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C₁₀ - C₃₂ Hydrocarbons in Soil - 8015AZ

09/25/98
Revision - 1.0

Analyte: C₁₀ - C₃₂ range Hydrocarbons

Method No.: 8015AZ

Matrix: Soil

Minimum Reporting Limits:

C₁₀ - C₂₂ 30 mg/Kg

C₂₂ - C₃₂ 100 mg/Kg

C₁₀ - C₃₂ (total) 130 mg/Kg

Procedure:

C₁₀ - C₃₂ Solvent extraction, GC-FID analysis

This method can also be used to quantitate C₆ - C₁₀ range at the Minimum Reporting Limit of 20 mg/Kg and C₆ - C₃₂ range at the Minimum Reporting Limit of 150 mg/Kg ([See Appendix A](#)).

C₆ - C₁₀ Purge and Trap or Solvent extraction, GC-FID analysis

C₆ - C₃₂ Solvent extraction, GC-FID analysis

1. METHOD REFERENCE

- 1.1 EPA Method 8015B, Nonhalogenated Organics Using GC/FID, SW-846 Update III, December 1996.
- 1.2 EPA Method 8000B, Gas Chromatography, SW846 Update III, December 1996.
- 1.3 EPA Method 5030A, Purge-and-Trap for Aqueous Samples, SW846 Update I, July 1992.
- 1.4 Modified DRO, Method for Determining Diesel Range Organics, Wisconsin DNR, PUBL-SW-141, July 1993.

2. DEFINITIONS

- 2.1 $C_{10} - C_{22}$, also known as DRO - Diesel Range Organics defined as the sum of the hydrocarbons that fall within the retention times of $C_{10} - C_{22}$. The retention time of C_{10} is defined by n-Decane and the retention time of C_{22} is defined by n-Docosane.
- 2.2 $C_{22} - C_{32}$, also known as ORO - Oil Range Organics defined as the sum of the hydrocarbons that fall within the retention times of $C_{22} - C_{32}$. The retention time of C_{22} is defined by n-Docosane and the retention time of C_{32} is defined by n- Dotriacontane.
- 2.3 LFB - Laboratory Fortified Blank defined as clean sand fortified by the laboratory with a known concentration of primary source standard, extracted, and analyzed with each batch of samples.
- 2.4 CCV - Continuing Calibration Verification defined as a mid-level primary source standard.

3. SYNOPSIS

See [Appendix A](#) for the quantitation of $C_6 - C_{10}$ and $C_6 - C_{32}$ hydrocarbons in soil and [Appendix B](#) for a table of carbon ranges versus acceptable analytical techniques

- 3.1 This method is an Arizona consensus method and was developed with collaboration among the Arizona Department of Health Services, Arizona Department of Environmental Quality and the Arizona Laboratory Association. This method replaces modified 8015, 418.1AZ and BLS-191 for compliance testing.

Although the compliance range in Arizona is $C_{10} - C_{32}$, this method can also be used to quantitate $C_6 - C_{10}$ and $C_6 - C_{32}$. **Please check with your clients for their needs.**

Report results from the individual ranges also, while reporting combination of ranges, for the added benefit to the clients. The results from the different analytical techniques cannot be combined for reporting a combination of carbon ranges. The same extraction solvent and analytical technique must be used. For e.g., Purge and Trap $C_6 - C_{10}$ cannot be combined with direct inject $C_{10} - C_{32}$ for reporting $C_6 - C_{32}$.

- 3.2 $C_{10} - C_{32}$ hydrocarbons may be extracted with hexane, methylene chloride or other appropriate solvent.

Note: Methanol is not an acceptable solvent to extract $C_{10} - C_{22}$ or $C_{22} - C_{32}$.

4. RANGES, SENSITIVITY, REPORTING LIMIT

- 4.1 This method is used for the detection of $C_{10} - C_{32}$ hydrocarbons in soil at the following concentrations. The minimum reporting limits (MRLs) of the individual hydrocarbon ranges are summed for reporting combination of ranges.

MINIMUM REPORTING LIMITS

$C_{10} - C_{22}$	30 mg/Kg
$C_{22} - C_{32}$	100 mg/Kg
$C_{10} - C_{32}$ (total)	130 mg/Kg

5. INTERFERENCES

- 5.1 Contamination by carryover can occur whenever high-level samples are analyzed. Whenever an unusually concentrated sample is encountered it should be followed by an analysis of solvent blank to check for cross contamination.
- 5.2 Hydrocarbons from animal and vegetable matter may co-extract with petroleum hydrocarbons. Silica gel is used to remove polar, nonpetroleum hydrocarbons.
- 5.3 Moisture from the sample may interfere with the extraction efficiency of the sample. Anhydrous sodium sulfate is used to remove moisture from the sample.

