Draft

Sampling Protocols and Analytical Methods for Determining Petroleum Products in Soil and Water

Prepared by the Oil Industry Environmental Working Group

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This document has been prepared by the Oil Industry Environmental Working Group. If you have any comments on this document, can you please send them to:

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Introduction

The objective of this guideline is to provide cost-effective, reliable information that will permit screening, assessment and where appropriate evaluation of the risks posed by contamination to human health and the environment.

This guideline specifies the sampling and analytical methods to be used for the testing required by the following guidelines for the Oil Industry:

- Above Ground Bulk Storage Tank Farm Containment System
- Surface Water Discharge
- Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand
- Procedures Manual for Underground Storage System Change of Ownership
- Code of Practice for the Design, Installation and Operation of Underground Petroleum Storage Systems and the Supplement for Existing Tanks.

The scope of this document includes:

- how samples should be taken
- holding time and preservation of samples and
- analytical methods.

The Surface Water Discharge and Contaminated Land guidelines address issues relating to the number of samples, sampling plan, contaminants of concern and selection of analytes.

It is important that there is consistency between standards for acceptable contamination levels, and the analytical methods selected to measure conformance.

A supplement to this document will be published later to address sampling and test methods relating to air contamination.

1.1 Scope of Analytical Methods

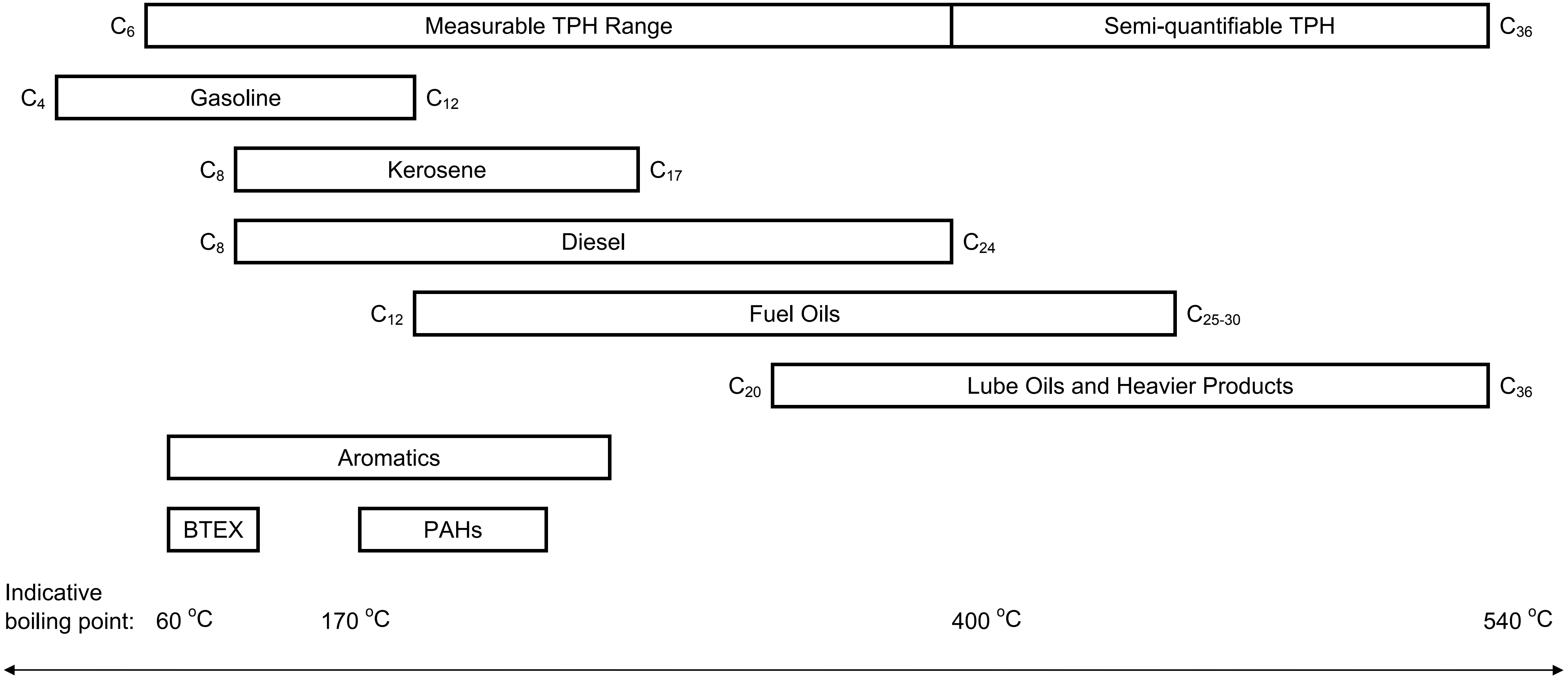
Sample	Analyte
Water	Suspended Solids Petroleum Hydrocarbons Volatile Hydrocarbons Semi-volatile Hydrocarbons Total Lead Organic Lead
Soil	Petroleum Hydrocarbons Volatile Hydrocarbons Semi-volatile Hydrocarbons Total Lead Organic Lead Toxicity Characteristic Leaching Procedure (TCLP) Analytes

Only petroleum hydrocarbons, volatiles and semi-volatiles are routinely analysed when dealing with contamination related to the oil industry. The other analytes would more commonly be analysed where contaminants other than hydrocarbons are involved.

The contaminated sites and surface water discharge guidelines provide guidance on when and where the analysis of the various analytes are required. The following figure illustrates the carbon ranges of typical fuels and oils.

This document pertains to the core methods most commonly used for the petroleum industry. Where a method is not specified, the latest version of the applicable US EPA (US EPA, 1992) or APHA (APHA, 1995) method should be used.

1.2 Carbon number, total petroleum hydrocarbons (TPH) and indicative boiling point range



This diagram shows the typical carbon number ranges of common products, together with indicative boiling points. This is contrasted against the detectable range of a TPH analysis.

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Soil sampling protocols

The collection and preparation of samples are important aspects of any assessment programme. They should be undertaken in a way that will avoid the introduction of bias, systematic or non-systematic errors. The methods of collection and sample size should be chosen to ensure that the sample obtained is representative of the environment from which it is taken. Physical techniques then need to be applied to make the sample homogeneous such that further sub-sampling will ensure the material taken for analysis is wholly representative.

The American Petroleum Institute (API) publication *A Guide to the Assessment and Remediation of Underground Petroleum Releases* (API, 1989) provides information on the selection of a drilling method suitable for the soil conditions and analyses required.

Samples can be sent for analysis by two general methods: soil cores (undisturbed samples with no headspace and only in situ voids) and sample container. Soil cores in inert liners can be capped, refrigerated and sent to the laboratory. If the sample container method is used, the collection method, container type, sample size and preservatives vary according to the analysis to be performed. The requirements for these are detailed in Section 5.

Soil samples should be visually inspected. The sample's general appearance and colour, presence of oils or other visual signs of petroleum hydrocarbons, soil texture (for example clay or sand) and odours should be recorded. Ideally, a duplicate sample should be taken for this inspection. Actual sampling of the soil should be completed in the minimum possible time, with the least possible handling before the sample is sealed in the container.

If soil samples are transferred to sample containers, roots and large stones, vegetation, sod and other non-soil materials should be removed from the sample. Samples for non-volatiles may be sieved to removed impurities larger than 10 mm in diameter. The percentage of material removed should be estimated so that the laboratory result can be related to site conditions. Samples for volatile analyses must remain as undisturbed as possible.

In collecting soil samples, particular care must be taken to prevent cross-contamination from one sample to another. This will require thorough cleaning of sampling equipment between sampling points or sampling sites. General field sampling quality assurance procedures that must be followed, including equipment cleaning procedures are detailed in Section 4. All field activities and observations should be documented in a field log (Section 4.6), and all samples listed on a chain of custody form (Section 4.7) that must accompany the samples to the laboratory.

2.1 Field screening

The main purpose of field screening is to define the general picture of soil contamination cost-effectively, and often as quickly as possible, before undertaking more expensive detailed chemical analysis of a limited number of samples.

