboratory quality control samples used for the data reported and results obtained; include information concerning surrogates, alkane standard, column performance, matrix spike and matrix spike duplicate samples, blank data, and reference samples.

8.4.3 Submission of Reports to Tank Owner or Operator

All reports must be submitted to the tank owner or operator by a qualified environmental professional as described in Section 2.1 of this chapter (Personnel and responsibilities). If submission of reports to ADEC is required under 18 AAC 78 or by ADEC, the qualified environmental professional must inform the tank owner or operator of the requirement.

SECTION 9. INTERNAL QUALITY CONTROL CHECKS

Required quality control (QC) checks include field QC check samples and laboratory QC samples. Comparison of acceptable tolerances and actually derived values for each required QC element must appear in each project report submitted, as discussed in Section 8.4.1 of this chapter (Information to be included in reports).

9.1 Field Quality Control Checks

This section defines the types of field QC checks that must be used and the circumstances in which each type is to be used. All field QC check samples must be analyzed, the results of the analysis used to calculate data quality indicators, and must be summarized as shown in Table 3 or a similar format. When used, QC measures must be performed, at a minimum, for the most volatile analyte under investigation.

TABLE 3
Example of Field Quality Control Summary

Quality Control Designation	Tolerance	Results This Project
<p>Holding time w/methanol GRO for soil Holding time GRO for water Holding time to extract DRO for soil Holding time to extract DRO for water Holding time to analyze DRO for soil Holding time to analyze DRO for water Holding time to extract RRO for soil Holding time to analyze RRO for soil Holding time to analyze; BTEX; soil Holding time BTEX for water Holding time to extract PAH for soil Holding time to extract PAH for water Holding time to analyze PAH for soil Holding time to analyze PAH for water Holding time Total VCS for soil Holding time Total VCS for water Holding time to extract PCB for soil Holding time to extract PCB for water Holding time to analyze PCB for soil Holding time to analyze PCB for water Holding time on digestate Total arsenic for soil Holding time on digestate Total arsenic for water Holding time on digestate Total cadmium for soil Holding time on digestate Total cadmium for water Holding time on digestate Total chromium for soil Holding time on digestate Total chromium for water Holding time on digestate Total lead for water</p>	<p>28 days 14 days at 4° ± 2° C 14 days at 4° ± 2° C 14 days at 4° ± 2° C Less than 40 days Less than 40 days 14 days at 4° ± 2° C Less than 40 days 14 days at 4° ± 2° C or per method requirements 14 days at 4° ± 2° C 14 days at 4° ± 2° C 7 days at 4° ± 2° C Less than 40 days Less than 40 days 14 days at 4° ± 2° C 14 days at 4° ± 2° C 14 days at 4° ± 2° C 7 days at 4° ± 2° C Less than 40 days Less than 30 days 6 months max. 6 months max 6 months max 6 months max 6 months max 6 months max 6 months max 6 months max</p>	
<p>Completeness Field Duplicate Decontamination Blank (s) Trip Blank (s) Methanol Trip Blank Field Blank Background Sample (s)</p>	<p>85% From ADEC project manager Less than practical quantitation limit Less than practical quantitation limit Less than practical quantitation limit Less than practical quantitation limit Assess background influence on final verification samples</p>	
<p>Legend: BTEX = Benzene, Toluene, Ethyl-benzene, Xylene; DRO = Diesel Range Organics; GRO = Gasoline Range Organics; RRO= Residual Range Organics; PAH = Polynuclear Aromatic Hydrocarbons; individual indicator PAH compounds PCB = Polychlorinated Biphenyls; VCS = Volatile Chlorinated Solvents.</p>		

9.1.1 Minimum Field QC Sample Requirements

Table 4 shows the minimum level of sample QC scrutiny that must be applied to field sampling. A description of each type of field QC sample appears in Sections 9.1.2. - 9.1.5 of this chapter. Reference to sets of samples in this and subsequent subsections refers to samples taken from the same site (or, for multiple sampling points within a single project, from the same area within a site that has uniform characteristics such as grain size and organic content) during the same sampling event during a discrete time period. It does not apply to sampling points from different sites, samples taken at significant time differences from each other, nor multiple samples from the same site, but with nonuniform site characteristics.

Table 4. Minimum Quality Control Scrutiny		
Minimum Field QC Samples Required	When Required	Allowable Tolerance
Field Duplicate (One per set of 10 samples, minimum of one)	All soil and water samples	Precision set by Project Manager
Decontamination or Equipment Blank (One per set of 20 similar samples, minimum of one)	All soil and water samples Where sampling equipment is decontaminated between samples	Less than the practical quantitation limit listed in Table 1
Trip Blank (One per set of 20 volatile samples, minimum of one)	All water samples Being analyzed for GRO, BTEX, or volatile chlorinated solvents.	Less than the practical quantitation limit listed in Table 1
Methanol Trip Blank (One per set of 20, minimum of one)	All soil samples Being analyzed for GRO, BTEX or volatile chlorinated solvents using AK101 or AK101AA field methanol preservation	Less than the practical quantitation limit listed in Table 1
Field Blank (One per set of 20, minimum of one)	Per project specifications. Used for highly contaminated sites with volatile organic contaminants	Less than the practical quantitation limit listed in Table 1

9.1.2 Field Duplicate Sample

Field duplicate samples are useful in documenting the precision (variability) of the sampling process and the site. They are independent samples collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently.

At least one field duplicate must be collected for every 10 samples for each matrix sampled, for each target compound. Duplicate water samples must be collected as close as possible to the same point in space and time and must be collected before any decontamination blanks are collected. Duplicate soil samples must be collected as close as possible to the same point in space and time. All field duplicates must be blind samples and must be given unique sample numbers just like any other field sample. Their collection should be adequately documented. The results from field duplicate samples must be used to calculate a precision value for field sampling quality control.

9.1.3 Decontamination or Equipment Blank

A decontamination or equipment blank is used to determine if contamination occurred from sampling equipment such as pumps and bailers and checks to make sure equipment decontamination procedures have been effective. This blank is a sample of contaminant-free media used to rinse sampling equipment. It must be collected after completion of decontamination procedures and before sampling. Decontamination blanks for water samples must be collected as described in Section 4.7.2 of this chapter (Sampling groundwater monitoring wells). Decontamination blanks for soil samples must be collected in a similar manner. Decontamination blanks would not be required if disposable bailers are used for each sample taken.

If decontamination blanks are required, at least one decontamination blank must be collected and analyzed for each set of water samples that might contain volatiles. In addition, at least one decontamination blank must be collected and analyzed for every 20 soil samples collected each day.

9.1.4 Trip Blank and Methanol Trip Blank

A trip blank is used to document if contamination occurred in the sample containers during shipping, transport, or storage procedures. This blank is a sample of contaminant-free media taken from the laboratory to the sampling site along with each batch of samples and returned to the laboratory **unopened**. An aqueous trip blank would contain organic free water and a methanol trip blank would contain methanol. This type of blank can be especially useful in documenting when trace volatile organic compounds are being investigated. A trip blank would be used for samples being analyzed for all volatile organic compounds such as GRO, BTEX, and volatile chlorinated solvents.

If a trip or methanol trip blank is required, at least one trip or methanol trip blank must accompany each set of 20 samples that might contain volatile organic contaminants.

9.1.5 Field Blank

A field blank is used to document if sample contamination occurred as a result of reagent and/or environmental contamination from contaminated air at the sample location. This blank is especially helpful for highly contaminated sites with volatile organic compounds. A field blank is a sample of contaminant-free media taken from the laboratory to the sampling site and **opened onsite** during the sampling procedure. The field blank is then sealed and appropriately labeled and returned to the laboratory for analysis with the sample batch. The field blank does not replace the trip blank. If required, a field blank must accompany each set of 20 samples destined for volatile organics analysis.

9.1.6 Background Sample

A background sample is optional and is taken to document and assess contaminant baseline or historical information. This sample is collected in an area judged to be free of a site contaminant. A background sample must be collected whenever, in the QA officer's judgment, it is required:

- (1) to document the occurrence of naturally occurring organics, especially when their presence might interfere with analytical tests;
- (2) to document the presence of contamination by migration of contaminants from off-site or non-UST-related sources; and
- (3) in a corrective action or treatment plan.

9.2 Laboratory Quality Control Samples

Laboratory quality control (QC) samples typically accompany the field samples during the laboratory preparation and analysis. The number of laboratory QC samples are dependent on the standard operating procedures of the method used. Labs do not generally charge for quality control analyses. The only laboratory quality control that would affect field sampling procedures would be the addition of a surrogate(s) that is included in the methanol preservation solution for use on soil samples being analyzed for volatile organic contaminants, especially GRO and BTEX using AK101 or AK101AA. . Example checklists for data and for quality control review for Alaska Petroleum Hydrocarbon Methods AK 101, AK 102, and AK 103 are found in Tables 5A-5F. A list of common laboratory QC samples are in Section 9.2.1 of this chapter:

TABLE 5A. AK 101 Gasoline Range Organics- Sample Result Check Sheet

SAMPLE INFORMATION

Matrix	<input type="checkbox"/> Aqueous	<input type="checkbox"/> Soil	<input type="checkbox"/> Sediment	<input type="checkbox"/> Other:
Containers	<input type="checkbox"/> Satisfactory	<input type="checkbox"/> Broken	<input type="checkbox"/> Leaking:	
Aqueous Preservation	<input type="checkbox"/> N/A	<input type="checkbox"/> pH<2	<input type="checkbox"/> pH>2	Comment:
Temperature	<input type="checkbox"/> Received on Ice	<input type="checkbox"/> Received at 4°C	<input type="checkbox"/> Other:	
Extraction Method	Water:	Soil:		

11 AK 101 ANALYTICAL RESULTS FOR FIELD SAMPLES

Field ID						
Lab ID						
Date Collected						
Date Received						
Date Extracted						
Date Analyzed						
Dilution Factor						
% Moisture (soil)						
Units						
RESULTS						
Total Gasoline Range Organics ¹ Results						
Field Sample Surrogate % Recovery						
Field Sample Surrogate Acceptance Range	50-150%	50-150%	50-150%	50-150%	50-150%	50-150%

¹Gasoline Range Organics data exclude concentrations of any surrogate(s) and/or internal standards eluting in that range

12 CERTIFICATION

1. Were all QA/QC procedures REQUIRED by the AK 101 Method followed? Yes No-Details attached

2. Were all performance/acceptance standards for the required QA/QC procedures achieved? Yes No-Details attached

3. Were any significant modifications made to the AK 101 method? No Yes-Details attached

SIGNATURE: _____

PRINTED NAME: _____ DATE: _____

Table 5B. AK 101 Gasoline Range Organics- Quality Assurance/Quality Control Sheet

SAMPLE INFORMATION

Matrix	<input type="checkbox"/> Aqueous	<input type="checkbox"/> Soil	<input type="checkbox"/> Sediment	<input type="checkbox"/> Other:
Extraction Method	Water:	Soil:		

13 AK 101 QUALITY CONTROL RESULTS FOR ANALYTICAL BATCH

Type	M. B.	LFB 1	LFB 2	CCS	CVS		
Field ID							
Lab ID							
Date Received							
Date Extracted							
Date Analyzed							
Dilution Factor							
% Moisture (soil)							
Units							
Method Blank Results							
Lab Fortified Blank (#1) % Recovery							
Lab Fortified Blank (#2) % Recovery							
LFB Acceptance Range		60-120%	60-120%				
LFB % RPD							
LFB % RPD Acceptance Limit			20%				
Continuing Calibration Sample Results							
CCS Acceptance Range				75-125%			
Curve Verification Sample (CVS) Results							
CVS Acceptance Range					75-125%		
Matrix Spike Result							
Matrix Spike Duplicate Result							
Surrogate % Recoveries for all QC							
Surrogate Acceptance Range	60-120%	60-120%	60-120%	60-120%	60-120%		

¹Gasoline Range Organics data exclude concentrations of any surrogate(s) and/or internal standards eluting in that range

14 CERTIFICATION

1. Were all QA/QC procedures REQUIRED by the AK 101 Method followed? Yes No-Details attached
2. Were all performance/acceptance standards for the required QA/QC procedures achieved? Yes No-Details attached
3. Were any significant modifications made to the AK 101 method? No Yes-Details attached

SIGNATURE: _____

PRINTED NAME: _____ DATE: _____

Table 5C. AK 102 Diesel Range Organics- Sample Result Check Sheet

SAMPLE INFORMATION

Matrix	<input type="checkbox"/> Aqueous	<input type="checkbox"/> Soil	<input type="checkbox"/> Sediment	<input type="checkbox"/> Other:
Containers	<input type="checkbox"/> Satisfactory	<input type="checkbox"/> Broken	<input type="checkbox"/> Leaking:	
Aqueous Preservation	<input type="checkbox"/> N/A	<input type="checkbox"/> pH<2	<input type="checkbox"/> pH>2	Comment:
Temperature	<input type="checkbox"/> Received on Ice	<input type="checkbox"/> Received at 4°C	<input type="checkbox"/> Other:	
Extraction Method	Water:	Soil:		

15 AK 102 ANALYTICAL RESULTS FOR FIELD SAMPLES

Field ID						
Lab ID						
Date Collected						
Date Received						
Date Extracted						
Date Analyzed						
Dilution Factor						
% Moisture (soil)						
Units						
RESULTS						
Total Diesel Range Organics ¹ Results						
Field Sample Surrogate % Recovery						
Field Sample Surrogate Acceptance Range	50-150%	50-150%	50-150%	50-150%	50-150%	50-150%

16 CERTIFICATION

1. Were all QA/QC procedures REQUIRED by the AK 102 Method followed? Yes No-Details attached

2. Were all performance/acceptance standards for the required QA/QC procedures achieved? Yes No-Details attached

3. Were any significant modifications made to the AK 102 method? No Yes-Details attached

SIGNATURE: _____

PRINTED NAME: _____ DATE: _____

Table 5D. AK 102 Diesel Range Organics- Quality Assurance/Quality Control Check Sheet

SAMPLE INFORMATION

Matrix	<input type="checkbox"/> Aqueous	<input type="checkbox"/> Soil	<input type="checkbox"/> Sediment	<input type="checkbox"/> Other:
Extraction Method	Water:	Soil:		

17 AK 102 Quality Control RESULTS FOR ANALYTICAL BATCH

Type	M. B.	LFB 1	LFB 2	CCS	CVS		
Field ID							
Lab ID							
Date Received							
Date Extracted							
Date Analyzed							
Dilution Factor							
% Moisture (soil)							
Units							
Method Blank Results							
Lab Fortified Blank (#1) % Recovery							
Lab Fortified Blank (#2) % Recovery							
LFB Acceptance Range		75-125%	75-125%				
LFB % RPD							
LFB % RPD Acceptance Limit			20%				
Continuing Calibration Sample Results							
CCS Acceptance Range				75-125%			
Curve Verification Sample (CVS) Results							
CVS Acceptance Range					75-125%		
Surrogate % Recoveries for all QC							
Surrogate Acceptance Range	60-120%	60-120%	60-120%	60-120%	60-120%		

¹Deisel Range Organics data exclude concentrations of any surrogate(s) and/or internal standards eluting in that range

18 CERTIFICATION

1. Were all QA/QC procedures REQUIRED by the AK 102 Method followed?	<input type="checkbox"/> Yes	<input type="checkbox"/> No-Details attached
2. Were all performance/acceptance standards for the required QA/QC procedures achieved?	<input type="checkbox"/> Yes	<input type="checkbox"/> No-Details attached
3. Were any significant modifications made to the AK 102 method?	<input type="checkbox"/> No	<input type="checkbox"/> Yes-Details attached
SIGNATURE: _____		
PRINTED NAME: _____ DATE: _____		

Table 5E. AK 103 Residual Range Organics- Sample Result Check Sheet

SAMPLE INFORMATION

Matrix	<input type="checkbox"/> Soil <input type="checkbox"/> Sediment <input type="checkbox"/> Other:
Containers	<input type="checkbox"/> Satisfactory <input type="checkbox"/> Broken <input type="checkbox"/> Leaking:
Temperature	<input type="checkbox"/> Received on Ice <input type="checkbox"/> Received at 4°C <input type="checkbox"/> Other:
Extraction Method	Soil:

19 AK 103 ANALYTICAL RESULTS FOR FIELD SAMPLES

Field ID						
Lab ID						
Date Collected						
Date Received						
Date Extracted						
Date Analyzed						
Dilution Factor						
% Moisture						
Units						
RESULTS						
Total Residual Range Organics ¹ Results						
Field Sample Surrogate % Recovery						
Field Sample Surrogate Acceptance Range	50-150%	50-150%	50-150%	50-150%	50-150%	50-150%

20 CERTIFICATION

1. Were all QA/QC procedures REQUIRED by the AK 103 Method followed?	<input type="checkbox"/> Yes <input type="checkbox"/> No-Details attached
2. Were all performance/acceptance standards for the required QA/QC procedures achieved?	<input type="checkbox"/> Yes <input type="checkbox"/> No-Details attached
3. Were any significant modifications made to the AK 103 method?	<input type="checkbox"/> No <input type="checkbox"/> Yes-Details attached
SIGNATURE: _____	
PRINTED NAME: _____ DATE: _____	

Table 5F. AK 103 Diesel Range Organics- Quality Control/Quality Assurance Check Sheet

SAMPLE INFORMATION

Matrix	<input type="checkbox"/> Soil <input type="checkbox"/> Sediment <input type="checkbox"/> Other:
Extraction Method	Soil:

21 AK 103 Quality Control RESULTS FOR ANALYTICAL BATCH

Type	M. B.	LFB 1	LFB 2	CCS	CVS		
Field ID							
Lab ID							
Date Received							
Date Extracted							
Date Analyzed							
Dilution Factor							
% Moisture							
Units							
Method Blank Results							
Lab Fortified Blank (#1) % Recovery							
Lab Fortified Blank (#2) % Recovery							
LFB Acceptance Range		60-120%	60-120%				
LFB % RPD							
LFB % RPD Acceptance Limit			20%				
Continuing Calibration Sample Results							
CCS Acceptance Range				75-125%			
Curve Verification Sample (CVS) Results							
CVS Acceptance Range					75-125%		
Surrogate % Recoveries for all Quality Control							
Surrogate Acceptance Range	60-120%	60-120%	60-120%	60-120%	60-120%		

¹Residual Range Organics data exclude concentrations of any surrogate(s) and/or internal standards eluting in that range

22 CERTIFICATION

1. Were all QA/QC procedures REQUIRED by the AK 103 Method followed? Yes No-Details attached

2. Were all performance/acceptance standards for the required QA/QC procedures achieved? Yes No-Details attached

3. Were any significant modifications made to the AK 103 method? No Yes-Details attached

SIGNATURE: _____

PRINTED NAME: _____ DATE: _____

9.2.1 List of Common Laboratory Quality Control Samples

Surrogates: The surrogate is analyzed and the recovery, expressed as a percentage, is intended to indicate the percent recovery of the contaminant. A surrogate is added to every sample that is being analyzed for organic compounds, including field quality control samples before sample preparation and analysis. In AK101, a methanol/surrogate solution is used in the field for preserving soil samples being analyzed for volatile organic compounds, especially, GRO and BTEX.

Retention time standard: A retention time standard is method specific and is used to verify the integration range. It also provides data for column performance. The elution pattern indicates expected boiling ranges for petroleum products that have boiling range production criteria.

Laboratory spike and laboratory spike duplicates samples: These samples are used to determine precision and accuracy of the analytical results through the percent recovery and relative percent difference. Quantities of stock solutions of the target contaminant(s) are added to laboratory matrix before it is extracted/digested and analyzed.

Matrix spike and matrix spike duplicate samples: These samples are used to assess and document the precision and bias of a method as a result of that specific sample matrix.

Reagent blank: The reagent blank is used to evaluate possible contamination of analytical process by target contaminants. No contaminant should be present in the reagent blank at a concentration greater than the method detection limit.

Bottle blanks: Bottle blanks may be used for diesel and gasoline organic analyses to determine if the bottles used are contaminant free.

Instrument blanks: The instrument blanks are used for diesel and gasoline analyses to determine if the instruments used are contaminant free.

SECTION 10. CORRECTIVE ACTIONS

Corrective actions are procedures and actions taken to correct unacceptable or unexpected deviations in sampling or analysis. An example is the re-analysis of one or more affected samples or the reporting of questionable data with a note of explanation on the situation. Ultimate responsibility for corrective actions rests with the qualified environmental professional. While appropriate corrective actions for out-of-control situations in the laboratory must be addressed by laboratory QA/QC documents, the owner or operator is responsible for ensuring that the qualified environmental professional shows that all corrective actions enable the data quality objectives to be met.

10.1 Handling Invalid Samples

If an invalid sample is taken, the following procedures must be followed:

- (1) if the completeness objective for the project is met and observations and field screening do not indicate the invalid sample was collected at a location with higher than the average contamination levels at the site, an explanatory note of the deviation from this chapter must

accompany the report and no further corrective action for deviation is required; and

(2) if the completeness objective for samples at the site is not met or observations and field screening indicate the invalid sample was collected at a location with higher than the average contamination levels at the site, sample(s) must be recollected at the proper location on the site, properly analyzed and reported, and an explanatory note of the deviation from this chapter must accompany the data report.

10.2 Field Instrument Failure and Improper Use

If field instruments are being improperly used (or are not used), field data must be re-collected.

10.3 Failures in Data Processing, Management, or Analysis

Problems with data processing, management, or analysis is typically discovered during data reduction, validation, and reporting (see Section 8 of this chapter). If these problems occur, the owner or operator shall ensure that the QA officer or another appropriate person is notified. Upon review of the problem, the owner or operator shall ensure that the QA officer or other appropriate person

(1) initiates actions to correct the improper procedure; and

(2) adheres to procedures outlined for notifying the QA officer and project manager of potential problems with data quality.

10.4 Corrective Actions with Laboratory

Normally, any corrective actions necessary in a laboratory are handled internally by the approved laboratory through its approved QA/QC procedures on file with ADEC. The need for corrective action in the laboratory is identified by

(1) the laboratory's internal QC checks;

(2) the data review conducted by the qualified environmental professional (see Section 8.3 of this chapter); or

(3) the laboratory's performance audits.

APPENDIX A

Site Assessment and Release Investigation Summary Form

This document summarizes information from site assessments and release investigation reports that are required by Alaska's Underground Storage Tanks Regulations (18 AAC 78). It is intended to ensure minimum requirements are met when submitting full reports to ADEC. It cannot be substituted for comprehensive site assessment or release investigation reports. Site assessments (as defined in AS 46.03.450) are conducted to check for the presence or absence of petroleum contamination. If contamination of soil or groundwater is identified, then a release investigation is required. Site assessments and release investigations must be conducted by a qualified environmental professional (as defined in 18 AAC 78) and in accordance with Chapter two of the *Underground Storage Tanks Procedures Manual (UST Manual)*.

How to fill out this form

Type or print in ink the requested information and sign in ink the "signature" blocks on page 7. Please attach this form to the comprehensive site assessment or release investigation report (or include it in the report introduction) and submit it to the nearest ADEC field operations office (Juneau, Anchorage, Fairbanks, or Soldotna).

1. General Information

**Purpose of
Site assessment/
Release investigation:**

(Closure, Change-in-service, Suspected or confirmed release, Compliance check, Other)

Owner of site:

Name of company/legal entity that owns the site Phone number

Mailing address City, State, Zip code

Operator of site:

Name of company/legal entity that operates the site Phone number

Mailing address of operator City, State, Zip code

Location of site:

Name of site (e.g. John Doe's Service Station) Phone number

Physical address of site (be as specific as possible) City, State, Zip code

Legal description of site Section/township/range

Type of business at site Facility ID # / Tank ID number(s)

Financial Assistance

Applications filed (this site only) Site assessment/tightness test ___ Tank cleanup ___ Tank upgrade ___ Tank closure ___

Reports on file with ADEC:

Tightness test ___ Closure notice ___ Other ___

2. System and tank status

Describe the status, size, and contents of the tanks that have been at the site:

Tank ID Number: Tank No. ___ Tank No. ___ Tank No. ___ Tank No. ___ Tank No. ___

Tank status (check one)

Currently in use _____

Temporarily closure _____

Closed/left in place _____

Closed/removed _____

Total capacity (gallons) _____

Contents (diesel, etc.) _____

3. Firm conducting site assessment and release investigation

Name of firm Phone number

Mailing address City, State, Zip code

Qualified environmental professional Person(s) collecting samples

4. Site history

Based on the best available knowledge, please check the appropriate box below:

Y N

- ___ ___ Was soil contamination observed or identified?
- ___ ___ Was groundwater contamination observed or identified?
- ___ ___ Did inventory control or prior tank repairs indicate a possible release?
- ___ ___ Has a tank tightness test been performed on any USTs on the site?
- ___ ___ Have any of the facility's USTs or piping ever failed a tightness test?
- ___ ___ Have there been any previous site assessments performed at this site?
- ___ ___ Do previous site assessments indicate any contamination has occurred?

If the answer to any of these questions is yes, please describe (or attach copy of report discussion). Give dates and circumstances, use continuation sheet if necessary:

5. Field screening analysis

Date(s) of field screening: _____ Temperature(s) during screening: _____
Estimated wind speeds: _____ Weather (clear, raining, etc.): _____
Type of field detection instrument used: _____
Brand: _____ Model: _____ Date calibrated: _____
Number of tests: _____ Range of results: _____

If an instrument wasn't used, what field detection method was used? _____
Number of tests: _____ Range of results: _____

6. Collection of soil samples

For site assessments done for USTs remaining in place

Check the appropriate boxes below (if not applicable, leave blank):

- | Y | N | |
|-----|-----|--|
| ___ | ___ | Were samples taken from borings (or test pits) within 5 feet of the UST? |
| ___ | ___ | Were samples collected from within 2 feet below the bottom of the UST? |
| ___ | ___ | Were dispensers connected to the UST system? |
| ___ | ___ | Were samples taken from borings (or test pits) adjacent to dispensers? |
| ___ | ___ | Were samples taken from borings (or test pits) adjacent to piping? |

How many borings/pits were made? _____ How many samples were analyzed? _____

For site assessments done at excavation and removal of USTs:

Check the appropriate boxes below (if not applicable, leave blank):

- | Y | N | |
|-----|-----|---|
| ___ | ___ | Were any areas of obvious contamination identified or observed? |
| ___ | ___ | Were samples taken from areas of obvious contamination? |
| ___ | ___ | Were at least two discrete analytical samples taken from excavated pit area? |
| ___ | ___ | Was at least one sample taken from below each dispensing island's piping? |
| ___ | ___ | Was at least one sample taken from the piping trench? |
| ___ | ___ | Were the samples referenced above collected taken from native soil within two feet below the bottom of the tank pit or dispenser/piping trench? |
| ___ | ___ | If multiple tanks were removed, were at least three samples collected? |
| ___ | ___ | Were additional samples collected for each 250 square feet of excavated pit over 250 square feet? |

Number of distinct points sampled: _____ Estimated excavation's surface area: _____

For all site assessments

Check the appropriate boxes below:

Y N

- Were field duplicate samples collected and analyzed?
- Were all samples kept at the appropriate temperature until analysis?
- Were all samples extracted & analyzed within recommended holding times?
- Did chain-of-custody/transfer logs accompany samples to laboratory?

