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 C_{25} to the end of C_{36}, 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 C_{36} 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 C_{25} and the peak end of C_{36}, 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 [41, 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 (C_{25}) and the peak end of n-hextriacontane (C_{36}). Quantitation is based on direct comparison of the area within this range to the total area of the motor oil standard within the same (C_{25} - C_{36}) range as determined from FID response using baseline-baseline integration. 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 (C_{25}) and n-hexatriacontane (C_{36}) which is analyzed once every 24 hour "day" or with each batch of samples, whichever is less frequent, not to exceed 20 samples per batch. This standard serves to define the retention time window for RRO.

3.7 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 Date Sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety should be available and should be identified for use by the analyst.

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

6. Apparatus and Materials

(Unless otherwise indicated, all apparatus and materials are 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-µL, 5-µl, 10-µL, 25-µL, and 100-µL 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 C_{24} from C_{25} in a midrange RCS and C_{36} 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 Sonabox 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 C_{25} and C_{36} 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 ± 2° C from the time of collection until extraction. Extraction must be performed on soils within 14 days.[1]. All analyses of extracts must take place within 40 days.

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

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

9. Procedure

9.1 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 C_{10}, if DRO (AK 102) is to be done simultaneously.

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

TZ = [(retention time C_{25} - retention time C_{24})/ (W ½ of C25 + W ½ of C24)] -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 C_{25}, $C_{36,}$ 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 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 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 C_{25} and the peak end of C_{36}. This blank is integrated over the RRO area in the same manner as for the field samples and is reported as the solvent blank (refer to 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:

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

Where: Cs = Concentration of RROs (mg/kg).
Ax = Response for the RROs in the sample, units in area.
RF = Response Factor from CCS (see Section 9.3. 1).
Ais = Response for the internal standard, units same as for Ax.
Cis = Internal standard concentration (mg/mL).
Vt = Volume of final extract in mL.
D = Dilution factor, if dilution was performed on the sample prior to analysis if no dilution was made, D = 1, dimensionless.
Vs = Amount of sample extracted in kg.

To calculate mg/dry kg for soil samples,

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

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

9.6.3 External Standard Calibration:

Soil samples:

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

Where: Cs = Concentration of RROs (mg/kg).
Ax = Response for the RROs in the sample, units in area.
As = Response for the external standard, units same as for Ax.
A = External standard concentration (mg/mL).
Vt = Volume of Final extract in mL.
D = Dilution factor, if dilution was performed on the sample prior to analysis. If no dilution was made, D = 1, dimensionless.
Vs = Amount of sample extracted in 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 C_{25} - C_{44} 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	500	116 ± 9
(S. E. Alaska Soils)		

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

1. USEPA, *Test Methods for Evaluating Solid Waste*, 3d Edition; Methods 8000, 8100, 3510, 3520, 3540, 3611 and 3550.

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

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

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

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

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

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

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

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

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

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

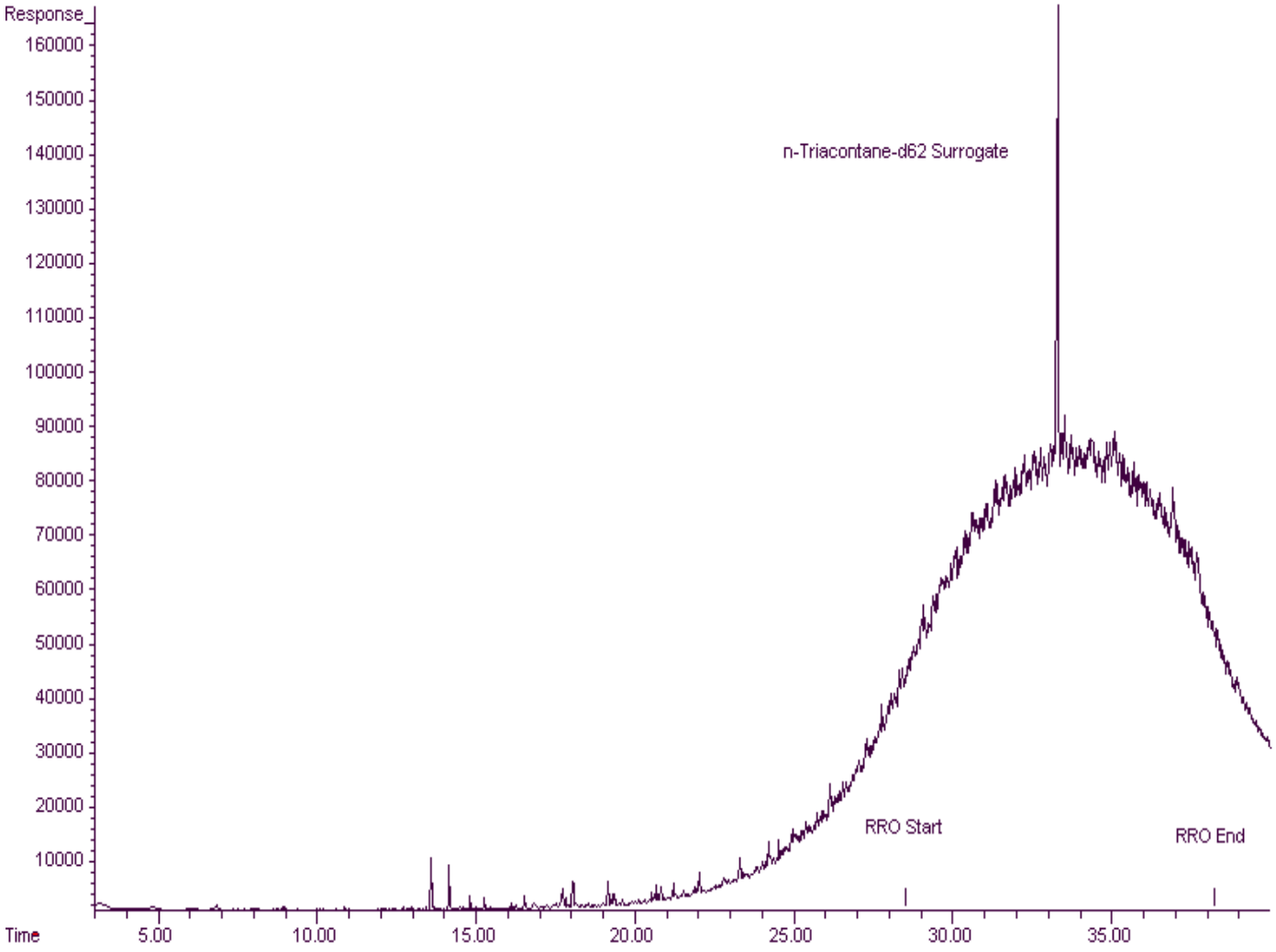
12. Research done by the State of Alaska, Department of Environmental Conservation, Division of Environmental Quality, State Chemistry Laboratory.

13. Carrell, Robert, "Method for the Determination of Extractable Petroleum Hydrocarbons", Laboratory Advisory Board Project Oversight Group, Duwamish Brownfields/TPI-I Project, September 1, 1997.

14. USEPA "Guidelines for Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act" (40 C.F.R. 136, Part VIII, July 1994).

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	
	Soil (mg/kg)	% Recovery	Relative % Difference
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	