2.1.1 Head space analysis of samples

Head space analysis for volatile organics is the most widely utilised field screening technique providing either a qualitative estimate of the total concentration of volatile contaminants present, or a semi-quantitative estimate of a limited number of compounds (e.g. BTEX) in the headspace.

Head space analysis, while generally carried out on soil samples, can also be utilised for the field screening of groundwater and surface water samples. In all cases, the field screening for volatile organics requires the collection of duplicate samples, and under no circumstances should field screening be carried out on the sample which is subsequently submitted for chemical analysis.

Headspace analysis of soil and water samples relies on the partitioning of any volatile organic compounds (VOCs) from the soil and aqueous phases into the gaseous. Consequently, head space analysis is limited to volatile compounds with the magnitude of the response dependent both on the volatility of the compound and its concentration in the soil/water.

The magnitude of the response is also dependent on the type of instrument being used, i.e., photo ionisation detector (PID) or flame ionisation detector (FID). In terms of using a PID, the response of the compound, and the ability of the instrument to detect the compounds is dependent on the photo-ionisation potential, i.e. ability of a compound to ionise when exposed to UV light. With PIDs, it is particularly important to choose an appropriate energy lamp to achieve for maximum analyte sensitivity.

To ensure that the instrument is providing accurate and repeatable results it is important that the instrument is regularly calibrated, before use and for example at two hour intervals during use.

Calibration procedures for the detection of volatile petroleum hydrocarbons involve calibration against a known standard. In most cases isobutylene span gas is used.

For headspace analysis of volatile organics, PIDs are the most widely used instrument. The primary advantages with PIDs are:

- extremely portable and easy to use
- instruments are generally intrinsically safe
- provide a very rapid analysis time and are not prone to contamination or build-up of contaminants and
- qualitative or semi-quantitative.

While FIDs are not necessarily intrinsically safe, FIDs have some advantages over PIDs which necessitate their use:

- FIDs can detect a wider range of volatile organics. PIDs are limited to chemicals that can be easily ionised with UV light, while a flame will ionise a large range of volatile organics. Photo-ionisation tables for organics should be consulted before analysis to determine the appropriate instrument. However, FIDs are prone to detecting volatile hydrocarbons sourced from non-petroleum matter (e.g. methane) and their use on sites underlain by organic materials (e.g. peat) is limited.
- For many volatiles, FIDs generally have lower detection limits (sub parts-per-million levels), and as such may be useful for detecting low concentrations of volatile organics.
- FIDs handle very wet samples and high humidity better than PIDs.

In general, headspace methods for soil and water samples involve the following standard method:

1. Fill a clean 0.5 litre or larger sample bottle half full of sample.
2. Seal the top with clean aluminium foil and place air tight lid on the container.
3. Ensure that the sample is at 15 to 25°C (optimum 25°C as Henry's Law constants are calculated at this temperature). A warm water bath can be utilised before testing if necessary.
4. Volatile hydrocarbon concentrations must be allowed to develop in the headspace of the sample jar for at least 5 minutes. During this headspace development period, the sample should be shaken vigorously for a total of 1 minute.
5. Remove the lid, and immediately pierce the aluminium foil seal with the probe of the PID or FID detector and read the highest (peak) measurement.

In some instances, where a semi-quantitative estimate of the concentration in the soil is sought static headspace methods are utilised for the headspace. In this instance the identical methodology to above is followed, however soil samples are enclosed in a bottle with distilled water and agitated before analysis. The distilled water serves to extract the contamination and there upon partition them from the aqueous phase into the gaseous phase. A known weight of soil and volume of water Henry's Law constant (as per water samples) can be used to estimate the concentration in the water phase and therefore within the soil. This methodology can also be directly applied to water samples.

Henry's Law $Cw = Pv/H$

Where:

H = Tabulated constants (at 25 °C).

Pv = The concentration within the gaseous phase over the solution.

Cw = The concentration within the aqueous phase.

In general, head space analysis is utilised as a semi-quantitative estimate of contamination only and is used to indicate areas and depths of elevated volatile organic compound concentrations. As such, this method has proven highly successful at providing general contamination patterns and allowing selective analysis of soil samples thereby considerably reducing analytical costs.

2.2 Soil sampling from a borehole

The following are minimum requirements. Depending on the site specific requirements, it may be necessary to take more samples.

Samples should be collected at intervals of not more than 1.5 metres. This is particularly important for field screening work.

1. Where practical, select a drilling method that does not introduce water or contaminating drilling fluids. Grease used on drill stem connections should not be petroleum based.

   Note: Drilling muds or water are sometimes required, for example to balance pressure differentials when drilling into a confined aquifer. The Regional Council should be consulted before drilling into a confined aquifer.

2. Sample within 300 mm of the surface grade and then at set intervals (e.g. 1 metre) and at geologic profile changes. Collect samples from the bottom of the borehole at each depth interval. Avoid using borehole cuttings for samples.
3. Samples can be field screened to determine which samples from each boring should be sent for analysis. Field screening techniques should be targeted toward the type of potential petroleum hydrocarbon release.
4. Select at least one to two samples for analysis from each boring as appropriate. The discrete samples should be selected from the area of highest apparent petroleum hydrocarbon concentration based on field screening techniques or soil discolouration and odour.
5. If there *is* field screening evidence of petroleum hydrocarbons and *no* groundwater or impervious layer is encountered, select a minimum of one discrete sample with the highest apparent hydrocarbon concentration based on field screening results.
6. If there *is* field screening evidence of petroleum hydrocarbons from field screening *and* groundwater or impervious layer is encountered, select a discrete sample with the highest apparent hydrocarbon concentration based on field screening results and an additional sample from immediately above the water table or impervious layer (0-150 mm).
7. If there is *no* evidence of petroleum hydrocarbons from field screening and *no* groundwater or impervious layer is encountered, select a discrete sample from the first 150 mm above the bottom of the borehole.

8. If there is *no* evidence of petroleum hydrocarbons *and* groundwater or impervious layer is encountered, select a discrete sample from the 0 to 150 mm zone above the water table or impervious layer.

2.2.1 Split spoon/push tube sampling

When using either a split spoon sampler or push tube, sample collection devices are attached to the end of the drill rods and lowered to the bottom of the borehole where the sampling device rests on the top of the fresh undisturbed formation. The sampling device is then driven into the formation to collect a relatively undisturbed sample.

The use of liners for the split spoon sampler is recommended to ensure a representative sample. After the split spoon or push tube has been withdrawn from the boring, the desired sample section should be removed from the sampling device and placed either into the appropriate sampling container or capped, awaiting analysis.

2.3 Test pits

Test pits are open pits dug with an excavator. They have the advantage that the sampler can view the extent of the contamination and select the most visually contaminated material to sample.

Test pits should not be entered unless the walls have been appropriately battered or shored to prevent cave-ins, and proper safety measures are taken to guard against being overcome by fumes.

1. The machinery used to excavate the pit must be free of oil and hydraulic fluid leaks. The bucket and boom must be steam cleaned before digging each test pit.
2. Sample the target material after removing all loose material from the bucket. Transfer a representative sample from the bucket to the sample jar using a properly cleaned trowel (refer to Section 4.2). Take care to select material that has not touched the sides of the bucket.

When backfilling a test pit with material excavated from the pit (i.e. not imported clean fill), ensure the material is placed back into the pit in the same order it came out; i.e. if contamination was observed at depth, ensure that the excavated contaminated soil is replaced at the same level, not left exposed at the surface or buried deeper.

2.4 Sediment sampling

Sediments will act as a sink for less soluble hydrocarbon components entering surface water ways. The sampling of these sediments will indicate if hydrocarbons are present that might affect organisms that use or come in contact with the sediment.

2.4.1 Sampling devices

Sediment samples can either be collected by a coring device, which is pushed into the sediment and holds it in place by suction pressure whilst being brought to the surface, or a grab sample, obtained by scooping sediment into a container. The greatest potential problem associated with sediment sampling is the loss of fine sediments that are washed out during the sample collection process. The sampling device must be designed and operated to minimise this disturbance. Examples of appropriate collection devices include an open ended tube which can be pushed into the sediment, then sealed at the exposed end (e.g. with a rubber bung) to create a suction pressure that holds the sediment in place during sample removal. Alternatively, grab samples may be collected with a sampling container with a spring loaded cap (e.g. the Ekman dredge) or a container with a porous end plate that allows the passage of water but the retention of fine sediments.