7. Laboratory analysis of soil samples

(see Table 1 of *UST Procedures Manual*)

Identify the possible contaminants (gasoline, BTEX, diesel, etc.): _____

Please list the analytical methods used to detect these contaminants in the soil samples, the number of samples analyzed by each method, and the range of results for each method:

Possible product	Analytical method	Number of samples	Range of results	Location(s) of sample point(s) w/highest level of contamination
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____
_____	_____	_____	_____	_____

8. Groundwater investigation

Check the appropriate boxes below:

Y N

- Was groundwater encountered during the excavation or drilling work?
- Were borings drilled/pits dug at least five feet below the USTs bottom?
- Is groundwater or seasonal high water table known or suspected to exist within five feet of the bottom of the USTs?

Y N

- Were samples taken from borings drilled/test pits dug to this water level?
- Were all these samples analyzed within recommended holding times?

How many groundwater/saturated-soil samples were collected & analyzed? _____

How many of these samples were taken from the top 6" of water table? _____

How many field QC samples were analyzed? _____
 Trip blanks Duplicates Decon blanks

9. Laboratory analysis of water samples
 (see Table 1 of *UST Procedures Manual*)

Identify the possible contaminants at the site: _____

Identify the analytical methods used to detect these contaminants in the water samples, the number of samples analyzed by each method, and the range of results for each method:

Analytical method	Number of samples	Range of results (ppm)	Location(s) of sample point with highest level of contamination
_____	_____	_____	_____
_____	_____	_____	_____
_____	_____	_____	_____

10. Disposal of material

Check the appropriate boxes below (if not applicable, leave blank):

- Y N
 Were tanks cleaned in accordance with API 2015 (Cleaning Petroleum Storage Tanks)?
 Were the tanks and piping removed and disposed in accordance with API 1604 (Removal and disposal of used petroleum Storage tanks)?

Where were the tanks and piping disposed? _____

Where was the tank sludge and rinsewater disposed? _____

11. Stockpiles

Check the appropriate boxes below:

- Y N
 Is any soil stockpiled at the site?
 Are soils stockpiled in accordance with 18 AAC 78.274?

12. Release investigation

Check the appropriate box below:

- Y N
 Was any petroleum contamination identified during site assessment?
 (Answer "yes" if any evidence a release occurred; if no, proceed to item 13)

If contamination was found, what was matrix score for site? _____
(Attach completed matrix score sheet to this form)

When did release occur? _____ When was release confirmed? _____
(Date & time) (Date & time)

When was ADEC notified? _____ List ADEC staff notified: _____
(Date & time) (Name)

What is status of UST that prompted the investigation? _____
In use Out-of-use, product still in system Out-of-use, system empty Permanently closed

Briefly describe (or attach copy of report discussion) the steps taken to prevent further migration of the release and steps taken to monitor and mitigate fire and safety hazards:

13. Site sketch

Sketch the site in the space below. Alternatively, attach a site map to the back of the form. The sketch (or accompanying narrative) should include the following information:

- | | |
|---|---|
| locations of all USTs, piping, and dispensers | soil types |
| distances from tanks to nearby structures | field screening locations and readings |
| property line locations | sampling locations, depths, & sample ID numbers |
| location and dimensions of excavation(s) | water wells and monitoring wells (if present) |
| type of backfill used to surround system | depth to groundwater/seasonal high location |
| locations of any known historical releases | locations of any stockpiled soils |
| locations of any observed contamination | north arrow |
| location of any boreholes and test pits | bar scale (specify feet or meters) |
| | current land use; human and environmental receptors |

For release investigations, in addition to the above information, show the groundwater gradient; surface drainages (including potential hydraulic connections with groundwater) and utility trenches.

14. Quality assurance

Check the appropriate boxes below:

- Y N
- ___ ___ Were there deviations from Chapter 2 of the *UST Procedures Manual*? (Note that any deviations must be documented in a section of the comprehensive report)
- ___ ___ Is a field quality control summary included in the reports?

___ ___ Is a laboratory QC summary included in the report for all samples used to verify cleanup standards have been met?

15. Certification

The following certification is to be signed by the Qualified Environmental Professional or Quality Assurance Officer:

I certify that except as specifically noted in this report, all statements and data appearing in this report are in conformance with the provisions of Chapter 2 of the *UST Procedures Manual*.

(Print name) (Title)

(Signature) (Date)

The following certification is to be signed by the UST owner/operator (or designated representative):

I certify that I have personally examined and am familiar with the information in this and all attached documents and based on my inquiry of the individuals immediately responsible for obtaining the information, I believe that the submitted information is true, accurate, and complete.

(Print name)

(Specify if owner, operator, representative)

(Signature) (Date)

(Street Address) (City, State, Zip)

16. Attachments

Please check the boxes showing any comprehensive reports attached to this summary:

- ___ Site Assessment Report (include if no release investigation is needed)
- ___ Release Investigation Report (include if release investigation is needed)

APPENDIX B

Laboratory Data Report Check Sheet

The following items are to be kept on file at the lab for ten years after analysis.

Reviewer _____ Date _____

Project _____

Laboratory _____

LAB INFORMATION

- | | |
|--|--|
| <input type="checkbox"/> Laboratory name | <input type="checkbox"/> UST Lab ID Number |
| <input type="checkbox"/> Address | <input type="checkbox"/> Telephone number |
| <input type="checkbox"/> Fax number | <input type="checkbox"/> Email |

METHOD AND SAMPLE INFORMATION

- | | |
|---|---|
| <input type="checkbox"/> Analyte of interest, or target analyte | <input type="checkbox"/> Lab file ID number |
| <input type="checkbox"/> Extraction method # | <input type="checkbox"/> Type of matrix |
| <input type="checkbox"/> Name | <input type="checkbox"/> Field sample number |
| <input type="checkbox"/> Extraction solvent used | <input type="checkbox"/> Lab sample number |
| <input type="checkbox"/> Site or project name | <input type="checkbox"/> Sample collection point |
| <input type="checkbox"/> Date sampled | <input type="checkbox"/> Date received |
| <input type="checkbox"/> Date extracted | <input type="checkbox"/> Date analyzed |
| <input type="checkbox"/> Ambient container temperature upon receipt of sample | <input type="checkbox"/> Time/date temperature measured |
| <input type="checkbox"/> Sample refrigerated | <input type="checkbox"/> Temperature |
| <input type="checkbox"/> Sample transfer log/release/chain-of-custody form | <input type="checkbox"/> Date/time |

RESULTS

- | | |
|---|--|
| <input type="checkbox"/> Concentration of analyte (mg/kg dry or mg/L) | <input type="checkbox"/> Volume of sample purged |
| <input type="checkbox"/> % solids analysis or explanation | <input type="checkbox"/> Case narrative summary |
| <input type="checkbox"/> Dilution factor | |

QC INFORMATION

- | | |
|---|--------------------------------------|
| <input type="checkbox"/> QA Officer Signature | <input type="checkbox"/> Report date |
| <input type="checkbox"/> Date signed | |
| <input type="checkbox"/> Method detection limit or method reporting limit indicated | |
| <input type="checkbox"/> Calculation examples/explanations | |
| <input type="checkbox"/> Identification of flags or qualifiers | |
| <input type="checkbox"/> All corrections and strikeouts initialed and dated | |
| <input type="checkbox"/> Precision and accuracy value for each sample set | |

APPENDIX B - LABORATORY DATA REPORT CHECK SHEET (Cont.)

FINAL REPORT

- Analyst's name on all report pages
- Date prepared
- Analyst's signature/initials on all chromatograms
- Report securely bound
- With sequentially numbered pages

CHROMATOGRAMS & INTEGRATIONS

- Original data package (with analyst's initials)
- Sample queue
- Chromatograms included
 - clearly labeled
 - baseline-baseline integrated
- Integration report included (clearly labeled)
- Integration range clearly indicated
- Date/time on all chromatograms

CALIBRATION INFORMATION

- 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

SURROGATE USED

- Surrogate properly identified
- % recovery for each sample
- Acceptable range indicated
- Outliers explained

APPENDIX B - LABORATORY DATA REPORT CHECK SHEET (Cont.)

COLUMN PERFORMANCE

- Alkane/window retention time standard analyzed
- Components properly identified
- Date determined
- Analyst's initials

SPIKES

- Spike/spike duplicate (if analyzed)
- Recoveries
- Relative % difference
- Acceptable range clearly indicated
- Narrative

BLANKS

- Method blank

OPTIONAL

- Reagent blank
- Bottle blank
- Reference (library) sample included
- Pattern match/narrative
- Summary

APPENDIX C

Alaska Series Laboratory Methods for the Analysis of Gasoline Range Organics (AK101), Diesel Range Organics (AK102), and Residual Range Organics (AK103) Forward for AK Methods 101, 102, and 103

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 specified in 18 AAC 60, 18 AAC 75, or 18 AAC 78**, 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 *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, 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 each method.

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 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

Version 04/08/02

1. Scope and Application

1.1 Analytes

- 1.1.1 This method is designed to measure the concentration of Gasoline Range Organics (GRO) in water and soil. This corresponds to an alkane range from the peak start of n-hexane (C₆) to the peak start of n-decane (C₁₀), and to a boiling point range between approximately 60°C and 170°C (see example of chromatogram in Figure 1 of this method).
- 1.1.2 Components with boiling points greater than or equal to C₁₀ present in products such as diesel or fuel oil are detectable under the conditions of the method.
- 1.1.3. With the optional photo ionization detector (PID), this method can be extended for specific determination of volatile aromatics (BTEX) as specified in EPA Method SW-846 8021B. **Please be aware that any reference to 8021B is in regard to apparatus and not sample preparation. All AK101 samples must be preserved with methanol.**

1.2 Quantitation Limits

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

1.3 Dynamic Range

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

1.4 Experience

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

2. Method Summary

- 2.1 This method provides gas chromatographic conditions for the detection of volatile petroleum fractions such as gasoline. Other nonpetroleum compounds with similar characteristics and boiling points may also be detected with this method. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. A flame ionization detector (FID), or PID/FID in series, provides detection. Quantitation must be performed by comparing the total chromatographic area between and including C₆ (n-hexane) and C₉ (n-nonane), to the peak start time of C₁₀ (n-decane), including resolved and unresolved components, based on FID response compared to a blended commercial gasoline standard (Section 3.2 of this method) and using forced baseline-baseline integration. (See Table 1 of this method for suggestions regarding purge-and-trap operating parameters.)
- 2.2 Water samples must be analyzed directly for GRO by purge-and-trap extraction and gas chromatography. Soil or waste samples are dispersed in methanol to dissolve and preserve the volatile organic constituents (see Table 2 of this method). A portion of the methanol solution is injected into water, and then analyzed in a manner similar to water analysis. Conversely, methanol extracts may be injected directly into the GC/PID/FID if all quality control criteria of the methods are met.
- 2.3 Special field sampling techniques are required to minimize the loss of volatile organic compounds from soil. Conventional sampling and sample handling techniques are not acceptable.
- 2.4 Benzene, toluene, ethylbenzene and total xylene isomers (BTEX) may be determined simultaneously with GRO if the gas chromatograph is outfitted with the optional PID detector, and all requirements of EPA SW-846 Method 8021B are met.
- 2.5 This version of the method was developed by Mary Jane F. Pilgrim, Ph.D. It is based, in part, on: U.S. EPA SW-846 [1] methods 5030, 8000, 8021B, 8015; a single laboratory method evaluation study conducted by the American Petroleum Institute (API) [2]; work by the EPA Total Petroleum Hydrocarbons Methods Committee [3]; and work by the Alaska Department of Environmental Conservation, State Chemistry Laboratory, with support from the Contaminated Sites Program.

3. Definitions

- 3.1 Gasoline Range Organics (GRO): All chromatographic peaks, both resolved and unresolved, eluting between the peak start time for C₆ (n-hexane) and the peak start time for C₁₀ (n-decane). Quantitation is based on a direct comparison of the baseline - baseline integrated area within this range to the total area of the calibration standard over the same (C₆ - C₁₀) range, using FID response. Surrogate peak areas shall be determined by valley to valley integration.
- 3.2 Gasoline Calibration Standard (GCS): An equal-weight mixture of regular, plus, and premium grades of commercial gasoline, mixed and diluted to appropriate concentrations, used to prepare a standard curve.
- 3.3 Calibration Verification Standard (CVS): A gasoline quality control standard (Certified, or equivalent) prepared as in Section 3.2 of this method but with product from a source other than that used to prepare the GCS. This standard serves as a quality control check to verify the accuracy of calibration.
- 3.4 Continuing Calibration Standard (CCS): A mid-range working standard diluted from the GCS, used to verify that the analytical system is operating in a manner comparable to that at the time of calibration.
- 3.5 Surrogate: The recommended surrogate is either bromofluorobenzene or α,α,α -trifluorotoluene. Other compounds may be used as a surrogate if they are non-polar, purgeable from water and methanol, and do not co-elute with any significant component of the GCS and elute prior to the start of C₁₁. Surrogates may be added in the field or the laboratory or both.
- 3.6 Surrogate Blank: A laboratory or field blank sample spiked with the surrogate used in the sample batch. The surrogate recovery is used to evaluate method control (see Section 7.3 of this method).
- 3.7 Laboratory Fortified Blank (LFB): A method blank sample spiked with a commercial gasoline or blend of gasoline. The spike recovery is used to evaluate method control. The CVS may be used as the Laboratory Fortified Blank.
- 3.8 Retention Time Window Standard: A normal alkane standard containing n-hexane and n-decane (C₆ and C₁₀) which is analyzed once per 24 hour day or with each batch of samples, whichever is less frequent, not to exceed 20 samples per batch. This standard is used to establish the retention time window for quantitation of GRO. The compounds of BTEX can be included if all quality control criteria are met (see Section 10 of this method).

- 3.9 Method Detection Limit (MDL): The minimum concentration of a compound that can be measured and reported with 99 percent confidence that the value is greater than zero, determined from analysis of a sample in a given matrix containing the analyte. (See 40 C.F.R. 136, Appendix B, for method of determining method detection limit.) Each laboratory must demonstrate and periodically update method detection limits for each analyte of interest. MDL's must be updated when a significant change in instrument, method, or personnel occurs.
- 3.10 Practical Quantitation Limit (PQL): Five times the MDL.
- 3.11 Instrument blank: Reagent water known to be free of purgeable compounds within the integration window. Analyzed prior to the start of an analytical batch to demonstrate the analytical system is free of contamination.
- 3.12 Other terms are as defined in SW-846 [1].

4. Interferences

- 4.1 High levels of heavier petroleum products such as diesel or heating fuel may contain some volatile components producing a response within the retention time range for GRO. Other organic compounds, including chlorinated solvents, ketones, and ethers are also detectable by this method. As defined in the method, the GRO results include these compounds.
- 4.2 Samples contaminated with a single compound which is detectable using this method (e.g., some solvents,) and which are quantitated against the GCS, may result in a value which is biased for that compound. This is caused by the difference in response factors for the GCS and various solvents. An alternative calibration, detection or quantitation procedure may be appropriate if the identity and quantity of the compound are specific project concerns.
- 4.3 Samples can become contaminated by diffusion of volatile organics during shipment and storage. A trip blank prepared from reagent water (for water samples) or methanol (for soil and sediment samples) and carried through sampling and subsequent storage and handling is highly recommended to serve as a check for such contamination.
- 4.4 Contamination by carryover can occur when high-level and low-level samples are sequentially analyzed. To reduce carryover, the sample syringe and purging device should be rinsed between samples with reagent water and methanol. If an unusually concentrated sample is encountered, analysis of a solvent blank or reagent water to check for contamination should follow it. For volatile samples containing high concentrations of water-soluble materials, suspended solids, high boiling compounds, or organohalides, it may be necessary to wash the syringe or purging device with a detergent solution, rinse with distilled water and methanol, and then dry in a 105° C oven between analyses. The

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

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

5. Safety Issues

- 5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in chemical analyses. Additional references to laboratory safety should be made available and identified for the information of the analyst. Some data (i.e., on methanol) is available from ADEC.

6. Apparatus and Materials

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

6.1 Glassware

- 6.1.1 40-mL glass vials with Teflon-lined septa and screw caps (a.k.a., VOA or VOC vials).
- 6.1.2 4-oz. amber glass wide mouth jars with Teflon-lined septa that are fused to the screw caps.
- 6.1.3 Volumetric flasks, class A: 10-mL, 50-mL, 100-mL, 500-mL, and 1000-mL with ground glass stoppers.
- 6.1.4 Disposable pipettes: Pasteur.

6.2 Syringes

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

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

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

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

6.4 Stainless steel spatula

6.5 Gas Chromatography

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

6.5.2 Columns:

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

6.5.2.2 Capillary columns may be essential to achieve necessary resolution. The column must resolve C₆ from the methanol solvent front in a mid-range LCS standard and, if BTEX is to be done simultaneously, must resolve ethylbenzene from m/p-xylene.

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

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

6.5.3.1 Purging chamber: The recommended purging chamber is designed to accept 5-mL samples with a water column at least 3-cm deep. The gaseous headspace between the water column and the trap should have a

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

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

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

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

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

7. Reagents and Standards

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

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

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

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

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

- 7.3.2 Recommended Surrogates: 50 µg/mL of bromofluorobenzene and / or α,α,α -trifluorotoluene. Add 5.0 µL of this surrogate directly into the 5-mL syringe with every sample and standard analyzed. Surrogate is spiked into soil samples during the extraction step (see Section 8.2.1 of this method). A second surrogate may be used in addition to, but not in place of, the surrogate sent to the field (Section 8.2.1). The use of alternate surrogates is optional. Surrogate compounds must be non-polar, purgeable from water, elute prior to the start of C₁₁ and must not co-elute with any significant component of gasoline. Surrogated methanol is prepared at a ratio of 2.5 mL of methanol to 0.5 mL of surrogate spiking solution at 50 µg/mL.
- 7.3.3 Retention Time Window Standard: This mixture of n-hexane and n-decane serves as a retention time window defining mix for GRO. The concentration of the individual components should not be less than 500 µg/mL and not more than 1000 µg/mL. Additional analytes may be added to this mix if 8021B is to be done concomitantly.
- 7.3.4 Calibration Standards: A mixture of equal weights of regular, plus, and premium grades of unleaded gasoline serves as the Gasoline Calibration Standard. Gasoline standards must be certified as non-oxygenate gasoline or the gasoline concentration must be adjusted to reflect the contribution from oxygenates. No fewer than 3 concentrations of the GCS are diluted directly into a 5-mL Luerlock syringe (linear range approximately 50 to 2,000 µg/L) at the time of calibration. BTEX calibration should meet the criteria specified in EPA SW-846 Method 8021B for waters and soils [1]. Other than one standard concentration near the practical quantitation limit, the expected range of concentrations found in the field samples should define the working range of the GC (see Section 9.3.2 of this method).
- 7.3.5 Stock Standard for Calibration Verification: From a blend of oxygenate free commercial gasoline other than those used to prepare the GCS, make an equal weight mixture as described in Section 7.3.4 of this method. Prepare a dilution of 500 ug/mL in methanol.

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

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

8.1 Aqueous Samples:

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

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

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

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

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

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

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

- 8.2.5 Soil for volatiles analysis can be collected using any coring device that minimizes soil disturbance. Any scraping, stirring, or similar activity will result in a loss of volatiles during sampling. A sufficient number of samples should be collected to provide for backup in case of breakage.
- 8.2.6 Although it is not necessary to refrigerate all methanol preserved samples at $4^{\circ} \pm 2^{\circ}$ C after collection and until analysis is complete, collected samples must be kept below 25° C.
- 8.2.7 A second surrogate, added to the methanol and soil mixture after sample collection, may be used in addition to, but not in place of, the surrogate with which the field methanol preservative was prepared.
- 8.2.8 A reagent methanol trip blank must be prepared in the same manner as the sample vials, and must contain surrogated methanol. One trip blank must be included with each shipping container and must be stored and analyzed with the field samples. Trip blank analysis is not required if all samples in a shipping container are less than the project specific cleanup level.
- 8.2.9 Field blanks may be added to the sampling protocol and are prepared in the field by addition of surrogated methanol to the prepared container, as required by the qualified environmental professional or the Project Manager.
- 8.2.10 A sample of the same soil to be analyzed for GRO should be collected into a moisture-proof container for per cent moisture determination. This sample should be processed as soon as possible upon arrival at the laboratory to assure that the resulting moisture determination is representative of the preserved sample as surveyed.
- 8.2.11 Trip blanks, field blanks, method blanks, etc. should be prepared from the same batch of solvent, reagents and vials as are used for sample preservation.
- 8.3 Twenty-eight days is the maximum holding time for soil and sediment samples collected under this section.
- 8.4 Because the jars are pre-weighed, it is extremely important that the sampler put evidence tape on the kit ONLY, or the bubble bags in which the sample bottles are shipped, and not on the individual bottles. Removal of evidence tape is extremely difficult and the additional weight biases final results. Also, the glue on the evidence tape can contribute to the volatiles concentration in the sample (per Rocky Mountain Analytical, direct communication).
- 8.5 Trip blanks, field blanks, and bottle blanks should be prepared as appropriate to meet the quality assurance goals of the project plan.

9. Procedure

- 9.1 Volatile compounds are introduced into the gas chromatograph by purge-and-trap (see exception, Section 2.2 of this method). Purge gas should be set at a flow rate of 25 - 40 mL/min. and purge time at 12 min., or conditions necessary to optimize the resulting chromatography.
- 9.2 Waters:
- 9.2.1 Purge-and-trap may be used directly on most water samples.
- 9.2.2 Water samples high in dispersed sediments (non-settling or slow settling solids) must NOT be filtered before analysis, as this results in loss of volatiles. Centrifugation also forces the gases out of the water matrix. In most cases, a muddy water sample can be left undisturbed until the solids settle out. An aliquot of the sample can then be taken with a 5-mL gas tight syringe, being careful not to disturb the sediment layer. Introduction of sediment into the purge device can result in occlusion of the frit, leading to incomplete purging of the sample and low-biased results. In any case, sample preparation should be noted, and an approximate volume given for the solids, if present.
- 9.3 Soils and Sediments:
- 9.3.1 Soils and solids are methanol extracted. An aliquot of the extract is added to reagent water and analyzed as in Section 9.10 of this method.
- 9.3.2 For best retention of volatile compounds, samples should be collected into tared, sample jars containing the methanol-surrogate solution (see Section 8.2 of this method).
- 9.3.3 The entire volume of soil must be submerged in the methanol-surrogate solution.
- 9.3.4 Weigh the sample jar upon receipt and record the total filled weight. Swirl the jar gently for 2 minutes to be sure that the soil sample is dispersed into the methanol, and allow the sediment to settle. It is recommended that the meniscus of the methanol be marked and dated on the outside of the jar.
- 9.3.5 Best results are obtained by allowing the sample volatiles to equilibrate with the methanol for at least 48 hours before continuing with the analysis. However, this is not always possible. In any case, note the time difference between when the methanol was delivered into the soil sample and when analysis was initiated.
- 9.4 Soils and Sediments Collected without Methanol Preservation:
- 9.4.1 When solids are collected by the sampling techniques described in SW-846 [1],

volatile results are biased low. Therefore, data from these samples (collected without methanol preservative) must be reported as “greater than or equal to” the calculated mg/kg GRO as gasoline and may not be accepted as valid by state project managers.

- 9.4.2 To prepare extracts from these types of collection containers, gently mix the contents of the sample container with a narrow metal spatula. Do not discard any supernatant liquids, as the entire contents of the sample container must be represented.
- 9.4.3 For sediment/soil and waste that are insoluble in methanol, weigh 10 g (wet weight) of sample into a tared 20-mL vial, using a top loading balance. Note and record the actual weight to 0.1 g.
- 9.4.4 Quickly add 9.5 mL of methanol and 0.5 mL of the 50 ug/mL surrogate spiking solution to the vial (or, after adding spiking solution, fill to the line on the volumetric flask), cap and swirl (do not shake) for 2 minutes.
- 9.4.5 Allow sediment to settle. The alternate sample preparation procedure must be noted on the data transmittal.

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

9.5 Methanol Soluble Solids:

- 9.5.1 For waste that is soluble in methanol weigh 1 g (wet weight), to the nearest 0.01 g into a tared 10-mL volumetric flask.
- 9.5.2 Quickly add 9.5 mL of methanol and 0.5 mL of the 50 µg/mL surrogate spiking solution to the vial (or, after adding spiking solution, fill to the line on the volumetric flask), cap and swirl for 2 minutes, to disburse the waste into the methanol.
- 9.5.3 Allow sediment to settle, pipette an aliquot to an amber glass vial for storage at 4° ± 2°C (zero headspace).

9.6 Sample Screening:

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

hexadecane extraction and screening method (SW-846 Method 3820 [1]).

9.7 Gas Chromatography Conditions (recommended)

9.7.1 Column 1: Set helium column pressure to 20#. Set column temperature to 30° C for 1 min., then ramp at a rate of 5° C/min. to 100° C, then 8° C/min. to 240° C and hold for 7.5 min. Conditions may be altered to improve the resolution of GRO. H₂ may be used as carrier gas, N₂ as purge gas. Conditions may be altered to accommodate the optional gases.

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

9.8 Calibration:

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

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

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

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

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

$$\text{Internal Standard Response Factor} = \frac{(A_x)(Q_{is})}{(Q_x)(A_{is})}$$

Where: A_x = Area response of analyte
 A_{is} = Area response of internal standard
 Q_{is} = Amount of internal standard
 Q_x = Amount of analyte

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

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

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

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

9.9 Retention Time Window

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

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

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

- 9.9.2.2 In those cases where the standard deviation for a particular analyte is zero, the laboratory should use ± 0.05 min. in place of the standard deviation.
- 9.9.3 The laboratory must calculate retention time windows for each standard on each GC column and when a new GC column type is installed or instrument conditions changed. The laboratory must retain the data for at least five years and update it at least once a year.
- 9.10 Gas Chromatograph Analysis: Generally, the analytical batch on a pre-calibrated instrument will follow this flow: Reagent Blank, Retention Time Window Standard, opening CCS, Method Blank, Field Samples, spikes, reps, etc. (20), LFB. Repeat sequence, then end with closing CCS.
- 9.10.1 Samples are analyzed by GC/FID. Water, with or without methanol extract, to be analyzed for GRO is introduced into the programmed gas chromatograph (Section 9.2) using purge-and-trap sample concentration.
- 9.10.2 If initial calibration (see Section 9.8 of this method) has been performed, verify the calibration by analysis of a mid-point CCS (see Section 9.8.6 of this method). After the last sample has been analyzed, the same CCS must be analyzed to demonstrate that the analytical system is still in control. With each day's run, open a 24 hour analysis window. This is done by running the Retention Time Window Standard.
- 9.10.3 An LFB at a concentration representative of the field samples being analyzed must also be run once every 20 samples. If the result does not fall within the range specified in Table 3 of this method, corrective action must be performed and all affected samples re-analyzed.
- 9.10.4 Calculate the percent difference of the response factor from the mid-point CCS from the mean response factor for each analyte to be quantitated (as in Section 9.8.4 of this method). This is done for GRO as a "group" from the CCS if GRO is to be quantitated (FID) and for each of the components in the Retention Time Window Standard if additional quantitation for BTEX is required (PID). If the response factors have a difference greater than 25%, corrective action must be taken and all samples re-analyzed.
- 9.10.5 A reagent water blank must be analyzed each day to determine the area generated from normal baseline noise under the conditions prevailing within the 24 hour period. Add up to 300 μL of methanol to the blank when soil or sediment extracts are to be analyzed. The noise area is generated by projecting a horizontal baseline between the retention times observed between the beginning of n-hexane and the beginning of n-decane. This lab control sample is integrated over the GRO area in the same manner as for the field samples and is reported as the reagent blank.

