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# Reference Method for the Canada-Wide Standard for Petroleum Hydrocarbons in Soil - Tier 1 Method

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*The Canadian Council of Ministers of the Environment (CCME) is the major intergovernmental forum in Canada for discussion and joint action on environmental issues of national, international and global concern. The 14 member governments work as partners in developing nationally consistent environmental standards, practices and legislation.*

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## *FOREWORD*

This analytical method was prepared by the Analytical Methods Technical Advisory Group (AMTAG) to the Petroleum Hydrocarbons Canada-Wide Standard (PHCs CWS) Development Committee reporting to the Canadian Council of Ministers of the Environment (CCME). AMTAG consists of representatives of various organizations and was appointed by CCME to prepare this method. Members are listed in Appendix 1. The method was written in response to a recommendation made to CCME to harmonize analysis of petroleum hydrocarbons.

CCME recognizes that technical progress and improved quality and efficiency can be achieved by allowing a performance-based approach. Some aspects of this Tier 1 Petroleum Hydrocarbons analysis method are performance-based. Some aspects are prescriptive and must be carried out exactly as written. With an aggregate parameter like petroleum hydrocarbons, comparability of analytical results across Canada can be accomplished only by prescribing many of the method details. Method details, such as purge and trap apparatus and Soxhlet extractors, are specified as benchmark methods, not as absolute requirements for the analysis.

Any method options selected for use by laboratories must be validated against these benchmarks as outlined in the method. Indeed, it is hoped that new techniques for extraction will increase the precision of this analysis. Any comparison should be designed to produce statistics, which allow meaningful comparisons between it and this benchmark method. Generally, the new method must be compared to this benchmark method using a variety of soil types including peaty soils and heavy clay soils. Otherwise, the comparison exercise may not be valid.

It is anticipated that suitable interlaboratory comparisons will become available in the near future from accreditation bodies in Canada. *Any method that is believed to be equivalent to this benchmark method must be approved by the appropriate jurisdiction*. Otherwise, it is recommended that this method be followed as closely as possible. Certain quality control criteria that must be met have also been specified.

## *1. SCOPE AND APPLICATION*

This analytical method is to be used for Tier 1 analysis of petroleum hydrocarbons for the application of the Canada-Wide Standard for Petroleum Hydrocarbons in Soil. The Canada-Wide Standard for Petroleum Hydrocarbons is designed for assessment and remediation of contaminated sites. This harmonized method is to replace the many different analysis methods previously used by various laboratories and jurisdictions in Canada. Tier 2 analyses may be developed for more detailed requirements when characterizing contaminated sites.

It is recognized that other chemicals for which soil quality criteria exist are often associated with PHC-contaminated sites. The most common of these are BTEX and certain PAHs. BTEX are the six compounds, benzene, toluene, ethylbenzene, and ortho, meta and para-xylene. These are mostly associated with gasoline. PAHs or Polycyclic Aromatic Hydrocarbons are also associated with petroleum products. Soil quality criteria exist for the following PAHs: naphthalene, phenanthrene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene and pyrene.[1] They are found in sources such as crude oils, tar oils, creosote and flare pits.

It is not intended that the results of the PHC analysis include either BTEX or PAHs. However, it is recommended that analysis of BTEX be performed at any site where volatile PHCs are suspected. It is also recommended that analysis for the above-mentioned PAHs be performed if there is any reasonable expectation that they may be present. [2] Note that any method chosen for naphthalene must ensure good recovery due to its volatility. Again, it is recommended that analysis for naphthalene be performed if there is some evidence that it may be present.[2] Often PAH analysis is performed simply to confirm PAHs are not present at a site.

The Canada-Wide Standard for Petroleum Hydrocarbons requires that four fractions be determined analytically to decide if the site meets acceptable criteria for various land uses. The four fractions, F1 through F4 are:

- F1, i.e., nC6 to nC10, as defined by this method, from which the results of a BTEX analysis have been subtracted, described as $F1_{-BTEX}$.
- F2, i.e., nC10 to nC16, as defined by this method from which naphthalene has been subtracted, described as $F2_{-napth.}$
- F3, i.e., nC16 to nC34, as defined by this method, less the PAHs phenanthrene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene and pyrene, if analyzed. This is described as $F3_{-PAH.}$
- F4, either as nC34 to nC50 obtained by gas chromatography from analysis of extractable hydrocarbons as defined by this method, or F4G, gravimetric heavy hydrocarbons, whichever is the greater result. See Section 11.4.

[1] Henceforth in this document, these are referred to as selected PAHs. If the CCME develops soil quality criteria for other PAHs, this list will have to reflect those additional PAHs.

[2] The basis for reasonable expectation of PAHs being present would normally be a past history of chemical manufacture or use on that site, e.g., wood preservation, tar oil manufacture.

**Note that not all samples will be analyzed for PAHs. The subtraction of PAHs will only be done if there are sufficient PAHs present to change the result from the PHC analysis.**
Each part of the method is defined by the analysis procedure and not by the chemistry of the samples. The procedure defined here should provide better consistency in data than is achieved by diverse analysis methods.

This method is not suitable for quantitation of individual hydrocarbons. BTEX and PAHs should be run by separate methods as appropriate to the jurisdiction where the sample was taken. The most recognized methods for BTEX involve purge and trap extraction followed by GC-MS. PAHs should be analyzed by solvent extraction followed by cleanup and GC-MS analysis. Normally, BTEX and PAHs would be subtracted from the PHC results derived by this method [1-4]. Sub-samples for the analysis of BTEX and PAHs should be taken from the same sample container or analyzed on the same sample taken for analysis of one of the appropriate hydrocarbon fractions.

This method is suitable for soil and sediment and has not been validated for other sample types. This method is not applicable to all PHC soil combinations. It is applicable to the majority of contaminated sites where refined products have been spilled. It is also applicable to many sites where crude oil operations have resulted in contamination. In those remaining sites where contamination by C50+ PHC is known or suspected, considerable deviation from this method may be required to satisfactorily extract and analyze a sample. In those cases, the calibration and quantitation should be as close as possible to this method to allow a valid comparison of results to the CWS PHC standard. Some advice is provided in Section 15.

### 1.1 Constraining PHC Quantitation Range

Inclusive procedures in the analytical method are provided on the assumption that PHC contamination may be "broad-band" and poorly characterized – as might occur in the case of a crude oil release, or when different product/waste streams coalesce in a downstream scenario. In some cases, however, reliable information exists to indicate that a PHC release is of a single type that is well characterized and confined to (1) three or less of the PHC CWS fractions, or (2) F1 to F3 plus only a portion of F4. The latter case is discussed in some detail in the analytical method - the go/no-go decision regarding extending chromatography beyond C50 or performing a gravimetric determination based on chromatogram characteristics and knowledge of release type.

In principle, similar approaches may be applied with respect to the first case. For example, if it is understood that PHC contamination is related to a recent release of a single grade of gasoline, and comprehensive gas chromatography of representative samples confirms this knowledge, F4 and possibly F3 can be eliminated from the analysis. Similarly, other simple fuel types may be confirmed by return of the chromatographic trace to the baseline region within the F3 envelope. In such cases, it may be unnecessary to extend chromatography to the C50 range.
Specific approved procedures must be confirmed with the jurisdictional authority.

## 2. METHOD SUMMARY

Fraction F1, C6 to C10 hydrocarbons, is determined by extracting a 5 g or greater soil sample with methanol, separating the methanol from the soil, then adding the methanol to a purging vessel or other equivalent or better apparatus used for determination of volatile organics. The sample is analyzed by gas chromatography with a 100% poly(dimethylsiloxane) (DB-1 or equivalent) column and a flame ionization detector. All area counts are integrated from the **beginning** of the nC6 peak to the **apex** of the nC10 peak to give F1. Standards containing nC6, nC10 and toluene are run. Toluene is used as calibration standard. The nC6 and nC10 response factors must be within 30% of the response factor for toluene. Note that only half of the nC10 peak is included in this analysis. The result of a BTEX analysis is subtracted to give the final result. Note that it may be possible to obtain very low or even negative numbers for PHCs in the presence of high concentrations of BTEX. $F1_{-BTEX}$ can never be less than zero. If a negative number occurs, report zero concentration for $F1_{-BTEX}$ .