The choice of sampling device will depend on the likely zone of hydrocarbon accumulation. For recent accumulations, near surface sediments should be targeted as they have the greatest bio-exposure potential. Grab samples will provide a sample of shallower sediments over a broader area.

A core sample is more site specific and provides deeper penetration into the sediments. Core samples may be more appropriate for studies of historical spillage incidents, or for investigations where the vertical differentiation of the sediment layers is important.

2.4.2 Sample location

Samples should be collected near the point of entry of hydrocarbons into the surface waterway and from depositional areas where fine sediments accumulate. These finer sediments will be found behind structures which create back eddies, in slower water on the downstream inside banks of river bends and in areas of still water conditions.

2.4.3 Sample collection

The focus of sediment sample collection is to minimise disturbance to the sediments before sampling, by undertaking the following steps:

1. Identify sampling locations and determine the order of sample collection. In general work from downstream to upstream and from least likely areas of contamination to most likely areas.
2. Prepare glass sampling jar, labels and equipment in dry conditions.
3. Carefully approach each sampling location to avoid sediment disturbance. Small shallow rivers and lakes may be sampled by wading into the water, approaching the sampling location from a downstream direction. In deeper waters a container attached to a pole may be used. Alternatively, divers may be used in deep water to carry out the sample collection.
4. Collect the sample using a grab or core sampler as appropriate. Carefully document the sample location and the depth of penetration.
5. Place sample in sampling jar, carefully remove any loose material from the rim and replace the lid firmly. No sediment is to be decanted from the sample jar.
6. Complete decontamination of sampling equipment before collection of next sample.

The specific sampling protocols required for the collection of soil and sediment samples for volatile, semi-volatile and metal analyses are detailed in Sections 2.5 through 2.8.

2.5 Sampling for volatile organic compounds (including gasoline contaminated petroleum hydrocarbons)

For volatile constituents, unless the cohesive-sample soil core method of sampling is used, a separate sample for volatile analysis must be collected. This sample must be separate to that collected for semi-volatile and metal analyses. In collecting the sample, the procedure must be performed rapidly and with minimal disturbance of the sample to minimise the loss of volatiles to the atmosphere. If the cohesive-sample soil core method is not used, the following procedure should be used:

1. Fill a 100 mL pre-cleaned borosilicate jar with soil. The sample should completely fill the sample container (no headspace).
2. Wipe the jar screw threads with a clean tissue to remove any sample article that adheres to the jar threads and that could affect the seal.
3. Cap the jar with a Teflon-lined cap, placing the coated side toward the sample.
4. Label the sample. Place it in a cooler with ice (not dry ice). Cool to 4ºC, and keep in the dark. Maintain temperature in transit to laboratory. A min/max thermometer should be included with the samples so temperatures during transportation can be verified.
5. A minimum of one field duplicate should be taken for every ten (or fewer) samples.

6. Samples should be shipped to the laboratory within 24 hours of collection so that the analysis can be performed within the required holding period.

2.6 Sampling for semi-volatile organic compounds and metals

1. Collect about 200 grams of soil sample (100 grams for metals and 100 grams for semi-volatiles) in a 250 mL pre-cleaned glass jar. Jars of other sizes can be used depending on the actual amount of sample collected.
2. Wipe the jar screw threads with a clean tissue to remove any sample that adheres to the thread to ensure a good seal.
3. Cap the jar with a Teflon-lined cap.
4. Label the sample. Place it in a cooler with ice (not dry ice). Cool to 4ºC, and keep in the dark. Maintain temperature in transit to laboratory. A max/min thermometer should be included with the samples so temperatures during transportation can be verified.
5. A minimum of one sample should be taken at each sampling point.
6. A minimum of one field duplicate should be taken for every ten (or fewer samples).

Note: PAHs are light sensitive. All samples collected for PAH analysis must therefore be stored in amber glass jars or kept in the dark to minimise photolytic decomposition.

2.7 Soil samples for hazardous waste determination by TCLP volatiles

For volatile constituents, unless the cohesive-sample soil core method of sampling is used, a separate sample for volatile analysis must be collected. This sample must be separate from that collected for semi-volatile and metal analyses. In collecting the sample, the procedure must be performed rapidly and with minimal disturbance of the sample to minimise the loss of volatiles to the atmosphere. If the cohesive-sample soil core method is not used, the following procedure should be used:

1. Fill a pre-cleaned borosilicate jar with soil. The sample should completely fill the sample container (no headspace).
2. Wipe the jar screw threads with a clean tissue to remove any sample that adheres to the thread to ensure a good seal.
3. Cap the jar with a Teflon-lined cap, placing the coated side toward the sample.
4. Label the sample. Place it in a cooler with ice (not dry ice). Cool to 4ºC, and keep in the dark. Maintain temperature in transit to laboratory. A max/min thermometer should be included with the samples so temperatures during transportation can be verified.
5. A minimum of one field duplicate should be taken for every ten (or fewer) samples.
6. Request the laboratory run TCLP for *volatiles using a zero headspace extractor (ZHE).*

2.8 Soil samples for hazardous waste determination by TCLP semi-volatiles and TCLP metals

Trace metals and semi-volatile organics can be determined on a single TCLP leachate.

1. Fill a 500 mL pre-cleaned borosilicate jar with 300 to 500 grams of soil. The amount of headspace in the jar is not critical.

2. Wipe the jar screw threads with a clean tissue to remove any sample that adheres to the thread to ensure a good seal.
3. Cap the jar with a Teflon-lined cap, placing the coated side toward the sample.
4. Label the sample. Place it in a cooler with ice (not dry ice). Cool to 4ºC, and keep in the dark. Maintain temperature in transit to laboratory. A max/min thermometer should be included with the samples so temperatures during transportation can be verified.
5. A minimum of one field duplicate should be taken for every ten (or fewer) samples.
6. Request the laboratory run a TCLP analysis for *semi-volatiles* and/or *metals*. (A zero headspace extractor should not be used.)

3

Water sampling protocols

The collection and preparation of samples are important aspects of any assessment programme. They should be undertaken in a way that will avoid the introduction of bias, systematic or non-systematic errors. The methods of collection and sample size should be chosen to ensure that the sample obtained is representative of the environment from which it is taken. Physical techniques then need to be applied to make the sample homogeneous such that further sub-sampling will ensure the material taken for analysis is wholly representative.

Groundwater sampling can be done by drilling bores and constructing monitoring wells, or using various alternative techniques, such as cone penetrometers or Geoprobes.

To install monitoring wells, a permit may be required by the Regional Council. Care must be taken when installing wells to ensure that they do not provide a pathway for contamination to move into deeper, uncontaminated aquifers.

Monitoring wells should be developed after they have been installed. This process removes the drilling fluids and sediment that may have moved through the filter pack and screen during construction. In addition, the well should be purged to remove stagnant water before each sampling event.

In collecting water samples, particular care must be taken to prevent cross-contamination from one sample to another. This will require thorough cleaning of sampling equipment between sampling points. General field sampling quality assurance procedures that must be followed, including equipment cleaning procedures are detailed in Section 4. All field activities and observations should be documented in a field log (Section 4.6), and all samples listed on a chain of custody form (Section 4.7) that must accompany the samples to the laboratory. The sample container type, sample size and preservatives vary according to the analysis to be performed. The requirements for these are detailed in Section 5.

3.1 Sampling groundwater from boreholes

Ideally, groundwater samples should be taken from a monitoring well. Where the installation of a monitoring well is not possible, groundwater can be sampled from a borehole as follows:

1. Take samples of the groundwater using a bottom fill bailer (Teflon, rigid PVC or stainless steel) or a positive-displacement or submersible pump. Peristaltic pumps may be used for sampling for non-volatiles.
2. Use dedicated sampling equipment or clean thoroughly between each sampling point (refer Section 4.2).
3. Preserve samples appropriately for the targeted analytes (see Section 6.1)

3.2 Preparation to sample monitoring wells

1. Measure depth to static water level before purging or sampling well. If not previously measured, measure and record depth of well.
2. Measure the thickness of any free product.
3. Calculate the volume of water in the well.
4. Purge a *minimum* of three well volumes of water by pumping or bailing, taking care not to pump the well dry. If water recovery is extremely slow, for example, requiring days, then evacuating one well volume is sufficient. Record the volume and rate of purging in the Field Log.