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

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

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

9.10.7.1 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature and pour the sample into the syringe using caution not to agitate the sample which would result in loss of volatiles. Replace the plunger and compress the sample. Invert the syringe so that the air bubble rises to the top (valve end) of the syringe. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Add 5 μ L 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 $4 \pm 2^\circ$ C with valve closed only until such time as the analyst has determined that the first sample has been analyzed successfully. If a second analysis is needed, it must be from the second syringe and must be analyzed within 24 hours of the opening of the original sample vial. Care must be taken to prevent air from leaking into (and to prevent volatiles from leaking out of) the syringe containing the backup aliquot.

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

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

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

9.10.9. Dilutions:

- 9.10.9.1 If the product concentration exceeds the linear range of the method as defined by the calibration curve, the sample (or extract or dilution) must be diluted and reanalyzed. The response of the major peaks should be kept in the upper half of the linear range of the calibration curve.
- 9.10.9.2 It is most desirable to adjust the volume of extract introduced into the reagent water as in Section 9.10.8.1 of this method to compensate for concentrated sample extracts. However, if that is not possible, the following procedure is appropriate for diluting samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe:
 - 9.10.9.3 Dilutions may be made in class A volumetric flasks (10-mL to 100-mL seem most useful), or other quantitative glassware with similar accuracy. Select the volumetric flask that will allow for the necessary dilution. Although intermediate dilutions may be necessary for highly concentrated samples, remember that the more transfers the sample makes, the greater the chance components will be lost.
 - 9.10.9.4 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this to the flask.
 - 9.10.9.5 Inject the proper aliquot of sample from the syringe prepared in Section 9.10.7.2 into the flask. Aliquots of less than 1-mL are not recommended for dilution of water samples using this method. Make sure aliquot is introduced well below the surface of the reagent water in the volumetric flask to minimize sample loss.
 - 9.10.9.6 Dilute the sample to the mark with reagent water, disturbing the surface as little as possible. Cap the flask and invert three times. Repeat the above procedure for additional dilutions. Analyze the diluted sample as in Section 9.10.7 of this method.

9.10.10 Alternative Dilution Technique:

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

samples.

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

9.11 Moisture Determination for Solids

- 9.11.1 Moisture determinations must accompany all soils data (reported in mg/dry kg) so the client can, at will, determine the results in the original soil condition. Reporting in mg/dry kg can best be done if an unpreserved portion of the sample (collected without methanol) is provided. Because of the potential for high gasoline or related compound concentrations in the soil, all drying should be done under a functioning hood.
- 9.11.2 To determine percentage of moisture, pre-weigh an aluminum weighing boat. Weigh 5-10 g of the sample into the boat and record both weights to the nearest 0.01 g. Dry the sample overnight in a warm (105° C) oven.
- 9.11.3 Remove the sample from the oven and cool in a desiccator until the sample reaches room temperature, and weigh to the nearest 0.01 g. Record the weight.

9.12 Calculations:

9.12.1 External Standard Calibration:

The concentration of Gasoline Range Organics in the sample is determined by calculating the absolute weight of analyte purged, from a summation of peak response for all chromatographic peaks, resolved and unresolved, eluting between the peak start time for C₆ (hexane) and the peak start time for C₁₀ (decane), using the calibration curve or the calibration factor determined in Section 9.8 of this method and baseline-baseline projection. Refer to Section 9.9 (Retention Time Window.)

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

Aqueous Samples:

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

Where: C_s = Concentration of Gasoline Range Organics

RF = Response factor, as described in Section 9.8.4

A_x = Response for the Gasoline Range Organics in the sample, units in

area
V_s = Volume of sample purged, in liters.
D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.

Solid samples (methanol extraction):

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

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

V_i = Volume of extract actually purged (μL)

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

A_x, 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 (%)

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

Where: A = weight of aluminum boat + wet sample

B = weight of boat

C = weight of boat + dry sample

9.12.3 Internal Standard Calibration.

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

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

- 10.1 The laboratory must demonstrate, through the analysis of quality control check standards, that the operation of the measurement system is in control. This must include the analysis of QC check samples plus the calculation of average recovery and the standard deviation of the recovery as outlined in this method and in Method 8000B, Section 8.0.
- 10.2 After successful calibration (Section 9.8 of this method), analyze a reagent blank sample. The reagent blank must be analyzed with every analytical batch. The surrogate recovery must be within established limits (see Table 3 of this method), or within the limits established by the project plan (whichever is more stringent). Also, the mid-point CCS must be analyzed at the beginning and end of each sequence, and compared to the successful calibration as described in Section 9.8.6 of this method, and fall within established limits (see Table 3 of this method). Method detection limits (MDL) must be established as specified in 40 C.F.R. 136, Appendix B, and renewed as specified in Section 3.9 of this method.

- 10.3 An LFB must be analyzed with every analytical batch, and also run once every 20 samples. The matrix for these samples should be reagent water for batches of aqueous samples or methanol for soil sample batch analyses. The accuracy and precision of the duplicates must be within established limits (see Table 3 of this method).
- 10.4 With every batch of samples extracted, the reagent blank must be analyzed. The reagent blank must have GRO less than the practical quantitation limit.
- 10.5 If any of the criteria in Sections 9.8, 10.2, 10.3, and 10.4 of this method are not met, corrective action must be taken before samples are analyzed.
- 10.6 Calculate the surrogate recovery in each sample. If recoveries are outside established limits (Table 3 of this method), verify calculations, dilutions, and standard solutions. Verify instrument performance.
- 10.6.1 High recoveries may be due to a co-eluting matrix interference -examine the sample chromatogram.
- 10.6.2 Low recoveries may be due to adsorption by the sample matrix (i.e., high humus soils).
- 10.6.3 Low recoveries may be due to a poor purge (clogged purge tube or frit). If this is suspected, check the purge tube with a blank before reanalyzing the sample.
- 10.6.4 If the surrogate recovery is outside established limits due to suspected matrix effects, GRO results must be flagged. If the surrogate recovery is less than 50%, and the calculated GRO results are within a factor of 2 of the action limit, the laboratory should recommend that the client resubmit the sample for matrix spike and matrix spike duplicate analysis. This is a recommendation, not a requirement of the method, and therefore, the onus is not on the analytical laboratory to absorb the cost of the additional analyses.
- 10.6.5 If surrogate recovery is low due to moisture dilution, results should be recalculated using a dilution factor determined by the following calculation:

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

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

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

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

10.9 Corrective Action

10.9.1 Calibration

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

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

10.9.2 Surrogates

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

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

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

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

Procedures Manual.

10.9.3.1 Instrument Blanks:

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

10.9.3.2 Trip Blank:

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

10.9.3.3 Field Blank:

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

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

10.9.4 Laboratory Fortified Blanks

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

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

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

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

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

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

11. Method Performance

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

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

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

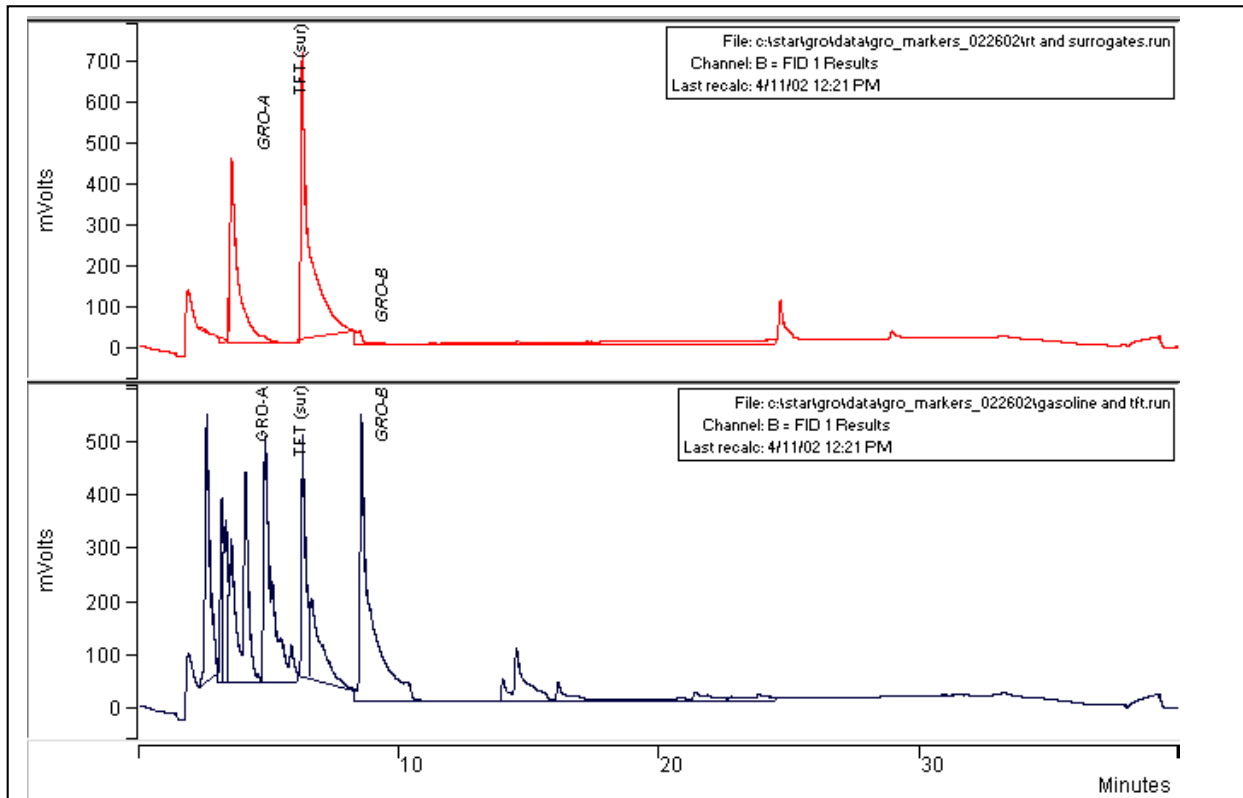
1. Analyses performed by Rocky Mountain Analytical. Gasoline used = API PS6.
2. Analyses performed by State of Alaska, ADEC Laboratory. Gasoline used = GCS.
3. All highly organic, high moisture soils matrices showed less than 30% analyte recovery.

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

12. References

1. USEPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846, 3d Edition; Methods 5030, 8000, 8015, 8020, and 8021B.
2. USEPA, *Sampling and Analysis of Gasoline Range Organics in Soils*, American Petroleum Institute Pub. #4516, October 1991.
3. USEPA, *Evaluation of Proposed Analytical Methods to Determine Total Petroleum Hydrocarbons in Soil and Groundwater*, prepared by Midwest Research Institute for USEPA Office of Underground Storage Tanks, August 14, 1990.
4. Urban, M.J., J.S. Smith, E.K. Schultz, R.K. Dickson, *Volatile Organic Analysis for a Soil, Sediment or Waste Sample in Fifth Annual Waste Testing and Quality Assurance Symposium*, USEPA, July 24-28, 1989.
5. Siegrist, R.L., and P.D. Jenssen, *Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils*, Environmental Science and Technology, Vol. 24, November 1990.
6. Fitzgerald, John, *On-site Analytical Screening of Gasoline Contaminated Media Using a Jar Headspace Procedure in Petroleum Contaminated Soils*, Vol. 2, 1989.
7. Senn, R.B., and M.S. Johnson, *Interpretation of Gas Chromatographic Data in Subsurface Hydrocarbon Investigations*, Ground Water Monitoring Review, 1987.
8. Hughes, B.M., D.E. McKenzie, C.K. Trang, L.S.R. Minor, *Examples of the Use of and Advanced Mass Spectrometric Data Processing Environment for the Determination of Sources of Wastes in Fifth Annual Waste Testing and Quality Assurance Symposium*; USEPA, July 24-28, 1989.
9. *Laboratory Study on Solubilities of Petroleum Hydrocarbons in Groundwater*, American Petroleum Institute Pub #4395, August 1985.
10. *Volatile Organic Analysis for a Soil, Sediment or Waste Sample (The Methanol Method)*, a symposium prepared by James S. Smith, Ph.D. for the State of Alaska, Department of Environmental Conservation, Underground Storage Tank/Leaking Underground Storage Tank program, August 16, 1993.
11. Carrell, Bob, *NWTPH-Gx, Volatile Petroleum Products Method for Soil and Water*, Manchester Environmental Laboratory, Dept. of Ecology, State of Washington, December 1996.
12. USEPA, *Guidelines for Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act (40 C.F.R.136), Part VIII*, October 26, 1984.

Figure 1. Gasoline Range Organics



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

Column:

HP-5MS, 30 meters, 32 microns ID

Carrier Gas Hydrogen

Program: 1. Hold at 30 deg C for 4.42 minutes.

2. 2 deg/min to 77 deg C

3. 50 deg/min to 230 deg.

4. Hold at 230 deg 1 minute.

Purge and desorb conditions as recommended in the method

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

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

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

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

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

Calculate appropriate dilution factor for concentrations exceeding this table.

- a. This number is determined by sample pre-screening.
- b. The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a total volume of 300 μL of methanol for each blank, sample and control.
- c. Dilute an aliquot of the methanol extract and then take 300 μL for analysis.

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

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

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

Method AK 102

For Determination of Diesel Range Organics

Version 04/08/02

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 C₁₀ to the beginning of C₂₅, and a boiling point range of approximately 170° C to 400°C. (See Figure 1 of this method)

1.1.2 Components with boiling points greater than the start of C₂₅ 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 must not exceed 20 mg/kg for soils and 800 µg/L for waters.

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 1 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 water or 25 grams of soil is the recommended sample size. 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 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 and including the peak start of C₁₀ to the peak start of C₂₅, including both resolved and unresolved

components, based on FID response compared to a diesel calibration standard (see Section 3.2 of this method). Integration must be performed using forced baseline-baseline integration.

- 2.2 This version of the method was developed by Mary Jane Pilgrim, Ph.D. 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 EPA Methods 8000 and 8100, SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* [1], adopted by reference in 18 AAC 78.090(i), 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 (C₁₀) and the peak start of n-pentacosane (C₂₅). Quantitation is based on direct comparison of the area within this range to the total area over the same (C₁₀ - C₂₅) range of the calibration standard as determined by FID response using forced baseline-baseline integration. Surrogate peak areas shall be determined by valley to valley integration.
- 3.2 Diesel Calibration Standard (DCS): Commercial #2 diesel fuel or equivalent hydrocarbon mixture in which greater than 95% of the hydrocarbon mass elutes within the diesel range diluted to appropriate concentrations in methylene chloride. The DCS serves as a calibration standard for DRO.
- 3.3 Surrogate: Ortho-terphenyl or equivalent. The surrogate must be spiked into all extracted samples and standards prior to extraction.
- 3.4 Calibration Verification Standard (CVS): A quality control standard, prepared as in Section 3.2 of this method, but with a diesel range hydrocarbon mixture from a source other than that used to prepare the Diesel Calibration Standard. It is used by the laboratory to verify the accuracy of calibration. Greater than 95 % of the hydrocarbon mass must elute between the diesel range.
- 3.5 Laboratory Fortified Blank (LFB): A method blank sample spiked with a commercial #2 diesel fuel the same as that used to make the Diesel Calibration Standard (see Section 3.2 of this method). The spike recovery is used to evaluate method control (see Table 1 of this method).
- 3.6 Retention Time Window Standard: A mixture of the normal alkanes n-decane and n-pentacosane (C₁₀ and C₂₅) 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.

- 3.7 Internal Standard: Alpha androstane, used to normalize DRO concentrations. Use of an internal standard is recommended, but not required.
- 3.8 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 samples.
- 3.9 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 initial calibration.
- 3.10 Method Detection Limit (MDL): The minimum concentration of a compound that can be measured and reported with 99 percent confidence that the value is greater than zero, determined from analysis of a sample in a given matrix containing the analyte. (See 40 C.F.R. 136, Appendix B, for method of determining method detection limit.) Each laboratory must demonstrate and periodically update method detection limits for each analyte of interest.
- 3.11 Practical Quantification Limit (PQL): is defined as 5 times the MDL.
- 3.12 Method Blank – also known as a procedural blank demonstrates that the apparatus and reagents used to perform the method are free from contamination.
- 3.13 Instrument Blank – demonstrates that the instrument is free from contamination.
- 3.14 Solvent Blank – demonstrates that the solvent (in this case methylene chloride) used in the method is free from contamination. It should not go through the procedure. It may also serve as an instrument blank.
- 3.15 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 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.

6.1.8 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 –Boiling chips must be decontaminated in a manner appropriate for the material.

6.3 Micro syringes 1- μ L, 5- μ L, 10- μ L, 25- μ L, and 100- μ L.

6.4 An analytical balance capable of accurately weighting 0.0001 g should be used for preparing standards and percent moisture determination. A top-loading balance capable of weighing to the nearest 0.01 g should be used for sample preparation and percent moisture determination.

6.5 Stainless steel spatula.

6.6 Gas Chromatography

6.6.1 Gas Chromatography: 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.

6.6.2 Columns

6.6.2.1 Column 1: HP5MS 30 M x 0.32 mm 0.25 micron film thickness or equivalent.

6.6.2.2 Other Columns may be used - capillary columns may be essential to achieve the necessary resolution. The column must resolve C₁₀ from the solvent front in a midrange DCS or CVS must resolve C₂₄ from C₂₅.

6.7 Sonication.

6.7.1 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 1/2inch Tapped Disrupter Horn) plus No. 2073/4inch Tapped Disrupter Horn, and No. 419 1/8 inch Standard tapered Microtip probe.

- 6.7.2 A Sonobox or equivalent is recommended with the above disrupter for decreasing sound (Heat Systems-Ultrasonics, Inc., Model 432 13 or equivalent).
- 6.8 Soxhlet extraction apparatus as described in SW-846, Method 3540 [1].
- 6.9 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 target analytes and interfering substances.
- 7.2 Methylene Chloride - 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 Section 7.2 above. 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. 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 µg/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 µg/mL ortho-terphenyl (OTP). A working solution is made at 20 µg/mL (recommended concentration) in methylene chloride.
- 7.4.3 Diesel Calibration Standard: 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. A mid-range dilution of this blend serves as the Continuing Calibration Standard.

- 7.4.4 Retention Time Window Standard: A stock solution of C₁₀ and C₂₅ each at a level of at least 2000 µg/mL. This blend of alkanes serves as a retention time window defining mix for DRO.
- 7.4.5 Stock Calibration Verification Standard (CVS): Provide a stock source of commercial diesel #2 other than that used to prepare the DCS, as described in Section 7.4.3 of this method. A working solution is made at a recommended concentration of 5000 µg/mL in methylene chloride.

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

- 8.1 Water samples are collected 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 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 Section 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, and the extraction solvent is methylene chloride.

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 (see Section 7.1 of this method) 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 (Section 7.4.2 of this method, recommended level of 20 µg/mL if o-terphenyl is used).
- 9.1.1.4 For every batch or 20 samples extracted (whichever is more frequent), prepare duplicate LFBs. 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 (approximately 10 minutes rest after shaking).
- 9.1.1.7 Drain the bottom layer (methylene chloride).
- 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 vessel as described in Section 9.1.1.7 of this method.

9.1.1.9 Concentrate extracts to 1 mL at a temperature not to exceed 55° C or that recommended by the manufacturer of concentration apparatus being used. Transfer extracts to GC vials for analysis. Extracts should be stored in a freezer at <10° C. Record the information for the extraction and concentration steps.

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

9.1.1.10 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 at <-10° C.

9.1.1.11 Record information for the extraction and concentration steps.

Note: The extraction and concentration steps must be performed under a hood. Methylene chloride a potential health hazard (see MSDS).

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 stainless steel or Teflon® spatula. 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 spiking solution 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, 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, dry the extract with anhydrous sodium sulfate. (This assures that the extract is water-free before concentration.)

9.1.2.7 Transfer extract into a clean concentration vessel and concentrate extracts to 1 mL at a temperature not to exceed 55° C or that recommended by the manufacturer of concentration apparatus being used. Transfer extracts to GC vials for analysis. Extracts should be stored in a freezer at <10° C. Record the information for the extraction and concentration steps.

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. 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 0.01 g. Dry the sample overnight in a warm (105°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 0.01 g. Record the weight.

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. (Refer to EPA SW-846 Method 8270C for storage temperature.)

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.

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 C₁₀.

9.2.2.2 The separation number, TZ, should be greater than 15 for C₂₄ and C₂₅, if RRO is to be analyzed concomitantly.

$$TZ = [(retention\ time\ C_{25} - retention\ time\ C_{24}) / (W\ \frac{1}{2}\ of\ C_{25} + W\ \frac{1}{2}\ of\ C_{24})] - 1$$

Where "W $\frac{1}{2}$ " = 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-C₁₉ from ortho-terphenyl and n-C₂₁ from 5 alpha-androstane at varying relative concentrations.

9.3 Calibration

9.3.1 Calibrate the GC, set up as in Section 9.2 of this method. A minimum of three concentrations of DCS (five concentrations are recommended).

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. Linearity of the calibration curve at the PQL must be determined.

9.3.3 Curve fit must be linear regression with a R² of 0.995 or better, quadratic fit with a R² of 0.995 or better, or if using response factors, the average percent relative standard deviation (%RSD) is less than 25% over the working range.

9.3.4 The calibration curve must be confirmed using the CVS (see Section 7.4.5 of this method). 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. The working RF or calibration curve must be verified on each working day (24 hours) by the injection of a CCS (see Section 7.4.3 of this method) 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.

9.4 Retention Time Window Definition:

9.4.1 Before establishing windows, be certain that the GC system is within optimum operating conditions (see Section 6.6 of this method). Make three injections of the Retention Time Window Standard (see Section 7.4.4 of this method) and surrogate 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 (RT) window for individual peaks is defined as the average RT plus or minus three times the standard deviation of the absolute retention times for each component.

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

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 μL using the conditions established in Section 9.2 of this method) 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 $\mu\text{g}/\text{mL}$ of sample extract. Twenty μL of 5-alpha androstane stock at 1000 $\mu\text{g}/\text{mL}$ 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 $\mu\text{g}/\text{mL}$ may lead to measurement bias due to coelution with the internal standard.**) Internal standard calibration should not be used when DRO exceeds 5,000 $\mu\text{g}/\text{mL}$ in the final extract.

9.5.3 If initial calibration (see Section 9.3 of this method) 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 (Section 7.4.4 of this method).

- 9.5.4 Calculate the percent difference of the response factor from the mean response factor as in Section 9.3.2 of this method. 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 solvent blank (methylene chloride) may 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 C₁₀ and the peak start of C₂₅. This 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 Section 4 of this method) **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 sample should be diluted or external standard calibration should be used. The response of the major peaks should be kept in the upper half of the linear range of the calibration curve

9.6 Calculations:

9.6.1 Percent 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 and Section 9.4 of this

method (Retention Time Window Definition). The concentration of DRO is calculated as follows:

Aqueous/Soil samples:

$$C_s = \frac{(A_x)(C_{is})(D)(V_t)}{(A_{is})(RF)(V_s)}$$

Where: C_s = Concentration of DRO (mg/L or mg/kg).

A_x = Response for the DRO in the sample, units in area.

RF = Response Factor from CCS (see Section 9.3.3).

A_{is} = Response for the internal standard, units same as for A_x .

C_{is} = Internal standard concentration (mg/mL).

V_t = 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.

V_s = Amount of sample extracted in L or kg.

9.6.3 To calculate mg/dry kg for soil samples,

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

The % moisture calculation must be included in the data package (see Section 9.6. 1). Some software programs are capable of performing these calculations with minimal analyst intervention.

9.6.4 External Standard Calibration:

Aqueous/Soil samples:

$$C_s = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_s)}$$

Where: C_s = Concentration of DRO (mg/L or mg/kg).

A_x = Response for the DRO in the sample, units in area.

A_s = Response for the external standard, units same as for A_x .

A = External standard concentration (mg/mL).

V_t = Volume of Final extract in mL.

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

V_s = Amount of sample extracted in L or kg.

9.6.5 Some software programs are capable of performing Sections 9.6.1 and 9.6.3 of this method, 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 of this method before field samples can be analyzed.

10. Quality Control

10.1 Curve Verification Standard (CVS)

10.1.1 The CVS is not extracted.

10.1.2 The CVS is analyzed once with calibration standards to verify calibration curve.

10.1.3 The CVS recovery requirement is 75-125% of true value.

10.2 Continuing Calibration Samples (CCS)

10.2.1 The CCS is not extracted.

10.2.2 The CCS is analyzed at the start and end of an analytical batch and for every 20 samples in that batch.

10.2.3 The CCS recovery requirement is 75-125% of true value.

10.3 Blanks

10.3.1 Instrument Blank may be analyzed with each analytical batch to demonstrate that the system is free from contamination.

10.3.2 Method Blank must be analyzed with each extraction batch.

10.3.3 BLANK SUBTRACTION IS NOT ALLOWED. Blanks are reported by value. This information is for data quality assessment purposes only.

10.3.4 Other blanks may be analyzed as necessary following the recommendations of Chapter 2 Section 9 of the *UST Procedures Manual*.

10.4 Lab Fortified Blanks (LFB)

10.4.1 LFB is extracted using the method procedure.

10.4.2 One LFB is analyzed with each analytical batch

10.4.3 The LFB recovery requirement is 75-125% of true value.

10.4.4 If any LFB recovery fails to meet method criteria, appropriate corrective action must be taken. See 10.7, "Corrective Actions".

10.5 Matrix Spike (MS) and Matrix Spike Duplicates (MSD)

10.5.1 MS & MSD are samples that are spiked with DCS to produce a known concentration greater than the sample background concentration. Both are processed as samples.

10.5.2 MS & MSD are analyzed only when requested.

10.5.3 There are no RPD or recovery requirements for MS and MSD.

10.6 Surrogate

10.210.6.1 The surrogate should be spiked at a level to produce a recommended extract

concentration of 20 µg/mL.

10.6.2 Surrogate recoveries must be 60-120% for laboratory control samples (CCS, CVS, method blank, LFB) and 50-150 % for field samples(all other samples).

10.6.3 If any surrogate recovery fails to meet method criteria, corrective action must be taken. See 10.7, "Corrective Actions".

10.6.4 If field samples show poor surrogate recovery which is not attributable to laboratory error, DRO results must be flagged. Re-sampling, matrix spikes or other remedial action is at the discretion of the client and is not the responsibility of the laboratory.

10.7 Corrective Action

10.7.1 The actions listed below are recommended and may not apply to a particular failure.

10.7.2 Check for matrix interference or carry-over.

10.7.3 Check for errors in calculation and that concentrations of surrogates and internal standards are correct.

10.7.4 Check that instrument performance meets method criteria.

10.7.5 Re-process the data.

10.7.6 Re-analyze the extracts.

10.7.7 Extract additional aliquots of the failing sample(s) and re-analyze.

10.7.8 Collect replacement samples

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) using a blend of different diesel products.