Note: Steps 5.2 and 5.3 are optional. Sodium sulfate and silica gel are added if found necessary.

- 5.4 Other organic compounds, including chlorinated hydrocarbons, phenols, and phthalate esters may be quantitated as petroleum hydrocarbon range(s).

6. SAMPLE HANDLING AND PRESERVATION

- 6.1 Soil samples analyzed for $C_{10} - C_{32}$ are collected in brass sleeves or glass jars with Teflon lined screw caps or any appropriate containers as specified by the Arizona Department of Environmental Quality.
- 6.2 Soil samples are to be immediately cooled to $4 \pm 2^{\circ}\text{C}$ until analysis.
- 6.3 The extraction and the analysis of the soil samples for $C_{10} - C_{32}$ must be completed within 14 days of sampling.

7. APPARATUS

- 7.1 Temperature programmable gas chromatograph, equipped with flame ionization detector and optional autosampler. The carrier gas for the analysis is Helium.

- 7.2 Autosampler vials with crimp seals.
- 7.3 30m, Rtx-5 or DB-5 fused silica capillary or megabore column or equivalent. These columns can be substituted with any other capillary or megabore columns that achieve adequate separation for identification and quantitation.

Recommended column and oven conditions are:

Injector: 300°C, Detector: 300°C, Oven: 35°C- hold for 3 minutes, ramp at 10°C/min to 310°C and hold until all the motor oil elutes.

Note: Follow manufacturer's recommendation for FID detector temperature.

- 7.4 Computer system equipped with chromatography software. An alternate integration technique can be used if demonstrated to be capable of appropriate quantitation.
- 7.5 Assorted micro syringes.
- 7.6 Sonicating bath, vortex, rotator, wrist action shaker or equivalent.
- 7.7 Screw capped vial.
- 7.8 Pasteur pipets or equivalent.

8. REAGENTS AND STANDARDS

- 8.1 Hexane, methylene chloride or other solvent proven to extract $C_{10} - C_{32}$ hydrocarbons. To prove the extraction efficiency of an alternate solvent, side by side comparison studies must be performed prior to the alternate solvent's incorporation into the method.
- 8.2 Sodium sulfate, anhydrous (see Section 5.3, EPA method 3550B, SW846, December 1996 for pretreatment).
- 8.3 Silica gel 60/200 mesh, Davidson grade 950 or equivalent.
- 8.4 Primary standard that contains the reference materials of interest.
- 8.5 Secondary standard that contains the reference materials of interest.

- 8.6 Surrogate: Suggested surrogate include o-Terphenyl for C₁₀ - C₂₂.
- 8.7 Retention Time Verification Standard: A mixture of, n-Decane (C₁₀), n-Docosane (C₂₂) and n-Dotriacontane (C₃₂) at 1000 ug/mL each in methylene chloride can be purchased from Supelco or equivalent vendor.

9. PROCEDURE

9.1 Extraction Procedure:

- 9.1.1 Add 1 - 3 grams each of anhydrous sodium sulfate and silica gel to an empty screw capped vial. The amount of sodium sulfate and silica gel added will depend upon the moisture and the non-petroleum hydrocarbon interferences present in the samples.

Note: Step 9.1.1 is optional. Silica gel and sodium sulfate are added if found necessary.

- 9.1.2 Remove sample from the refrigerator and immediately weigh a representative subsample of 10 grams into the previously prepared screw capped vial avoiding excessive disturbance of the sample. Start duplicate matrix spikes.

- 9.1.3 Additional amounts of silica gel may be used to remove non-petroleum hydrocarbon interferences.

- 9.1.4 Spike LFB and selected samples at appropriate level with primary source standard.

- 9.1.5 Spike all samples, matrix spikes, method blank, LFB with appropriate surrogate.

Note: Spike surrogate and matrix spike solutions directly on to the soil before adding the extraction solvent.

- 9.1.6 Immediately add 10 mL of hexane, methylene chloride, or appropriate solvent to the vial. Verify that the solvent covers the material being extracted. If the solvent does not completely cover the extracted material, prepare another subsample reducing the mass being extracted.

- 9.1.7 If a sonicating water bath is used, seal the vial and wet the soil with the solvent by inverting the vial by hand approximately three times. Extract by sonicating in the water bath (no heat is applied) for 10 - 15 minutes.

Note: Ensure the sample is kept cool to minimize loss of extraction solvent.

Other extraction techniques such as wrist action shaker, vortex and rotator may be used. Alternate extraction techniques can be used if they have proven to extract C₁₀ - C₃₂ range hydrocarbons.

To prove the extraction efficiency of an alternate extraction, side by side comparison studies must be performed prior to implementing its use in the method.