5. Monitor and record an indicator parameter (pH or conductivity) using fixed volumes of water withdrawn from the well to determine when the well has reached equilibrium. The well is considered stabilised when two consecutive indicator readings are within ten percent of each other.

3.3 Sampling monitoring wells

Collect groundwater samples once the well has stabilised (normally within two hours of well purging). For slow recovery wells, the well must at least recover above the bottom of the screen.

Either pumps or bailers can be used for groundwater sampling. Air-lift pumps should not be used when sampling for volatiles or components that are air-sensitive because the sample is brought into contact with the air. Peristaltic pumps should not be used to sample volatiles because of the risk of degassing. Only pumps that can be disassembled and decontaminated are suitable for this.

If bailers are used they must be constructed of Teflon, rigid PVC or stainless steel. The samples should be transferred to the sample container with little or no agitation so that volatiles are not lost.

Sampling equipment must be thoroughly cleaned and decontaminated between sampling points and between purging and sampling.

1. Prior to sampling, take a field blank in the same manner that the groundwater samples will be collected. An equipment blank should also be collected (see Section 4.4).
2. As soon as possible after purging, take samples of the groundwater using a bottom-fill bailer or a positive displacement or submersible pump. Bailers should be lowered into the water slowly.
3. Preserve sample appropriately for the targeted analytes, depending on the goals of the project and the suspected contamination.

3.4 Sampling of oily-water separators

Samples must be collected as running samples from the outlet. If this is not possible, samples may be extracted from the bottom of the last chamber, adjacent to the outlet.

3.5 Sampling surface water

In turbulent waters, collect sample from the top 20 mm. With laminar or no flow conditions, collect three samples from top, middle and bottom of the water column.

Immerse sample bottles into the water at an angle of 45 degrees to the surface.

Middle samples	Use a pole with a mark at the mid-depth level as a guide. Immerse the bottle pointing up, with the cap still in place, so that the neck is at the required depth. Slowly unscrew the cap, allow to the bottle to fill and replace the cap before removing the bottle from the water.
Bottom samples	Take care not to disturb the sediment at the bottom. Immerse the capped bottle, pointing up, to just above the bottom. Slowly unscrew the cap and allow the bottle to fill. Replace the cap before removing the bottle from the water.
Floating product	If floating product or a sheen is present, a sample taken at the surface will be required if the floating product is to be analysed.

An intermediate container may need to be used for the middle and bottom samples to avoid flushing preservative from a final sample container that has been pre-dosed with preservative.

The specific sampling protocols required for the collection of water samples for volatile, semi-volatile and metal analyses are detailed in Sections 3.6 through 3.8.

3.6 Water sampling for volatile organic compounds

For volatile constituents a separate sample for volatile analysis must be collected. This sample must be separate to that collected for semi-volatile and metal analyses. In collecting the sample, the procedure must be performed rapidly and with minimal disturbance of the sample to minimise the loss of volatiles to the atmosphere.

Trip blanks are mandatory for volatile hydrocarbon analysis in water (see Section 4.4).

1. Use a pre-cleaned 40 mL VOC bottle with a Teflon-coated septum. In some instances the sample may be collected directly into the VOC bottle.
2. If the sample is to be transferred to the VOC bottle, use a volatile-transfer spigot.
3. Slightly overfill the bottle so that the surface is convex.
4. Gently cap the bottle, invert and gently tap against the palm of hand to check for air bubbles.
5. If bubbles are present, uncap the bottle and add more sample to eliminate bubbles.
6. Label the sample and place it in a cooler with ice (not dry ice). Cool to 4ºC, and keep in the dark. Maintain temperature in transit to laboratory. A max/min thermometer should be included with the samples so temperatures during transportation can be verified.
7. Samples should be shipped to the laboratory within 24 hours of collection so that analysis can be performed within the required holding period

3.7 Water sampling for semi-volatile organic compounds

1. Collect groundwater samples in pre-cleaned glass bottles with Teflon-lined screw caps. The sample bottle should *not* be pre-rinsed with the sample before collection. If collecting composite samples, they should be collected in refrigerated containers (4 ° C) and the automatic sampling equipment should not contain Tygon tubing.
2. Fill the bottle (it is permissible to leave a small air gap).
3. Gently cap the bottle with a Teflon-lined cap, placing the coated side towards the sample.
4. Label the sample. Place it in a cooler with ice (not dry ice). Cool to 4ºC, and keep in the dark. Maintain temperature in transit to laboratory. A max/min thermometer should be included with the samples so temperatures during transportation can be verified.
5. If amber bottles are not used, store the samples in the dark to minimise photolytic decomposition of PAHs.
6. Collect at least one duplicate sample for every ten (or fewer) samples. Duplicates should be collected in separate bottles.

3.8 Water sampling for metals

Water samples taken for the analysis of *dissolved* metals should be filtered *in the field*. Preferential filtration is 0.45 μm in-line filter assemblies which can use the pump pressure to filter. If organics are known or suspected to be present (for example evidence of free product), organically based filters made of cellulose nitrate, cellulose acetate, or polycarbonate should *not* be used. Instead, nylon or Teflon filters should be used.

After a filter pad is changed, the first 50 to 100 millilitres should be discarded as a rinse. Field sampling personnel should exercise care in field filtration procedures because sloppy techniques can cause solids breakthrough and bias sample results.

1. Collect samples in pre-cleaned plastic or glass bottles.

2. If sampling for *dissolved* metals, filter the sample through a 0.45 µm filter in the field before collection and preservation. In-line filters or other field filtration devices can be used. Use a new filter with *each* sample. Discard the initial 50 to 100 millilitres of sample after each filter change.
3. If sampling for *total* metals, do not filter.
4. Add sufficient 1:1 nitric acid:distilled water preservative so that the pH is ≤ 2. Sulphuric acid should not be used as a preservative for metals.
5. Gently cap the bottle, and label the sample. Place it in a cooler with ice (not dry ice). Cool to 4ºC, and keep in the dark. Maintain temperature in transit to laboratory. A max/min thermometer should be included with the samples so temperatures during transportation can be verified.
6. Samples should be sent to the laboratory so that analyses can be performed within the required holding period.

4

Field sampling quality assurance

4.1 Avoiding contamination of samples

To obtain *representative* samples care must be taken to ensure that the integrity of the sample to be analysed is not compromised. Anything that comes into contact with the sample should be carefully chosen and monitored to eliminate or minimise any source of contamination *to* the sample and sample area or the removal of analyte *from* the sample. A potential major problem encountered in field sampling is contamination from inadequately cleaned equipment and samplers, surrounding surfaces (ground and clothing), lubricants, well construction materials, solvents, motors, pumps, or from automobile exhausts being too close to the sampling area.

The following steps should be taken to help prevent or minimise all sources of field contamination.

- **Sampling equipment** should be made of relatively *inert materials* such as stainless steel, carbon steel, rigid PVC, fluorocarbon resin (Teflon) or glass. Likewise, monitoring wells must use inert materials in their construction. The use of other plastics in samplers, bottles, bailers, or tubing can contaminate the sample with phthalate esters and other plasticisers. Tubing, fittings, and equipment made of the following materials should *not* be used in pumps, wells, and drilling or sampling equipment: neoprene, Tygon, silicone rubber, Viton, or polypropylene.
- **Plastic sheeting** should be placed around the sampling area or wellhead to prevent contact between the soil or drilling cutting and any sampling materials (bailer rope, water level tape, and tubing).
- **Disposable PVC gloves** and, where possible, clothing shield should be used for cleaning samplers and sampling equipment. Clean gloves should be used for *each* sampling point and should be discarded between samples. In no case should gloves worn for equipment cleaning be used for taking samples.
- **Disposable or dedicated sampling equipment** should be used wherever possible for separate sample points to prevent cross contamination. Dedicated samplers (and sometimes pumps) are more often used in well monitoring scenarios than in soil sampling. Porous materials, such as rope and wooden blocks, cannot be decontaminated properly.
- **Inert non-hydrocarbon-based lubricants** should be used if soil boring equipment needs lubricating greases to function properly. Samples of lubricating greases or muds should be taken and analysed as a Quality Control precaution to ensure that contamination is not being introduced into the sample zone.
- **Volatile contaminants** should not be introduced into the sampling area. For example, gasoline or diesel powered vehicle or motor exhaust fumes close to or upwind of the sampling area can cause problems when sampling for volatiles and petroleum hydrocarbons. If an air drilling technique is used for boring, the appropriate air filtering devices should be used and changed regularly to avoid introducing down-hole contamination from the petroleum lubricants used in air compressor equipment.