23 24	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

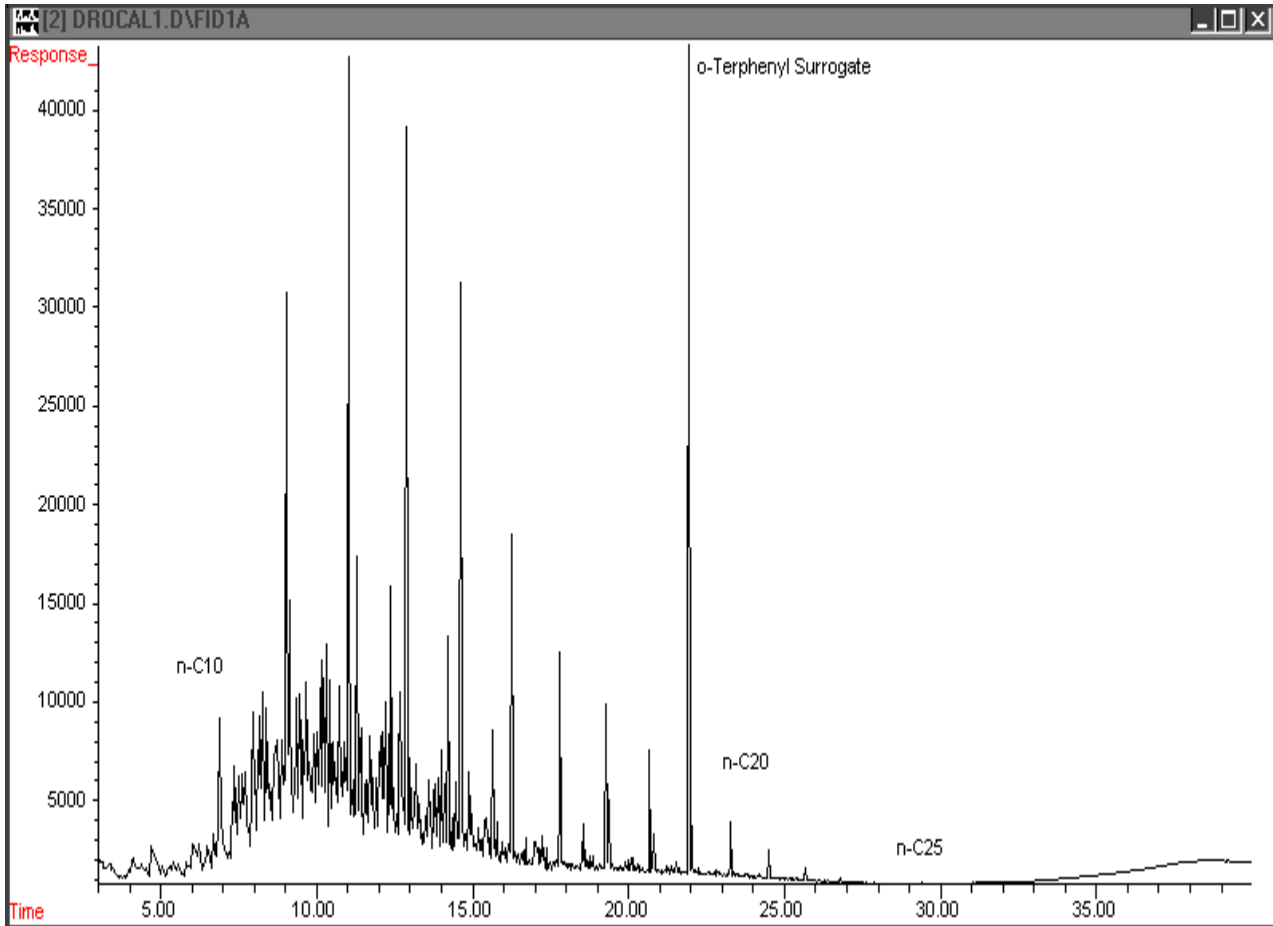
Notes: Analyses performed by State of Alaska, DEC Laboratory. Diesel used =A mixture made of a blend of equal weights (1:1:1) of arctic diesel, diesel #1, and diesel #2, mixed together to form a composite diesel fuel. All highly organic soil matrices showed high analyte recovery due to naturally occurring DROs.

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

12. References

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13. Carrell, Robert, "Method for the Determination of Extractable Petroleum Hydrocarbons". Laboratory Advisory Board Project Oversight Group, Duwamish Brownfields/TPH Project, September 1, 1997.
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Figure 1. Diesel Range Organics, Fuel Oil #2



**Method AK102, Table 1
Acceptance Criteria for Quality Control**

	Analyze Spike Concentration		Control Limits	
	Water (mg/L)	Soils (mg/Kg)	% Recovery	Relative% Difference
Lab Fortified Blanks	0.5-2.0		75-125	20
Continuing Calibration			75-125	
Calibration Verification			75-125	
Surrogate Recovery:				
Laboratory Control Sample**:	0.02	0.8	60-120	
Field Sample:	0.02	0.8	50-150	

- Suggested concentrations. May vary with matrix.
- **Laboratory Control Sample is any laboratory prepared sample used for quality control except calibration standards.

Field criteria from voluntary contribution of method performance information from Approved laboratories, and method performance at SCL.

Method AK 103

For Determination of Residual Range Organics

Version 04/08/02

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 C₂₅ to the end of C₃₆, and compounds with boiling points from approximately 400° C to 500° C. (See Figure 1 of this method.)

1.1.2 The method is primarily designed to measure lubricating or motor oils or other heavy petroleum products. Components greater than C₃₆ present in products such as asphalts, and mid-range boiling point 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 AK 102. All quality control requirements of both methods (Section 10 of this method) must be met. Reasonable modification 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 in extracts.

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 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 C₂₅ and the peak end of C₃₆, both resolved and unresolved components, based on FID response, and using forced baseline-baseline integration, compared to a blended commercial standard called the Residuals Calibration Standard (see Section 3.2 of this method).
- 2.2 This version of the method was developed by Mary Jane Pilgrim, Ph.D. and is based in part on US EPA Methods 8000 and 8100, SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* [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 340-122-3 50 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 (C₂₅) and the peak end of n-hextriacontane (C₃₆). Quantitation is based on direct comparison of the area within this range to the total area of the motor oil standard within the same (C₂₅ - C₃₆) range as determined from FID response using baseline-baseline integration. Surrogate peak areas shall be determined by valley to valley 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. If the source of the spill is known, it is suggested that the known source be used as the calibration standard.
- 3.3 Surrogate: n-Triacontane d62 or equivalent. A demonstration of suitability must be performed. Any variance from this surrogate must be approved by the ADEC Approval Authority.

- 3.4 Calibration Verification Standard (CVS): A commercial motor oil blend, prepared as in Section 3.2 of this method but with products from a source other than those used to prepare the RCS. It is used by the laboratory to verify the accuracy of the calibration. If the source of the spill is known, it can be used to verify the curve if the calibration standards are prepared from a second source. Greater than 95% of the hydrocarbons must elute between the retention time markers.
- 3.5 Laboratory Fortified Blank (LFB): A method blank sample spiked with diluted RCS (Section 3.2 of this methods) . The spike recovery is used to evaluate method control (see Table 1 of this method).
- 3.6 Retention Time Window Standard: A mixture of the normal alkanes n-pentacosane (C₂₅) and n-hexatriacontane (C₃₆) 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.
- 3.7 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.
- 3.8 Standard Soil: Ottawa sand or other standard soil with characteristics that match the field samples as closely as possible, used in quality control standards.
- 3.9 Continuing Calibration Standard (CCS): A mid-range working standard diluted from the RCS (Section 3.2 of this method), used to verify that the analytical system is operating in a manner comparable to that at the time of calibration.
- 3.10 Method Detection Limit (MDL): The minimum concentration of a compound that can be measured and reported with 99 percent confidence that the value is greater than zero, determined from analysis of a sample in a given matrix containing the analyte. (See 40 C.F.R. 136, Appendix B, for method of determining method detection limit.) Each laboratory must demonstrate and periodically update method detection limits for each analyte of interest.
- 3.11 Practical Quantification Limit (PQL): is defined as 5 times the MDL.
- 3.12 Method Blank – also known as a procedural blank demonstrates that apparatus and reagents used to perform the method are free from contamination
- 3.13 Instrument Blank – demonstrates that the instrument is free from contamination.
- 3.14 Solvent Blank – demonstrates that the solvent (in this case methylene chloride) used in the method is free from contamination. It should not go through the procedure. It may also serve as an instrument blank.
- 3.15 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 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 Data 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 recommended, not required.)

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 2-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: 1- μ L, 5- μ L, 10- μ L, 25- μ L, and 100- μ L or as needed.
- 6.4 An analytical balance capable of accurately weighing 0.0001 g should be used for preparing standards. A top-loading balance capable of weighing to the nearest 0.01 g should be used for sample preparation.
- 6.5 Stainless steel spatula.
- 6.6 Gas Chromatography
 - 6.6.1 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.
 - 6.6.2 Columns
 - 6.6.2.1 Column 1: J&W DB-1 30m x 0.32 mm, 0.25 film
 - 6.6.2.2 Alternate columns: DB-5 30m x 0.32 mm, 0.25 micron film thickness.
 - 6.6.2.3 Other Columns may be used - capillary columns may be required to achieve the necessary resolution. The column must resolve C₂₄ from C₂₅ in a midrange RCS and C₃₆ must be clearly identified. See Section 9.2.2 of this method for additional column performance criteria.
- 6.7 Sonication
 - 6.7.1 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 ¾ inch Tapped Disrupter Horn, and No. 419 1/8 inch Standard tapered Microtip probe.

- 6.7.2 A Sonobox or equivalent is recommended with the above disrupter for decreasing sound (Heat Systems-Ultrasonics, Inc., Model 432 13 or equivalent).
- 6.8 Soxhlet extraction apparatus as described in SW-846 Method 3540 [1].
- 6.9 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 target analytes and interfering substances.
- 7.2 Methylene Chloride, 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 Section 7.2 above. Standards preparation should follow guidelines in SW-846 [1]. All standards prepared by the laboratory should be stored at -10 to -20° C and protected from light. Marking of the meniscus is helpful in maintaining stock standard integrity. Standards should be checked no more than six months prior to use to assure their integrity.
- 7.4.1 Recommended Surrogate: 5000 µg/mL n-Triacontane-d62 (dTC). A working solution is made at 500 µg/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 C₂₅ and C₃₆ n-alkanes with each component at a level of at least 10,000 µg/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 (see Section 7.4.2). Prepare a stock solution of 25,000 µg/mL in methylene chloride. A working solution is made at a recommended concentration of 5,000 µg/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 $4 \pm 2^\circ$ 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, and the extraction solvent must be methylene chloride.

9. 1.1 Soil Preparation - Soxhlet Extraction

9. 1. 1.1 Decant any water layered on the sample. Refer to method AK 102, Section 9.1.2 if DRO is to be done simultaneously. Mix the sample well and note any foreign objects or anomalies (variable 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 stainless steel or Teflon spatula, 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.

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

9.1.1.4 Prepare an LFB from the RCS and 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 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 Dry the extract with anhydrous sodium sulfate (This assures that the extract is water-free before concentration.)

9.1.1.7 Concentrate extract to 1 mL at a temperature not to exceed 55 ° C or that recommended by the manufacturer of concentration apparatus being used. Transfer extracts to GC vials for analysis. Extracts should be stored in a freezer <-10° C. Record the information for extraction and concentration steps.

Note: The extraction and concentration steps must be performed under a hood. Methylene chloride is a potential health hazard (See MSDS.)

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. 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 (105°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 0.01g. Record the weight.

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 120° 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.

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 C₁₀, if DRO (AK 102) is to be done simultaneously.

9.2.2.2 The separation number, TZ, should be greater than 15 for C₂₄ and C₂₅ if DRO is to be analyzed concomitantly.

$$TZ = [(\text{retention time } C_{25} - \text{retention time } C_{24}) / (W \frac{1}{2} \text{ of } C_{25} + W \frac{1}{2} \text{ of } C_{24})] - 1$$

Where "W ½ " = peak width at half-height

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

9.3 Calibration

9.3.1 Calibrate the GC, set up as in Section 9.2 of this method, with a minimum of three concentrations of RCS (five concentrations are recommended).

9.3.2 Choose Residual Calibration Standard concentrations to cover the RRO range expected in the samples, or the linear range of the instrument, whichever is less. Linearity of the calibration curve at the PQL must be documented.

9.3.3 Curve fit must be linear regression with a R² of 0.995 or better, quadratic fit with a R² of 0.995 or better, or if using response factors the average percent relative standard deviation (%RSD) is less than 25% over the working range.

9.3.4 The calibration curve must be confirmed using the CVS (see Section 7.4.4 of this method). 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 response factor or calibration curve must be verified on each working day (24 hours) by the injection of a CCS (see Section 7.4.2 of this

method) 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.

9.4 Retention Time Window Definition

9.4.1 Before establishing windows, be certain that the GC system is within optimum operating conditions (see Section 9.2 of this method). Make three injections of the Retention Time Window Standard (see Section 7.4.3 of this method) and surrogate 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 C₂₅, C₃₆, and the surrogate.

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

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

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 μ L using the conditions established in Section 9.2 of this method) 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 (Section 9.3 of this method) has been performed, verify the calibration by analysis of a mid-point CCS (see Section 9.3.5 of this method). With each day's run, open a 24 hour analysis window. This is done by running the Retention Time Window Standard (Section 7.4.3 of this method).

9.5.4 Calculate the percent recovery of the CCS concentration. This is done for RRO 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 solvent blank may 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 C₂₅ and the peak end of C₃₆. 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 Section 4 of this method). 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 µg/mL in the final extract. The sample should be diluted or external standard calibration should be used.

9.6 Calculations:

9.6.1 Percent 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

The % moisture calculation must be included in the data package.

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 of this method. Also refer to Section 9.4 of this method (Retention Time Window Definition).

The concentration of RRO is calculated as follows:

Soil samples:

$$C_s = \frac{(A_x)(C_{is})(D)(V_t)}{(A_{is})(RF)(V_s)}$$

Where: C_s = Concentration of RROs (mg/kg).

A_x = Response for the RROs in the sample, units in area.

RF = Response Factor from CCS (see Section 9.3. 1).

A_{is} = Response for the internal standard, units same as for A_x .

C_{is} = Internal standard concentration (mg/mL).

V_t = 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.

V_s = Amount of sample extracted in kg.

To calculate mg/dry kg for soil samples,

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

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

9.6.3 External Standard Calibration:

Soil samples:

$$C_s = \frac{(A_x)(A)(V_t)(D)}{(A_s)(V_s)}$$

Where: C_s = Concentration of RROs (mg/kg).

A_x = Response for the RROs in the sample, units in area.

A_s = Response for the external standard, units same as for A_x .

A = External standard concentration (mg/mL).

V_t = 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.

V_s = Amount of sample extracted in kg.

9.6.4 Some software programs are capable of performing moisture calculations with minimal analyst intervention.

10. Quality Control

10.1 Curve Verification Standard (CVS)

10.1.1 The CVS is not extracted.

10.1.2 The CVS is analyzed once with calibration standards to verify the calibration curve.

10.1.3 The CVS recovery requirement is 75-125% of true value.

10.2 Continuing Calibration Samples (CCS)

10.2.1 The CCS is not extracted.

10.2.2 The CCS is analyzed at the start and end of an analytical batch and for every 20 samples in that batch.

10.2.3 The CCS recovery requirement is 75-125% of true value.

10.3 Blanks

10.3.1 Instrument Blank may be analyzed with each analytical batch to demonstrate that the system is free from contamination.

10.3.2 Method Blank must be analyzed with each extraction batch.

10.3.3 BLANK SUBTRACTION IS NOT ALLOWED. Blanks are reported by value. This information is for data quality assessment purposes only.

10.3.4 Other blanks may be analyzed as necessary following the recommendations of Chapter 2, Section 9 of the *UST Procedures Manual*.

10.4 Lab Fortified Blanks (LFB)

10.4.1 LFB is extracted using the method procedure.

10.4.2 One LFB is analyzed with each analytical batch

10.4.3 The LFB recovery requirement is 60-120% of true value.

10.4.4 If any LFB recovery fails to meet method criteria, appropriate corrective action must be taken. See Section 10.7 of this method, "Corrective Actions".

10.5 Matrix Spike (MS) and Matrix Spike Duplicates (MSD)

10.5.1 MS & MSD are samples that are spiked with RCS to produce a known concentration greater than the sample background concentration. Both are processed as samples.

10.5.2 MS & MSD are analyzed only when requested.

10.5.3 There are no RPD or recovery requirements for MS and MSD.

10.5.4 The recovery and relative percent difference (RPD) for the MS and MSD are for informational purposes only.

10.6 Surrogate

10.6.1 Surrogate recoveries must be 60-120% for laboratory control samples (CCS, CVS, method blank, LFB) and 50-150 % for field samples (all other samples).

10.6.2 If any surrogate recovery fails to meet method criteria, corrective action must be taken. See Section 10.7 of this method, "Corrective Actions".

10.6.3 If field samples show poor surrogate recovery which is not attributable to laboratory error, RRO results must be flagged. Re-sampling, matrix spikes, or other remedial action is at the discretion of the client and is not the responsibility of the laboratory.

10.7 Corrective Action

- 10.7.1 The actions listed below are recommended and may not apply to a particular failure.
- 10.7.2 Check for matrix interference or carry-over.
- 10.7.3 Check for errors in calculation and that concentrations of surrogates and internal standards are correct.
- 10.7.4 Check that instrument performance meets method criteria.
- 10.7.5 Re-process the data.
- 10.7.6 Re-analyze the extracts.
- 10.7.7 Extract additional aliquots of the failing sample(s) and re-analyze.
- 10.7.8 Collect replacement samples.

11. Method Performance

11.1 Specific method performance data for Revision 3.0 of AK 103, Residual Range Organics, is not available at this time. Information on method performance for the C₂₅ - C₄₄ range (Revision 2.1) follows.

11.1.1 The method performance data presented, other than the performance evaluation samples, 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.

11.1.2 Results for motor oil spikes (methylene chloride extraction direct injection, soils) are 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
Performance Samples 2001	1231	104 ± 14
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

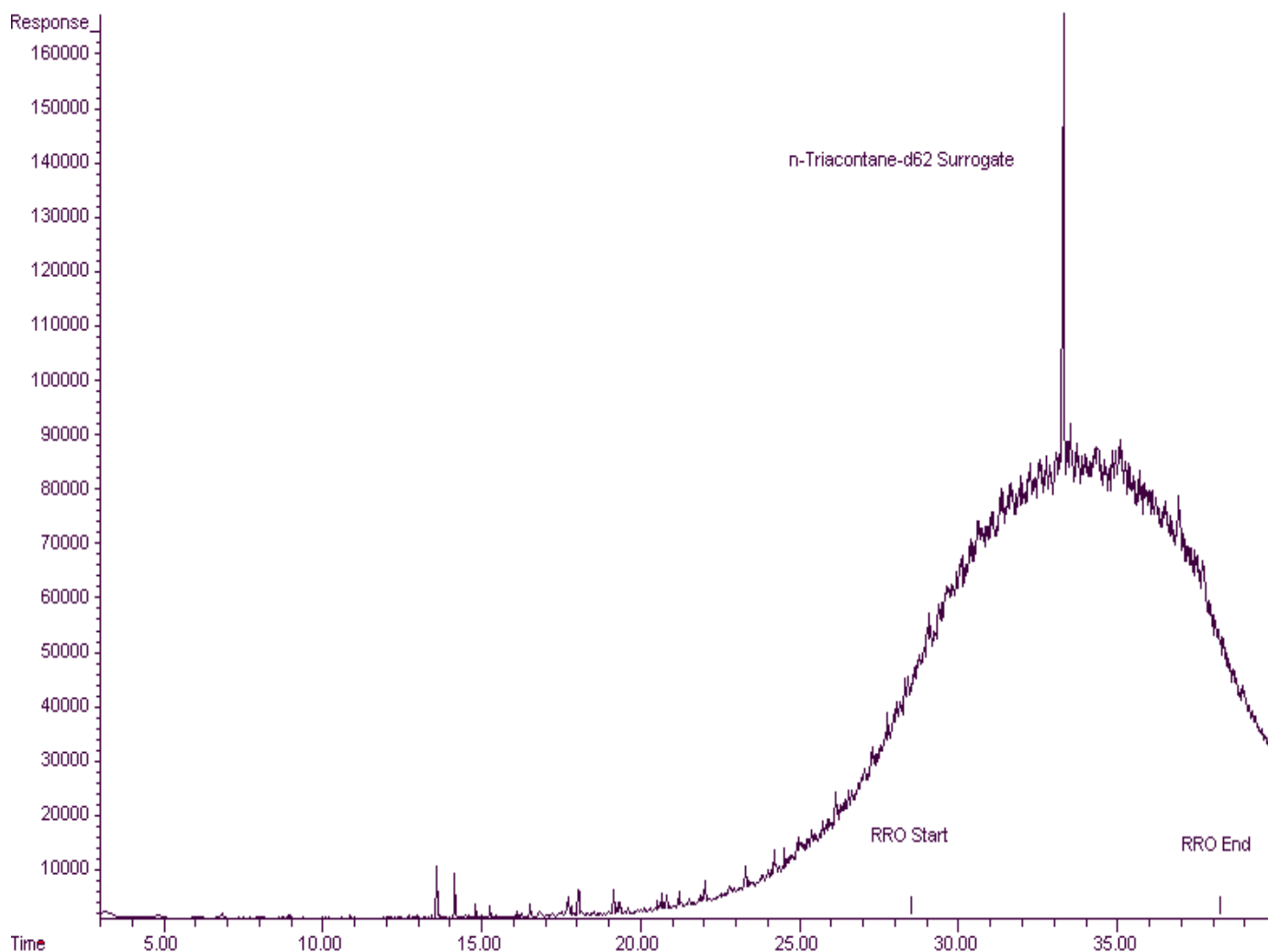
11.1.3 The method detection limit for soil calculated according to 40 C.F.R. 136, Appendix B (1994) was 51 mg/kg (external standard calibration).

12. References

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Figure 1. Residual Range Organics at 25 mg/mL, or 25,000,000 ug/L

Chromatogram is based on 25mg/mL of RRO standard made from 1:1 mixture of Valvoline 30 wt and Valvoline 40 wt motor oil. 100 ug/mL of n-Triacontane-d62 surrogate. GC conditions: HP 5890 series II GC/FID, HP-5 column 30m x 0.32mm x 0.25um, H2 carrier gas, Merlin high pressure microseal septum, Injector temperature - 320°C, Detector temperature - 330°C Oven temperature program - 45°C for 3 minutes, 8°C/minute to 320°C hold for 2.63 minutes for total run time of 40 minutes.



Method AK 103, Table 1
ACCEPTANCE CRITERIA FOR QUALITY CONTROL

ANALYTE	SPIKE CONCENTRATION		CONTROL LIMITS	Relative % Difference
	Soil (mg/kg)	% Recovery		
Lab Fortified Blank Residual Range Organics	500 mg/kg		60-120	20
CVS/CCS Residual Range Organics	2000 mg/L		75-125	
Surrogate Control Samples n-Triacontane-d62	50 mg/kg		60-120	
Surrogate Recovery (field samples) n-Triacontane-d62	50 mg/kg		50-150	

APPENDIX D

Alaska Series Laboratory Methods for the Analysis of Aliphatic and Aromatic Gasoline Range Organics (AK101AA), Aliphatic and Aromatic Diesel Range Organics (AK102AA), and Aliphatic and Aromatic Residual Range Organics (AK103AA)

Forward for AK Methods 101AA, 102AA, 103AA

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.

In order to obtain approval for the AK Series "AA" Methods, AK101AA, AK102AA, AK103AA, laboratories must pass a performance evaluation audit for each method as outlined in the Underground Storage Tank Regulations, 18 AAC 78.800-815. Guidelines for the performance evaluation sampling for these methods are outlined below.

- 1) One sample for each hydrocarbon range (GRO, DRO, RRO) and above the reporting limit for both aromatic and aliphatic compounds and below 500X the reporting limit shall be analyzed for each reporting matrix within the ADEC defined time period. The aromatics should be fortified in the mixtures such that they are no less than 40% of the total hydrocarbon to ensure the ability to detect them in low concentration samples.
- 2) All volatiles samples can be mixed using methanol.
- 3) Soil semivolatile standards should be relatively simple. The sample concentrates can be made up in hexane or methylene chloride. ADEC suggests hexane for the semivolatile samples as it will be easier to quantitatively transfer without losses due to evaporation.
- 4) Semivolatile water standards require a concentrate that can be mixed with water and will not adversely affect the SiO₂ or Al₂O₃ partitioning. ADEC experience has shown small amounts of methanol or acetone cause significant breakthrough on the columns. To attempt to alleviate the concern of using a non-miscible solvent, we suggest the following possibilities. Of these options the first two are the most desirable.
 - a) Create concentrates in water. Make up 50 or 100mL water concentrates and require the labs to quantitatively measure 40 or 80mL of water standard into a liter of "clean" water. This has been relatively easy for the lower concentrations, but the higher pose a slight problem.
 - b) Send full 1L samples to each lab. It is the same as the labs are used to seeing from their clients. Preservatives may be necessary.
 - c) Create concentrates in hexane. Hexane rather than methylene chloride will be better since it does not drop to the bottom of a continuous extractor. It would have to be extracted both from the top of the water and in the water allowing some equilibrium to be established. Either way, if a shakeout is used, an equilibrium is established during the process of shaking the sample.
- 5) Results required for these Performance Evaluation samples include:
 - a) standard deviation;
 - b) two and three sigma limits;
 - c) true values; and
 - d) percent recoveries.

Method AK101AA

Method for the Determination of Aromatic and Aliphatic Hydrocarbons in Gasoline Range Organics

Version 3-1-99

1 Scope & Application

1.1 This method is used for the extraction, fractionation, and quantification of aromatic and aliphatic compounds in the gasoline range. Adopted methodology by the Alaska Department of Environmental Conservation (ADEC) has established guidelines defining gasoline range organics (GRO), diesel range organics (DRO), and residual range organics (RRO) for gross organic measurements by Gas Chromatography. The intention of this method is to use these existing criteria and provide guidance for the fractionation of aromatic and aliphatic compounds within the gasoline range.

1.2 This, and most other volatiles aliphatic aromatic, fractionation methods are based on the EPA SW-846 Method 8015 & 8020 and related techniques employed throughout the petroleum industry.

1.3 This method provides guidance for laboratories interested in performing aromatic and aliphatic fractionation. It also defines general quality control guidelines and control limits to be used until statistical data is available.

1.4 This method is designed for the fractionation of aromatic / aliphatic compounds in the gasoline range. This has been defined as the beginning of C₆ to the beginning of C₁₀. This range includes gasolines of various types, naphthas, etc.

1.5 It is important to note fuels are crude oil distillates. This method is designed to accurately measure aliphatic compounds that fall only between the listed n-alkane hydrocarbon markers and specific C₆ to C₉ benzene and alkyl benzenes. Because distillates are complex mixtures of hydrocarbons, they may extend beyond the ranges defined by the ADEC.

1.6 This is a performance-based method. On October 6, 1997, EPA published guidelines for performance-based methodology -- 62 FR 52098. The intention is to encourage method development within the laboratory community that will 1) decrease costs of analysis, 2) increase analytical precision and accuracy, 3) allow laboratories to better fit methods to data quality objectives.

1.7 Being a performance-based method, heavy reliance on performance evaluation samples will be required. Laboratories shall request, analyze, and submit performance evaluation samples on a periodic basis to retain ADEC approval.