Fractions F2, F3 and F4, extractable hydrocarbons in the range C10 to C50, are determined by extracting a 5 g dry weight or greater soil sample with 50:50 hexane:acetone[3] in a Soxhlet apparatus or other equivalent or better apparatus. The solvent recovered from the extracted sample is dried using sodium sulphate and treated either in situ or by column chromatography with silica gel to remove polar material.[4] The sample is analyzed by gas chromatography with a 100% poly(dimethylsiloxane) column and a flame ionization detector in the following three ranges.

- C10 to C16 hydrocarbons are determined by integration of all area counts from the apex of the nC10 peak to the apex of the nC16 peak. The average response factor for nC10, nC16 and nC34 hydrocarbons is used for primary calibration. This result gives Fraction F2. This result after naphthalene has been subtracted gives $F2_{-naphth}$.
- F3 result, C16 to C34 hydrocarbons, are determined by integration of all area counts from the apex of the nC16 peak to the apex of the nC34 peak. The average response factor for nC10, nC16 and nC34 hydrocarbons is used for primary calibration. This result after subtraction of selected PAHs, (phenanthrene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene and pyrene) if analyzed, gives Fraction $F3_{-PAH}$.
- F4 result, C34 to C50 hydrocarbons, are determined by integration of all area counts from the apex of the nC34 peak to the apex of the nC50 peak. The average response factor for nC10, nC16 and nC34 hydrocarbons is used for primary calibration. The GC response factor of the nC50 must within 30% of the average response factor of the nC10, nC16 and nC34 hydrocarbons. This result gives fraction F4 **provided** that the chromatogram descends to baseline by the retention time of nC50. **Note** that only half of the nC10 and half of the nC50 peaks are included in these analyses. Similarly, the nC16 and nC34 peaks are each split between two fractions.

[3] This solvent mixture was chosen since it will allow extraction of wet soils. Dichloromethane was rejected, as it can also extract organic compounds other than hydrocarbons. It is recognized that, as hydrocarbons degrade, the resulting mix contains polar species. In reality, there is no perfect solvent. Hexane:acetone was felt to be the best compromise. DCM was rejected partly as efforts are in place in some labs to reduce or eliminate DCM as part of an effort to "green" laboratories.

[4] The use of silica gel to remove polar compounds must be performed carefully with well defined procedures. Otherwise hydrocarbons will be lost.

- Gravimetric heavy hydrocarbons,F4G, **must** be determined only if the chromatogram of the C34 to C50 hydrocarbons indicates that hydrocarbons greater than C50 are present as evidenced by the chromatogram failing to return to baseline at or above C50. A 5 g or greater soil sample is extracted with 50:50 hexane:acetone. The solvent is evaporated and the weight of residue determined. If the result is less than 50% of the CWS PHC criteria for the soil type and proposed use, stop the analysis and report this result. If the result is higher than 50% of the CWS PHC criteria, the sample can then be reconstituted in 50:50 dichloromethane:hexane, treated with silica gel one time only, re-evaporated and the weight of residue determined. Both the C34 to C50 GC result and the gravimetric result F4G or F4G-sg are reported but the greater result is reported as Fraction F4. **Gravimetric heavy hydrocarbon data obtained on soil samples is known to be highly variable. The gravimetric heavy hydrocarbon result is not added to the gas chromatographic result.**

**Note:** Alternatively, if acceptable to the jurisdiction, a high temperature gas chromatographic analysis[5] may be done in addition to the nC10 to nC50 analysis described in this method to determine the exact quantity of hydrocarbons greater than nC34. F4 will then be the result of all hydrocarbons greater than nC34 as measured by high temperature gas chromatography. This would normally be part of the Tier 2 approach. If analyzed, this method would give $F4_{HTG.}$

Percent moisture is determined by carefully heating a 5 g or greater soil sample in an oven at 101°C to 110°C overnight or until a constant weight is achieved. **Percent moisture includes loss of volatile hydrocarbons.**

## *3. SAFETY CONSIDERATIONS*

The testing and analysis of samples using this method may require the use of equipment and materials that could be hazardous. Anyone using this method is responsible for consulting the appropriate authorities and establishing appropriate health and safety practices in conjunction with any applicable regulatory requirements prior to its use. CCME neither assumes nor accepts any responsibility for any injury or damage that may occur during or as a result of the analyses wherever performed.

This method does not address all safety issues associated with its use. Please refer to material safety data sheets (MSDSs) for reagents used in this method.

Petroleum hydrocarbons are flammable and certain components of petroleum products can pose other hazards to human health.

Gasoline generally contains significant levels of aromatic hydrocarbons, which may be carcinogens.

[5] The ASTM D6352-98, "Standard Test Method for Boiling Point Distribution of Petroleum Distillates in Boiling Range from 174 to 700ºC by Gas Chromatography", may be useful in developing an in-house laboratory method for this purpose.

This method specifies heating and drying of samples. Do not put hydrocarbon-containing samples or solvent extracts directly into the oven as this may cause fire or liberation of toxic vapours. Rather, air-dry the sample first in a fume cupboard and then carefully place it in the oven after the organic vapours have evaporated.

## *4. LOSS/CONTAMINATION CONTROL*

Collect soil samples quickly in wide mouth glass jars with aluminium foil or Teflon-lined lids. Completely fill the sample bottles, leaving no headspace and transport them to the laboratory as soon as possible.

Glassware, reagents and solvents are potential sources of contamination or elevated baselines. All materials should be of the highest quality possible. Glassware should be rinsed with hexane and air-dried.

Any volatile or extractable substance is a potential interference.

Run glassware blank with every batch of samples.

To avoid losses in the C6 to C10 fraction, carry out the methanol extraction of the samples within 48 hours of sample receipt or a maximum of 7 days from sample collection. For the C10 to C50 fractions, again holding times should be minimized but they should be extracted no later than 14 days of sample receipt and extracts held no more than 7 days.

## *5. SAMPLING, SAMPLE SIZE, PREPARATION AND WEIGHING PROCEDURE*

Sampling must be done by qualified personnel, experienced in sampling activities and working under standard documented operating conditions. The objective of sampling is to collect a set of samples that is suitable for chemical analysis to assess compliance with the targets set by CCME. Since compliance decisions are made from analysis of the sample, it is important that the sample be properly taken in a quality-controlled manner for submission to a laboratory and that the sample be representative of the area being sampled.

Many components of petroleum hydrocarbons are volatile and biodegradable. Collect soil samples as quickly as practicable in wide mouth glass jars with aluminum foil or Teflon-lined lids and cool to $4^{o}C$ as soon as possible. Completely fill the sample bottles, leaving minimal headspace. Collect a single bottle of sample. No chemical preservation is used. Transport samples to the laboratory as soon as possible.

Label samples clearly with the date and time of sampling, location or source of the sample, whether the sample is a grab or composite, analysis required and the identity of the individual who collected the sample. Fill out labels in indelible ink and affix to the sample container to ensure that it will not fall off when wet or during transport.

When a sample could be considered as evidence in an investigation, chain of custody procedures are required. Chain of custody requires demonstration that samples have not been tampered with at

any point in handling or shipping and that the individuals in charge of the samples can be identified at every stage in the sampling and analysis operation.

In the analytical laboratory, take four separate samples from the same sample bottle for determination of C6 to C10 hydrocarbons, C10 to C50 hydrocarbons, gravimetric heavy hydrocarbons and moisture content. The sample size should be a minimum of 5 g of dry weight for each of the four samples taken. Total wet weight to be taken should be estimated when the % moisture is unknown. Note that sub-samples for both BTEX and PAH analysis should also be taken from the same sample.

Effective sample handling requires good judgment. Minimal sample manipulation helps to avoid losses of volatile components. The water content of certain samples may require the use of diatomaceous earth as a water sorbent. The use of sodium sulphate as a drying agent for wet soil samples could lead to an exothermic reaction resulting in loss of C10 and other volatile materials.