4.2 Equipment cleaning

Drilling equipment should be decontaminated before and after arrival at the site, between drilling locations, and before leaving the site. To avoid cross contamination, any tools or equipment (drilling and sampling) which can potentially come into contact with soil and groundwater samples must be stringently cleaned between each boring or sampling location. If the drilling involves penetrating an upper contaminated zone followed by a lower uncontaminated zone, further decontamination is necessary. Decontamination procedures should be done in a designated area at a sufficient distance from the sampling point.

Any solvent waste generated in the field during cleaning of equipment must not be allowed to flow into the soil, pervious areas or storm water drainage. The waste should be collected in suitable containers and disposed of properly. Likewise, decontamination and drilling wastes can be collected in drums for proper disposal, depending on the nature of the waste.

Equipment blanks should be collected and labelled. Then, if the sampling data is suspect, the equipment blanks can be analysed to check for any indication of field contamination.

The use of pre-packaged water in the field can contribute contaminants such as phthalates that may show up during an analysis for polynuclear aromatic hydrocarbons (PAHs). In particular, black 20 litre containers should not be used. The deionized water blank, should be analysed on a regular basis to ensure that no contamination is being introduced from rinsing the sampling equipment. Analytical laboratory distilled or deionised water should also be checked periodically.

The following decontamination procedure should be used for all field equipment:

- Steam clean or wash with non-phosphate detergent (disassemble equipment before cleaning).
- Rinse with potable water (deionised or distilled water should be used if there is any doubt about the quality of the potable water).

For equipment that will be in contact with the samples the following additional measures are required:

- If sampling for metals, rinse with 10% hydrochloric or nitric acid (note, dilute nitric acid may oxidise stainless steel).
- Rinse liberally with deionized/distilled water.
- Wrap with inert material (e.g. aluminium foil) if the equipment is not to be used promptly.

4.3 Sample vessel pre-cleaning

To eliminate the introduction of contamination, sample containers and caps need to be cleaned and dried before sampling.

Some sample vessels can be supplied ‘sterilised’ and if it can be demonstrated with blank vessels that contamination is absent, pre-cleaning of the vessel is not required.

- ***BTEX & VOC bottles***
  Each screw top borosilicate glass bottle and septum should be thoroughly washed with laboratory-grade phosphate-free detergent (e.g. Decon 90) and water and then rinsed with deionized water. The bottles should then be oven-dried at 105 °C for at least one hour. *Do not heat the septum for extended periods of time (more than 1 hour) because the silicone begins to slowly degrade at 105 °C.*
- ***Sample bottles and jars for organics***
  Each glass sample container should be thoroughly washed with laboratory-grade phosphate-free detergent (e.g. Decon 90) and water and then rinsed with deionized water. The containers may then be heated at 400 °C for about 15 to 30 minutes until dry, or solvent rinsed with pesticide quality hexane and acetone and oven dried at 80-100 °C.
- ***Containers for groundwater sampling of metals***
  Each sample container (glass or plastic) should be thoroughly washed with laboratory-grade phosphate-free detergent (e.g. Decon 90) and water, rinsed with

deionized water, followed by a rinse with a 1:1 solution of nitric or hydrochloric acid:distilled water, and finally rinsed with deionized water and air dried (glass containers may also be oven dried).

4.4 Quality control samples

Trip blanks	Test samples of analyte-free media (distilled or deionised water) supplied by the laboratory, taken to the sampling site, and returned to the laboratory unopened. Trip blanks must be taken for volatile hydrocarbon analysis of groundwater.
Field blanks	Distilled or deionised water is taken to the sampling site and poured into the sample container prior to sample collection. The sample container remains open throughout the collection of samples and is then sealed and returned to the laboratory with the other samples.
Equipment blanks	Equipment blanks are deionized water solutions that are transported to the site, opened in the field, and poured over or through the sample collection device, collected in a sample container, and returned to the laboratory. Equipment blanks are used to check the cleanliness of the sampling device.
Field Duplicates	A second sample taken from the same position as the first sample. The analysis of field duplicates provide some information on the sampling variability, as well as laboratory precision for the analytical method. A minimum of one field duplicate should be collected for every ten (or fewer) samples. Guidance on where and when field duplicates are required to be collected are given in the document *Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand* (MfE, 1999).

4.5 Sample labels

The following information will be recorded on each sample label:

1. Job name
2. Field sample number
3. Date and time of collection
4. Name of sampler
5. Preservatives used

4.6 Field log

Information recorded in the Field Log Book should include, but is not limited to:

- Name and address of site
- Name and address of field contacts on site
- Date and time of arrival at, and departure from the site
- Purpose of sampling
- Site information
- References (site drawings, photographs)
- Description of sampling point
- Method of sample collection
- Record of where samples were taken

- Water level prior to water sampling
- Depth to bottom of casing/borehole
- Calculations to determine well bore volume
- Volume and rate of well purging
- Measurement of well-purging parameters
- Details of any waste generated and its fate
- Number and volume of samples taken
- Description of soil samples (e.g. size, matrix, lithology, texture, colour)
- Odour of samples
- Date and time of collection
- Field sample numbers (these should be referenced to specific sampling points and times)
- Collector's name
- Field measurements made (e.g. PID readings, conductivity)
- Field observations (weather, humidity, soil type)
- Field treatment of samples (e.g. filtration of samples for *dissolved* metals)
- Field preservation of samples
- Unusual situations or problems.

4.7 Chain of custody

A Chain of Custody record must accompany the samples to the laboratory and a copy should be faxed to the originator by the laboratory upon receipt of the samples. Its purpose is to trace sample possession from the time of collection through analysis. The following should be recorded as a minimum on each Chain of Custody record:

- Field sample number(s)
- Name of sample collector
- Sample collector's signature
- Date and time of collection
- Location of site
- Type of sample(s) (e.g. soil, groundwater, surface water, leachate, saline)
- Field pH or electrical conductivity if measured
- Analyses requested (if chain of custody form is also used as analysis request form)
- Expected range for results if known, or an indication of likely level of contamination (e.g. from highly contaminated area, from background site etc). This helps to avoid laboratory cross-contamination between samples, and gross contamination of laboratory glass ware and equipment.
- Signatures of people involved in the chain of possession (sampler, carrier, laboratory person who accepts sample)
- Date and time when sample(s) received by carrier
- Date and time when sample(s) received by laboratory.

An example of a typical Chain of Custody is given in Appendix 4.

5

Analytical methods

5.1 Recommended methods

The current versions of the analytical methods specified in the tables below, together with their updates, are the **recommended** methods for use in assessing petroleum products in soil and water. The methods given in the tables are not intended to be a definitive compilation of all published methods for measuring the parameters listed. Rather, they are the methods that are most commonly used by New Zealand laboratories for this type of work.

The methods specified may be modified, provided that the method performance is checked as described in Section 7.0. Any method modifications must be recorded with the modified method's performance criteria.

The following methods will frequently be required in assessing contamination levels (see Module 3 of *Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand* (MfE, 1999).

Parameter	Media	Acceptable Test Methods
Petroleum Hydrocarbons	Water	TPH[1,2]
	Soil	TPH[1,2]
Volatiles (including BTEX)	Water	US EPA 8020 US EPA 8240 US EPA 8260 US EPA 524 US EPA 624
	Soil	US EPA 8020 US EPA 8240 US EPA 8260
Semi-volatiles (including PAH)	Water	US EPA 8270 US EPA 625
	Soil	US EPA 8270

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[1] In the context of this document, TPH is used as a generic term to refer to the Petroleum Hydrocarbon by Gas Chromatography (PHGC) method given in Appendix 3.