1.8 This is meant to be a guidance document; it shall not take the place of an individual laboratory Standard Operating Procedure or training program. Each laboratory shall maintain a Standard Operating Procedure that thoroughly describes the method, techniques employed, and verification of method performance. The laboratory shall, also, maintain training records for analysts who perform tasks related to this method. Major variances from this method shall be disclosed on data report forms.

2 Summary of Method

2.1 While several techniques are available for aromatic and aliphatic fractionation analysis that may produce the desired results, the method listed has been found preferable.

2.2 The quantification of gasoline range aromatic and gasoline range aliphatic hydrocarbons are described.

2.3 A soil, water, or sludge sample is appropriately diluted, extracted (if a soil) with methanol, and analyzed by gas chromatography. The gas chromatograph (GC) must be equipped with a dynamic headspace concentrator, e.g. a purge and trap device, and detection system capable of detecting both aromatic and aliphatic hydrocarbons, a Photoionization Detector (PID) and Flame Ionization Detector (FID) in series is recommended.

2.4 Compounds measured using the FID or other "carbon counter" style detector, when used for fuels analysis, may be quantified as a total area as traditionally done by method AK101. Analytes measured by PID or similar detector preferential for aromatic hydrocarbons must be individually identified and quantified.

2.5 This method relies on the fact that the only aromatic compounds that elute between C₆ and C₉ on a typical volatiles chromatographic column are the compounds commonly referred to as BTEX. Most of the remaining C₉ aromatics elute between the C₉ and C₁₀ alkane markers; two, however, do not, but shall be included in this analysis.

2.6 This method has been demonstrated to reduce many of the problems associated with using the PID/FID detector combination for gasoline range aromatics/aliphatics fractionation. It reduces the error caused by analyzing a transitional hydrocarbon (e.g. arctic diesel or jet fuel) or an aged gasoline using the volatiles method. Often, one can not tell the difference between a highly degraded gasoline where high levels of aromatics exist and the light ends of a light diesel range distillate. Using the patterns of the C₉ alkyl benzenes, one has the tools to assist in making this determination.

Hydrocarbon compounds that elute between C₉ and C₁₀ are difficult to analyze. Previous methods have used the gross difference between the amount of analyte reported by the FID and the PID to determine aromatic and aliphatic hydrocarbons present. The PID is not sufficiently selective for larger molecules and does not adequately report gross aromatic values in this range. Further, unsaturated gasoline range compounds (olefins) will also cause false positive results on the PID.

This method quantifies C₆, C₇, C₈, and C₉ alkyl benzenes as aromatics. No aromatic compounds which elute earlier than these are observed, hence, identification of these compounds provide a high degree of confidence in quantification of aromatic compounds.

3 Definitions

3.1 Gasoline Range Organics - Organic compounds which elute by gas chromatography between the beginning of n-C₆ and the beginning of n-C₁₀.

3.2 Diesel Range Organics - Organic compounds which elute by gas chromatography between the beginning of n-C₁₀ and the beginning of n-C₂₅.

3.3 Residual Range Organics - Organic compounds which elute by gas chromatography between the beginning of n-C₂₅ and the end of n-C₃₆.

3.4 Instrument Blank - A clean solvent analyzed to demonstrate the cleanliness of the analytical system.

3.5 Analytical Batch - A set of samples, not to exceed 20, which are extracted, concentrated, and fractionated together. Each analytical batch shall consist of 20 or fewer samples, a method blank, two laboratory control samples, and a matrix spike.

3.6 Method Blank - A sample of clean sand or clean water that is spiked with surrogate compounds and extracted and fractionated along with the analytical batch of samples.

3.7 Retention Time Marker - A standard used to demonstrate the integration ranges for GRO, DRO, and RRO.

3.8 Initial Calibration - A set of standards used to define the concentration calibration range of the gas chromatograph. The concentration of the lowest standard must be between 3 and 5 times the method detection limit for this analysis. The initial calibration mixture is a mixture of several compounds within the proper range. These compounds shall span the entire GRO, DRO, or RRO ranges.

3.9 Calibration Verification - A standard, independent of the initial calibration mixture, used to verify the accuracy of the initial calibration. For this method it is common to use a gasoline.

3.10 Continuing Calibration - A mid-range calibration standard used to verify the initial calibration while analyzing samples. A continuing calibration standard shall be analyzed with every 10 analytical injections on the gas chromatograph and at the end of an analytical run even if fewer than 10 samples were analyzed since the previous continuing calibration.

3.11 Surrogate Standard Compounds - Compounds not typically present in GRO, DRO, or RRO hydrocarbons, which are placed in known quantities in each sample, method blank, laboratory control sample, and matrix spike to determine the recovery and accuracy of the analysis. The surrogate mixture shall contain, at a minimum, one aromatic compound and one aliphatic compound. A secondary use of the surrogate standard is to demonstrate the effectiveness of the fractionation. Control limits shall be placed on the amount of surrogate breakthrough observed in each sample, method blank, laboratory control sample, and matrix spike.

3.12 Matrix Spiking / Laboratory Control Compounds - A combination of aromatic

and aliphatic compounds added to laboratory control samples and matrix spikes to demonstrate laboratory precision and accuracy.

3.13 Aromatic Compounds - Hydrocarbon compounds which are related to benzene.

3.14 Aliphatic Compounds - Paraffins, olefins, branched paraffins, and cyclic paraffins. These compounds have no or few carbon - carbon double bonds and make up the majority of fuels

3.15 Polar Compounds - Typically associated with biomass. In the terms of this method, they are considered undesirable compounds and are removed if proper corrective action techniques are used.

3.16 Method Detection Limit (MDL) – The minimum concentration of a compound that can be measured and reported with 99 percent confidence that the value is greater than zero, determined from analysis of a sample in a given matrix containing the analyte. (See 40 C.F.R. 136, Appendix B, for method of determining method detection limit. Each laboratory must demonstrate and periodically maintain method detection limits for each analyte of interest. A method detection limit is a statistical quantity defined as the point where one has a 99% confidence they are not seeing either a false positive or a false negative. Near the MDL the confidence in quantification is very low.)

3.17 Quantification Limit - Practical quantitation limit (PQL) is a certain point where one has a 95% confidence in the quantification of a substance. Practical quantitation limits (PQL) for this method for analysis of GRO must not exceed 20 mg/kg for soils and 20 µg/L for waters.

3.18 Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS/LCSD) - These samples are used by the laboratory to demonstrate a method's precision and accuracy. These are samples identical to a method blank with the exception they are spiked with a known amount of analyte. They are taken through the entire extraction and analytical process.

3.19 Matrix Spike - An actual sample that is spiked with a known amount of analyte. This sample can give valuable information about the behavior of analytes in this sample and may be extrapolated to other samples from the same area.

4 Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interference under the conditions of the analysis, by analyzing reagent and method blanks.

4.2 High purity reagents must be used to minimize interference problems.

4.3 Washing all glassware with hot soapy water and then rinsing with warm tap water and methanol reduces method interferences.

4.4 Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. Whenever an unusually concentrated sample is analyzed, it

must be followed by the analysis of a system blank to check for cross-contamination.

4.5 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interference will vary considerably from one source to another depending upon the nature and diversity of the site being sampled.

4.6 Chromatographic columns typically “bleed” stationary phase material at high temperatures. Typically, the use of a column compensation program by the gas chromatograph will yield satisfactory results.

4.7 Many compounds elute along with the C₈ and C₉ alkyl benzenes. Chromatography should be adequate to determine these compounds from aliphatic compounds. Interpretation should be supervised and reviewed by experienced chemists.

5 Health and Safety

The toxicity and carcinogenic nature of each reagent used in this method has not been precisely defined. 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 safety program to minimize exposure and potential hazards from personnel. A reference file of material safety data sheets (MSDS) shall be made available to all personnel.

6 Apparatus and Materials

6.1 Equipment

6.1.1 Gas Chromatograph (GC): An analytical system with temperature programmable gas chromatograph for use with capillary columns is required. The data system must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.1.2 Recommended chromatographic column: A J&W DB-5MS 30m x 0.32mm ID x 1.0µm stationary phase has been successfully used. Any moderately polar column may be used (listed below is a sample of stationary phases evaluated). The choice of column must be demonstrated to be capable of separating gasoline range compounds and eluting the aromatic compounds listed in Section 6.4.2 of this method with minimal column bleed.

DB-5
Hp-5
DB-VRX

6.1.3 A dynamic headspace apparatus capable of purging a sample with an inert gas and trapping analytes on a solid packing, then heating the trap and eluting the analytes into the gas chromatograph.

6.1.5 Analytical balances:

6.1.5.1 An analytical balance capable of measuring 0.0001g is required for standards preparation.

6.1.5.2 An analytical balance capable of measuring 0.01g is required for measuring sample weights.

6.1.6 Drying oven: an oven capable of maintaining 150°C is used for drying of glassware and syringes.

6.2 Glassware

6.2.1 20 & 40mL VOA vials.

6.2.2 Syringes - 10, 25, 100, 500, 1000, 5000, and 10,000µL.

6.3 Reagents

6.3.1 Methanol – purge and trap grade or better, must be demonstrated to be below method detection limits for gasoline range contaminants.

6.3.2 Ottawa sand - cleaned beach sand used for soil method blanks.

6.4 Standards

6.4.1 Retention time marker - shall consist of a minimum of n-C₆ and n-C₁₀. More n-alkanes are recommended. This mixture is typically injected into the GC at a concentration of 50µg/mL for each compound.

6.4.2 Initial calibration mixtures - The use of a FID or other “carbon counting” detector for hydrocarbons allows a free association between hydrocarbon compounds providing little or no injector discrimination is present, hence, the gasoline standards commonly used in association with AK101 are adequate. Aromatic compounds must be individually calibrated on the PID.

For PID: Calibrate for the following on an individual basis:

Benzene
Toluene
Ethylbenzene
o-, m-, & p-xylenes
1,2,3-Trimethylbenzene
1,3,5-Trimethylbenzene
1,2,4-Trimethylbenzene
1-ethyl-2-methylbenzene
1-ethyl-3-methylbenzene

1-ethyl-4-methylbenzene
n-propylbenzene
Isopropylbenzene

A minimum of five dilutions of this mixture must be used for calibration purposes. The lowest concentration standard shall be within a factor of three to five of the method detection limit or at the reporting limit, whichever is lower. The highest concentration shall define the upper limit to the calibration. Sample extracts that contain concentrations higher than the calibration curve shall be diluted and reanalyzed.

6.4.3 Calibration verification mixture – Use similar standards as were used for initial calibration, but originate from a separate source.

6.4.4 Continuing calibration mixture - A mid-level standard using the same or similar compounds used in the initial calibration mixture should be prepared for this purpose. The calibration verification mixture may be used.

6.4.5 Surrogate standard mixture - A surrogate mixture shall be made in methanol. Working standards should be prepared to yield a concentration of 100µg/mL of the proper surrogate in each of the final fractions. A minimum of two surrogate compounds must be spiked into each sample, method blank, LCS/LCSD, and matrix spike. Bromofluorobenzene and $\alpha\alpha\alpha$ -trifluorotoluene have been successfully used for this purpose.

6.4.6 Internal standard mixture (optional) – Fluorobenzene or another compound may be used as an optional internal standard if deemed necessary by the analyst.

6.4.7 Laboratory control sample / matrix spike mixture - A mixture of aromatic and aliphatic compounds -- a minimum of three each -- shall be used as a laboratory control sample / matrix spike mixture. The mixture shall contain both aromatic and aliphatic compounds and have a concentration sufficient such that a final concentration in each extract fraction is 50µg/mL of each component. For example, if five aromatics and five aliphatics are used then the final concentration of each fraction should be 250µg/mL.

7 Sample Collection, Preservation, and Handling

7.1 Aqueous samples are collected in 40mL glass bottles with Teflon-lined screw caps known as VOA vials.

7.2 Soil and sediment samples are collected in 4 oz. (120 mL) amber wide-mouth glass jars with Teflon-lined septum screw caps. They should be approximately 25g and have added an aliquot of methanol preservative consisting of methanol spiked with one of the above surrogates.

7.3 Aqueous samples must be preserved at the time of sampling by the addition of a suitable acid to reduce the pH of the sample to less than 2.0. This may be accomplished

by the addition of a few drops of 1:1 HCl to a 40mL sample. The use of alternative acids is permissible. Following collection and addition of acid, the sample must be cooled to 4°C.

7.4 A chain of custody form must accompany all aqueous, soil, and sediment samples, documenting the time and date of sampling and any preservative additions.

7.5 Aqueous samples must be analyzed within 14 days of collection.

7.6 Soil and sediment samples must be analyzed within 28 days of collection.

8 Procedure

8.1 Sample Preparation – Samples or sample extracts are measured into a 5mL syringe, adjusted to 5.0mL, and added to the sample chamber of a purge and trap apparatus.

8.1.1 Water analysis

8.1.1.1 If analyst does not deem dilution necessary, pour water sample into the plunger portion of a 5mL volumetric syringe and adjust to 5.0mL.

8.1.1.2 Add surrogate standard solution through the open end of the syringe.

8.1.1.3 Place sample in sample chamber of the purge and trap.

8.1.2 Soil analysis

8.1.2.1 Allow field sample to equilibrate for 48 hours.

8.1.2.2 Fill and adjust a 5mL syringe with water. If sample does not require dilution, place up to 250µL of methanol extract into clean water and add lab surrogate/internal standard solution.

8.1.2.3 Place in purge and trap sampling apparatus.

8.2 Quantification

8.2.1 Analyze sample in the same manner as typical AK101 / EPA8021B samples.

8.2.2 Calibrate the instrument using standards listed above.

8.2.3 Quantify the individual aromatic compounds and sum their concentrations. This is the gasoline range aromatic result.

8.2.4 Quantify the “total GRO” as described by AK101.

8.2.5 Subtract the aromatic result from the total GRO result to obtain the aliphatic result.

Note this result consists of non-aromatic compounds and may include aliphatics (or paraffins), cyclic paraffins, olefins, ketones, aldehydes, etc.

8.3 Analytical

8.3.1 Gas Chromatograph Conditions (Recommended)

Parameter	Setting
Gas	Helium
Linear velocity	60 - 65cm/s
Initial Temp.	35°C
Initial Time	4min.
Rate	8°C/min.
Final Temp.	250°C
Hold	5 - 10min.
Injector Temp.	250°C
Detector Temp.	255°C

8.3.2 Gas Chromatograph Sequencing - A typical GC sequence must include a 24 hour retention time marker, a continuing calibration standard for every 10 injections -- that is, a beginning CC, and one after each subsequent 10 injections - - and an ending continuing calibration standard. Each sample batch should be analyzed in one sequence on the same instrument.

8.3.3 Calibration - A minimum of 5 concentrations of standard must be used to define the calibration curve. The concentration of each standard is the total of the concentrations of analytes present in that standard, hence, 5 analytes at 50µg/mL has a total concentration of 250µg/mL.

8.3.3.1 The lowest standard shall be equivalent to the reporting limit or a value three to five times the method detection limit, whichever is lower.

8.3.3.2 The highest concentration standard shall define the highest extract concentration that may be reported without dilution.

8.3.3.3 Whenever possible, use a least squares linear regression for calibration. Quadratic curves and average of response factors are acceptable provided adequate quality control and performance parameters are consistently met.

9 Calculations

9.1 Response Factors

Eq. 1

Where

$A_{x, \text{std}}$ = Area of analyte in standard.
 $C_{x, \text{std}}$ = Concentration of analyte in
Standard in $\mu\text{g/mL}$.

9.2 Concentrations

9.2.1 Soil External Standard (example) – many software packages will report concentrations of extracts without any problem. The following is for those cases where this is not done. It requires an average of response factors.

$$\text{Concentration in Soil (mg / Kg)} = \frac{(\text{Area}_x)(df)(V_f)(1000\mu\text{g / mg})}{(rf)(m_f)(W_i)} \quad \text{Eq. 2}$$

Where

A_x = Area of analyte in extract.
 df = Dilution Factor of extract.
 V_f = Final volume of extract after
concentration step.
 rf = Response factor.
 m_f = Fractional dry mass (%
Dryness)
 W_i = Initial Weight of soil sample.

Note: If instrument reports concentration in extract; that value can replace the (Area_x/rf) portion of the equation.

9.2.2 Water External Standard (example) – many software packages will report concentrations of extracts without any problem. The following is for those cases where this is not done. It requires an average of response factors.

$$\text{Concentration in Water}(\mu\text{g} / \text{L}) = \frac{(\text{Area}_x)(df)(V_f)}{(rf)(V_i)} \quad \text{Eq. 3}$$

Where

A_x = Area of analyte in extract.
 df = Dilution Factor of extract.
 V_f = Final volume of extract after concentration step.
 rf = Response factor.
 V_i = Initial volume of water (aqueous) sample.

Note: If instrument reports concentration in extract; that value can replace the (Area_x/rf) portion of the equation.

9.3 Fractional Mass of a soil – This is the fractional version of %Dryness for use in soil calculations.

$$\text{Fractional Mass} = \frac{(m_d)}{(m_s)} \quad \text{Eq. 4}$$

Where

m_d = Weight of dried soil.
 m_s = Weight of sample before drying.

9.4 Relative Percent Difference (RPD)

$$RPD = \frac{(X_1 - X_2)}{\frac{(X_1 + X_2)}{2}} * 100\%$$

Eq. 5

10 Quality Control

10.1 Retention Time Markers

10.1.1 A retention time marker must be analyzed at least once every 24-hour period or once each day of instrument operation.

10.1.2 The analyst must combine use of the retention times for the ranges of interest from three separate retention time markers to determine acceptable retention time variation.

10.1.3 The retention time window for the beginnings and ends of the hydrocarbon ranges must be calculated as follows from the beginning of C₆ to the end of C₁₀.

10.1.4 If the retention time of a retention time marker standard falls outside the established window, the retention time must be updated and a new retention time window established.

10.2 Initial Calibration – A minimum five-point calibration must be performed to establish the working range of the Gas Chromatograph.

10.2.1 An initial calibration must be made up for each fraction – aromatic and total gasoline range hydrocarbons.

10.2.2 The lowest concentration must be between 3 and 5 times the method detection limit concentration or at the reporting limit concentration, whichever is lower.

10.2.3 The highest concentration will define the upper limit concentration that may be reported without extract dilution.

10.2.4 If a linear regression is used (recommended) the coefficient of correlation must be 0.98 or higher.

10.2.5 If an average of response factors is used the maximum %RSD must be no greater than 15%.

10.2.6 A quadratic calibration may be used if the GC software allows this type of calibration. The coefficient of correlation must not fall below 0.98.

10.2.7 All data points in the calibration should be weighted equally.

10.2.8 Corrective Actions

- a) If the initial calibration is outside the control limits, analysis shall not be performed.
- b) Reintegrate all standards.
- c) Prepare and reanalyze a new curve.

10.3 Second Source Calibration Verification – A standard used to verify the initial calibration.

10.3.1 The second source calibration verification may be made up from a standard similar to the initial calibration at an intermediate level.

10.3.2 The second source compounds must be obtained from a separate source other than the initial calibration compounds.

10.3.3 The second source calibration verification standard may also be used as the continuing calibration standard.

10.3.4 The recovery of the second source calibration verification must be +/- 15% of the true value.

10.3.5 Corrective Actions

- a) If the second source verification standard is outside the control limits analysis shall not be performed.
- b) Reanalyze the second source calibration verification standard.
- c) Prepare a new standard.
- d) Prepare and analyze a new initial calibration.

10.4 Instrument Blank

10.4.1 Must be below reporting limits before proceeding with further analysis.

10.4.2 Must be analyzed at least once every 24 hours of instrument operation.

10.4.3 An instrument blank is recommended after samples high in concentration.

10.4.4 Corrective Actions

- a) **If an instrument blank is outside the limits, all samples associated with that blank must be reanalyzed.**

10.5 Continuing Calibration Standard

10.5.1 The Continuing Calibration Standard may be made up from a standard similar to the initial calibration at an intermediate level.

10.5.2 The continuing calibration standard may also be used as the second source calibration verification.

10.5.3 The recovery of the second source calibration verification must be +/- 15% of the true value.

10.5.4 A continuing calibration standard must be analyzed at the beginning of an

analytical run, once every 10 injections on the GC, and at the close of the run.

10.5.5 Corrective Actions

- (a) If a CCV is outside the limits, all samples associated with that standard must be reanalyzed.**
- (b) Be certain CCV is fresh and within limits.**

10.6 Method Blank

10.6.1 The method blank must be made up from a matrix similar to the samples within the analytical batch (e.g. water for aqueous, sand for sandy soil, clean loam for mossy high biomass samples)

10.6.2 Surrogate standards must be added to all method blanks and must fall within the window of 70 – 120% of the true values.

10.6.3 The method blank must be free of contamination (below reporting limits) within the specified range.

10.6.4 Corrective actions

- a) Reanalyze method blank being sure no instrument carryover is present.**
- b) If a problem persists, or surrogates are outside acceptable ranges, associated analytical batch must be re-extracted and analyzed.**

10.7 Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS/LCSD).

10.7.1 The LCS/LCSD/Matrix Spike working standard must be made up of a synthetic mixture of analytes. A minimum of three aromatic and three aliphatic compounds must be used for each range (DRO, RRO, GRO).

10.7.2 The LCS/LCSD should be made up from a matrix similar to the samples within the analytical batch (e.g. water for aqueous, sand for sandy soil, clean loam for mossy high biomass samples)

10.7.3 Surrogate standards must be added to all LCS/LCSD and must fall within the window of 70 – 120% of the true values.

10.7.4 Matrix spike/LCS compounds must be added to all LCS/LCSD samples and must fall within the window of 70 – 120% of the true values.

10.7.5 The duplicate must have a relative percent difference of less than 20%.

10.7.6 Corrective actions

- a) Reanalyze LCS/LCSD being sure no instrument carryover is present.**
- b) If problem persists, or surrogates are outside acceptable ranges, associated analytical batch must be re-extracted, re-fractionated, and/or re-analyzed.**

10.8 Matrix Spike

10.8.1 The LCS/LCSD/Matrix Spike working standard should be made up of a synthetic mixture of analytes. A minimum of three aromatic and three aliphatic compounds must be used for each range (DRO, RRO, and GRO) and the true values of each must be documented.

10.8.2 The matrix spike must be made up from a sample within the analytical batch.

10.8.3 Surrogate standards must be added to all matrix spike samples and should fall within the window of 50 - 150% of the true values.

10.8.4 Matrix spike/LCS compounds must be added to all matrix spike samples and should fall within the window of 50 - 150% of the true values

10.8.5 Corrective actions: No corrective actions are required for a matrix spike that is out of compliance.

10.9 Surrogate Spikes

10.9.1 At least two surrogate compounds which do not co-elute or otherwise interfere with the analytes of interest must be added to each sample, method blank, LCS/LCSD, and matrix spike.

10.9.2 The recovery of surrogate standards must not be outside the range 70 – 120% for method blanks and LCS/LCSD samples.

10.9.3 The recovery of surrogate standards should not be outside the range 50 - 150% for all remaining samples and matrix spikes.

10.9.4 Corrective Actions

- a) **If the surrogates for a sample are out of limits, then that sample must be re-analyzed.**
- b) **If a surrogate is out of limits in the same direction (e.g. low both times) for a second time, then the report shall reflect a matrix effect.**
- c) **If a surrogate compound is out of limits for a method blank or LCS/LCSD sample, then that sample must first be re-analyzed. If it is still out, the entire analytical batch must be re-extracted, re-fractionated, and re-analyzed.**

11 References

- 11.1** Alaska Department of Environmental Conservation, Methods AK101.
- 11.2** The Federal Register, 62 FR 52098, Oct 1997.
- 11.3** Massachusetts Department of Environmental Protection and ABB Environmental Services, Inc., Wakefield, MA "Interim Petroleum Policy: Development of Health-based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter", August 1994.
- 11.4** USEPA, "Measurement of Petroleum Hydrocarbons: Report on Activities to Develop a Manual" Prepared by Midwest Research Institute, Falls Church, VA, under EPA Contract #68-WO-0015, WA No. 4; submitted to USEPA Office of Underground Storage Tanks, Washington, DC; November 20, 1990.
- 11.5** USEPA Regulations 40 CFR Part 136, Appendix B, "Guidelines Establishing Test procedures for the Analysis of Pollutants", July 1992.
- 11.6** USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 8000: Gas Chromatographic Methods; September 1986.
- 11.7** USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 8015: Method for General Volatiles Analysis; September 1986
- 11.8** USEPA Test Methods for Evaluating Solid Waste (SW-846); Method 8020; Aromatic Compounds by Gas Chromatography; September 1986
- 11.9** USEPA, "Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring", EPA 821-B-93-001; U.S. Government Printing Office, Washington D.C., June, 1993.

Figure 1: GCMS trace of typical gasoline.

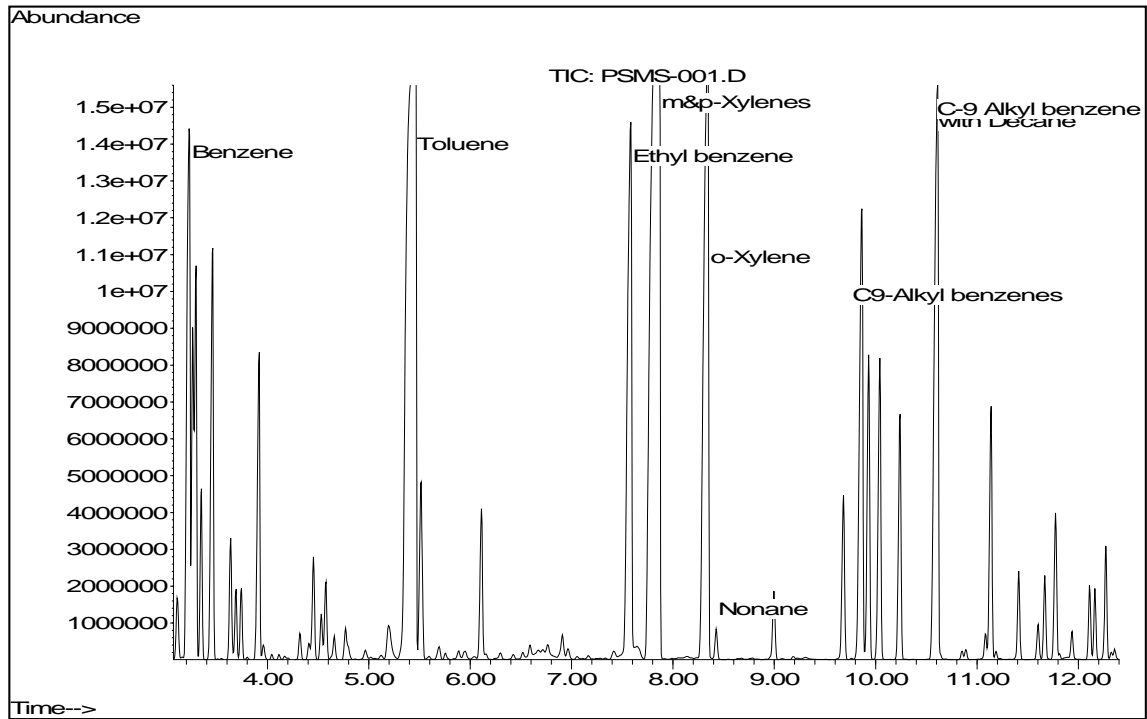


Figure 1: A fresh gasoline analyzed by GCMS to determine compounds present in the C₆ to C₁₀ range. BTEX compounds are commonly analyzed by volatiles methodology. Nonane elutes soon after o-Xylene. A single peak at 9min appears to be an olefin and the next 6 peaks are C₉ alkyl benzenes with the last one co-eluting with Decane.