The sample should be at about 4$^{o}$C when opened to take sub-samples for analysis to minimize loss of volatile materials. Mix the sample with a spatula very quickly to homogenize the sample while minimizing loss of volatile material. Avoid non-representative material such as sticks and stones while taking the sample.

In the event that other analyses are required on the same sample, they should be taken from the same sample container or analyzed on the same sample taken for analysis of one of the hydrocarbon fractions.

Collect soil samples in a manner that minimizes sample handling and agitation. If possible, do not collect samples from soil exposed to direct sunlight. This may mean removing some surface soil to obtain a fresh sample. The use of specially designed airtight collection samplers is recommended. All soil must be removed from the threads of jars and vials to ensure an adequate seal. Samples must be cooled to 4$^{o}$C immediately after collection. They must be kept at 4$^{o}$C or below during shipment and until analyzed. Freezing may cause glass sample bottles to break, thus rendering the samples useless. Ship samples to the laboratory as fast as possible. Several references are recommended for developing suitable standard operating procedures for collecting samples [5-8].

## 6. PRESCRIPTIVE ELEMENTS OF THE METHOD

The following general elements of this method are mandatory and must be carried out exactly as outlined in this method. Additional prescriptive elements are described in the sample analysis sections.

Although this document is a performance-based method, which permits some flexibility in how the method is carried out, a laboratory must have a valid written laboratory SOP documenting how the method is carried out in that laboratory. Laboratories must use a documented quality system conforming to ISO Guide 25[6] or CAN/CSA-Z753 [9] or equivalent.

Validation of performance-based method options chosen by a laboratory must be carried out on reference samples that have been previously validated by this analytical method.

Solvents specified in the method must be used. Although the solvents specified in this method may not always be the best solvents for all situations, their consistent use should result in comparability between laboratories using this Tier 1 hydrocarbon analysis method.

Method validation, as described in Appendix 2, must be carried out and documented.

A minimum sample size of 5 g dry weight for each analysis is required unless limited by insufficient sample. Samples for analysis must be able to be handled and weighed as a solid sample, as this method is not validated for liquids, slurries or other sample types.

Method detection limits must be determined experimentally, as outlined in Appendix 3.

GC performance criteria described in Sections 10.1 and 11.1 of this method must be rigorously met. Interlaboratory testing has confirmed that failure to meet the required QC performance criteria results in poor quality data.

## 7. PERFORMANCE-BASED ELEMENTS OF THE METHOD

The following general elements of the method are performance-based and allow laboratories to select method options suitable to their situation and increase efficiency and technical improvements. Additional performance-based elements are described in Sections 10 and 11.

The use of surrogate chemicals is optional. Surrogates are used, however, only to detect mechanical problems in the analysis and should not be used to correct the data. One candidate for an internal standard is 5-a-androstane, often used in identification of petroleum analyses.[7]

Petroleum products should be selected by the laboratory for quality control purposes to cover the applicable carbon ranges and the product types typical of samples common to that laboratory. These products are used for confirming validity of the calibration standards, MDL determination,

[6] ISO Guide 25 was replaced by ISO Standard 17025 as of January 2000.
[7] Note that the integration program will have to be modified to eliminate the added 5-a-androstane.

and retention time range markers for product identification and as spiking materials. Quality control criteria for calibration and method quality control must be within acceptable limits for the analysis to proceed and for data to be reported.

If desired, a single sample can be taken for C10 to C50 hydrocarbons and gravimetric heavy hydrocarbons provided that, when the sample is split for analysis after extraction, extracted material corresponding to a minimum of 5 g dry weight of original sample is taken for each analysis.

## *8. QUALITY CONTROL CRITERIA*

The following quality control criteria are mandatory and must be demonstrated before and during analysis:

Method Detection Limits (MDLs) must be met as follows:

- F1,C6 to C10 hydrocarbons **10.7 mg/kg**
- F2, C10 to C16 hydrocarbons **3.9 mg/kg**
- F3, C16 to C50 hydrocarbons **9.0 mg/kg**
- F4G (gravimetric) based on motor oil **29 mg/kg**

The MDL calculation must be similar to ACS, USEPA, Quebec MEF and Ontario MOE procedures. It is not an instrument detection limit.

Data quality objectives for laboratory precision must be repeated analysis of a single, homogenous sample at levels greater than 10 times MDL for the analyses as:

- C6 to C10 hydrocarbons 30%
- C10 to C16 hydrocarbons 20%
- C16 to C34 hydrocarbons 20%
- C34 to C50 hydrocarbons 20%
- Gravimetric heavy hydrocarbons 30%

## *9. QUALITY CONTROL SAMPLES*

At a minimum, the laboratory quality control samples as described in this section must be run with each 20 samples analyzed. Quality control samples must be processed through the entire analytical method and be reported with the data. Quality control samples must be run for each of the analyses. The laboratory should generate quality control statistics for each quality control sample type.

A method blank is prepared using all reagents and equipment, but with no sample. Method blanks must give results that are less than the MDL.

A duplicate is a second portion of sample taken from the same sample bottle and processed through the same analytical run.

A petroleum product is used for preparing spiked samples. A good choice of product is the material used for the determination of MDL.

A performance sample is a blank or clean soil that is spiked or fortified with an appropriate product as determined by the laboratory and analyzed as though it were a sample. Alternately, reference samples with values previously validated by the CWS PHC method can be used as performance samples. A performance sample should be recovered within ±20%. Performance samples are also available from commercial companies as gasoline or diesel in soil. They should be used with caution, however, as the methods used to analyze them may not be comparable to this method.

As an option, laboratories can prepare a spiked sample, which is a second sample taken from the same sample bottle and fortified with an appropriate product as determined by the laboratory and analyzed as though it were a sample.

Sampling personnel should be encouraged to generate field quality control samples to be submitted to the laboratory along with the samples for analysis. Field quality control can be duplicate samples taken in the field and field blanks, which can be blank soils provided by the laboratory, taken to the field and returned.

## *10. SAMPLE ANALYSIS – C6 TO C10 HYDROCARBONS (F1)*

### 10.1 Prescriptive Elements

- Use gas chromatography with flame ionization detector and 100% poly(dimethylsiloxane) low bleed chromatography columns, 15 m minimum length and 0.53 mm maximum diameter, to analyze the C6 to C10 hydrocarbons. The chromatography system must separate the nC6 peak from the solvent peak.
- Use methanol extraction to analyze the C6 to C10 hydrocarbons.
- Ensure that the soil is dispersed in the methanol.
- As light hydrocarbons are not stable in soil samples, ensure that the sample is extracted with methanol within 48 hours of sample receipt or a maximum of 7 days from sample collection.
- Toluene is the primary calibration standard for C6 to C10 hydrocarbons.
- Mandatory instrument performance criteria for C6 to C10 is that the nC6 and nC10 response factors must be within 30% of the response factor for toluene.
- Perform BTEX analysis on a second sub-sample or simultaneously, e.g., by using a column splitter to an MS detector, if volatile PHCs are suspected. Alternatively, the same extract can be used if it does not compromise the required MDLs.

## 10.2 Performance-based Elements

- Purge and trap is the benchmark method for C6 to C10 hydrocarbons, but other suitable methods can be substituted provided that validation data demonstrates that the substitute method provides data comparable to the benchmark method.[8]
- If headspace analysis is to be used as an alternative to purge and trap, consider salting the sample in the headspace unit to improve the recovery of aromatic compounds, which are known to be biased low compared to aliphatics in headspace analysis.
- It is best to minimize the quantity of methanol taken for analysis, while at the same time taking sufficient sample to achieve desired MDLs.

## 10.3 Reagents

- All chemicals used in the method should be ACS reagent grade or better.
- Perform calibration and retention time marking for the C6 to C10 hydrocarbons using a mixture of approximately equal weights of toluene, nC6 and nC10 dissolved in methanol.
- Products used as control standards or linearity checks should cover the applicable carbon ranges for the analysis.
- MDL determination for the C6 to C10 hydrocarbons is determined experimentally using gasoline added to clean soil.