[2] Infrared based methods (such as US EPA 418.1 and APHA 5520C) are considered no longer to be appropriate for TPH analysis due to the requirement for these methods to use a freon extraction solvent.

The following methods would be used only in special cases:

Parameter	**Media**	**Acceptable Test Methods**
Total Dissolved Solids	Water	US EPA 160.1
Total Suspended Solids	Water	US EPA 160.2 APHA 2540D
BOD	Water	US EPA 405.1
COD	Water	US EPA 410.4
Total Lead	Water	US EPA 3015 US EPA 3010
	Soil	US EPA 3051 US EPA 3050
Organic Lead	Water	to be confirmed
	Soil	to be confirmed
TCLP - Metals		US EPA 1311
TCLP - Semi-volatiles		US EPA 1311
TCLP - Volatiles		US EPA 1311 using ZHE

TCLP tests can be used to provide data for reference with acceptance criteria for soil disposal at landfills.

A brief description of each test method is provided in Appendix 1. The quality assurance requirements for laboratories applying these methods for the determination of petroleum products in soil and water are described in Section 7.0.

Soil sample concentrations should be reported in mg/kg (equivalent to parts-per-million) on a dry weight basis, with the moisture content included in the report. Water samples should be reported in mg/L (equivalent to parts-per-million).

In addition to contaminant concentration data, laboratories must also report the following:

- date samples received at the laboratory, date extracted and holding times.
- results of laboratory quality control samples analysed with each batch of field samples.
- analytical method validation data where appropriate.

5.2 Immunoassay tests and new technology

Immunoassay testing and other technology may be used to provide on site screening. This work shall only be carried out by properly trained personnel, using equipment and protocols demonstrated and accepted in New Zealand. Ideally, the method should be pre-calibrated against gas chromatography laboratory analyses with typical samples taken from the site under investigation.

6

Sample storage and preparation

6.1 Containers, preservatives and holding times

Information on sample volumes, type of sample containers, recommended container size, preservatives and holding times for soil and water samples are provided in Tables 6.1 and 6.2 respectively.

The number of samples and containers can be reduced if the preservation procedure and the sample collection container is the same for each of the analytes. However, for volatile constituents, unless the cohesive-sample soil core method of sampling is used, a separate sample for volatile analysis must be collected.

Care must be taken to prevent water-containing samples from freezing because this can cause degassing, fracturing of the sample, or separation of slightly immiscible phase. Preservatives should be prepared in the laboratory using analytical grade chemicals and distilled water and stored in tightly sealed containers, away from sources of contamination. If sample containers are not pre-preserved in the laboratory, aqueous preservatives can be taken to the field in small dropper bottles to facilitate field preservation procedures.

Table 6.1 Sample Volumes, Bottles, Preservatives and Holding Times for Soil Samples

PARAMETER	CONTAINER TYPE, NUMBER and SUGGESTED VOLUME	PRESERVATION	MAX HOLDING TIME UNTIL EXTRACTION (from date of collection)	MAX HOLDING TIME UNTIL ANALYSIS (from date of collection)
Volatile Organics	1 x 100 mL glass jar with Teflon-lined cap	Cool to ≤ 4°C (No headspace)	N/A	7 days (from date of collection) *
Semi Volatiles	1 x 250 mL glass jar with Teflon-lined cap	Cool to ≤ 4°C	14 days	40 days
Petroleum Hydrocarbons by GC	1 x 250 mL glass jar with Teflon-lined cap	Cool to ≤ 4°C	3 days	14 days *
Total Lead	1 x 250 mL glass jar with Teflon-lined cap	Cool to ≤ 4°C	N/A	6 months
Organic Lead	1 x 500 mL glass jar with Teflon-lined cap	Cool to ≤ 4°C	14 days	14 days *
TCLP (for volatiles)	1 x 500 mL glass jar with Teflon-lined cap	Cool to ≤ 4°C (No headspace)	7 days	N/A
TCLP (for semi-volatiles and metals)	1 x 500 mL glass jar with Teflon-lined cap	Cool to ≤ 4°C	Organics: 14 days Metals: 6 months	N/A

* These samples should be shipped within 24 hours of collection.

Table 6.2 Sample Volumes, Bottles, Preservatives and Holding Times for Water Samples

PARAMETER	CONTAINER TYPE, NUMBER and SUGGESTED VOLUME	PRESERVATION	MAX HOLDING TIME UNTIL EXTRACTION (from date of collection)	MAX HOLDING TIME UNTIL ANALYSIS (from date of collection)
Volatile Organics	2 x 40 mL VOC bottles Teflon-coated septum	Cool to $\leq 4^{o}C$ (No headspace)	N/A	7 days (from date of collection) *
Semi Volatiles	1 x 1 litre amber glass jar with Teflon-lined cap	Cool to $\leq 4^{o}C$ Store in dark	7 days	40 days
Petroleum Hydrocarbons by GC	1 x 500 mL glass jar with Teflon-lined cap	Cool to $\leq 4^{o}C$	3 days	14 days *
Total Lead	1 x 500 mL plastic bottle, or glass jar with Teflon-lined cap	HNO_3 to pH < 2 Cool to $\leq 4^{o}C$	N/A	6 months
Organic Lead	1 x 500 mL plastic bottle, or glass jar with Teflon-lined cap	Cool to $\leq 4^{o}C$	14 days	30 days *
BOD	1 x 500 mL glass or plastic bottle	Cool to $\leq 4^{o}C$	N/A	2 days
COD	1 x 500 mL glass or plastic bottle	Cool to $\leq 4^{o}C$ H_2SO_4 to pH < 2	N/A	28 days
Total Dissolved Solids	1 x 1 litre plastic bottle	Cool to $\leq 4^{o}C$	N/A	7 days *
Total Suspended Solids	1 x 1 litre plastic bottle	Cool to $\leq 4^{o}C$	N/A	7 days *

* These samples should be shipped within 24 hours of collection.

6.2 Laboratory sample preparation

To obtain reproducible results it is essential that laboratories use standardised procedures for the preparation of samples. However, it is important to ensure that no bias is introduced in the analytical results. For example, certain oil industry contaminants can be driven off or modified during drying or handling procedures. Volatile organics may evaporate and PAHs are photosensitive.

6.2.1 Soil and sediment sample preparation

Where the amount of material required for an analysis is greater than 10g, samples may be analysed on an "as received" (i.e. wet) basis after removal of any stones and other large objects, and thorough mixing of the samples. Any superficial water should be decanted from sediment samples prior to mixing. Any analyses for volatile contaminants such as petroleum hydrocarbons, must be carried out on, as received, wet samples to avoid losses during drying.

For samples which are highly heterogeneous, or when test portions less than 10g are required, samples should be dried, ground and sieved prior to collection of the analytical portion. Samples should be air dried (≤30°C, <65% relative humidity, 16h or longer if required) and ground so that less than 5% is retained on a 2mm sieve.

If composite samples are to be analysed, these should be prepared from equal quantities of sub-samples taken through the full drying and sieving process. No more than 5 sub-samples should be used to form a composite, to avoid excessive dilution of individual samples.

Extreme care should be taken to avoid cross contamination during the sample preparation process and to minimise spread of dust in the laboratory. Equipment and containers used must be thoroughly cleaned before each sample to prevent cross-contamination. Cleaning procedures will vary according to the analytes being determined. Generally detergent washing, followed by deionised distilled water rinsing and oven drying will suffice. For trace metal analysis it may be necessary to incorporate soaking in dilute acid before distilled water rinsing. Solvent rinsing followed by air drying will normally be required prior to homogenising samples for organics analysis. Frequent laboratory reagent blank analyses will be required to check for contamination.

WARNING: Grinding of soils and sediments to fine dimensions may produce airborne particles which present a health hazard. Preparation should be performed in a fume hood, and appropriate respiratory protection should be worn.