Method AK 102AA
For Determination of Aromatic and Aliphatic
Hydrocarbons in Diesel Range Organics
Version 6-30-98

1. Scope & Application

1.1 This method is used for the extraction, fractionation, and quantification of aromatic and aliphatic compounds in the diesel range. Adopted methodology by the Alaska Department of Environmental Conservation (ADEC) has established guidelines defining gasoline range organics (GRO), diesel range organics (DRO), and residual range organics (RRO) for gross organic measurements by Gas Chromatography. The intention of this method is to use these existing criteria and provide guidance for the fractionation of aromatic and aliphatic compounds within these ranges.

1.2 This, and most other aliphatic aromatic, fractionation methods are based on the EPA SW-846 Method 3630 and related techniques employed throughout the petroleum industry.

1.3 This method provides guidance for laboratories interested in performing aromatic and aliphatic fractionation. It also defines general quality control guidelines, reporting limits, and control limits to be used until statistical data is available.

1.4 This method is designed for the fractionation of aromatic / aliphatic compounds in the diesel range. This has been defined as the beginning of C₁₀ to the beginning of C₂₅. This range includes: kerosene, several types of jet fuel, several types of motor fuels commonly referred to as diesel fuels, and several light heating oils.

1.5 It is important to note fuels are crude oil distillates. This method is designed to accurately measure aromatic and aliphatic compounds that fall only between the listed n-alkane hydrocarbons. Because distillates are complex mixtures of hydrocarbons, they may extend beyond the ranges defined by the ADEC.

1.6 This is a performance-based method. EPA has recently published guidelines for performance-based methodology -- 62 FR 52098. The intention is to encourage method development within the laboratory community that will 1) decrease costs of analysis, 2) increase analytical precision and accuracy, 3) allow laboratories to better fit methods to data quality objectives.

1.7 Being a performance-based method, heavy reliance on performance evaluation samples will be required. Laboratories shall request, analyze, and submit performance evaluation samples on a periodic basis to retain ADEC approval.

1.8 This document is meant to be a guidance document; it shall not take the place of an individual laboratory Standard Operating Procedure or training program. Each laboratory shall maintain a Standard Operating Procedure that thoroughly describes the method, techniques employed, and verification of method performance. The laboratory shall, also, maintain training records for analysts who perform tasks related to this method. Major variances from this method shall be disclosed on data report forms.

2 Summary of Method

2.1 While several techniques are available for aromatic and aliphatic fractionation analysis that may produce the desired results, the method listed has been found preferable.

2.2 The extraction, fractionation, and quantification of diesel range aromatic and diesel range aliphatic hydrocarbons are described.

2.3 Hydrocarbons extracted from a water, soil, or sludge sample are extracted with methylene chloride and concentrated in accordance with AK102.

2.4 Methylene chloride in the extracts is exchanged for n-hexane or another appropriate non-polar solvent and passed through a bed of silica gel. The silica gel is first washed with the non-polar solvent to collect the aliphatic hydrocarbons, then with a moderately polar solvent to collect aromatic hydrocarbons. The washes are concentrated for analysis.

2.5 Concentrated aromatic and aliphatic samples are analyzed by gas chromatography (GC). The GC shall be equipped with an oven capable of temperature programming and an analytical column capable of separating diesel range compounds within the specifications outlined in this document. It shall also be equipped with a detector capable of detecting carbon or carbon ions -- the typical detector is the Flame Ionization Detector (FID), an Atomic Emission Detector (AED), or other detector capable of measuring the amount of carbon present in a sample independent of compound may be used. Data shall be collected by a data collection system capable of providing a chromatographic trace and integration of the selected hydrocarbon range.

3 Definitions

3.1 Gasoline Range Organics - Organic compounds which elute by gas chromatography between the beginning of n-C₆ and the beginning of n-C₁₀.

3.2 Diesel Range Organics - Organic compounds which elute by gas chromatography between the beginning of n-C₁₀ and the beginning of n-C₂₅.

3.3 Residual Range Organics - Organic compounds which elute by gas chromatography between the beginning of n-C₂₅ and the end of n-C₃₆.

3.4 Instrument Blank - A clean solvent analyzed to demonstrate the cleanliness of the analytical system.

3.5 Analytical Batch - A set of samples, not to exceed 20, which are extracted, concentrated, and fractionated together. Each analytical batch shall consist of 20 or fewer samples, a method blank, two laboratory control samples, and a matrix spike.

3.6 Method Blank - A sample of clean sand or clean water that is spiked with surrogate compounds, extracted, and fractionated along with the analytical batch of samples.

3.7 Retention Time Marker - A standard used to demonstrate the integration ranges for GRO, DRO, and RRO.

3.8 Initial Calibration - A set of standards used to define the concentration calibration

range of the gas chromatograph. The concentration of the lowest standard must be between 3 and 5 times the method detection limit for this analysis. The initial calibration mixture is a mixture of several compounds within the proper range. These compounds shall span the entire GRO, DRO, or RRO ranges.

3.9 Calibration Verification - A standard, independent of the initial calibration mixture, used to verify the accuracy of the initial calibration. For this method it is common to use a diesel fuel #2 since over 95% of these compounds elute within the DRO range.

3.10 Continuing Calibration - A mid-range calibration standard used to verify the initial calibration while analyzing samples. A continuing calibration standard shall be analyzed with every 10 analytical injections on the gas chromatograph.

3.11 Surrogate Standard Compounds - Compounds not typically present in GRO, DRO, or RRO hydrocarbons, which are placed in known quantities in each sample, method blank, laboratory control sample, and matrix spike to determine the recovery and accuracy of the analysis. The surrogate mixture shall contain, at a minimum, one aromatic compound and one aliphatic compound. A secondary use of the surrogate standard is to demonstrate the effectiveness of the fractionation. Control limits shall be placed on the amount of surrogate breakthrough observed in each sample, method blank, laboratory control sample, and matrix spike.

3.12 Matrix Spiking / Laboratory Control Compounds - A combination of aromatic and aliphatic compounds added to laboratory control samples and matrix spikes to demonstrate laboratory precision and accuracy.

3.13 Silica Gel Breakthrough – Defined as the effect of using either inactive silica gel, too much solvent, inappropriate solvent, or overloading on silica gel column. Surrogate compounds are typically used to determine whether column breakthrough has occurred.

3.14 Aromatic Compounds - Hydrocarbon compounds which are related to benzene.

3.15 Aliphatic Compounds - Paraffins, olefins, branched paraffins, and cyclic paraffins. These compounds have no or few carbon - carbon double bonds and make up the majority of fuels

3.16 Polar Compounds – Typically, associated with biomass. In the terms of this method, these are considered undesirable compounds and are removed if proper corrective action techniques are used.

3.17 Method Detection Limit (MDL) – The minimum concentration of a compound that can be measured and reported with 99 percent confidence that the value is greater than zero, determined from analysis of a sample in a given matrix containing the analyte. (See 40 C.F.R. 136, Appendix B, for method of determining method detection limit. Each laboratory must demonstrate and periodically maintain method detection limits for each analyte of interest. A method detection limit is a statistical quantity defined as the point where one has a 99% confidence they are not seeing either a false positive or a false negative. Near the MDL the confidence in quantification is very low.)

3.18 Quantification Limit - Practical quantitation limit (PQL) is a certain point where

one has a 95% confidence in the quantification of a substance. Practical quantitation limits (PQL) for this method for analysis of DRO must not exceed 20 mg/kg for soils and 2 µg/L for waters.

3.19 Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS/LCSD) - These samples are used by the laboratory to demonstrate a method's precision and accuracy. These are samples identical to a method blank with the exception they are spiked with a known amount of analyte. They are taken through the entire extraction and analytical process.

3.20.1 Matrix Spike - An actual sample that is spiked with a known amount of analyte. This sample can give valuable information about the behavior of analytes in this sample and may be extrapolated to other samples from the same area.

4 Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interference under the conditions of the analysis, by analyzing reagent and method blanks.

4.2 High purity reagents must be used to minimize interference problems.

4.3 Washing all glassware with hot soapy water and then rinsing with warm tap water, acetone, and methylene chloride reduces method interferences.

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

4.5 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interference will vary considerably from one source to another depending upon the nature and diversity of the site being sampled. Many polar compounds commonly attributed to "biogenic" sources should be removed by the silica gel if properly used. Several petroleum precursors are present in aging vegetation and peat; these compounds will not be removed using this technique.

4.6 The leaching of plasticizers and other compounds have been observed from commercially available silica gel cartridges used to fractionate DRO and RRO sample extracts. Concerns of this nature must be continuously monitored and documented by analysis of Laboratory Method Blanks.

4.7 Many compounds elute along with the C₈ and C₉ alkyl benzenes. Chromatography should be adequate to determine these compounds from aliphatic compounds. Interpretation should be supervised and reviewed by experienced chemists.

5 Health and Safety

The toxicity and carcinogenic nature of each reagent used in this method has not been

precisely defined. 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 safety program to minimize exposure and potential hazards from personnel. A reference file of material safety data sheets (MSDS) shall be made available to all personnel.

6 Apparatus and Materials

6.1 Equipment

6.1.1 Gas Chromatograph: An analytical system with temperature programmable gas chromatograph for use with capillary columns is required. The data system must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.1.2 Recommended chromatographic column: A J&W DB-5MS 30m x 0.32mm ID x 0.10 μ m stationary phase has been successfully used. Any column capable of separating diesel and residual range compounds with minimal column bleed may be used.

6.1.3 A concentration apparatus capable of using clean air or nitrogen to remove excess solvent from samples shall be used. These systems range from a combination of Kuderna-Danish concentrators and N-Evap apparatus, to automated Turbo-Vap systems.

6.1.4 Soil extraction equipment: Soxhlet continuous extractors and ultrasonic cell disrupters have been used for the extraction of soil samples.

6.1.5 Analytical balances:

6.1.5.1 An analytical balance capable of measuring 0.0001g is required for standards preparation.

6.1.5.2 An analytical balance capable of measuring 0.01g is required for measuring sample weights.

6.1.6 Drying oven: an oven capable of maintaining 150°C is used for drying of sodium sulfate and activation of silica gel.

6.2 Glassware

6.2.1 Beakers - 250mL or 400mL.

6.2.2 2L separatory funnels or equivalent (continuous extractors, etc.).

6.2.2 Long stemmed funnels.

6.2.3 Kuderna-Danish concentrator or equivalent (Turbo Vap tubes, etc.).

6.2.4 10mL graduated disposable pipettes or equivalent.

6.2.5 Graduated cylinders - 50mL & 100mL.

6.2.6 Graduated centrifuge tubes or equivalent - 10mL or 15mL.

6.2.7 Autosampler vials or extract containers.

6.1.8 Syringes - 10, 25, 100, 500, and 1000 μ L.

6.3 Reagents

6.3.1 Methylene chloride - analytical grade or better, must be demonstrated to be below method detection limits for diesel and residual range contaminants.

6.3.2 n-Hexane - analytical grade or better, must be demonstrated to be below method detection limits for diesel and residual range contaminants.

6.3.3 Ottawa sand - cleaned beach sand used for soil method blanks.

6.3.4 Sodium sulfate - Anhydrous, granulated, used for drying soil samples and all methylene chloride extracts.

6.3.5 Silica gel - Anhydrous, 60 - 100 mesh has been used successfully. Prepacked extraction cartridges may be used provided they meet the quality control performance criteria listed in this document.

IMPORTANT: silica gel should be activated by placing in a 150°C oven prior to use, prolonged exposure to moist air will cause high surrogate breakthrough in samples, method blanks, laboratory control samples, and matrix spikes.

6.3.6 Glass wool - Pesticide grade or better.

6.4 Standards

6.4.1 Retention time marker - shall consist of a minimum of n-C₁₀, n-C₂₅, and n-C₃₆ (if the optional RRO analysis is used concurrently with DRO). More n-alkanes are recommended. This mixture is typically injected into the GC at a concentration of 50 μ g/mL for each compound.

6.4.2 Initial calibration mixtures: Since it is impractical and nearly impossible to use a commercial diesel range distillate for calibration a synthetic mixture must be used. The use of a Flame Ionization Detector or other "carbon counting" detector allows a free association between fuel-derived hydrocarbon compounds providing little or no injector discrimination is present.

Choose a minimum of three -- recommend five or more -- which span the entire diesel range. The concentration of the standard is the total of all the individual compounds.

Each compound should be in the same concentration as the others in solution. A minimum of five dilutions of this mixture must be used for calibration purposes. The lowest concentration standard shall be within a factor of three to five of the method detection limit or at the reporting limit, whichever is lower. The highest concentration shall define the upper limit to the calibration. Sample extracts that

contain concentrations higher than the calibration curve shall be diluted and reanalyzed.

6.4.2.1 Aromatic - A minimum of three aromatic compounds, which span the diesel range, should be used for calibration purposes. Polynuclear aromatic hydrocarbons (PAHs) generally suit the purpose of this calibration.

6.4.2.2 Aliphatic - A minimum of three aliphatic compounds, which span the diesel range, should be used for calibration purposes. N-alkanes: C₁₁, C₁₅, C₁₇, C₁₈, and C₂₄ have been successfully used.

6.4.3 Calibration verification mixture - A #2 diesel fuel diluted to 1000µg/mL has been successfully used. Any hydrocarbon mixture where more than 95% of the hydrocarbon elutes in the diesel range and is independent of the initial calibration may be used.

6.4.4 Continuing Calibration mixture - A mid-level standard using the same or similar compounds used in the initial calibration mixture should be prepared for this purpose.

6.4.5 Surrogate standard mixture - A surrogate mixture shall be made in methylene chloride and shall contain compounds from the three major fractions present in most samples -- aliphatic, aromatic, and polar. Working standards should be prepared to yield a concentration of 100µg/mL of the proper surrogate in each of the final fractions.

6.4.5.1 Squalane has been successfully used for the aliphatic surrogate; although it elutes in the residual range no problems have been observed.

6.4.5.2 o-Terphenyl has been used as an aromatic surrogate with great success; few interference problems have been observed.

6.4.5.3 Tetrahydronaphthol has been successfully used as a polar surrogate to monitor the elution of polar compounds with the aromatic fraction.

Note: The surrogate standard mixture shall be made up in methylene chloride or hexane, NOT methanol or acetone, even small amounts of these solvents greatly affect the polarity of the final solutions and will be detrimental to the fractionation.

6.4.6 Internal standard mixture (optional) - 5- α -Androstane may be used as an optional internal standard if deemed necessary by the analyst.

6.4.7 Laboratory control sample / matrix spike mixture - A mixture of aromatic and aliphatic compounds -- a minimum of three each -- shall be used as a laboratory control sample / matrix spike mixture. The mixture shall contain both aromatic and aliphatic compounds and have a concentration sufficient such that a final concentration in each extract fraction is 50µg/mL of each component. For example, if five aromatics and five aliphatics are used then the final concentration

of each fraction should be 250 μ g/mL.

Note: The laboratory control sample / matrix spike mixture must be made up in methylene chloride or hexane, NOT methanol or acetone, even small amounts of these solvents greatly affect the polarity of the final solutions and will be detrimental to the fractionation.

7 Sample Collection, Preservation, and Handling

7.1 Aqueous samples are collected in 1-liter amber glass bottles with Teflon-lined screw caps.

7.2 Soil and sediment samples are collected in 4 oz. (120 mL) amber wide-mouth glass jars with Teflon-lined screw caps.

7.3 Aqueous samples must be preserved at the time of sampling by the addition of a suitable acid to reduce the pH of the sample to less than 2.0. This may be accomplished by the addition of 5 mL of 1:1 HCl to a 1 liter sample. The use of alternative acids is permissible. Following collection and addition of acid, the sample must be cooled to 4°C.

7.4 Soil and sediment samples must be cooled to 4°C immediately after collection.

7.5 A chain of custody form must accompany all aqueous, soil and sediment samples, documenting the time and date of sampling and any preservative additions.

7.6 Aqueous samples must be extracted within 7 days of collection, and analyzed within 40 days of extraction.

7.7 Soil and sediment samples must be extracted within 14 days of collection, and analyzed within 40 days of extraction.

8 Procedure

8.1 Sample Preparation - Samples are extracted using methylene chloride, and, later, solvent-exchanged into hexane. An acceptable extraction procedure for water samples is a separatory funnel liquid/liquid extraction technique based upon SW-846 Method 3510A; continuous liquid/liquid extraction has also proven effective. For soil or sediment samples, use of a Soxhlet or Soxtec technique is recommended. Alternative extraction procedures are acceptable, provided that the laboratory can document acceptable performance.

8.1.1 Water Extraction

8.1.1.1 Mark the meniscus on the 1-liter sample bottle (for later volume determination) and transfer it to a 2-liter separatory funnel. For blanks and quality control samples, pour 1 liter of reagent water into the separatory funnel. Check the pH of the sample with wide-range pH paper. Note the pH in a laboratory logbook or preparatory sheet.

The pH of the sample need not be adjusted.

8.1.1.2 Add 1.0 mL of the surrogate spiking solution to all samples, blanks, laboratory control samples, and matrix spikes. For samples selected for spiking, add laboratory control sample / matrix spike solution.

8.1.1.3 Add 60mL methylene chloride to the sample bottle to rinse the inner walls of the container and add this solvent to the separatory funnel.

8.1.1.4 Seal and shake each separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, venting into a hood should be done immediately after the separatory funnel has been sealed and shaken once.

8.1.1.5 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase fractionation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

8.1.1.6 Prepare a filtration apparatus by suspending a funnel with either filter paper or a plug of glass wool and bed of sodium sulfate over a receiving vessel (a Kuderna-Danish vessel or Turbo-Vap tube).

8.1.1.7 Pour organic extract through the sodium sulfate bed and allow to drain into the receiving vessel. Be sure to rinse sodium sulfate thoroughly with methylene chloride after it had drained.

8.1.1.8 Repeat the extraction two more times using additional 60 mL portions of solvent. Combine the three solvent extracts in a 250-mL Erlenmeyer flask. (Steps 8.1.1.3 to 81.1.5)

8.1.1.9 For sample volume determination add water to the sample bottle to the level of the meniscus previously marked then transfer this water to a graduated cylinder.

8.1.2 Soil Extraction using ultrasonic probe

8.1.2.1 Weigh approximately 25g of soil into a 250mL beaker.

8.1.2.2 Add surrogate standard solution to all samples, blanks, laboratory control samples, and matrix spikes. Add laboratory control sample / matrix spike mixture to appropriate samples.

8.1.2.2 Mix anhydrous sodium sulfate into soil using a metal spatula. This should be done until the soil / sodium sulfate mixture has the consistency of beach sand.

8.1.2.3 Add approximately 60mL of methylene chloride until solids have

been covered to a depth of about ½ inch.

8.1.2.4 Place mixture under ultrasound horn and start sonication for two minutes.

8.1.2.5 Prepare a filtration apparatus by suspending a funnel with either filter paper or a plug of glass wool and bed of sodium sulfate over a receiving vessel (a Kuderna-Danish vessel or Turbo-Vap tube).

8.1.2.6 When sonication has finished, pour the solvent through the sodium sulfate bed and allow to drain into the receiving vessel. Be sure to rinse sodium sulfate thoroughly with methylene chloride after it has drained.

8.1.2.7 Repeat steps 8.1.2.3 - 8.1.2.6 two more times.

8.1.2.8 Go to sample concentration and solvent exchange step.

8.1.2.9

8.1.3 Extract concentration and solvent exchange

8.1.3.1 Using concentration apparatus, concentrate sample until its volume is less than 3mL.

8.1.3.2 Add nonpolar solvent (n-hexane); be sure to thoroughly mix the solution since methylene chloride may tend to stay at the bottom of the container.

8.1.3.3 Concentrate extract down to 5mL.

8.2 Aromatic / Aliphatic Fractionation

8.2.1 Cut the top off a 10mL disposable volumetric Pasteur pipette using a triangular file.

8.2.2 Place a small plug of glass wool into the pipette and slide it down into the taper.

8.2.3 Add a few grams of Ottawa sand to cover the glass wool and provide a flat bed for the silica gel.

8.2.4 Add silica gel to the pipette, with occasional shaking to ensure uniform packing, up to the 3mL mark.

8.2.5 Add another few grams of Ottawa sand to provide some protection to the silica gel bed.

8.2.6 Note the mark where the top of the silica gel is. Add n-hexane to the pipette up to one of the marks on the pipette where the analyst can track the volume of hexane.

8.2.7 When hexane begins to drip out the bottom of the pipette note the volume of hexane added to the top and the volume left. This will be the column volume. Allow one more column volume to pass through to rinse the silica gel and discard

the hexane.

8.2.8 When the hexane level has reached the top of the sand, add 1.0mL of hexane extract. Allow this to flow down into the sand before adding more hexane. Begin collecting hexane in graduated 15mL-centrifuge tube or volumetric Kuderna-Danish tube when $\frac{1}{2}$ to $\frac{3}{4}$ of a column volume of hexane has passed through the column.

8.2.9 Each solvent wash should consist of 1.5 to 2.5 column volumes to eliminate break through. With experience, the analyst should be able to determine the amount of wash needed.

8.2.10 When the hexane level has dropped into the sand, slowly add pure methylene chloride to the top of the column.

8.2.11 When $\frac{1}{2}$ to $\frac{3}{4}$ of a column wash of methylene chloride has passed through the silica gel, change collection tubes and mark the hexane fraction as Aliphatic.

8.2.12 Continue adding methylene chloride until 1.5 to 2.5 volumes have passed.

8.2.13 If the polar compounds are of interest, add a third wash of 5 - 10% methanol in methylene chloride. Otherwise, finish the methylene chloride wash with one additional column volume. Remove this fraction and label it Aromatic.

Note: The amount of solvent in each receiver should be approximately the same as the calculated column volume times the multiplication factor in use for the lab (1.5 to 2.5).

Note: Column overloading is a common occurrence. Dilution of samples prior to fractionation may be necessary to avoid unwanted breakthrough.

8.2.14 Using an appropriate concentration device, concentrate each fraction down to 1.0mL. If internal standard is used, add it now. Samples are ready for analysis.

8.3 Analysis

8.3.1 Gas Chromatograph Conditions (Recommended)

Parameter	Setting
Gas	Helium
Linear velocity	60 - 65cm/s
Initial Temp.	35°C
Initial Time	4min.
Rate	15°C/min.
Final Temp.	250°C
Hold	0min.
Rate II	25°C/min.
Final Temp. II	350°C
Hold II	5 - 10min.
Injector Temp.	310°C; Note: higher temperatures cause thermal cracking of hydrocarbons.
Detector Temp.	355°C

8.3.2 Gas Chromatograph Sequencing - A typical GC sequence must include a 24 hour retention time marker, a continuing calibration standard for every 10 injections -- that is, a beginning continuing calibration standard, and one after each subsequent 10 injections -- and an ending continuing calibration standard. Each sample batch should be analyzed in one sequence on the same instrument.

8.3.3 Calibration - A minimum of 5 concentrations of standard must be used to define the calibration curve. The concentration of each standard is the total of the concentrations of analytes present in that standard, hence, 5 analytes at 50µg/mL has a total concentration of 250µg/mL.

8.3.3.1 The lowest standard shall be equivalent to the reporting limit or a value three to five times the method detection limit, whichever is lower.

8.3.3.2 The highest concentration standard shall define the highest extract concentration that may be reported without dilution.

8.3.3.3 Whenever possible use a least squares linear regression for calibration. Quadratic curves and average of response factors are acceptable provided adequate quality control and performance parameters are consistently met.

9. Calculations

9.1 Response Factors

$$\text{Response Factor} = \frac{(Area_{x, std})}{(C_{x, std})} \quad \text{Eq. 1}$$

Where

$A_{x, std}$ = Area of analyte in standard.
 $C_{x, std}$ = Concentration of analyte in Standard in $\mu\text{g/mL}$.

9.2 Concentrations

9.2.1 Soil External Standard (example) – many software packages report concentrations of extracts without any problem. The following is for those cases where this is not done. It requires an average of response factors.

$$\text{Concentration in Soil (mg / Kg)} = \frac{(Area_x)(df)(V_f)(1000\mu\text{g / mg})}{(rf)(m_f)(W_i)} \quad \text{Eq. 2}$$

Where

A_x = Area of analyte in extract.
 df = Dilution Factor of extract.
 V_f = Final volume of extract after concentration step.
 rf = Response factor.
 m_f = Fractional dry mass (% Dryness)
 W_i = Initial Weight of soil sample.

Note: If instrument reports concentration in extract; that value can replace the $(Area_x/rf)$ portion of the equation.

9.2.2 Water External Standard (example) – many software packages report concentrations of extracts without any problem. The following is for those cases where this is not done. It requires an average of response factors.

$$\text{Concentration in Water } (\mu\text{g / L}) = \frac{(Area_x)(df)(V_f)}{(rf)(V_i)} \quad \text{Eq. 3}$$

Where

$A_x =$	Area of analyte in extract.
$df =$	Dilution Factor of extract.
$V_f =$	Final volume of extract after concentration step.
$rf =$	Response factor.
$V_i =$	Initial volume of water (aqueous) sample.

Note: If instrument reports concentration in extract; that value can replace the (A_{x}/rf) portion of the equation.

9.3 Fractional Mass of a soil – This is the fractional version of %Dryness for use in soil calculations.

$$\text{Fractional Mass} = \frac{(m_d)}{(m_s)} \quad \text{Eq. 4}$$

Where

$m_d =$	Weight of dried soil.
$m_s =$	Weight of sample before drying.

9.4 Relative Percent Difference

$$RPD = \frac{(X_1 - X_2)}{\frac{(X_1 + X_2)}{2}} * 100\% \quad \text{Eq. 5}$$

10 Quality Control

10.1 Retention Time Markers

10.1.1 A retention time marker must be analyzed at least once every 24-hour period or once each day of instrument operation.

10.1.2 The analyst must use the retention times for the ranges of interest from three separate retention time markers to determine acceptable retention time variation.

10.1.3 If the retention time of a retention time marker standard falls outside the established window, the retention time must be updated and a new retention time window established.

10.2 Initial Calibration – A minimum five-point calibration must be performed to establish the working range of the Gas Chromatograph.

10.2.1 An initial calibration must be made up for each fraction – aromatic and aliphatic – and must contain a minimum of three compounds.

10.2.2 The initial calibration should contain hydrocarbons representative of the particular fraction to be analyzed.

10.2.3 The lowest concentration must be between 3 and 5 times the method detection limit concentration or at the reporting limit concentration, whichever is lower.

10.2.4 The highest concentration will define the upper limit concentration that may be reported without extract dilution.

10.2.5 If a linear regression is used (recommended) the coefficient of correlation must be 0.98 or higher.

10.2.6 If an average of response factors is used the maximum %RSD must be no greater than 15%.

10.2.7 A quadratic calibration may be used if the GC software allows this type of calibration. The coefficient of correlation must not fall below 0.98.

10.2.8 All data points in the calibration should be weighted equally.

10.2.9 Corrective Actions

- a) If the initial calibration is outside the control limits, analysis shall not be performed.**
- b) Reintegrate all standards.**
- c) Prepare and reanalyze a new curve.**

10.3 Second Source Calibration Verification – A standard used to verify the initial calibration.

10.3.1 The second source calibration verification may be made up from a standard similar to the initial calibration at an intermediate level.