## 10.4 Analysis Procedure

- Take a minimum sample size of 5 g dry weight for C6 to C10 hydrocarbons as quickly as possible while still at 4$^{o}$C to avoid losing volatile components. Transfer this sample to a tared glass vial with cap, and weigh it. If BTEX is also being analyzed, it is advantageous to weigh out a second sample immediately.
- Quickly add methanol in an amount that will ensure a methanol:wet solid ratio of approximately 2:1 or greater and recap the vial. Mix the vial on a mechanical shaker for one hour. Ensure that the soil is dispersed in the methanol.
- Allow the solids to settle, recover the methanol for analysis and store a portion of the methanol at 4$^{o}$C for reanalysis if required.
- Measure an appropriate volume of methanol into a purge vessel containing clean water. Purge the sample into an appropriate gas chromatograph with flame ionization detector and a 100% poly(dimethylsiloxane) column. Different volumes of methanol extract can be run to get a chromatogram in the range of the calibration curve, but the reported MDL must be adjusted accordingly.
- Integrate the area under the chromatogram from the beginning of the nC6 peak to the apex of the nC10 peak as a single peak. Ensure that baseline drift between chromatograms is accounted for during integration.

[8] Methods using methanol usually provide better recoveries than straight purge and trap methods, especially for toluene and xylenes.

- The following are GC conditions used in two laboratories, which resulted in acceptable recovery of nC6 and nC10.

| | |
|---|---|
| Column: | DB1 (0.25 mm id, 1.0 µm film, 60 m length) |
| Carrier gas: | Helium |
| Head pressure: | 13 psi at 35°C |
| Column flow: | Constant pressure |
| Injector temperature: | 250°C |
| Injector mode: | Purge and trap<br>10 minutes purge<br>4 minutes dry purge<br>6 minutes desorb, Vocarb 4000 trap |
| Solvent: | Water with methanol extract dissolved |
| Sample volume: | 5 mL water |

| | |
|---|---|
| Column: | 100% poly(dimethylsiloxane) column (0.53mm id, 1.5 µm film, 30 m length) |
| Carrier gas: | Helium |
| Head pressure: | 5.0 psi at 36°C |
| Column flow: | 7.48 mL/min, constant flow recommended |
| Injector temperature: | 200°C |
| Injector mode: | Split/splitless or on column inlet |
| GC liner: | 4 mm id splitless liner with silanized glass wool |
| Initial inlet purge: | Off |
| Inlet purge on time: | 0.3 minutes |
| Oven program: | 36°C for 3 minutes, 5°C per minute to 150°C, 15°C per minute to 240°C, then hold 6 minutes |
| Detector temperature: | 250°C (See Section 11.4) |
| Solvent: | Methanol |
| Injection volume: | 1 to 2 µL |

**10.5 Calibration Procedure**

- Perform calibration and retention time marking for the C6 to C10 hydrocarbons using a mixture of approximately equal weights of toluene, nC6 and nC10 dissolved in methanol.[9]
- For the C6 to C10 hydrocarbons, run a minimum of a 3-point calibration curve using toluene and a blank before analysis begins. Although calibration is based on integration of area under the chromatogram between retention time markers, the highest standard must give a higher peak height than the highest peak height in the samples to be run. Dilute samples so that the peak height of the largest sample peak is less than the peak height of the highest calibration standard. Verify instrument calibration using reference standards procured from a second source.

[9] It is useful to prepare a second set of calibration standards, either from a separate source or made up of pure chemicals by a second person. The second set can be used to verify the primary standards over a long period.

- Linearity of the detector response must be established using a product such as gasoline and with the single compound calibration standards. Linearity must be within 15% in each of the calibrated carbon ranges for products and within 10% for single compounds.
- At a minimum, run a daily check of the lowest calibration standard and the midpoint calibration standard to confirm stability of the calibration curve. Rerun the calibration curve if the low standard deviates by more than 20% from the curve or if the midpoint calibration standard deviates by more than 15% from the curve.

### 10.6 Calculations

**Calculation of average response factor ($RF_{avg}$) -** For the toluene standards in each of the calibration curves, calculate a response factor (RF) and take an average of all these response factors.

$$RF = \frac{A_{tol}}{C_{tol}}$$

Where $A_{tol}$ = Area under the toluene peak for a calibration standard
$C_{tol}$ = Micrograms of toluene standard injected

The average response factor is calculated as:

$$RF_{avg} = \frac{\text{sum of individual RF values}}{\text{number of RF values used}}$$

Be sure to use the same units at all times for RF calculations.

**Calculation of F1 C6 to C10 petroleum hydrocarbons in a sample -** The average RF is used to calculate the C6 to C10 hydrocarbons as follows:

$$C6-C10 \text{ hydrocarbons (mg/kg)} = \frac{A_{C6-C10} * Vol * F}{RF_{avg} * W_d * Ext}$$

Where $Area_{C6-C10}$ = The integration of all area counts from the beginning of the C6 peak to the apex of the nC10 peak
Vol = Volume of methanol including any extracted water from the sample (mL)
F = Dilution factor applied to bring the samples and standards into appropriate peak height range
$RF_{avg}$ = Average response factor calculated above
$W_d$ = Dry weight of sample taken (g)
Ext = Volume of sample extract (methanol and water) taken for analysis (mL)

**BTEX must be analyzed separately and subtracted from the C6 to C10 hydrocarbon result to give the $F1_{-BTEX}$ result.**

Note that the volume used (Vol) must be the volume of methanol including any extracted water from the sample. This volume can be calculated from the volume of methanol used and the % moisture calculated in Section 13 as follows:

$$\text{Vol} = \text{Volume of Methanol} + \frac{\text{Wet weight of sample} * \%\text{Moisture}}{100}$$

## *11. SAMPLE ANALYSIS – C10 TO C50 HYDROCARBONS (F2, F3 and F4)*

### 11.1 Prescriptive Elements

- Use gas chromatography with flame ionization detector and 100% poly(dimethylsiloxane) low bleed chromatography columns, 15 m minimum length and 0.53 mm maximum diameter for analysis of the C10 to C50 hydrocarbons. The chromatography system must separate the nC10 peak from the solvent peak.
- The primary calibration standard for the C10 to C50 hydrocarbons is a mixture of approximately equal amounts of nC10, nC16 and nC34 normal hydrocarbons.
- Mandatory instrument performance criteria for C10 to C50 are that nC50 response factor must be a within 30% of the average of nC10, nC16 and nC34 response factors and the nC10, nC16 and nC34 response factors must be within 10% of each other. This performance criterion must be met by any injection system used for hydrocarbon analysis and confirmed on a daily basis.
- 100% activated silica gel must be used to clean up the C10 to C50 hydrocarbons. Use 0.6 g of 100% activated silica gel for each gram of sample taken.

### 11.2 Performance-based Elements

- Either split/splitless, on column or other injection methods are allowed, subject to meeting quality criteria for C50 recovery in Section 11.1.
- Soxhlet extraction apparatus is the benchmark method for the C10 to C50 hydrocarbons, but other suitable extraction methods can be substituted provided that validation data demonstrate that the substitute method provides data comparable to the benchmark method.
- Other elements of the method, such as the rotovap, shaker apparatus and ovens, can be substituted provided that the quality control criteria listed in Section 8 are met and that validation data has been generated to support the method changes.

### 11.3 Reagents

- All chemicals used in the method should be reagent grade or better.
- All single compound chemical calibration standards should be pure and of the highest quality available. The nC10, nC16 and nC34 hydrocarbons are prepared in toluene. The nC50 is also prepared in toluene but is only soluble to about 15 µg/mL.
- Products used as control standards or linearity checks should cover the applicable carbon ranges for the analysis.
- MDL for the C10 to C50 hydrocarbons is determined experimentally using a weathered diesel product added to clean soil.
- Silica gel should be pure, 60 to 200 mesh and should be 100% activated by drying at >101$^{o}$C overnight and used immediately.