- 9.1.8 Allow sample extracts to settle.
- 9.1.9 Transfer extract to a clean, labeled vial and seal.
- 9.1.10 Extracts must be stored at <6_C with minimum headspace until analysis.

9.2 Analytical Procedure:

- 9.2.1 Analysis is performed by GC-FID.

10. CALIBRATION

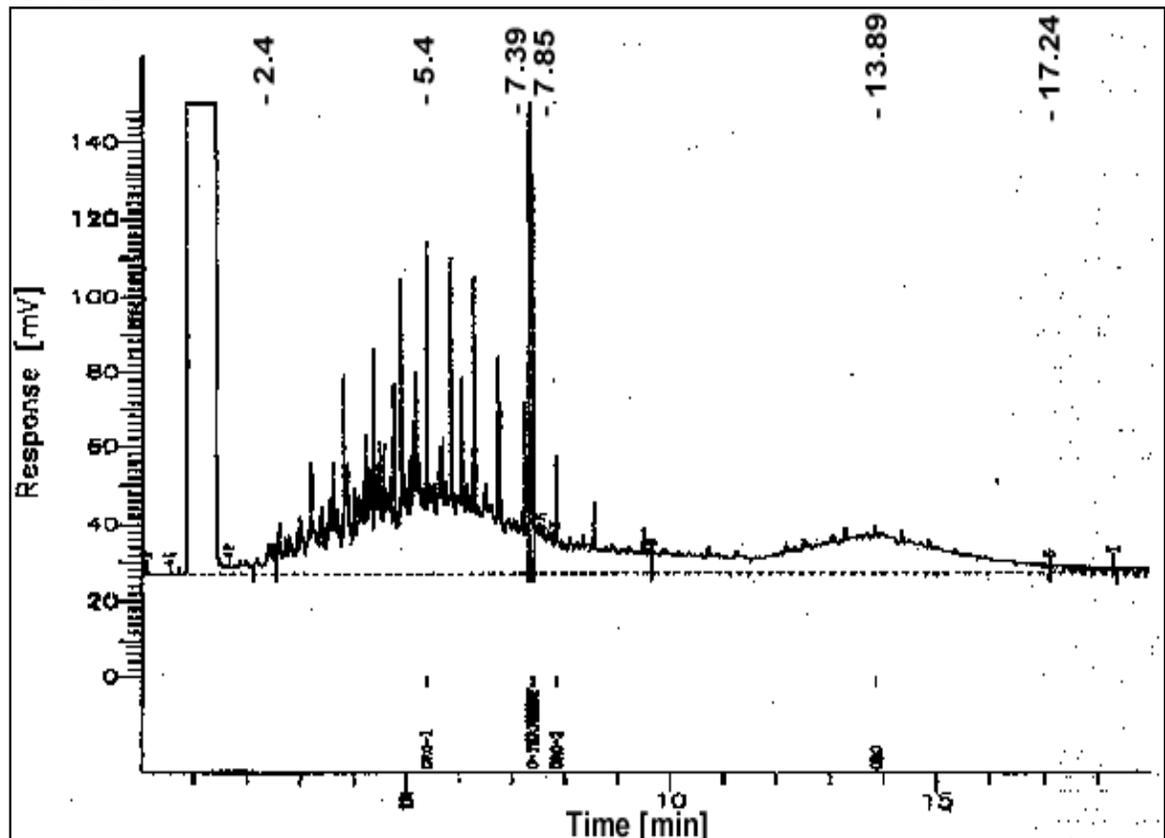
- 10.1 A five point calibration curve is generated using diesel and 10W30 motor oil (or equivalent) as reference materials. The reporting limit concentrations of the individual hydrocarbon ranges are to be included as part of the calibration curve ([see section 4 for limits](#)). Diesel reference materials must be purchased from an analytical standard manufacturer. For C₂₂ - C₃₂, 10W30 (or equivalent) is used as the reference material.
- 10.2 A five point calibration curve is generated for surrogates.

- 10.3 The initial calibration is verified at the beginning of each analytical run, after every 10 samples and at the end of the day. If the CCV recovery does not fall within 70% and 130% of true value, all samples analyzed after the valid CCV must be repeated. If the repeat CCV is also outside the acceptance range, a new calibration curve must be generated.
- 10.4 A mixture of C_{10} , C_{22} and C_{32} marker compounds is injected after the calibration curve and as frequently as needed through out the run for retention time verification of individual hydrocarbon ranges. A mix containing these marker compounds can be purchased from an analytical standard manufacturer.

11. CALCULATION

- 11.1 A common baseline is drawn from the beginning to the end of the required carbon range, such that the petroleum "hump" is included in the quantitation (see Figure 1). The common baseline is drawn in the direction of the baseline drift. The quantitation is done on $C_{10} - C_{22}$ and $C_{22} - C_{32}$ hydrocarbon ranges individually and summed for combination of ranges. Report results from the individual ranges also, while reporting combination of ranges.