10.3.2 The second source compounds must be obtained from a separate source than the initial calibration compounds.

10.3.3 A middle diesel range distillate may be used in the place of a synthetic calibration standard provided more than 95% of the hydrocarbon area elutes within the ADEC defined diesel range.

10.3.4 The second source calibration verification standard may also be used as the continuing calibration standard.

10.3.5 The recovery of the second source calibration verification must be +/- 15% of the true value.

10.3.6 Corrective Actions

- a) If the second source verification standard is outside the control limits, analysis shall not be performed.**
- b) Reanalyze the second source calibration verification standard.**

- c) **Reprepare a new standard.**
- d) **Reprepare and analyze a new initial calibration.**

10.4 Instrument Blank

10.4.1 Must be below reporting limits before proceeding with further analysis.

10.4.2 Must be analyzed at least once every 24 hours of instrument operation.

10.4.3 An instrument blank is recommended after samples high in concentration.

10.4.4 Corrective Actions

- a) **If an instrument blank is outside the limits all samples associated with that blank must be reanalyzed.**

10.5 Continuing Calibration Standard

10.5.1 The Continuing Calibration Standard may be made up from a standard similar to the initial calibration at an intermediate level.

10.5.2 A middle diesel range distillate (e.g. DF-2) may be used in the place of a synthetic calibration standard provided more than 95% of the hydrocarbon area elutes within the ADEC defined diesel range.

10.5.3 The continuing calibration standard may also be used as the second source calibration verification.

10.5.4 The recovery of the second source calibration verification must be +/- 15% of the true value.

10.5.5 A continuing calibration standard must be analyzed at the beginning of an analytical run, once every 10 injections on the GC, and at the close of the run.

10.5.6 Corrective Actions

- a) **If a Continuing Calibration Verification is outside the limits, all samples associated with that standard must be reanalyzed.**
- b) **Be certain Continuing Calibration Verification is fresh and within limits.**

10.6 Method Blank

10.6.1 The method blank must be made up from a matrix similar to the samples within the analytical batch (e.g. water for aqueous, sand for sandy soil, clean loam for mossy high biomass samples)

10.6.2 Surrogate standards must be added to all method blanks and must fall within the window of 70 – 120% of the true values.

10.6.3 The method blank must be free of contamination (below reporting limits) within the specified range.

10.6.4 Corrective actions

- a) **Reanalyze method blank being sure no instrument carryover is present.**
- b) **If problem persists, or surrogates are outside acceptable ranges, associated analytical batch must be re-extracted and analyzed.**

10.7 Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS/LCSD).

10.7.1 The LCS/LCSD/Matrix Spiking working standard must be made up of a synthetic mixture of analytes. A minimum of three aromatic and three aliphatic compounds must be used for each range (DRO, RRO, GRO).

10.7.2 The LCS/LCSD should be made up from a matrix similar to the samples within the analytical batch (e.g. water for aqueous, sand for sandy soil, clean loam for mossy high biomass samples)

10.7.3 Surrogate standards must be added to all LCS/LCSD and must fall within the window of 70 – 120% of the true values.

10.7.4 Matrix spiking/LCS compounds must be added to all LCS/LCSD samples and must fall within the window of 70 – 120% of the true values.

10.7.5 Compounds from the other fraction must not exceed 10% (e.g. the aliphatic LCS/LCSD samples may not have more than 10% recovery of any single aromatic LCS/LCSD/Matrix Spiking compound or visa versa).

10.7.6 The duplicate must have a relative percent difference of less than 20%.

10.7.7 Corrective actions

- a) **Reanalyze LCS/LCSD being sure no instrument carryover is present.**
- b) **If problem persists, or surrogates are outside acceptable ranges, associated analytical batch must be re-extracted, re-fractionated, and/or re-analyzed.**

10.8 Matrix Spike (MS)

10.8.1 The LCS/LCSD/Matrix Spiking working standard must be made up of a synthetic mixture of analytes. A minimum of three aromatic and three aliphatic compounds must be used for each range (DRO, RRO, GRO).

10.8.2 The matrix spike must be made up from a sample within the analytical batch.

10.8.3 Surrogate standards must be added to all matrix spike samples and should fall within the window of 50 - 150% of the true values.

10.8.4 Matrix spiking/LCS compounds must be added to all matrix spike samples and should fall within the window of 50 - 150% of the true values.

10.8.5 Compounds from the other fraction must not exceed 10% recovery (e.g. the

aliphatic matrix spike samples may not have more than 10% recovery of any single aromatic LCS/LCSD/Matrix Spiking compound or visa versa).

10.8.6 Corrective actions

No corrective actions are required for a matrix spike that is out of compliance.

10.9 Surrogate Spikes

10.9.1 At least one aromatic and one aliphatic surrogate compound which does not coelute or otherwise interfere with the analytes of interest must be added to each sample, method blank, LCS/LCSD, and matrix spike.

10.9.2 Since diesel and residual range compounds are often analyzed together, one compound per fraction will suffice for the modified AK102/103 combined method.

10.9.3 The recovery of surrogate standards must not be outside the range 70 – 120% for method blanks and LCS/LCSD samples.

10.9.4 The recovery of surrogate standards should not be outside the range 50 - 150% for all remaining samples and matrix spikes.

10.9.5 Surrogate compounds from the other fraction must not exceed 10% recovery in a given fraction (e.g. the aliphatic samples or matrix spikes may not have more than 10% recovery of any single aromatic surrogate compound or visa versa).

10.9.6 The polar surrogate shall not be observed above 10% recovery in any sample, method blank, LCS/LCSD, or matrix spike.

10.9.7 Corrective Actions

- a) If the surrogates for a sample are out of limits, that sample must be re-extracted, re-fractionated, and/or re-analyzed.**
- b) If a surrogate is out of limits in the same direction (e.g. low both times) for a second time, the report shall reflect a matrix effect.**
- c) If a surrogate is higher than limits for the opposing fraction, that sample shall be re-extracted, re-fractionated, and/or re-analyzed. Care must be taken to ensure the quality and the activity of the silica gel or alumina or other adsorptive material in the fractionation column.**
- d) If a surrogate compound is out of limits for a method blank or LCS/LCSD sample, that sample must first be re-analyzed; then, if still out, the entire analytical batch must be re-extracted, re-fractionated, and re-analyzed.**

11. References

- 11.01** Alaska Department of Environmental Conservation, Methods AK102 & AK103.
- 11.02** The Federal Register, 62 FR 52098, Oct 1997.
- 11.03 Massachusetts** Department of Environmental Protection and ABB Environmental Services, Inc., Wakefield, MA "Interim Petroleum Policy: Development of Health-based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter", August 1994.
- 11.04** USEPA, "Measurement of Petroleum Hydrocarbons: Report on Activities to Develop a Manual" Prepared by Midwest Research Institute, Falls Church, VA, under EPA Contract #68-WO-0015, WA No. 4; submitted to USEPA Office of Underground Storage Tanks, Washington, DC; November 20, 1990.
- 11.05** USEPA Regulations 40 C.F.R. 136, Appendix B, "Guidelines Establishing Test procedures for the Analysis of Pollutants", July 1992.
- 11.06** USEPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846), Method 3510: Separatory Funnel Liquid-Liquid Extraction; September 1986.
- 11.07** USEPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846), Method 3540: Soxhlet Extraction; September 1986
- 11.08** USEPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846), Method 3630: Silica Gel Cleanup; September 1986
- 11.09** USEPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846), Method 8000: Gas Chromatography; September 1986
- 11.10** USEPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846), Method 8100: Polynuclear Aromatic Hydrocarbons; September 1986
- 11.11** Wisconsin Department of Natural Resources, "Modified DRO - Method for Determining Diesel Range Organics", PUBL-SW-141, 1992
- 11.12** USEPA, "Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring", EPA 821-B-93-001; U.S. Government Printing Office, Washington D.C., June, 1993

Method AK 103AA
For Determination of Aromatic and Aliphatic Hydrocarbons in
Residual Range Organics
Version 6-30-98

1 Scope & Application

1.1 This method is used for the extraction, fractionation, and quantification of aromatic and aliphatic compounds in the residual range. Adopted methodology by the Alaska Department of Environmental Conservation (ADEC) has established guidelines defining gasoline range organics (GRO), diesel range organics (DRO), and residual range organics (RRO) for gross organic measurements by Gas Chromatography. The intention of this method is to use these existing criteria and provide guidance for the fractionation and quantification of aromatic and aliphatic compounds within these ranges.

1.2 This, and most other aliphatic aromatic, fractionation methods are based on the EPA SW-846 Method 3630 and related techniques employed throughout the petroleum industry.

1.3 This method provides guidance for laboratories interested in performing aromatic and aliphatic fractionation. It also defines general quality control guidelines and control limits to be used until statistical data is available.

1.4 This method is designed for the fractionation of aromatic / aliphatic compounds in the residual range. This has been defined as the beginning of C₂₅ to the end of C₃₆. This range includes heavy heating oils, lubricating oils, and hydraulic fluids. This method is typically employed along with its diesel range organic counterpart in a combination analysis.

1.5 It is important to note fuels are crude oil distillates. This method is designed to accurately measure aromatic and aliphatic compounds that fall only between the listed n-alkane hydrocarbons. Because distillates are complex mixtures of hydrocarbons, they may extend beyond the ranges defined by the ADEC.

1.6 This is a performance-based method. EPA has recently published guidelines for performance-based methodology -- 62 FR 52098. The intention is to encourage method development within the laboratory community that will 1) decrease costs of analysis, 2) increase analytical precision and accuracy, 3) allow laboratories to better fit methods to data quality objectives.

1.7 Being a performance-based method, heavy reliance on performance evaluation samples will be required. Laboratories shall request, analyze, and submit performance evaluation samples on a periodic basis to retain ADEC approval.

1.8 This document is meant to be a guidance document; it shall not take the place of an individual laboratory Standard Operating Procedure or training program. Each laboratory shall maintain a Standard Operating Procedure that thoroughly describes the method, techniques employed, and verification of method performance. The laboratory shall,

also, maintain training records for analysts who perform tasks related to this method. Major variances from this method shall be disclosed on data report forms.

2 Summary of Method

2.1 While several techniques are available for aromatic and aliphatic fractionation analysis that may produce the desired results, the method listed has been found preferable.

2.2 The extraction, fractionation, and quantification of residual range aromatic and residual range aliphatic hydrocarbons are described.

2.3 Hydrocarbons extracted from a water, soil, or sludge sample are extracted with methylene chloride and concentrated in accordance with AK102 and AK103.

2.4 Methylene chloride in the extracts is exchanged for n-hexane or another appropriate non-polar solvent and passed through a bed of silica gel. The silica gel is first washed with the non-polar solvent to collect the aliphatic hydrocarbons, then with a moderately polar solvent to collect aromatic hydrocarbons. The washes are concentrated for analysis.

2.5 Concentrated aromatic and aliphatic samples are analyzed by gas chromatography (GC). The GC shall be equipped with an oven capable of temperature programming and an analytical column capable of separating residual range compounds within the specifications outlined in this document. It shall also be equipped with a detector capable of detecting carbon or carbon ions -- the typical detector is the Flame Ionization Detector (FID), an Atomic Emission Detector (AED), or other detector capable of measuring the amount of carbon present in a sample independent of the final component that may be observed. Data shall be collected by a data collection system capable of providing a chromatographic trace and integration of the selected hydrocarbon range.

3 Definitions

3.1 Gasoline Range Organics - Organic compounds which elute by gas chromatography between the beginning of n-C₆ and the beginning of n-C₁₀.

3.2 Diesel Range Organics - Organic compounds which elute by gas chromatography between the beginning of n-C₁₀ and the beginning of n-C₂₅.

3.3 Residual Range Organics - Organic compounds which elute by gas chromatography between the beginning of n-C₂₅ and the end of n-C₃₆.

3.4 Instrument Blank - A clean solvent analyzed to demonstrate the cleanliness of the analytical system.

3.5 Analytical Batch - A set of samples, not to exceed 20, which are extracted, concentrated, and fractionated together. Each analytical batch shall consist of 20 or fewer samples, a method blank, two laboratory control samples, and a matrix spike.

3.6 Method Blank - A sample of clean sand or clean water that is spiked with surrogate compounds, extracted, and fractionated along with the analytical batch of samples.

3.7 Retention Time Marker - A standard used to demonstrate the integration ranges for GRO, DRO, and RRO.

3.8 Initial Calibration - A set of standards used to define the concentration calibration range of the gas chromatograph. The concentration of the lowest standard must be between 3 and 5 times the method detection limit for this analysis. The initial calibration mixture is a mixture of several compounds within the proper range. These compounds shall span the entire GRO, DRO, or RRO ranges.

3.9 Calibration Verification - A standard, independent of the initial calibration mixture, used to verify the accuracy of the initial calibration. Since the residual range is somewhat abbreviated and a single oil or other heavy distillate where over 95% of the hydrocarbon elutes within the carbon range limits, a synthetic calibration verification standard is recommended.

3.10 Continuing Calibration - A mid-range calibration standard used to verify the initial calibration while analyzing samples. A continuing calibration standard shall be analyzed with every 10 analytical injections on the gas chromatograph.

3.11 Surrogate Standard Compounds - Compounds not typically present in GRO, DRO, or RRO hydrocarbons, which are placed in known quantities in each sample, method blank, laboratory control sample, and matrix spike to determine the recovery and accuracy of the analysis. The surrogate mixture shall contain, at a minimum, one aromatic compound and one aliphatic compound. A secondary use of the surrogate standard is to demonstrate the effectiveness of the fractionation. Control limits shall be placed on the amount of surrogate breakthrough observed in each sample, method blank, laboratory control sample, and matrix spike.

3.12 Matrix Spiking / Laboratory Control Compounds - A combination of aromatic and aliphatic compounds added to laboratory control samples and matrix spikes to demonstrate laboratory precision and accuracy.

3.13 Silica Gel Breakthrough – Defined as the effect of using either inactive silica gel, too much solvent, inappropriate solvent, or overloading on silica gel column where compounds which should be retained on the silica gel breakthrough into the fraction. Surrogate compounds are typically used to determine whether column breakthrough has occurred.

3.14 Aromatic Compounds - Hydrocarbon compounds which are related to benzene.

3.15 Aliphatic Compounds - Paraffins, olefins, branched paraffins, and cyclic paraffins. These compounds have no or few carbon - carbon double bonds and make up the majority of fuels

3.16 Polar Compounds – Typically, associated with biomass. In the terms of this method, these are considered undesirable compounds and are removed if proper corrective action techniques are used.

3.17 Method Detection Limit (MDL) – The minimum concentration of a compound that can be measured and reported with 99 percent confidence that the value is greater than zero, determined from analysis of a sample in a given matrix containing the analyte. (See 40 C.F.R. 136, Appendix B, for method of determining method detection limit. Each laboratory must demonstrate and periodically maintain method detection limits for each analyte of interest. A method detection limit is a statistical quantity defined as the point where one has a 99% confidence they are not seeing either a false positive or a false negative. Near the MDL the confidence in quantification is very low.)

3.18 Quantification Limit - Practical quantitation limit (PQL) is a certain point where one has a 95% confidence in the quantification of a substance. Practical quantitation limits (PQL) for this method for analysis of RRO must not exceed 20 mg/kg for soils.

3.19 Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS/LCSD) - These samples are used by the laboratory to demonstrate a method's precision and accuracy. These are samples identical to a method blank with the exception they are spiked with a known amount of analyte. They are taken through the entire extraction and analytical process.

3.19 Matrix Spike - An actual sample that is spiked with a known amount of analyte. This sample can give valuable information about the behavior of analytes in this sample and may be extrapolated to other samples from the same area.

4 Interferences

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines causing misinterpretation of gas chromatograms. All of these materials must be demonstrated to be free from interference under the conditions of the analysis, by analyzing reagent and method blanks.

4.2 High purity reagents must be used to minimize interference problems.

4.3 Washing all glassware with hot soapy water and then rinsing with warm tap water, acetone, and methylene chloride reduces method interferences.

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

4.5 Matrix interferences may be caused by contaminants that are co-extracted from the

sample. The extent of matrix interference will vary considerably from one source to another depending upon the nature and diversity of the site being sampled. Many polar compounds commonly attributed to "biogenic" sources should be removed by the silica gel if properly used. Several petroleum precursors are present in aging vegetation and peat; these compounds will not be removed using this technique.

4.6 The leaching of plasticizers and other compounds have been observed from commercially available silica gel cartridges used to fractionate DRO and RRO sample extracts. Concerns of this nature must be continuously monitored and documented by analysis of Laboratory Method Blanks.

4.7 Chromatographic columns typically "bleed" stationary phase material at high temperatures. This bleed may interfere with the residual range causing elevated method detection and reporting limits. The analyst should take precautions to either eliminate this or correct for it. Typically, the use of a column compensation program by the gas chromatograph will yield satisfactory results.

5 Health and Safety

The toxicity and carcinogenic nature of each reagent used in this method has not been precisely defined. 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 safety program to minimize exposure and potential hazards from personnel. A reference file of material safety data sheets (MSDS) shall be made available to all personnel.

6 Apparatus and Materials

6.1 Equipment

6.1.1 Gas Chromatograph: An analytical system with temperature programmable gas chromatograph for use with capillary columns is required. The data system must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.1.2 Recommended chromatographic column: A J&W DB-5MS 30m x 0.32mm ID x 0.10µm stationary phase has been successfully used. Any column capable of separating diesel and residual range compounds with minimal column bleed may be used.

6.1.3 A concentration apparatus capable of using clean air or nitrogen to remove excess solvent from samples shall be used. These systems range from a combination of Kuderna-Danish concentrators and N-Evap apparatus, to automated Turbo-Vap systems.

6.1.4 Soil extraction equipment: Soxhlet continuous extractors and ultrasonic cell disrupters have been used for the extraction of soil samples.

6.1.5 Analytical balances:

6.1.5.1 An analytical balance capable of measuring 0.0001g is required for

standards preparation.

6.1.5.2 An analytical balance capable of measuring 0.01g is required for measuring sample weights.

6.1.6 Drying oven: an oven capable of maintaining 150°C is used for drying of sodium sulfate and activation of silica gel.

6.2 Glassware

6.2.1 Beakers - 250mL or 400mL.

6.2.2 2L separatory funnels or equivalent (continuous extractors, etc.).

6.2.2 Long stemmed funnels.

6.2.3 Kuderna-Danish concentrator or equivalent (Turbo Vap tubes, etc.).

6.2.4 10mL graduated disposable pipettes or equivalent.

6.2.5 Graduated cylinders - 50mL & 100mL.

6.2.6 Graduated centrifuge tubes or equivalent - 10mL or 15mL.

6.2.7 Autosampler vials or extract containers.

6.1.8 Syringes - 10, 25, 100, 500, and 1000 μ L.

6.3 Reagents

6.3.1 Methylene chloride - analytical grade or better, must be demonstrated to be below method detection limits for diesel and residual range contaminants.

6.3.2 n-Hexane - analytical grade or better, must be demonstrated to be below method detection limits for diesel and residual range contaminants.

6.3.3 Ottawa sand - cleaned beach sand used for soil method blanks.

6.3.4 Sodium sulfate - Anhydrous, granulated, used for drying soil samples and all methylene chloride extracts.

6.3.5 Silica gel - Anhydrous, 60 - 100 mesh has been used successfully. Prepacked extraction cartridges may be used provided they meet the quality control performance criteria listed in this document.

IMPORTANT: silica gel should be activated by placing in a 150°C oven prior to use, prolonged exposure to moist air will cause high surrogate breakthrough in samples, method blanks, laboratory control samples, and matrix spikes.

6.3.6 Glass wool - Pesticide grade or better.

6.4 Standards

6.4.1 Retention time marker - shall consist of a minimum of n-C₁₀ (required only if used in conjunction with DRO analysis), n-C₂₅, and n-C₃₆. More n-alkanes are recommended. This mixture is typically injected into the GC at a concentration of 50 μ g/mL for each compound.

6.4.2 Initial calibration mixtures: Since it is impractical and nearly impossible to use a commercial residual range distillate for calibration a synthetic mixture must be used. The use of a Flame Ionization Detector or other “carbon counting” detector allows a free association between fuel-derived hydrocarbon compounds providing little or no injector discrimination is present.

Choose a minimum of three -- recommend five or more -- which span the entire residual range. The concentration of the standard is the total of all the individual compounds.

Each compound should be in the same concentration as the others in solution. A minimum of five dilutions of this mixture must be used for calibration purposes. The lowest concentration standard shall be within a factor of three to five of the method detection limit or at the reporting limit, whichever is lower. The highest concentration shall define the upper limit to the calibration. Sample extracts that contain concentrations higher than the calibration curve shall be diluted and reanalyzed.

6.4.2.1 Aromatic - A minimum of three aromatic compounds, which span the residual range, should be used for calibration purposes. Polynuclear aromatic hydrocarbons (PAHs) and their homologues generally suit the purpose of this calibration.

6.4.2.2 Aliphatic - A minimum of three aliphatic compounds, which span the residual range, should be used for calibration purposes. N-alkanes: C₂₆, C₂₈, C₃₀, C₃₂, and C₃₄ have been successfully used.

6.4.3 Calibration verification mixture - A synthetic blend of compounds which elute in the residual range is recommended. Any hydrocarbon mixture where more than 95% of the hydrocarbon elutes in the residual range and is independent of the initial calibration may be used.

6.4.4 Continuing Calibration mixture - A mid-level standard using the same or similar compounds used in the initial calibration mixture should be prepared for this purpose.

6.4.5 Surrogate standard mixture - A surrogate mixture shall be made in methylene chloride and shall contain compounds from the three major fractions present in most samples -- aliphatic, aromatic, and polar. Working standards should be prepared to yield a concentration of 100µg/mL of the proper surrogate in the each of the final fractions.

6.4.5.1 Squalane has been successfully used for the aliphatic surrogate; although it elutes in the residual range no problems have been observed.

6.4.5.2 o-Terphenyl has been used as an aromatic surrogate with great success; few interference problems have been observed.

6.4.5.3 Tetrahydronaphthol has been successfully used as a polar surrogate to monitor the elution of polar compounds with the aromatic fraction.

Note: The surrogate standard mixture shall be made up in methylene

chloride or hexane, NOT methanol or acetone, even small amounts of these solvents greatly affect the polarity of the final solutions and will be detrimental to the fractionation.

6.4.6 Internal standard mixture (optional) - 5- α -Androstane may be used as an optional internal standard if deemed necessary by the analyst.

6.4.7 Laboratory control sample / matrix spike mixture - A mixture of aromatic and aliphatic compounds -- a minimum of three each -- shall be used as a laboratory control sample / matrix spike mixture. The mixture shall contain both aromatic and aliphatic compounds and have a concentration sufficient such that a final concentration in each extract fraction is 50 μ g/mL of each component. For example, if five aromatics and five aliphatics are used then the final concentration of each fraction should be 250 μ g/mL.

Note: The laboratory control sample / matrix spike mixture must be made up in methylene chloride or hexane, NOT methanol or acetone, even small amounts of these solvents greatly affect the polarity of the final solutions and will be detrimental to the fractionation.

7 Sample Collection, Preservation, and Handling

7.1 Aqueous samples are collected in 1-liter amber glass bottles with Teflon-lined screw caps.

7.2 Soil and sediment samples are collected in 4 oz. (120 mL) amber wide-mouth glass jars with Teflon-lined screw caps.

7.3 Aqueous samples must be preserved at the time of sampling by the addition of a suitable acid to reduce the pH of the sample to less than 2.0. This may be accomplished by the addition of 5 mL of 1:1 HCl to a 1 liter sample. The use of alternative acids is permissible. Following collection and addition of acid, the sample must be cooled to 4°C.

7.4 Soil and sediment samples must be cooled to 4°C immediately after collection.

7.5 A chain of custody form must accompany all aqueous, soil and sediment samples, documenting the time and date of sampling and any preservative additions.

7.6 Aqueous samples must be extracted within 7 days of collection, and analyzed within 40 days of extraction.

7.7 Soil and sediment samples must be extracted within 14 days of collection, and analyzed within 40 days of extraction.

8 Procedure

8.1 Sample Preparation - Samples are extracted using methylene chloride, and, later, solvent-exchanged into hexane. An acceptable extraction procedure for water samples is a separatory funnel liquid/liquid extraction technique based upon SW-846 Method 3510A; continuous liquid/liquid extraction has also proven effective. For soil or sediment samples, use of a Soxhlet or Soxtec technique is recommended. Alternative

extraction procedures are acceptable, provided that the laboratory can document acceptable performance.

8.1.1 Water Extraction

8.1.1.1 Mark the meniscus on the 1-liter sample bottle (for later volume determination) and transfer it to a 2-liter separatory funnel. For blanks and quality control samples, pour 1 liter of reagent water into the separatory funnel. Check the pH of the sample with wide-range pH paper. Note the pH in a laboratory logbook or preparatory sheet.

The pH of the sample need not be adjusted.

8.1.1.2 Add 1.0 mL of the surrogate spiking solution to all samples, blanks, laboratory control samples, and matrix spikes. For samples selected for spiking, add laboratory control sample / matrix spike solution.

8.1.1.3 Add 60mL methylene chloride to the sample bottle to rinse the inner walls of the container and add this solvent to the separatory funnel.

8.1.1.4 Seal and shake each separatory funnel vigorously for 2 minutes with periodic venting to release excess pressure.

NOTE: Methylene chloride creates excessive pressure very rapidly; therefore, venting into a hood should be done immediately after the separatory funnel has been sealed and shaken once.

8.1.1.5 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, the analyst must employ mechanical techniques to complete the phase fractionation. The optimum technique depends upon the sample and may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods.

8.1.1.6 Prepare a filtration apparatus by suspending a funnel with either filter paper or a plug of glass wool and bed of sodium sulfate over a receiving vessel (a Kuderna-Danish vessel or Turbo-Vap tube).

8.1.1.7 Pour organic extract through the sodium sulfate bed and allow to drain into the receiving vessel. Be sure to rinse sodium sulfate thoroughly with methylene chloride after it has drained.

8.1.1.8 Repeat the extraction two more times using additional 60 mL portions of solvent. Combine the three solvent extracts in a 250-mL Erlenmeyer flask. (Steps 8.1.1.3 to 8.1.1.5)

8.1.1.9 For sample volume determination, add water to the sample bottle to the level of the meniscus previously marked, then transfer this water to a graduated cylinder.

8.1.2 Soil Extraction using ultrasonic probe

8.1.2.1 Weigh approximately 25g of soil into a 250mL beaker.

8.1.2.2 Add surrogate standard solution to all samples, blanks, laboratory control samples, and matrix spikes. Add laboratory control sample / matrix spike mixture to appropriate samples.

8.1.2.2 Mix anhydrous sodium sulfate into soil using a metal spatula. This should be done until the soil / sodium sulfate mixture has the consistency of beach sand.

8.1.2.3 Add approximately 60mL of methylene chloride until solids have been covered to a depth of about ½ inch.

8.1.2.4 Place mixture under ultrasound horn and start sonication for two minutes.

8.1.2.5 Prepare a filtration apparatus by suspending a funnel with either filter paper or a plug of glass wool and bed of sodium sulfate over a receiving vessel (a Kuderna-Danish vessel or Turbo-Vap tube).