1. Non-volatile or 'Stable' Analytes. Samples can be air dried for this analysis.
   - (a) examine visually and record observations
   - (b) obtain a representative sub-sample of the laboratory sample, of at least 50% of the sample or 200g, whichever is the smaller, taking into consideration amounts required for repeat analyses, other analyses to be carried out on this same sample and the moisture content of the sample
   - (c) remove large stones (>5mm) and vegetation and record the proportion by weight, together with the description, of each fraction of material removed
   - (d) air-dry or in draught oven (≤30°C, <65% relative humidity)
   - (e) grind sample (mortar and pestle) and sieve to <2mm (weigh and retain the larger particles for later analysis if required)
   - (f) mix and quarter (if necessary) the fraction <2 mm diameter
   - (g) transfer to sealed glass container
   - (h) store at 4^{o}C in the dark, pending extraction and analysis.
2. Semi-volatile Analytes. For this analysis, drying may lead to loss of analytes.
   - (a) follow steps (a), (b) and (c) above
   - (b) grind sample in a mortar and pestle to produce a homogeneous test sample

(c) transfer to sealed, air tight glass container and store at 4°C in the dark, pending extraction and analysis

(d) dry a separate, weighed portion of the original sample to determine moisture content. Report the moisture content with the analytical result so that the analyte concentrations may be reported on a “dry-weight” basis.

3. Volatile Analytes

It is necessary that samples taken for analysis of volatiles be separate from those taken for semi-volatile or non-volatile analytes. This will allow for volatile analysis to be repeated, if necessary, on samples which have not been homogenised or otherwise inappropriately treated.

When a sample container (chilled) is opened to allow an analytical sub-sample to be taken, the operation must be performed rapidly and with minimal disturbance of the sample. Preferably the sub-sample should be taken by using a corer.

(a) the representativeness of the analytical sub-sample should be demonstrated by analysis of multiple portions, rather than attempting to homogenise the sample and risk analyte losses

(b) the presence of large stones or particles (obviously >5 mm) and vegetation may prohibit sub-sampling with a coring device. If so, an analytical sub-sample should be taken by other means, but rapidly and with minimal disturbance so as to avoid the risk of significant analyte losses. For these samples, it is recommended that, after measurement of volatiles in the analytical sub-sample, the proportion by weight of each type of material in the sub-sample should be determined

(c) dry a separate, weighed portion of the original sample to determine moisture content. Report the moisture content with the analytical result so that the analyte concentrations may be reported on a “dry-weight” basis.

6.2.2 Liquid sample preparation

For samples collected for semi-volatile or metal analysis, samples containing visible amounts of particulate should be filtered before analysis, unless the method is intended to cover the total amounts of contaminant present in the sample. Even in this case it may be preferable to analyse the particulate separately from the liquid, because a “total” concentration will be affected by the relative amounts of particulate and liquids in any sub-samples taken.

(a) filter out solids

(b) stabilise as necessary by cooling to 4°C

(c) separate distinct liquid phases, if present, for separate analysis. If liquid phase is present, this must be reported.

Samples collected for *dissolved* metal analysis should have been filtered in the field (see Section 3.8). For these samples, subsequent laboratory filtration should not be required.

Samples collected for volatile analysis must not be filtered.

7

Laboratory quality assurance

Quality assurance procedures during analytical work are essential for the provision of meaningful results. This includes procedures for sample storage, preservation and sub-sampling, the preparation of analyte calibration standards and the analysis of quality control samples. Each of these is discussed briefly below, but laboratories should also examine the more comprehensive coverage provided in some of the major references (e.g. API, 1987; CCME, 1993; MfE and MoH, 1997; US EPA, 1992).

7.1 Sample preparation and sub-sampling

Many of the samples collected from oil industry sites will be heterogeneous in nature and it is important that these be properly processed and sub-sampled prior to analysis to ensure representative results. The requirements for each type of sample are discussed in Section 6.2.

7.2 Analyte calibration standards

Many of the laboratory based methods covered in this document require some form of calibration to ensure the accuracy of the results. This will normally be achieved through the use of working standards, which are prepared as part of the analytical procedure. However, it is important that these standards be cross-referenced to primary standards, and preferably to externally sourced reference materials.

Inter-laboratory check sample programmes have consistently shown that the most common source of major bias in analytical data is inaccurate concentrations, or even identifications, of analytes in calibration standards. Consequently, laboratory QA/QC systems and quality audits must put great emphasis on this area. It is essential that detailed procedures are in place to manage and document the traceability and validity of reference materials and derived solution standards used in analytical methods. Documentation should include:

- A suitable coding system for uniquely identifying all primary and derived standards.
- Records of receipt for all primary reference compounds or certified standards including source, purity and expiry date.
- Records of preparation for all stock standard solutions including dates of preparation and expiry, weight of reference material, final volume and solvent of dilution, signature of check by laboratory manager or person responsible for quality assurance policy in the laboratory.
- Record of preparation for all primary dilution and calibration (working) standard solutions including aliquot volume(s) or weight(s) of stock standard(s), final volume and solvent of dilution, expiry date, signature of check by laboratory manager.
- Records of confirmation of identity and concentrations of analytes in standard solutions including GCMS, comparisons of concentrations with those of previous standards and comparisons of concentrations with those of standard solutions exchanged with other laboratories.

7.3 Recommended quality control procedures

It is recommended that the QC steps described in Chapter 1, “Quality Control” of “Test Methods for Evaluating Solid Waste”, US EPA Publication SW-846 (US EPA, 1992), be adopted for all soils analyses and are also applicable to most water analyses.

In particular, it is expected that analysts would implement the following QC steps with each analytical batch, or with each twenty samples, whichever is the smaller:

1. **Laboratory reagent blank**: - at least one determination of a blank to establish the contribution to the analytical signal by reagents, glassware etc. The blank should be subtracted from the gross analytical signal for each analysis before calculation of sample analyte concentration.
2. **Replicate analysis**: - duplicate analysis of at least one sample from the batch. The variation between replicate analyses should be recorded for each batch to provide an estimate of the precision of the method.
3. **Quality control sample**: - analysis of at least one control sample, which comprises either a standard reference material, a laboratory reference material or a control matrix fortified with analytes representative of the analyte class. In all of these QC samples, the analytes should be present or fortified at concentrations which are easily quantified but within the range of concentrations expected for real samples.
4. **Surrogate analytes**: - surrogate analytes should be used in analytical procedures where it is appropriate (typically chromatographic methods of analysis for organic compounds). Surrogate spikes are known additions **to each sample and matrix spike or reference sample analysis**, of compounds that are similar to the analytes of interest in terms of:

    (a) extraction,

    (b) recovery through clean-up procedures, and

    (c) response to chromatographic or other determinations, but which

    (d) are not expected to be found in real samples,

    (e) will not interfere with quantification of any analyte of interest, and

    (f) may be separately and independently quantified by virtue of, for example, chromatographic separation or production of different mass ions in a GCMS system.

    Surrogate analytes are added to the analysis portion **before extraction** to provide a means of checking, for every analysis, that no gross errors have occurred at any stage of the procedure leading to significant analyte losses.
5. **Internal standards** - the use of internal standards is highly recommended for methods based on chromatographic analysis (typically for the determination of organic chemicals). Internal standards are added to each final extract solution, **once all extraction, clean-up and concentration steps are completed**. The addition is a constant amount of one or more compounds with similar qualities to 4(d), 4(e) and 4(f) above.

    The purpose of internal standards is to check the consistency of the analytical step (e.g.: injection volumes, instrument sensitivity and retention times for chromatographic systems) and provide a reference against which results may be adjusted in case of variation. The instrument is usually calibrated using the ratio of peak height or area for analytes compared with that for the internal standard(s). Surrogates are treated as analytes for quantification purposes.

Internal standards and surrogate analytes are of most use in the trace analysis of organic chemicals, where analyte losses that can occur during the extraction or chromatography steps, and the small final volumes that are frequently involved can give rise to considerable errors. They are of less use for the analysis of samples with very high concentrations of analytes, as the responses of small quantities of added standards are likely to be ‘swamped’ by the analytes in the sample, or to be ‘diluted-out’ and lost in the dilution of final extracts.