FIGURE 1



11.2 Calculations are done as follows:

$$C_s = (C_{ex} \times V_t) / (W_s)$$

Where:

C_s = Concentration in the sample

C_{ex} = Concentration in the final extract

V_t = Total volume of the concentrated extract

W_s = Weight of the sample extracted

Express the final results in mg/Kg. See Section 7.10, EPA method 8000B, for a detailed description.

12. QUALITY CONTROL

- 12.1 Samples for C_{10} - C_{32} must be extracted and analyzed within 14 days of sampling.
- 12.2 Extraction solvents other than hexane and methylene chloride may be used, but method performance verification must be done.
- 12.3 Minimum of one method blank must be analyzed for every batch up to 20 samples or less.
- 12.4 Minimum of one LFB must be analyzed for every batch up to 20 samples or less. The spiking solutions must be derived from the same source as the calibration curve. Acceptance range for LFB recovery is between 70% and 130% of true value.

- 12.5 Minimum of one matrix spike and a matrix spike duplicate must be analyzed for every batch up to 20 samples or less. The spiking solutions must be derived from the same source as the calibration curve. The laboratory shall use 70 - 130% as an interim acceptance criteria for matrix spike recoveries of spiked analytes, until the in-house limits are developed. Calculate precision (RPD) as per section 8.5.3.2 of EPA method 8000B.
- 12.6 Acceptance range for surrogate recovery is between 70% and 130% of true value.
- 12.7 The correlation coefficient of a calibration curve must be greater than or equal to 0.995 ($r \geq 0.995$). An external standard quantitation must be performed. An average response factor may be used if the relative standard deviation is less than 20% ($RSD < 20\%$).
- 12.8 A secondary source standard is injected after a calibration curve. Acceptance range for secondary source standard recovery is between 80% - 120% of true value.
- 12.9 A Retention Time Verification Standard is injected after a calibration curve and as frequently as needed ([see section 10.4](#)).
- 12.10 A CCV must be analyzed at the beginning of each analytical run and after every ten samples analyzed. The recovery of the CCV should be between 70% and 130% of true value. If the CCV recovery does not fall within the specified range, all samples analyzed after the last valid CCV must be repeated. A closing CCV must be analyzed.
- 12.11 In lieu of a Minimum Detection Limit (MDL) study, a Reporting Limit Verification (RLV) study must be performed initially and then annually. The study is to contain at least seven replicates of soil samples spiked at the reporting limits (see section 4 for limits) and extracted. Each replicate must have recovery between 70% and 130% of true value. No statistical analysis is performed on the recoveries of this RLV study. The purpose of the study is to prove that the minimum reporting limit can be extracted and analyzed consistently.

APPENDIX A

$C_6 - C_{10}$ and $C_6 - C_{32}$ Hydrocarbons in Soil

1. METHOD REFERENCE

- 1.1 EPA Method 8015B, Nonhalogenated Organics Using GC/FID, SW-846 Update III, December 1996.
- 1.2 EPA Method 8000B, Gas Chromatography, SW846 Update III, December 1996.
- 1.3 EPA Method 5030A, Purge-and-Trap for Aqueous Samples, SW846 Update I, July 1992.
- 1.4 Modified GRO, Method for Determining Gasoline Range Organics, Wisconsin DNR, PUBL-SW-141, July 1993.
- 1.5 ELAC Technical Sub-committee draft document titled "Soil Sampling Guidance for Methanol Field Preservation".

2. DEFINITIONS

- 2.1 $C_6 - C_{10}$, also known as GRO - Gasoline Range Organics defined as the sum of the hydrocarbons that fall within the retention times of $C_6 - C_{10}$. The retention time of C_6 is defined by n-Hexane and the retention time of C_{10} is defined by n-Decane. If the Purge and Trap technique is used, C_6 is defined by benzene and C_{10} is defined by naphthalene.
- 2.2 $C_6 - C_{32}$ is the sum of the hydrocarbons that fall within the retention times of $C_6 - C_{32}$ and is the combined result of hydrocarbon ranges $C_6 - C_{10}$, $C_{10} - C_{22}$ and $C_{22} - C_{32}$.
- 2.3 LFB - Laboratory Fortified Blank defined as clean sand fortified by the laboratory with a known concentration of primary source standard, extracted, and analyzed with each batch of samples.
- 2.4 CCV - Continuing Calibration Verification defined as a mid-level primary source standard.

3. SYNOPSIS

- 3.1 $C_6 - C_{10}$ hydrocarbons in soil is not a compliance range in Arizona but is often a requested range for suspected gasoline contamination investigation. For the analysis of $C_6 - C_{10}$ this procedure in Appendix A applies.