### 11.4 Analysis Procedure

For C10 to C50 hydrocarbons, weigh a minimum sample size of 5 g dry weight into a tared Soxhlet thimble or equivalent apparatus. **If sample requires drying, mix with sufficient amount of diatomaceous earth until mixture is free-flowing.**

- Set up the equipment to extract the sample with 50:50 n-hexane:acetone at a minimum 20:1 solvent:dry soil ratio. The extraction should proceed for 16 to 24 hours with the Soxhlet operating at 4 to 6 cycles per hour.
- Recover the solvent and pass it through 8 to 9 g of dried sodium sulphate in a column. Rinse the sodium sulphate through with 5 to 10 mL of hexane.
- Add 1 to 2 mL[10] of toluene to the recovered solvent in an evaporating vessel. Evaporate the solvent to a volume of 1 to 2 mL. Evaporation conditions must be demonstrated to avoid the loss of the nC10 hydrocarbon. At this point, a physical separation of water may be required.
- For silica gel cleanup, use either of the following options (in-situ or column).[11]

**Option A - In-situ Silica Gel Cleanup**

- Add a minimum of 20 mL of 50:50 n-hexane:dichloromethane to the recovered solvent.
- Add 100% activated silica gel to the hexane/DCM/toluene mixture in an amount of 0.6 g silica gel per gram of dry sample[12]. Stir or shake the mixture for a minimum of 5 minutes, then recover the solvent mixture.
- Add 1 to 2 mL of toluene to the recovered solvent in an evaporating vessel. Evaporate the solvent to a volume of 1 mL. If volume reduction is needed to meet the required MDL, place the solvent in an evaporating apparatus such as a rotary evaporator. Evaporation conditions must be demonstrated to avoid the loss of the nC10 hydrocarbon.

[10] Note that it is important to minimize the amount of toluene added. If 2 mL is added twice, then it will be difficult to reduce the volume to less than 3 to 4 mL.

[11] It is recognized that use of silica gel may reduce the nominal value of the result. Care must be taken to ensure that only non-hydrocarbons are retained on the column. An alternative to adding silica gel to the solvent mixture is to use a 5 g silica gel column. See Section 15.1 for the rare situation when silica gel cleanup may not be the best approach.

[12] When the total quantity of extractable organics from a sample is estimated to exceed 500 mg, it is recommended that an appropriate quantitative fraction of the sample be cleaned up. This prevents saturation of silica gel, which will occur only with samples that contain extremely high levels of organics. If only a portion of a sample is cleaned up, ensure that this is considered as a dilution during calculations.

**Option B – Silica Gel Column Cleanup**

- Prepare a silica gel column for each sample. Place a small quantity of glass wool into the bottom of a glass column with an internal diameter of approximately 15 to 20 mm., then dry-pack the column with (5.0±0.2) g of 100% activated silica gel. Add about 1 cm of anhydrous sodium sulphateto the top of the silica gel. The column dimensions must be such that the bed depth of the silica gel exceeds 20 mm. Clean and wet the column by eluting at least 10 mL of 50:50 hexane:DCM through the column. Do not collect this eluant.
- Quantitatively transfer the extract onto a silica gel column.[13] Collect all further eluant from the silica column in an evaporating vessel. Allow the solvent level to drop below the top of the silica bed, and then elute the column with a minimum of 20 mL of 50:50 hexane:DCM.
- Add 1 to 2 mL of toluene if required to the recovered solvent, using a rotary evaporator or other evaporation apparatus reduce collected solvent to a volume of approximately 2 to 5 mL. Quantitatively transfer the extract to a smaller vial and concentrate further to an accurate final volume of 2 mL, or to a larger final volume if appropriate. Evaporation conditions must be demonstrated to avoid the loss of the nC10 hydrocarbon.
- If the extract is not to be chromatographed immediately, transfer the extract to a vial and store in the dark at 4°C or less. Bring the extract back to room temperature before GC analysis.
- Integrate the area under the chromatogram from the apex of the nC10 peak to the apex of the nC16 peak, from the apex of the nC16 peak to the apex of the nC34 peak and from the apex of the nC34 peak to the apex of the nC50 peak. If the chromatogram returns to baseline by the end of the C34 fraction and no heavier material is suspected, then subsequent analyses on samples from the same site may be terminated at this point.[14] Note whether the chromatogram has returned to baseline[15] at nC50 to determine whether gravimetric heavy hydrocarbons are required. Ensure that baseline drift due to column bleed between chromatograms is accounted for during integration either by blank subtraction or by column compensation.
- The following are GC conditions used in two laboratories, which resulted in acceptable recovery of nC50.

| | |
|---|---|
| Column: | DB1ht (0.32 mm id, 0.1 µm film, 30 m length) |
| Carrier gas: | Hydrogen |
| Head pressure: | 18.4 psi at 40°C |
| Column flow: | 9.96 mL/min at 40°C, constant flow |
| Injector temperature: | 300°C |
| Detector temperature: | 340°C |

[13] The silica gel cleanup is intended to selectively remove naturally occurring polar organics without removing most petroleum hydrocarbons. It is recognized that some petroleum hydrocarbons and their degradation products may also be removed to some extent Adequate rinsing of the silica gel column, however, will minimize these losses. See Section 15.1 for the rare situation when silica gel cleanup may not be the best approach.

[14] Information about the sample and professional judgement are required to ensure an accurate result in these cases.

[15] Note: "Returned to baseline" is defined as: less than 5% of the total C10 to C50 hydrocarbon "envelope" elutes past the C50 retention time compared to a solvent blank.

| | |
|---|---|
| Injector mode: | Split/splitless, 4 mm liner with silanized glass wool |
| Solvent: | Toluene |
| Injection volume: | 2 µL |
| Oven program: | 40°C for 1 minute, then 15°C per minute to 340°C, hold 20 minutes |

| | |
|---|---|
| Column: | SPB1 (0.53 mm id, 0.15 µm film, 15 m length) |
| Carrier gas: | Helium |
| Head pressure: | 2.7 psi at 35°C |
| Column flow: | 7.6 mL/min at 35°C |
| Injector temperature: | 35°C |
| Detector temperature | 320°C |
| Injector mode: | On column |
| Solvent: | Hexane |
| Injection volume: | 1 µL |
| Oven program: | 35°C for 2 minutes, then 30°C per minute to 300°C, hold 10 minutes |

### 11.5 Calibration Procedure

- Perform calibration and retention time marking for the C10 to C50 hydrocarbons using approximately equal weights of nC10, nC16 and nC34 hydrocarbons dissolved in toluene.[16]
- A solution of nC50 in toluene is used as retention time and response factor standard for the C10 to C50 hydrocarbons.
- For the C10 to C50 hydrocarbons, run a minimum of a 3-point calibration curve using the nC10, nC16 and nC34 hydrocarbons and a blank before analysis begins. Although calibration is based on integration of area under the chromatogram between retention time markers, the highest standard must give a higher peak height than the highest peak height in the samples to be run. Dilute samples so that the peak height of the largest sample peak is less than the peak height of the highest calibration standard.
- Establish linearity of the detector response using products such as diesel or motor oil and with the single compound calibration standards. Linearity must be within 15% in each of the calibrated carbon ranges for products and within 10% for single compounds.
- At a minimum, run a daily check of the lowest calibration standard and the midpoint calibration standard to confirm stability of the calibration curve. Rerun the calibration curve if the low standard deviates by more than 20% from the curve or if the midpoint calibration standard deviates by more than 15% from the curve.

### 11.6 Calculations

**Calculation of average response factor ($RF_{avg}$)** - For each of the hydrocarbon standard alkanes (nC10, nC16 and nC34) within each of the minimum 3-point calibration curve runs, calculate a response factor (RF) and take an average of all these response factors. For example, if you use a 5-point calibration curve, you will average 15 individual RFs.

[16] Note: It is better laboratory practice to match the solvents of calibration solutions to that of sample extracts. However, solubility requirements may require standards to be made up in one solvent and diluted into another, e.g., nC34 can be made up into cyclohexane and then diluted into toluene for the working solution.