8.1.2.6 When sonication has finished, pour the solvent through the sodium sulfate bed and allow to drain into the receiving vessel. Be sure to rinse sodium sulfate thoroughly with methylene chloride after it had drained.

8.1.2.7 Repeat steps 8.1.2.3 - 8.1.2.6 two more times.

8.1.2.8 Go to sample concentration and solvent exchange step.

8.1.3 Extract concentration and solvent exchange

8.1.3.1 Using concentration apparatus, concentrate sample until its volume is less than 3mL.

8.1.3.2 Add nonpolar solvent (n-hexane); be sure to thoroughly mix the solution since methylene chloride may tend to stay at the bottom of the container.

8.1.3.3 Concentrate extract down to 5mL.

8.2 Aromatic / Aliphatic Fractionation

8.2.1 Cut the top off a 10mL disposable volumetric Pasteur pipette using a triangular file.

8.2.2 Place a small plug of glass wool into the pipette and slide it down into the taper.

8.2.3 Add a few grams of Ottawa sand to cover the glass wool and provide a flat bed for the silica gel.

8.2.4 Add silica gel to the pipette, with occasional shaking to ensure uniform packing, up to the 3mL mark.

8.2.5 Add another few grams of Ottawa sand to provide some protection to the silica gel bed.

8.2.6 Note the mark where the top of the silica gel is. Add n-hexane to the pipette up to one of the marks on the pipette where the analyst can track the volume of hexane.

8.2.7 When hexane begins to drip out the bottom of the pipette, note the volume of hexane added to the top and the volume left. This will be the column volume. Allow one more column volume to pass through to rinse the silica gel and discard the hexane.

8.2.8 When the hexane level has reached the top of the sand, add 1.0mL of hexane extract. Allow this to flow down into the sand before adding more hexane. Begin collecting hexane in graduated 15mL-centrifuge tube or volumetric Kuderna-Danish tube when $\frac{1}{2}$ to $\frac{3}{4}$ of a column volume of hexane has passed through the column.

8.2.9 Each solvent wash should consist of 1.5 to 2.5 column volumes to eliminate break through. With experience, the analyst should be able to determine the amount of wash needed.

8.2.10 When the hexane level has dropped into the sand, slowly add pure methylene chloride to the top of the column.

8.2.11 When $\frac{1}{2}$ to $\frac{3}{4}$ of a column wash of methylene chloride has passed through the silica gel, change collection tubes and mark the hexane fraction as Aliphatic.

8.2.12 Continue adding methylene chloride until 1.5 to 2.5 volumes have passed.

8.2.13 If the polar compounds are of interest, add a third wash of 5 - 10% methanol in methylene chloride. Otherwise, finish the methylene chloride wash with one additional column volume. Remove this fraction and label it Aromatic.

Note: The amount of solvent in each receiver should be approximately the same as the calculated column volume times the multiplication factor in use for the lab (1.5 to 2.5).

Note: Column overloading is a common occurrence. Dilution of samples prior to fractionation may be necessary to avoid unwanted breakthrough.

8.2.14 Using an appropriate concentration device, concentrate each fraction down to 1.0mL. If internal standard is used, add it now. Samples are ready for analysis.

8.3 Analysis

8.3.1 Gas Chromatograph Conditions (Recommended)

Parameter	Setting
Gas	Helium
Linear velocity	60 - 65cm/s

Initial Temp.	35°C
Initial Time	4min.
Rate	15°C/min.
Final Temp.	250°C
Hold	0min.
Rate II	25°C/min.
Final Temp. II	350°C
Hold II	5 - 10min.
Injector Temp.	310°C; Note: higher temperatures cause thermal cracking of hydrocarbons.
Detector Temp.	355°C

8.3.2 Gas Chromatograph Sequencing - The GC sequence must include a 24 hour retention time marker, a continuing calibration standard for every 10 injections -- that is, a beginning continuing calibration standard, and one after each subsequent 10 injections -- and an ending continuing calibration standard. Each sample batch should be analyzed in one sequence on the same instrument.

8.3.3 Calibration - A minimum of 5 concentrations of standard must be used to define the calibration curve. The concentration of each standard is the total of the concentrations of analytes present in that standard, hence, 5 analytes at 50µg/mL has a total concentration of 250µg/mL.

8.3.3.1 The lowest standard shall be equivalent to the reporting limit or a value three to five times the method detection limit, whichever is lower.

8.3.3.2 The highest concentration standard shall define the highest extract concentration that may be reported without dilution.

8.3.3.3 Whenever possible, use a least squares linear regression for calibration. Quadratic curves and average of response factors are acceptable provided adequate quality control and performance parameters are consistently met.

9 Calculations

9.1 Response Factors

$$Response\ Factor = \frac{(Area_{x, std})}{(C_{x, std})}$$

Eq. 1

Where

$A_{x, \text{std}}$ = Area of analyte in standard.
 $C_{x, \text{std}}$ = Concentration of analyte in Standard in $\mu\text{g/mL}$.

9.2 Concentrations

9.2.1 Soil External Standard (example) – many software packages will report concentrations of extracts without any problem. The following is for those cases where this is not done. It requires an average of response factors.

$$\text{Concentration in Soil (mg / Kg)} = \frac{(Area_x)(df)(V_f)(1000\mu\text{g / mg})}{(rf)(m_f)(W_i)} \quad \text{Eq. 2}$$

Where

A_x = Area of analyte in extract.
 df = Dilution Factor of extract.
 V_f = Final volume of extract after concentration step.
 rf = Response factor.
 m_f = Fractional dry mass (% Dryness)
 W_i = Initial Weight of soil sample.

Note: If instrument reports concentration in extract; that value can replace the $(Area_x/rf)$ portion of the equation.

9.2.2 Water External Standard (example) – many software packages will report concentrations of extracts without any problem. The following is for those cases where this is not done. It requires an average of response factors.

$$\text{Concentration in Water } (\mu\text{g / L}) = \frac{(Area_x)(df)(V_f)}{(rf)(V_i)} \quad \text{Eq. 3}$$

Where

A_x = Area of analyte in extract.
 df = Dilution Factor of extract.
 V_f = Final volume of extract after concentration step.
 rf = Response factor.
 V_i = Initial volume of water (aqueous) sample.

Note: If instrument reports concentration in extract; that value can replace the

(Area_x/rf) portion of the equation.

9.3 Fractional Mass of a soil – This is the fractional version of %Dryness for use in soil calculations.

$$\text{Fractional Mass} = \frac{(m_d)}{(m_s)} \quad \text{Eq. 4}$$

Where

m_d = Weight of dried soil.
 m_s = Weight of sample before drying.

9.4 Relative Percent Difference

$$RPD = \frac{(X_1 - X_2)}{\frac{(X_1 + X_2)}{2}} * 100\% \quad \text{Eq. 5}$$

10 Quality Control

10.1 Retention Time Markers

10.1.5 A retention time marker must be analyzed at least once every 24-hour period or once each day of instrument operation.

10.1.6 The analyst must use the retention times for the ranges of interest from three separate retention time markers to determine acceptable retention time variation.

10.1.7 If the retention time of a retention time marker standard falls outside the established window, the retention time must be updated and a new retention time window established.

10.2 Initial Calibration – A minimum five-point calibration must be performed to establish the working range of the Gas Chromatograph.

10.2.1 An initial calibration must be made up for each fraction – aromatic and aliphatic – and must contain a minimum of three compounds.

10.2.2 The initial calibration should contain hydrocarbons representative of the particular fraction to be analyzed.

10.2.3 The lowest concentration must be between 3 and 5 times the method detection limit concentration or at the reporting limit concentration, whichever is lower.

10.2.4 The highest concentration will define the upper limit concentration that

may be reported without extract dilution.

10.2.5 If a linear regression is used (recommended), the coefficient of correlation must be 0.98 or higher.

10.2.6 If an average of response factors is used, the maximum %RSD must be no greater than 15%.

10.2.7 A quadratic calibration may be used if the GC software allows this type of calibration. The coefficient of correlation must not fall below 0.98.

10.2.8 All data points in the calibration should be weighted equally.

10.2.9 Corrective Actions

- a) If the initial calibration is outside the control limits, analysis shall not be performed.**
- b) Reintegrate all standards.**
- c) Prepare and reanalyze a new curve.**

10.3 Second Source Calibration Verification – A standard used to verify the initial calibration.

10.3.1 The second source calibration verification may be made up from a standard similar to the initial calibration at an intermediate level.

10.3.2 The second source compounds must be obtained from a separate source than the initial calibration compounds.

10.3.3 A residual range distillate may be used in the place of a synthetic calibration standard provided more than 95% of the hydrocarbon area elutes within the ADEC defined residual range.

10.3.4 The second source calibration verification standard may also be used as the continuing calibration standard.

10.3.5 The recovery of the second source calibration verification must be +/- 15% of the true value.

10.3.6 Corrective Actions

- a) If the second source verification standard is outside the control limits, analysis shall not be performed.**
- b) Reanalyze the second source calibration verification standard.**
- c) Reprepare a new standard.**
- d) Reprepare and analyze a new initial calibration.**

10.4 Instrument Blank

10.4.1 Must be below reporting limits before proceeding with further analysis.

10.4.2 Must be analyzed at least once every 24 hours of instrument operation or when a sample when instrument carryover is suspected.

10.4.3 An instrument blank is recommended after samples high in concentration.

10.4.4 Corrective Actions

- a) If an instrument blank is outside the limits, all samples associated with that blank must be reanalyzed.**

10.5 Continuing Calibration Standard

10.5.1 The Continuing Calibration Standard may be made up from a standard similar to the initial calibration at an intermediate level.

10.5.2 A residual range distillate may not be used in the place of a synthetic calibration standard since more than 95% of the hydrocarbon area of any known distillate will elute within the ADEC defined residual range.

10.5.3 The continuing calibration standard may also be used as the second source calibration verification.

10.5.4 The recovery of the second source calibration verification must be +/- 15% of the true value.

10.5.6 A continuing calibration standard must be analyzed at the beginning of an analytical run, once every 10 injections on the GC, and at the close of the run.

10.5.7 Corrective Actions

- a) If a Continuing Calibration Verification is outside the limits, all samples associated with that standard must be reanalyzed.**
- b) Be certain Continuing Calibration Verification is fresh and within limits.**

10.6 Method Blank

10.6.1 The method blank must be made up from a matrix similar to the samples within the analytical batch (e.g. water for aqueous, sand for sandy soil, clean loam for mossy high biomass samples)

10.6.2 Surrogate standards must be added to all method blanks and must fall within the window of 70 – 120% of the true values.

10.6.3 The method blank must be free of contamination (below reporting limits) within the specified range.

10.6.4 Corrective actions

- a) Reanalyze method blank being sure no instrument carryover is present.**
- b) If problem persists, or surrogates are outside acceptable ranges, associated analytical batch must be re-extracted and analyzed.**

10.7 Laboratory Control Sample and Laboratory Control Sample Duplicate (LCS/LCSD).

10.7.1 The LCS/LCSD/Matrix Spike working standard must be made up of a synthetic mixture of analytes. A minimum of three aromatic and three aliphatic compounds must be used for each range (DRO, RRO, and GRO).

10.7.2 The LCS/LCSD should be made up from a matrix similar to the samples within the analytical batch (e.g. water for aqueous, sand for sandy soil, clean loam for mossy high biomass samples).

10.7.3 Surrogate standards must be added to all LCS/LCSD and must fall within the window of 70 – 120% of the true values.

10.7.4 Matrix spike/LCS compounds must be added to all LCS/LCSD samples and must fall within the window of 70 – 120% of the true values.

10.7.5 Compounds from the other fraction must not exceed 10% (e.g. the aliphatic LCS/LCSD samples may not have more than 10% recovery of any single aromatic LCS/LCSD/Matrix Spike compound or visa versa).

10.7.6 The duplicate must have a relative percent difference of less than 20%.

10.7.7 Corrective actions

a) Reanalyze LCS/LCSD being sure no instrument carryover is present.

b) If problem persists, or surrogates are outside acceptable ranges, associated analytical batch must be re-extracted, re-fractionated and/or re-analyzed.

10.8 Matrix Spike (MS)

10.8.1 The LCS/LCSD/Matrix Spike working standard must be made up of a synthetic mixture of analytes. A minimum of three aromatic and three aliphatic compounds must be used for each range (DRO, RRO, and GRO).

10.8.2 The matrix spike must be made up from a sample within the analytical batch.

10.8.3 Surrogate standards must be added to all matrix spike samples and should fall within the window of 50 - 150% of the true values.

10.8.4 Matrix spiking/LCS compounds must be added to all matrix spike samples and should fall within the window of 50 - 150% of the true values.

10.8.5 Compounds from the other fraction must not exceed 10% recovery (e.g. the aliphatic matrix spike samples may not have more than 10% recovery of any single aromatic LCS/LCSD/Matrix Spiking compound or visa versa).

10.8.6 Corrective actions

No corrective actions are required for a matrix spike that is out of compliance.

10.9 Surrogate Spikes

10.9.1 At least one aromatic and one aliphatic surrogate compound which does not coelute or otherwise interfere with the analytes of interest must be added to each sample, method blank, LCS/LCSD, and matrix spike.

10.9.2 Since diesel and residual range compounds are often analyzed together, the compounds one compound per fraction will suffice for the modified AK102AA/103AA combined method.

10.9.3 The recovery of surrogate standards must not be outside the range 70 – 120% for method blanks and LCS/LCSD samples.

10.9.4 The recovery of surrogate standards should not be outside the range 50 - 150% for all remaining samples and matrix spikes.

10.9.5 Surrogate compounds from the other fraction must not exceed 10% recovery in a given fraction (e.g. the aliphatic samples or matrix spikes may not have more than 10% recovery of any single aromatic surrogate compound or visa versa).

10.9.6 The polar surrogate shall not be observed above 10% recovery in any sample, method blank, LCS/LCSD, or matrix spike.

10.9.7 Corrective Actions

- a) **If the surrogates for a sample are out of limits, that sample must be re-extracted, re-fractionated, and/or re-analyzed.**
- b) **If a surrogate is out of limits in the same direction (e.g. low both times) for a second time, the report shall reflect a matrix effect.**
- c) **If a surrogate is higher than limits for the opposing fraction, that sample shall be re-extracted, re-fractionated, and/or re-analyzed. Care must be taken to ensure the quality and the activity of the silica gel or alumina or other adsorptive material in the fractionation column.**
- d) **If a surrogate compound is out of limits for a method blank or LCS/LCSD sample, that sample must first be re-analyzed; then, if still out, the entire analytical batch must be re-extracted, re-fractionated, and re-analyzed.**

11 References

11.1 Alaska Department of Environmental Conservation, Methods AK102 & AK103.

11.2 The Federal Register, 62 FR 52098, Oct 1997.

11.3 Massachusetts Department of Environmental Protection and ABB Environmental Services, Inc., Wakefield, MA "Interim Petroleum Policy: Development of Health-based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter", August 1994.

11.4 USEPA, "Measurement of Petroleum Hydrocarbons: Report on Activities to Develop a Manual" Prepared by Midwest Research Institute, Falls Church, VA, under EPA Contract #68-WO-0015, WA No. 4; submitted to USEPA Office of Underground Storage Tanks, Washington, DC; November 20, 1990.

11.5 USEPA Regulations 40 C.F.R. 136, Appendix B, "Guidelines Establishing Test procedures for the Analysis of Pollutants", July 1992.

11.6 USEPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846), Method 3510: Separatory Funnel Liquid-Liquid Extraction; September 1986.

11.7 USEPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846), Method 3540: Soxhlet Extraction; September 1986

11.8 USEPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846), Method 3630: Silica Gel Cleanup; September 1986

11.9 USEPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846), Method 8000: Gas Chromatography; September 1986

11.10 USEPA, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846), Method 8100: Polynuclear Aromatic Hydrocarbons; September 1986

11.11 Wisconsin Department of Natural Resources, "Modified DRO - Method for Determining Diesel Range Organics", PUBL-SW-141, 1992

11.12 USEPA, "Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring", EPA 821-B-93-001; U.S. Government Printing Office, Washington D.C., June, 1993

APPENDIX E

Alaska Department of Environmental Conservation Hazard Ranking Evaluation Form

Purpose of this form

This form is used only for sites with underground storage tanks that are subject to regulation under AS 46.03.365. The form is based on the "Alaska Hazard Ranking Model" which ADEC uses to prioritize its investigation and cleanup efforts. It is used to collect preliminary information on the relative risk a contaminated site may pose to human health and the environment.

Explanation of how sites are scored

The box below explains how a site will be scored after ADEC receives this form. Note that although the form contains values for "unknown" elements, a minimum combination of the following data elements are needed for adequately distinguishing between sites: toxicity, quantity, air exposure, ground water exposure, and surface water exposure. Also note that scores cannot be calculated in the following instances:

1. If too many data elements are unknown; or,
2. If both the toxicity and the quantity data elements are unknown; or,
3. If all exposure elements are unknown.

Scoring procedure for risk evaluation Form

The Preliminary Risk Evaluation Form contains 14 different questions. Each question deals with a particular "data element" (shown below) that is considered in scoring the site. The alternatives to each question are assigned a value and then these values are entered into the formulas below to calculate the final score.

Question # Data Element

1. Toxicity
2. Quantity
3. Release Information
4. Site Access
5. Air Exposure
- 6a. Population Density (within one mile)
- 6b. Population Proximity (500 feet)
7. Ground Water Usage
8. Ground Water Exposure
9. Surface Water Use
10. Surface Water Exposure
11. Surface Water Environment
12. Environmental/Recreational Area
13. Observed Environmental Impact
14. Multiple Sources or Contaminants

Scoring

Ranking Score = Substance Factor x (Human Target + Environmental Target)

Substance Factor = (#1) x (#2) x (#3)

Human Target = (#4 + Air Target Population + Adj. Ground Water Use + Adj. Surface Water Use)

Air Target Population = (#5) x (#6a) x (#6b)

Adj. Ground Water Use = (#7) x (#8) x (#6a)

Adj. Surface Water Use = (#9) x (#10) x (#6a)

Environmental Target = (#11) + (#12)

or, if (#11) + (#12) = 0, use value in (#13)

If there are **multiple contaminants** (answer is "yes" to #14), multiply Ranking Score by 1.2.

(Numbers in parentheses refer to the 14 "data elements" identified above.)

Return completed form to: ADEC Underground Storage Tank Section
555 Cordova Street, Anchorage, Alaska 99501-2617
Telephone: (907) 269-7503 FAX (907) 269-7649

ADEC Hazard Ranking Evaluation Form

Please type, or print in ink, all the requested information on this page.

General Information

Name of Site: _____

Facility ID Number: _____

Tax ID Number: _____

Applicant:

Facility:

Name: _____ Name: _____

Address: _____ Address: _____

Telephone: _____ Telephone: _____

Owner of Tank (if not the same as applicant): Owner of Land (if not the same as applicant):

Name: _____ Name: _____

Address: _____ Address: _____

Telephone: _____ Telephone: _____

Preparer:

Name: _____

Title: _____

Firm: _____

Telephone: _____

Please provide any additional information that may assist in processing the Preliminary Risk Evaluation Form (i.e. directions to the site if it does not have a physical address, uncertainties over how to answer particular questions, etc.). Please use additional pages, if necessary.

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HAZID #

ADEC Hazard Ranking Evaluation Form

(Values for scoring are in parentheses following each option)

On pages 3-6, please fill in the letter of the correct choice in the box preceding each question

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1. ___

1. **What type of product was released or detected?**

If more than one substance is present, use the one that will score the highest substance factor.

- a. Chlorinated solvents, other halogenated hydrocarbons, synthetic chlorinated organic pesticides. (4)
- b. Metals, gasoline, aviation gas, naphtha, non-chlorinated pesticides. (3)
- c. Unknown substances. (2.1)
- d. Diesel fuel, jet fuels, (JP-4, JP-5), kerosene, non-chlorinated phenols, non-chlorinated solvents, crude oil. (2)
- e. Waste lubricating oils, heavy fuel oils (No. 6, etc.), inorganic acids/bases, tar. (1)

2. ___

2. **What quantity of product was released?**

- a. < 10 drums or 549 drum or tank gallons, < 500 spilled gallons, < 100 cubic yards or tons, < 100 ft². (1)
- b. 10-99 drums or 550 - 5,499 drum or tank gallons, 500 - 9,999 spilled gallons, 100 - 499 cubic yards or tons, 100 - 9,999 ft². (2)
- c. Unknown quantity. (2.1)
- d. 100 - 999 drums or 5,500 - 54,999 drum or tank gallons, 10,000 - 39,999 spilled gallons, 500 - 1,999 cubic yards or tons, 10,000 - 43,559 ft². (3)
- e. \geq 1,000 drums or \geq 50,000 drum or tank gallons, \geq 40,000 spilled gallons, \geq 2,000 cubic yards or tons, \geq 1 acre (43,560 ft²). (4)

Note: < means "less than" (i.e. 1 < 10, or one is less than ten)
> means "greater than" (i.e. 10 > 1, or 10 is greater than one)
 \geq means "greater than or equal to" (i.e. 11 \geq 10, or 11 is greater than or equal to 10)

3. ___

3. **Has a release at the site been documented?**

- a. Documented releases indicate contamination due to disposal practices or failure of containment at the site, regardless of quantity. (1)
- b. Containment management practices exist which may pose a significant threat, but there is no documentation of a release. (.5)
- c. An unknown potential for site release exists, or off-site contamination is not clearly linked to the site. (.2)
- d. There is a documented absence of a release at the site. (.1)

4. ___

4. **How controlled is access to this site?**

- a. A school is present within 500 feet, and, site access is partially controlled or uncontrolled, and, wastes are present at the surface. (3)
- b. Access to the site is uncontrolled, and, wastes are present at the surface. (2)
- c. Access to the site is partially controlled, or, surrounding features restrict site access, or, contaminated soil is stockpiled (presumed covered) on site. (1)
- d. There is an underground tank, or waste is not present at the surface, or access to the site is completely controlled. (0)

5.____

 5. **Have contaminants been released to the atmosphere?**

- a. A documented release of particulate or gases from the site has been confirmed. (1)
- b. A release may have occurred at the site based on existing physical evidence, including uncovered stockpiles of excavated soils. (.2)
- c. No significant air releases have been identified at the site and waste management practices indicate no substantial possibility. (.1)

6a.____

 6a . **What is the predominant population density within 1 mile radius?**

- a. Urban residential use (in or adjacent to population > 35,000, single family lots < 1/4 acre). (10)
- b. Suburban residential areas (lots 1/4 - 1 acre), or, cities with population between 2,000 - 35,000, or, industrial/commercial areas. (8)
- c. Villages (<2,000 people), or, low density housing (one unit per acre), or, low density commercial use, or, few permanent residents, but intensive seasonal use. (5)
- d. Rural use, with some occupied buildings. No villages or associated commercial/industrial areas within 1 mile (3)
- e. Isolated areas with no population present. (0)

6b.____

 6b. **What is the predominant population in proximity to the site (within 500 feet)?**

(Also count workers at site, residents of military barracks or lodges, and students at a school.)

- a. Occupied buildings or dwellings present within 500 feet of site. (1)
- b. No occupied buildings within 500 feet. (0.5)

7.____

 7. **What is the ground water usage within 1 mile?**

- a. Within a 1 mile radius, a majority of the population is served by municipal wells or other public water supply wells serving > 25 individuals. (1)
- b. Within a 1 mile radius, a majority of the population is served primarily by community or private wells. (.8)
- c. A majority of the population is served by drinking water supplies originating greater than a mile from the site, but other public water supply wells serving more than 25 individuals are located within one mile of the site. (.6)
- d. A majority of the population is served by drinking water supplies that are > 1 mile from the site, or there are no known wells within one mile, but the possibility of use of drinking water exists. (.4)
- e. Ground water as a source of drinking water or is not used. (.1)

8.____

 8. **Has there been any documentation of ground water contamination?**

- a. Documented contamination of a drinking water supply at the tap exceeds the MCL. (4)
- b. Documented contamination of a drinking water supply at the tap, does not exceed the MCL. (2)
- c. Ground water contamination has been detected but actual contamination at the tap has not been documented. (1)
- d. Ground water contamination is unknown, either at the tap or at the ground water source. (.4)
- e. Ground water is documented to be free of contamination, or, waste and site characteristics indicate a low potential for contamination. (0)

9.____

9. **What is the primary use of surface water within 1 mile?**

- a. Surface water is used as a drinking water source supplied by intakes within 1 mile of site. *Assign this value if surface drinking water supplies within one mile of the site have been abandoned due to site contamination.* (1)
- b. Use of surface water as a source of drinking water, from intakes within 1 mile, is unknown, but likely. (.5)
- c. Use of surface water as a source of drinking water is unknown but is unlikely, or, there is no use of surface water as a drinking water source within a 1 mile radius. (.2)

10.____

10. **Has surface water been contaminated by a release from the site?**

- a. Documented contamination of surface drinking water supply at the tap, exceeds the MCL due to releases of hazardous material from the site. (4)
- b. Documented contamination of surface drinking water supply at the tap does not exceed the MCL. (2)
- c. Surface water contamination has been detected at a drinking water source, but actual contamination of drinking water supply at the tap has not been documented. (1)
- d. Surface water contamination is unknown. (4)
- e. Surface water is not used as a source of drinking water, or, surface water is documented to be free of contamination, or site and waste characteristics indicate a low potential for contamination of surface water. (0)

11.____

11. **What type of surface water environment exists within 1/4 mile of the site?**

- a. Fresh or marine water or wetlands are present within 1/4 mile, and evidence of death or stress to fish or wildlife exists, which is strongly suspected as a result of the presence of hazardous substances. (5)
- b. Fresh or marine waters or wetlands are present within 1/4 mile, and evidence of death or stress to plants exists, which is strongly suspected as a result of the presence of hazardous substances. (3)
- c. Fresh or marine waters or wetlands are present within 1/4 mile, but there is no evidence of death or stress to fish, wildlife, or plants. (2)
- d. No fresh or marine waters or wetlands are present within 1/4 mile. (0)

12.____

12. **Is the site in an environmental/recreation area?**

- a. The site is in an environmental/recreation area and evidence exists of death or stress to fish or wildlife, which is strongly suspected as a result of the presence of hazardous substances. (5)
- b. The site is an environmental/recreation area and evidence exists of death or stress to plants, which is strongly suspected as a result of the presence of hazardous substances. (3)
- c. The site is in an environmental/recreation area and there is no evidence of death or stress to fish, wildlife, or plants. (2)
- d. The site is not in an environmental/recreation area. (0)

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13. _____

If your answer to both questions 11 and 12 was "d", and there are documented impacts to the environment which are not within 1/4 mile of surface waters or located within 1/4 mile of an environmental or recreation area, then proceed to question number 13. Otherwise, skip 13, and proceed to question 14.

13. **What are the observed environmental impacts to surface waters not within 1/4 mile, or which are not within environmental/recreational areas?**

- a. There is evidence of death or stress to fish or wildlife, which is strongly suspected as a result of the presence of hazardous substances. (5)
- b. There is evidence of death or stress to plant life, which is strongly suspected as a result of the presence of hazardous substances. (3)
- c. There is no evidence of death or stress to wildlife or plant life. (0)

14. _____

14. **Are there multiple sources of contamination present at the site? Yes or No**
(A yes answer will result in the final score being multiplied by 1.2, otherwise there will be no adjustment to the final score.)

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Scores assigned

by: _____