- 3.2 If $C_6 - C_{32}$ hydrocarbons are requested, the combined result of hydrocarbon ranges $C_6 - C_{10}$, $C_{10} - C_{22}$ and $C_{22} - C_{32}$ is reported. Report results from the individual ranges also, while reporting combination of ranges, for the added benefit to the clients. The results from the different analytical techniques cannot be combined for reporting a combination of carbon ranges. The same extraction solvent and analytical technique must be used. For e.g., Purge and Trap $C_6 - C_{10}$ cannot be combined with direct inject $C_{10} - C_{32}$ for reporting $C_6 - C_{32}$.
- 3.3 $C_6 - C_{10}$ hydrocarbons can be analyzed by extraction followed either by direct injection or by Purge and Trap technique.
- 3.4 Methanol extraction is only acceptable for $C_6 - C_{10}$ that will be analyzed on a Purge and Trap system.
- 3.5 $C_6 - C_{10}$ and $C_6 - C_{32}$ hydrocarbons analyzed by direct injection may be extracted with methylene chloride or other appropriate solvent. Hexane is not a suitable extraction solvent for the quantitation of $C_6 - C_{10}$ hydrocarbons due to its interference.
- 3.6 Gasoline can be quantitated using GC/PID, if it meets all the method criteria of 8015AZ. **It should be reported as gasoline and not as $C_6 - C_{10}$.** The laboratory must do side by side studies to prove that a PID does not yield statistically lower results for fresh and degraded gasoline contaminated samples compared to a FID.
- 3.7 Simultaneous analysis of BTEX can be performed if it meets all the method criteria of 8021B.
- 3.8 The Arizona Environmental Laboratory Advisory Committee draft guidance document "Suggested Soil Sampling Guidance for Methanol Field Preservation" is applicable for the analysis of volatiles and gasoline, if requested by certain programs of Arizona Department of Environmental Quality.

4. RANGES, SENSITIVITY, REPORTING LIMIT

- 4.1 This method is used for the detection of $C_6 - C_{10}$ and $C_6 - C_{32}$ hydrocarbons in soil at the following concentration.

- 4.2 The minimum reporting limits (MRLs) of the individual hydrocarbon ranges are summed for reporting the combination of ranges for $C_6 - C_{32}$.

MINIMUM REPORTING LIMITS

$C_6 - C_{10}$	20 mg/Kg
$C_6 - C_{32}$ (total)	150 mg/Kg

5. INTERFERENCES

- 5.1 Contamination by carryover can occur whenever high-level samples are analyzed. Whenever an unusually concentrated sample is encountered it should be followed by an analysis of solvent blank to check for cross contamination.
- 5.2 Hydrocarbons from animal and vegetable matter may co-extract with petroleum hydrocarbons. Silica gel is used to remove polar, nonpetroleum hydrocarbons.
- 5.3 Moisture from the sample may interfere with the extraction efficiency of the sample. Anhydrous sodium sulfate is used to remove moisture from the sample.

Note: Steps 5.2 and 5.3 are optional. Sodium sulfate and silica gel are added if found necessary.

- 5.4 Other organic compounds, including chlorinated hydrocarbons, phenols, and phthalate esters may be quantitated as petroleum hydrocarbon range(s).
- 5.5 The presence of heavy hydrocarbons ($C_{10} - C_{22}$, $C_{22} - C_{32}$) could affect the extraction efficiency of $C_6 - C_{10}$ compounds if methanol is used as the extraction solvent. It is highly recommended to extract the samples for $C_6 - C_{10}$ with solvent such as methylene chloride or any other appropriate solvent and analyze by direct injection if the presence of heavy hydrocarbons is suspected.

6. SAMPLE HANDLING AND PRESERVATION

- 6.1 Soil samples analyzed for C₆ - C₃₂ are collected in brass sleeves or glass jars with Teflon lined screw caps or any appropriate containers as specified by the Arizona Department of Environmental Quality. Glass jars are not appropriate for C₆ - C₁₀ range contaminated samples. The container must contain as little headspace as possible.
- 6.2 Soil samples are to be immediately cooled to 4 Å 2_C until analysis.
- 6.3 The extraction and the analysis of the soil samples for C₆ - C₃₂ must be completed within 14 days of sampling. The samples for C₆ - C₁₀ analysis only must be extracted within 72 hours and analyzed within 14 days of sampling. This holding time limit of 72 hours between sample collection and extraction for soil samples is a policy decision which is part of the site characterization guidance from the Underground Storage Tank (UST) Section of the Arizona Department of Environmental Quality.