Each individual RF is calculated as:

$$RF = \frac{A_{n-alk}}{C_{n-alk}}$$

Where $A_{n\text{-}alk}$ = area under the individual n-alkane peak
$C_{n\text{-}alk}$ = concentration of the individual n-alkane standard

The average response factor is calculated as:

$$RF_{avg} = \frac{\text{sum of individual RF values}}{\text{number of RF values used}}$$

Be sure to use the same units at all times for RF calculations.

**Calculation of petroleum hydrocarbons in a sample** - The average RF is used to calculate the hydrocarbons in each of the ranges C10 to C16, C16 to C34 and C34 to C50.

**F2**

$$\text{C10} - \text{C16 hydrocarbons (mg/kg)} = \frac{A_{C10-C16} * Vol * F}{RF_{avg} * W_d}$$

If naphthalene is analyzed, it must be subtracted from the F2 result and reported as $F2_{\text{-napth}}$.

**F3**

$$\text{C16} - \text{C34 hydrocarbons (mg/kg)} = \frac{A_{C16-C34} * Vol * F}{RF_{avg} * W_d}$$

If PAHs (phenanthrene, benz(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene and pyrene) are analyzed, they must be subtracted from this result to give the F3 result, to give $F3_{\text{-PAH}}$.

**F4 Note:** See the second paragraph in Section 2 to decide if this result or the result from the Gravimetric Heavy Hydrocarbon analysis, F4G, is used for F4.

$$\text{C34} - \text{C50 hydrocarbons (mg/kg)} = \frac{A_{C34-C50} * Vol * F}{RF_{avg} * W_d}$$

Where:

| | | |
|---|---|---|
| $Area_{C10-C16}$ | = | The integration of all area counts from the apex of the C10 peak to the apex of the nC16 peak |
| $Area_{C16-C34}$ | = | The integration of all area counts from the apex of the C16 peak to the apex of the nC34 peak |
| $Area_{C34-C50}$ | = | The integration of all area counts from the apex of the C34 peak to the apex of the nC50 peak |
| Vol | = | Final volume of sample extract (mL) |

| | | |
|---|---|---|
| F | = | Dilution factor applied to bring the samples and standards into appropriate peak height range |
| $RF_{avg}$ | = | Average response factor calculated above |
| $W_d$ | = | Dry weight of sample taken (g) |

## *12. SAMPLE ANALYSIS – GRAVIMETRIC HEAVY HYDROCARBONS (F4G)*

### 12.1 Prescriptive Elements

- 50:50 n-hexane:acetone must be used as the solvent.
- The final determination is gravimetric.

### 12.2 Performance-based Elements

- Soxhlet extraction apparatus is the benchmark method for the gravimetric heavy hydrocarbons, but other suitable extraction methods can be substituted provided that validation data demonstrates that the substitute method provides data comparable to the benchmark method.

### 12.3 Reagents

- All chemicals used in the method should be reagent grade or better.
- MDL for the gravimetric heavy hydrocarbons is determined experimentally using a 30-weight, non-detergent grade motor oil product added to clean soil.
- Silica gel should be pure, 60 to 200 mesh and should be 100% activated by drying at >101$^{o}$C overnight and used immediately.

### 12.4 Analysis Procedure

- Weigh a minimum sample size of 5 g dry weight for gravimetric heavy hydrocarbons into a tared Soxhlet thimble or equivalent apparatus.
- Set up the equipment to extract the sample with 50:50 n-hexane:acetone at a minimum 20:1 solvent-to-dry-soil ratio. Proceed with the extraction for 16 to 24 hours with the Soxhlet operating at 4 to 6 cycles per hour.
- Recover the solvent and evaporate it in a tared aluminium dish in a fume hood, then further evaporate it in an oven at 101$^{o}$C to 110$^{o}$C to remove water and light hydrocarbons. Do not put samples containing volatile hydrocarbons directly into the oven without first evaporating fumes.
- Cool to constant weight in a desiccator and weigh to the nearest 0.0001 g or better.
- Calculate gravimetric heavy hydrocarbons. **If the result obtained is 50% or less of the applicable CWS PHC criteria for the soil type and lands use, if known to the analyst, stop the analysis and report the result.**
- If separation of polar from non-polar material is desired or requested, redissolve the material in the aluminium pan in 50:50 dichloromethane:hexane. Add 100% activated silica gel to the hexane/DCM mixture in an amount of 0.6 g silica gel per gram of sample. Stir or shake the mixture for a minimum of 5 minutes. This silica gel cleanup procedure can be carried out one time only for each sample. **Caution:** silica gel cleanup has limitations when applied to soils of high organic content.

- Recover the solvent and evaporate it in a tared aluminium dish in a fume hood, then further evaporate it in a oven at 101 to 110$^{o}$C.
- Cool to constant weight in a dessicator and weigh to the nearest 0.0001 g or better.
- Calculate silica gel treated gravimetric heavy hydrocarbons.

### 12.5 Calibration Procedure

- Use Class S weights for confirmation of calibration of the balance for the gravimetric heavy hydrocarbons.

### 12.6 Calculations

Calculation of gravimetric heavy hydrocarbons (GHH), F4G, with and without silica gel treatment, F4G-sg, is carried out using the following equation. All weights must be corrected for tare weight of the apparatus by the laboratory.

$$\text{GHH (mg/kg)} = \left( \frac{W_x(g)}{W_d(g)} \right) * 10^6$$

Where $W_x$ = weight of extractable material after drying
$W_d$ = dry weight of sample

$$\text{GHH after silica gel (mg/kg)} = \left( \frac{W_{sq}(g)}{W_d(g)} \right) * 10^6$$

Where $W_{sg}$ = weight of extractable material after silica gel treatment and drying
$W_d$ = dry weight of sample

The result from the gravimetric heavy hydrocarbon, F4G, analysis **must** be substituted for the result for F4 if it is greater than the value obtained by gas chromatography for nC34 to nC50 from the extractable hydrocarbons described in Section 11.2. However, both the results from the GHH and the GC analysis are reported. See also the note in paragraph 2 of Section 2.

## *13. SAMPLE ANALYSIS – MOISTURE DETERMINATION*

### 13.1 Prescriptive Elements

- The sample must be dried in an oven at 101 to 110$^{o}$C. Note that moisture determination includes loss of water plus loss of volatile hydrocarbons.

### 13.2 Performance-based Elements

- None

### 13.3 Reagents

- None

### 13.4 Analysis Procedure

- Transfer a minimum of 5 g of sample for moisture determination to a tared aluminium pan or similar apparatus and weigh it to the nearest 0.01 g or better.
- Evaporate moisture and other volatiles from the fume hood if necessary, then dry in an oven at 101 to 110$^{o}$C overnight or until a constant weight is achieved. Do not put samples containing volatile hydrocarbons directly into the oven without first evaporating fumes.
- Transfer the sample to a desiccator where it is cooled to room temperature for 30 minutes or more.
- Weigh the sample on an analytical balance with a sensitivity of 0.01 g or better.

### 13.5 Calibration Procedure

- Use Class S weights for confirmation of the balance calibration.

### 13.6 Calculations

Calculate percent moisture from the loss of weight according to the following equation. Note that all the weights must be corrected for tare weights of apparatus by the laboratory.

$$\%\ Moisture = \left( \frac{S_b(g) - S_a(g)}{S_b(g)} \right) * 100\%$$

where $S_b$ = weight of sample before drying, in grams
$S_a$ = weight of sample after drying, in grams

Calculate dry weight using the following equation for use in calculating the other hydrocarbon values:

$$W_d(g) = W_t \left( 1 - \frac{\%\ Moisture}{100} \right)$$

Where $W_d$ = dry weight of sample, in grams
$W_t$ = weight of the sample taken from bottle, in grams.

## *14. REPORTING OF DATA*

For Tier 1 hydrocarbon analysis, include the following items in each data report.