7. APPARATUS

- 7.1 Temperature programmable gas chromatograph, equipped with flame ionization detector and optional autosampler. The carrier gas for the analysis is Helium.
- 7.2 Autosampler vials with crimp seals.
- 7.3 30m, Rtx-5 or DB-5 fused silica capillary or megabore column or equivalent. These columns can be substituted with any other capillary or megabore columns that achieve adequate separation for identification and quantitation.

Recommended column and oven conditions are:

Injector: 300°C, Detector: 300°C, Oven: 35°C- hold for 3 minutes, ramp at 10°C/min to 310°C and hold until all the motor oil elutes.

Note: Follow manufacturer's recommendation for FID detector temperature.

- 7.4 Computer system equipped with chromatography software. An alternate integration technique can be used if demonstrated to be capable of appropriate quantitation.
- 7.5 Assorted micro syringes.
- 7.6 Sonicating bath, vortex, rotator, wrist action shaker or equivalent.

- 7.7 Screw capped vial.
- 7.8 Pasteur pipets or equivalent.

8. REAGENTS AND STANDARDS

- 8.1 Methanol for the extraction of $C_6 - C_{10}$, for Purge and Trap analysis.
- 8.2 For direct inject analysis, methylene chloride or other solvent proven to extract $C_6 - C_{32}$ and $C_6 - C_{10}$ hydrocarbons. To prove the extraction efficiency of an alternate solvent, side by side comparison studies must be performed prior to the alternate solvent's incorporation into the method.
- 8.3 Sodium sulfate, anhydrous (see Section 5.3, EPA method 3550B, SW846, December 1996 for pretreatment).
- 8.4 Silica gel 60/200 mesh, Davidson grade 950 or equivalent.
- 8.5 Primary standard that contains the reference materials of interest.
- 8.6 Secondary standard that contains the reference materials of interest.
- 8.7 Surrogate: Suggested surrogate include trifluorotoluene (TFT) for $C_6 - C_{10}$.
- 8.8 Suggested Retention Time Verification Standards for $C_6 - C_{10}$:

For direct injection: A mixture of n- hexane (C_6) and n-Decane (C_{10})

For Purge and Trap: A mixture of benzene (C_6) and naphthalene (C_{10})

at 1000 ug/mL each in methylene chloride can be purchased from Supelco or equivalent vendor.

9. PROCEDURE

9.1 Extraction Procedure:

- 9.1.1 Preparation of the soil sample for analysis is performed immediately after being removed from the refrigerator and continuing as quickly as possible through the rest of the process to avoid excessive loss of volatile hydrocarbons.
- 9.1.2 Add 1 - 3 grams each of anhydrous sodium sulfate and silica gel to an empty screw capped vial. The amount of sodium sulfate and silica gel added will depend upon the moisture and the non-petroleum hydrocarbon interferences present in the samples.

Note: Step 9.1.2 is optional. Silica gel and sodium sulfate are added if found necessary.

- 9.1.3 Remove sample from the refrigerator and immediately weigh a representative subsample of 10 grams into the previously prepared screw capped vial avoiding excessive disturbance of the sample. Start duplicate samples or duplicate matrix spikes.
- 9.1.4 Additional amounts of silica gel may be used to remove non-petroleum hydrocarbon interferences.
- 9.1.5 Spike LFB and selected samples at appropriate level with primary source standard.
- 9.1.6 Spike all samples, method blanks, spikes and LFB with appropriate surrogate.

Note: Spike surrogate and matrix spike solutions directly on to the soil before adding the extraction solvent.

- 9.1.7 Immediately add 10 mL of methylene chloride or appropriate solvent to the vial for the direct inject analysis and methanol for the Purge and Trap analysis of C₆ - C₁₀. Verify that the solvent covers the material being extracted. If the solvent does not completely cover the extracted material, prepare another subsample reducing the mass being extracted. Methanol can also be added to the samples in the field. See ELAC Technical Sub-Committee Draft Document titled "Soil Sampling Guidance for Methanol Field Preservative".

- 9.1.8 If a sonicating water bath is used, seal the vial and wet the soil with the solvent by inverting the vial by hand approximately three times. Extract by sonicating in the water bath (no heat is applied) for 10 - 15 minutes.

Note: Ensure the sample is kept cool to minimize loss of volatiles.

Other extraction techniques such as wrist action shaker, vortex and rotator may be used. Alternate extraction techniques can be used if they have proven to extract C₆ - C₁₀ range hydrocarbons. To prove the extraction efficiency of an alternate extraction, side by side comparison studies must be performed prior to implementing its use in the method.

- 9.1.9 Allow sample extracts to settle.

- 9.1.10 Transfer extract to a clean, labeled vial and seal.

- 9.1.11 Extracts must be stored at <6_C with minimum headspace until analysis.