A hydrocarbon result expressed as mg/kg **on a dry weight basis** for:

- $FL_{BTEX}$ = C6 to C10 hydrocarbons – BTEX
- F2 = C10 to C16 hydrocarbons or $F2_{-napth,}$ if naphthalene has been measured and subtracted.
- F3 = C16 to C34 hydrocarbons or, $F3_{-PAH,}$ C16 to C34 hydrocarbons – PAHs (if analyzed)
- F4 = C34 to C50 hydrocarbons
- F4G = gravimetric heavy hydrocarbons (if chromatogram does not descend to baseline at C50). Note: **both** F4G and F4 by gas chromatography results should be reported with a note indicating that the higher should be used for interpreting the CWS PHC Tier 1 approach.
- $F4G_{-sg}$, if silica gel cleanup was applied to the F4G extract.
- % moisture.
- If requested, a professional judgement as to what the product is (gasoline, diesel, crude, etc. based on profiles and retention times of products run and experience of analyst). When included in a report, opinions and interpretations shall be clearly separated from the test results. The laboratory must be able to show that it has documented the basis upon which the opinions and interpretations have been made.
- Statement that the data for QC samples is available on request.
- Were QC criteria in Sections 10.1, 10.5, 11.1 and 11.5 met? (Y/N)
- Was the method modified in any way to accommodate the sample? If so, details should be supplied.
- Was Total Organic Carbon analyzed? Express the result as mg/kg of Carbon (see Section 15.)
- A CCME Petroleum Hydrocarbon Reporting Template appears in Appendix 4.

## 15. *SPECIAL CONSIDERATIONS*

**This section is intended to provide guidance for special situations when the CWS PHC method is not applicable in its entirety.**

Soil composition can vary widely, from extremely heavy clay soils to soils very high in organic content. Although the judgement of the regulating authority and experts managing the site on behalf of the site owners must be paramount, some advice is provided in this section to illustrate the types of problems for which the professional judgement and experience of the analyst must be taken into consideration. In arriving at what is a “true” result for PHCs, interferences from natural organic carbon and from soil amendment procedures must be considered. Several examples are given to highlight problems that may exist for the analyst.

### 15.1 High Organic Carbon Soils

Soils containing high organic carbon content may give rise to false positives. This can occur if a high organic carbon soil is extracted as for the C10 to C50 fraction. The chromatogram will contain peaks that may appear to be hydrocarbons. In such cases, it is recommended that the extract be analyzed by GC-MS to confirm that there are hydrocarbons present. Alternatively, a comparison soil should be sampled from a site known to be free of contamination. This second or "blank" soil should be extracted in a manner similar to the contaminated sample. After analysis, the two chromatograms should be compared. If possible, the "blank" chromatogram should be subtracted from the "contaminated" chromatogram, either by physical comparison of the two chromatograms or by using a computer.[17] If the results from the blank are similar or higher than the contaminated sample, then it must be assumed that there is no hydrocarbon present.

If there is evidence of hydrocarbon present, the best approach may be to conduct the analysis without silica gel cleanup on both the contaminated soil and an uncontaminated soil of the same type from a nearby location. Subtraction of the "blank" soil from the contaminated soil will give an estimate of the hydrocarbon levels. Normally there is some other evidence of hydrocarbon contamination, such as a distinct odour or definite information regarding a spill. Furthermore, it is recommended that in assessing high organic carbon soils, the organic content should be measured. Various techniques are given in reference [10]. The consensus is that methods based on the Leco furnace (or equivalent) are the most reliable [11].

### 15.2 Soils Remediated with Manure

Soils that have been bioremediated with manure can give higher than expected values. Uncontaminated soils treated with manure can have values ranging from 80 to 3000 mg/kg, depending on the length of time since manure was added. In these situations, it is essential to compare results from an uncontaminated control site with soils from the contaminated sites. It is assumed that both the contaminated and uncontaminated sites are treated in a similar manner.

### 15.3 Soils Containing Partially Degraded Hydrocarbons

Crude and partially weathered or degraded hydrocarbons can contain significant quantities of polar compounds. It is almost impossible to determine the degree of weathering without extensive analysis. Generally, silica gel cleanup, if performed correctly, will remove most polar compounds. However, this cleanup could lower results. An assessment of the degree of weathering can be obtained by laboratory weathering of a similar product or crude. An estimate of the impact of silica gel cleanup can be obtained by chromatographing part of the sample before and after cleanup. However, not all polar material will elute from a GC column. In order to obtain a reasonable estimate of contamination, it may again be useful to compare a contaminated soil with an uncontaminated soil of the same type from a nearby location. Both should be analyzed without silica gel cleanup. Subtraction of the "clean" soil from the contaminated soil will again give an estimate of the contamination.

[17] Computer subtraction is only possible if there are no retention time shifts, which may occur if the sample and the blank soil are run on different dates.

## *16. REFERENCES*


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2. Ontario Ministry of the Environment, “The Determination of Volatile Organohalides and Hydrocarbons in Sediments, Sludges and Kiln Dusts by Headspace Capillary Gas Chromatography (GC)”, Method LFHS/S-E3254A, 1994.

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6. U.S. Environmental Protection Agency, “Description and Sampling of Soils, A Field Pocket Guide”, EPA/625/12-91-002, November, 1991.

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11. Ontario Ministry of the Environment, “Determination of Total Carbon in Soil and Sediments by the Leco Carbon Analyzer”, Laboratory Services Branch, Method CARBONTC-E3142A, June 12, 1997. (Contact Cammy L Mack at 416-235-6005 to obtain copies.)

## *APPENDIX 1 – AMTAG MEMBERS*

The following members of the Analytical Methods Technical Advisory Group (AMTAG) of the CCME contributed to the establishment and validation of this method.

| | |
|---|---|
| Richard Turle | Environment Canada (AMTAG Chair) |
| Renée Gauthier | Ministère de l'Environnement du Québec |
| Scott Hannam | ASL Analytical Service Laboratories Ltd. |
| George Kanert | Ontario Ministry of the Environment |
| Abdel Kharrat | Alberta Research Council |
| Don Laberge | Envirotest Laboratories (CAEAL representative) |
| Todd Arsenault | New Brunswick Department of Environment and Local Government |
| Tim Munshaw | Philip Analytical (IAETL representative) |
| Carol Drury | Shell Canada (Petroleum industry representative) |
| Ileana Rhodes | Equilon Enterprises LLC (Petroleum industry representative) |
| François Messier | CEAEQ, Ministère de l'Environnement du Québec |
| Dave Morse | Ontario Ministry of the Environment |
| Peter Fowlie | Cornerstone Science |

## *APPENDIX 2 – METHOD VALIDATION*

Validation of the CCME Tier 1 Method for Analysis of Petroleum Hydrocarbons in Soils must be done at the following levels:

- use of the accepted method as required by CCME;
- validation of method or options chosen by laboratories;
- validation in the hands of individual staff members; and
- validation of each set of data.

**Use of the accepted method as required by CCME**
This analytical method must form the basis of chemical analysis for petroleum hydrocarbons in soil required for the CWS for PHC activities. This method has been established to provide data that is more consistent than what has been generated in the past by several diverse hydrocarbon methods. All required or prescriptive elements of the analysis outlined in the method must be carried out exactly. Performance-based method options selected must be validated. All quality control criteria listed in Section 8 must also be satisfied.

**Validation of the method or options chosen by laboratories**
Each laboratory must initially validate the CWS PHC hydrocarbon method and the method options chosen to demonstrate that the method can provide acceptable data under conditions prevailing in that laboratory. This must include the following.

- It must be demonstrated that instrumentation can achieve the prescribed responses for toluene, nC6, nC10, nC16, nC34 and nC50 as required in the method. Interlaboratory testing has demonstrated that it is essential to achieve the prescribed chromatographic responses in order to achieve good analytical data for samples.
- Chromatographic linearity must be demonstrated.
- Comparability of the method options chosen must be demonstrated at least once before analysis is carried out by analyzing a minimum of four reference samples. The reference samples must be analyzed by the exact CWS PHC reference method and by the method with the chosen options at least in triplicate. The data for both methods must within 20% for all the samples.
- Accuracy must be assessed by obtaining acceptable recoveries of each hydrocarbon fraction from samples previously validated by the CCME method, interlaboratory round robins using the CCME method must be participated in and certification and accreditation activities must also be participated in when they are available.
- Method detection limits must be determined experimentally as outlined in Appendix 3 and must meet the criteria listed in Section 8.
- Precision of soil samples or spiked soil samples must be within the data quality objectives stated in Section 8.

**Validation in the hands of individual staff members**
Each analyst who carries out the method must demonstrate the ability to achieve comparable data by successfully analyzing reference samples.

**Validation of each set of data**

Each set of data must be validated by running a set of quality control samples along with the batch of analytical samples. The quality control samples must meet the control criteria established by the laboratory.

## *APPENDIX 3 – METHOD DETECTION LIMIT*

The Method Detection Limit (MDL) for the analysis must be determined experimentally by the laboratory before analyzing samples and must be repeated at least annually or whenever there is a substantial change in the method or instrumentation used. The MDL must meet the criteria outlined in Section 8.

The MDL described here is consistent with the CAEAL approach, the USEPA approach and the Ontario MISA program. It is a method detection limit in that it incorporates all aspects of the analytical method, including extraction, concentration and quantification. It is not simply an instrument detection limit.

- For the F1 C6 to C10 fraction, the MDL determination is done using soil contaminated or spiked with gasoline at a concentration of 50 to 200 mg/kg. The same MDL shall be applied to the $F1_{-BTEX}$ fraction.

- For the F2 C10 to C16, F3 C16 to C34 and F4 C34 to C50 fractions, the MDL determination is done using soil contaminated or spiked with weathered diesel fuel at a concentration of 20 to 100 mg/kg. The results for the three fractions are summed and that result is applied to each of the three fractions. This approach is practical, although not accurate for each fraction. The same MDLs shall be applied to the$F2_{-PAH}$ and $F3_{-PAH}$ fraction.

- For F4 by the gravimetric heavy hydrocarbons, the MDL determination is done using soil contaminated or spiked with a 30-weight, non-detergent grade motor oil product at a concentration of 2,000 to 10,000 mg/kg. The MDL determination must include the silica gel cleanup i.e. procedure as for $F4G_{-sg}$. The same MDL shall be applied to the F4G parameter.

For each of the above cases, the MDL is determined by carrying out a minimum of 7 replicate measurements on the contaminated or spiked soil. The standard deviation of replicates is calculated. The MDL is the value determined to be statistically different from zero at the 99% confidence limit.

## *APPENDIX 4 – CCME PETROLEUM HYDROCARBON REPORTING TEMPLATE*

**Header information to identify the laboratory and the sample**
Name and address of laboratory:
Name and address of client:
Report number:
Identification of test sample:
Description of test sample:
Identification of test method:
Dates of sampling and reporting:

**Hydrocarbon results expressed on a dry weight basis**
F1 C6 to C10 hydrocarbons in mg/kg, $F1_{-BTEX}$ after BTEX is subtracted:
F2 C10 to C16 hydrocarbons in mg/kg, $F2_{-napth}$ after naphthalene is subtracted
F3 C16 to C34 hydrocarbons in mg/kg, $F3_{-PAH}$ after PAHS are subtracted:
F4 C34 to C50 hydrocarbons in mg/kg:
F4G by gravimetric heavy hydrocarbons in mg/kg, if analyzed: (Note that both of the two results for F4 and F4G are reported for F4 and a statement added to the report to effect that the greater of the two numbers are to be used in application to the CWS PHC.
$F4G_{-sg}$, if analyzed, is the result of gravimetric heavy hydrocarbons after silica gel treatment in mg/kg:
% moisture:
Total Organic Carbon, if requested
Method detection limits:
Validator signature:
A note stating that gravimetric heavy hydrocarbons cannot be added to the C6 to C50 hydrocarbons.
A note stating that BTEX and selected PAHs have been subtracted from the appropriate fractions.

**Comments that are clearly separated from the results of analysis:**
A statement that the method complies with the Reference Method for the CWS PHC and is validated for use in the laboratory.
All deviations from the method required are to be noted and reported for any particular sample.
Qualifications on results:
Subcontractors used:
Did the chromatogram descend to baseline by the retention time of nC50?
Were the quality criteria met?

- nC6 and nC10 response factors within 30% of response factor for toluene:
- nC10, nC16 and nC34 response factors within 10% of each other:
- C50 response factors within 70% of nC10 + nC16 + nC34 average:
- Linearity is within 15%:

Statement that the data for QC samples is available on request or the data for QC samples:

- Blank:
- Duplicate:
- Reference Sample:
- Spiked sample:

Extraction and analysis limits for holding time were met (Y/N)
Professional judgement, if requested, of what the material is, based on information that is stated (product profiles, retention times, professional experience, etc.)

## *APPENDIX 5 – SINGLE LABORATORY METHOD VALIDATION*

A validation of the method was conducted in the Emergency Science Division laboratory of the Environmental Technology Centre, during the fall and winter of 2000/01[*]. The purpose of this study was to estimate precision of several aspects of the method, determine method detection limits, and verify that standards were stable over a reasonable length of time. This information is provided to assist individual laboratories as they implement the CWS PHC method.

The main findings from this study are summarized as follows*:*

1. Linearity Study

Excellent linear relationship between the concentrations and GC responses are clearly demonstrated for the target compounds of Fractions 1 (C6-C10), 2 (C10-C16), 3 (C16-C34), and 4 (C34-C50) in the studied concentration range.

2. Precision Estimation Study

(1) Precision Estimation for Standards: for Fraction F1, the target compounds (benzene and toluene) demonstrated reasonable reproducibilities with the relative standard deviation (RSD) being around 12% at 0.05 ppm and 7.5% at 0.2 ppm, respectively.

The RSDs obtained from 8 determination of the C8-C30 standard were under 4%. The RSD for C50 (n = 8) was determined to be 7.3% at 25 ppm.

(2) Precision Estimation for Complete Method (gasoline spiked soil): The average recoveries were determined to be 82% at 50 ppm and 88% at 400 ppm of gasoline, respectively. The method precision from 8 measurements was determined to be 7.5% (RSD) at 50 ppm and 8.4% (RSD) at 400 ppm of gasoline, respectively.

(3) Precision Estimation for Complete Method (diesel and motor oil spiked soil): The relative standard deviations were determined to be 5.0% for F2, 3.4% for F3, and 3.5% for F4 of diesel and motor oil spiked soil samples, respectively.

Method Detection Limit (MDL) for F1 Using Gasoline-spiked Soil

The MDL determination was done using a spiked soil at a concentration of 50 µg/g soil. The SD and RSD from 8 replicate analyses were determined to be 0.37and 7.5%, respectively. Therefore, the MDL for whole gasoline is determined to be 0.37x3.14 (the appropriate one-sided 99% t-statistic) = 1.16 µg/g soil or 1.16 ppm.

Method Detection Limit (MDL) for F2, F3, and F4 Using Diesel-spiked Soil

The MDL were determined to be 3.9, 9.0, and 0.6 µg/g soil for F2, F3, and F4 (10.0 g of soil was spiked with 0.5 mg of diesel), respectively.

5. Determination of Method Detection Limit (MDL) for F4G (Motor Oil-spiked Soil) Using Gravimetric Method

The MDL (MDL = $t_{(n-1,\ a=0.99)}$ s) by gravimetric method was determined to be 0.29 mg/g soil or 290 mg/kg soil (5.0 mg of motor oil was added to 5.0 g of soil, equivalent to 1000 mg/kg of soil).

6. Stability Study

Around 100% and 85% of recoveries for all target compounds in the C6-C10 range were demonstrated at 7 days and at 38 days, respectively.

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[*] Lab Validation Study Results for the "Referencemethod for the Canada Wide Standard for Petroleum Hyrocarbons in Soil-Tier 1 Method", Zhendi Wanag and Ken Li, Environmental Science and Technology Divsison, Environmental Technology Centre, Environment Caanda, Ottawa K1A 0H3, March 2001.

Excellent stabilities were demonstrated for the standard C10-C50 in 62 days period with the RSDs (4 measurements at 4 different dates) being under 4%.