9.2 Analytical Procedure:

- 9.2.1 For Direct Inject Analysis:

- 9.2.1.1 Analysis is performed by GC-FID.

- 9.2.2 For Purge and Trap analysis:

- 9.2.2.1 An aliquot of methanol from 9.1.10 is added to 5 mls of water and EPA method 5030A is followed.

- 9.2.2.2 Analysis is performed by GC-FID. PID can be used in place of a FID for the analysis of gasoline if equivalency with a PID has been proven.

10. CALIBRATION

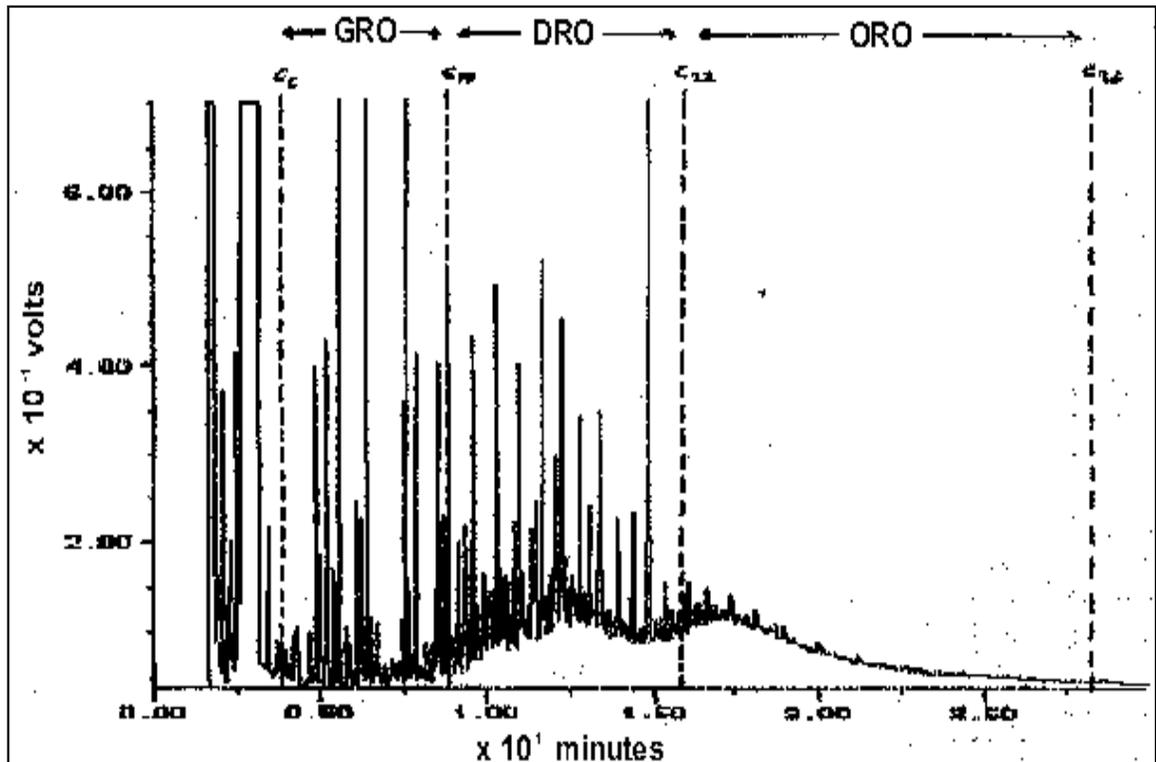
- 10.1 A five point calibration curve is generated using gasoline as reference material. The reporting limit concentration of the individual hydrocarbon range is to be included as part of the calibration curve (see section 4 for limit). Gasoline reference material can be purchased from an analytical standard manufacturer.

- 10.2 A five point calibration curve is generated for surrogates.
- 10.3 The initial calibration is verified at the beginning of each analytical run, after every 10 samples and at the end of the day. If the CCV recovery does not fall within 70% and 130% of true value, all samples analyzed after the valid CCV is repeated. If the repeat CCV is also outside the acceptance range, a new calibration curve is generated.
- 10.4 A mixture of C_6 and C_{10} marker compounds is injected after the calibration curve and as frequently as needed through out the run for retention time verification of individual hydrocarbon range. A mix containing these marker compounds can be purchased from an analytical standard manufacturer.

11. CALCULATION

- 11.1 A common baseline is drawn from the beginning to the end of the required carbon range, such that the petroleum "hump" is included in the quantitation (See Figure 2). The common baseline is drawn in the direction of the baseline drift. The quantitation is done on $C_6 - C_{10}$ and other hydrocarbon ranges, as needed, individually and summed for combination of ranges. Report results from the individual ranges also, while reporting combination of ranges.

FIGURE 2



11.2 Calculations are done as follows:

$$C_s = (C_{ex} \times V_t) / (W_s)$$

Where:

C_s = Concentration in the sample

C_{ex} = Concentration in the final extract

V_t = Total volume of the concentrated extract

W_s = Weight of the sample extracted

Express the final results in mg/Kg. See Section 7.10, EPA method 8000B, for a detailed description.

12. QUALITY CONTROL

- 12.1 Sample must contain a minimum of headspace and be subsampled before any other analysis is performed if GRO and BTEX are requested.
- 12.2 Samples for $C_6 - C_{32}$ are extracted and analyzed within 14 days of sampling. The samples for $C_6 - C_{10}$ analysis only must be extracted within 72 hours and analyzed within 14 days of sampling. This holding time limit of 72 hours between sample collection and extraction for soil samples is a policy decision which is part of the site characterization guidance from the Underground Storage Tank (UST) Section of the Arizona Department of Environmental Quality.
- 12.3 Extraction solvents other than methylene chloride may be used, but method performance verification must be done. Methanol is used as the extraction solvent for Purge and Trap technique. Hexane is not a suitable extraction solvent for direct inject analysis of $C_6 - C_{10}$.
- 12.4 Minimum of one method blank is analyzed for every batch up to 20 samples or less.
- 12.5 Minimum of one LFB is analyzed for every batch up to 20 samples or less. The spiking solutions is derived from the same source as the calibration curve. Acceptance range for LFB recovery is between 70% and 130% of true value.

- 12.6 Minimum of one matrix spike is analyzed for every batch up to 20 samples or less. The spiking solution is derived from the same source as the calibration curve. The laboratory can use 70 - 130% as an interim acceptance criteria for matrix spike recoveries of spiked analytes, until the in-house limits are developed.
- 12.7 Minimum of one sample duplicate or a duplicate sample spike is analyzed for every batch up to 20 samples or less. Calculate precision (RPD) as per section 8.5.3.2 of EPA method 8000B.
- 12.8 Acceptance range for surrogate recovery is between 70% and 130% of true value.
- 12.9 The correlation coefficient of a calibration curve is greater than or equal to 0.995 (r greater than or equal 0.995). An external standard quantitation is performed. An average response factor may be used if the relative standard deviation is less than 20% ($RSD < 20\%$).
- 12.10 A secondary source standard is injected after a calibration curve. Acceptance range for secondary source standard recovery is between 80% - 120% of true value.
- 12.11 A Retention Time Verification Standard is injected after a calibration curve and as frequently as needed.
- 12.12 A CCV is analyzed at the beginning of each analytical run and after every ten samples analyzed. The recovery of the CCV is between 70% and 130% of true value. If the CCV recovery does not fall within the specified range, all samples analyzed after the last valid CCV will be repeated. A closing CCV is analyzed.
- 12.13 In lieu of a Minimum Detection Limit (MDL) study, a Reporting Limit Verification (RLV) study is performed initially and then annually. The study is to contain at least seven replicates of soil samples spiked at the reporting limits (see section 4 for limits) and extracted. Each replicate recovery is between 70% and 130% of true value. No statistical analysis is performed on the recoveries of this RLV study. The purpose of the study is to prove that the minimum reporting limit can be extracted and analyzed consistently.
- 12.14 The laboratory specifies the sample introduction technique for $C_6 - C_{10}$ compounds in their final report.

APPENDIX B

TABLE OF CARBON RANGES VS ACCEPTABLE ANALYTICAL TECHNIQUES

CARBON RANGE	EXTRACTION/ANALYSIS METHOD	REPORT
C ₆ - C ₁₀	Solvent extraction: Direct Inj; GC/FID Methylene chloride or equivalent (No hexane or methanol) Methanol extraction: P & T; GC/FID	C ₆ - C ₁₀
C ₁₀ - C ₂₂	Solvent extraction: Direct Inj; GC/FID Methylene chloride, hexane, or equivalent (No methanol)	C ₁₀ - C ₂₂
C ₂₂ - C ₃₂	Solvent extraction: Direct Inj; GC/FID Methylene chloride, hexane, or equivalent (No methanol)	C ₂₂ - C ₃₂
C ₆ - C ₃₂	Solvent extraction: Direct Inj; GC/FID Methylene chloride or equivalent (No hexane or methanol)	C ₆ - C ₃₂ C ₆ - C ₁₀ C ₁₀ - C ₂₂ C ₂₂ - C ₃₂
C ₁₀ - C ₃₂	Solvent extraction: Direct Inj; GC/FID Methylene chloride, hexane, or equivalent (No methanol)	C ₁₀ - C ₃₂ C ₁₀ - C ₂₂ C ₂₂ - C ₃₂

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