In addition to the above within batch QC samples, it is also strongly recommended that the laboratory participate in inter-laboratory sample exchange and collaborative study programmes and periodically analyse certified reference materials. These QC activities provide invaluable experience and external reference to validate analytical methodologies and give confidence in the quality of data produced.

It is also recommended that a field control sample spiked with analytes in the mid-range of anticipated sample concentrations, be analysed for every matrix type from a site assessment study. Such samples provide information on the potential of the matrix to cause positive or negative bias. For soil and sediment samples, the spike should be applied to fresh material which has already been dried, ground and sieved. An unspiked duplicate sample must also be analysed to establish the naturally occurring analyte concentrations.

7.4 Method validation

This is the process of obtaining data on a method in order to determine its characteristic performance and to establish confidence in the use of the method to obtain reliable results (ANZECC, 1996). Method validation specific to each laboratory's operations needs to be performed before the method can be adopted and applied to the analysis of actual samples. The minimum validation data required are:

- accuracy
- precision
- percent recovery
- limits of detection and reporting.

7.4.1 Accuracy

Accuracy is a measure of the closeness of an analytical result obtained by a method to the 'true' value. The following levels of accuracy should generally be achievable from a screening or reference method.

-screening method: within ± 30 % of:

i) the expected value of a certified reference material of similar matrix; or

ii) the value obtained by a separately validated and recognised quantitative method for the sample matrix.

-reference method: within ± 15 % of:

i) the expected value of a certified reference material of similar matrix; or

ii) the value obtained by a separately validated and recognised quantitative method for the sample matrix.

It is recognised, however, that coefficients of variation for a procedure can be expected to be higher for low concentrations of analytes, e.g. those below ten times the minimum detectable concentration.

7.4.2 Precision

Precision is a measure of the variation in data obtained from an analytical method. It is a combination of two components, repeatability and reproducibility.

Repeatability

This is the precision that measures the variation in the method's results produced by the same analyst under conditions which are as close as possible using the same equipment in the one laboratory and within a short interval of time. Repeatability is expressed as a standard deviation. The smaller the standard deviation the better the repeatability. Determine the standard deviation as follows:

> Perform at least 5 replicate analysis of each sample type expected to be analysed routinely. This should be repeated over at least three different analyte concentrations,

across the range normally expected. From these results, calculate the standard deviation, s, for each concentration, c, as follows:

$s_c = [\Sigma(x_i - x')^2/(n-l)]^{1/2}$

where: x = concentration of analyte of the replicate
x' = mean concentration of n replicate analytes
n = number of replicate analyses for that concentration

The acceptable repeatability of an analyte determination is, in general, two standard deviations of the mean value.

Confidence limit and confidence interval

When the results are assigned to the ± S_c multiples, they are the confidence limits e.g.. 10±4 mg/kg indicates the confidence limits are 6 and 14, while values from 6 to 14 represent the confidence interval.

Reproducibility

This is the precision that measures the variation in the method's results produced by different analysts in different laboratories under different conditions and using different equipment. It measures the 'ruggedness' of the method. Reproducibility data are best obtained through interlaboratory comparisons and proficiency studies. It is recognised that it may not always be practical, but it is recommended that as far as possible, reproducibility data are obtained as part of the validation procedure. Reproducibility is also expressed as a standard deviation.

7.4.3 Percent recovery

Percent recovery describes the capability of the method to recover a known amount of analyte added to a sample. This is the most realistic and useful term to be applied to the daily quality control of the analytical performance. Spike the sample with a known quantity of the analyte such that the combined added and suspected natural concentration of the analyte is within the working range of the method. The longer the residence time of the spiked analyte before extraction or digestion, the closer is the simulation in recovering the analyte from the natural sample. Calculate the percent recovery as follows.

$$\%\ \text{Recovery} = \frac{c-a}{b} x100$$

where: a = natural concentration of analyte determined in the sample
b = concentration of analyte added to the sample

c = concentration of analyte determined in the spiked sample.

Note: If a is known beforehand, c should be approximately twice a, or b should be approximately equal to a.

In general, at least 80 % recovery should be achievable from a reference method. Lower recoveries may be expected for low concentrations of analytes.

7.4.4 Limits of detection and reporting

Limit of Detection (LD)

This is the concentration of analyte which, when the sample is processed through the complete method, produces a response with a 95 % probability that it is different from the blank. Determine the standard deviation, s_{LD}, of at least 5 replicates of the sample with a concentration close to the estimated detection limit. The limit of detection (LD) is then calculated as follows:

$$LD = \text{t-statistic x } s_{LD}$$

where: t-statistic = 2.13 for 5 replicates.

7.5 Data management

Effective data management is an essential final stage of any analytical procedure to ensure the overall validity of the results. This can involve the following steps:

- Data recording and documentation, including data custody records and checks on any data transfer operations.
- Data validation, including checking that all calculations are correct, identification of outliers and instrument drift.
- Data verification, which includes checking that all the data is present and correct.
- Data handling, which includes data rounding and treatment of significant figures, in accordance with recognised methodologies.

This subject is more fully discussed in API (1989), CCME (1993) and MfE and MoH (1997) publications.

Each laboratory that uses the methods specified in this guideline is required to operate a formal quality assurance programme and be externally audited for compliance to ISO Technical Guideline 25.

8

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9

Glossary

APHA	American Public Health Association
API	American Petroleum Institute
ASTM	American Society of Testing and Materials
BOD	Biochemical Oxygen Demand
Borehole	Holed drilled purely for soil sampling, or as precursor to installing a monitoring well
BTEX	Benzene, Toluene, Ethyl benzene and Xylene
COD	Chemical Oxygen Demand
US EPA	United States Environmental Protection Agency
FID	Flame Ionisation Detector
GC	Gas Chromatography
GCMS	Gas Chromatography Mass Spectrometry
ISO	International Standards Organisation
MDL	Method Detection Limit
Monitoring Well	Slotted pipe installed in a borehole to allow proper well development and sampling
MS	Mass Spectrometry
Observation Well	Well installed in tank pit backfill
PAH	Polycyclic Aromatic Hydrocarbon
Petroleum Hydrocarbons	Mineral oils only (excludes naturally occurring organics)
Pre-cleaned	Equipment cleaned in the laboratory, before going to site
PID	Photo Ionisation Detector
ppm	Parts-per-million
PHGC	Petroleum Hydrocarbons by Gas Chromatography. Draft method for the analysis of soil and water for total petroleum hydrocarbons
TCLP	Toxicity Characteristic Leaching Procedure
TPH	Total Petroleum Hydrocarbons. A generic term that, in the context of this document, refers to the PHGC method given in Appendix 3.
VOC	Volatile Organic Compound
ZHE	Zero Headspace Extractor

Appendix 1

Description of test methods

APHA 2540D	Gravimetric procedure for determining total suspended solids in water and wastewater. The sample is filtered through a glass fibre filter and the residue retained dried to a constant weight at 103 to 105 °C. The increase in weight of the filter with the trapped residues represents the total suspended solids.
TPH	Draft method for petroleum hydrocarbons by gas chromatography (PHGC). The method is designed to provide data for the carbon ranges from C_{10} to C_{36} that can be used in a risk assessment. Full method provided in Appendix 3.
US EPA 405.1	Biochemical oxygen demand (BOD) test used for determining the oxygen uptake over 5 days of surface waters, domestic and industrial wastes.
US EPA 410.4	Colorimetric method for determining the chemical oxygen demand (COD) in drinking, surface and waste waters.
US EPA 160.1	Gravimetric procedure for the determination of residue, filterable (dissolved solids) in water.
US EPA 160.2	Gravimetric procedure for the determination of residue, non-filterable, (suspended solids) in water.
US EPA 524	GCMS method used for detection of extremely low levels of halocarbons and aromatic hydrocarbons in drinking water.
US EPA 624	GCMS method used for detection of parts-per-billion levels of halocarbons and aromatic hydrocarbons in wastewater or groundwater.
US EPA 625	Covers the determination of base/neutral and acid organic compounds in wastewater. The sample is serially extracted with organic solvent under alkaline and acidic conditions and the base/neutral and acids fractions separately analysed by gas chromatography mass spectrometry.
US EPA 1311[a]	Toxicity Characteristic Leaching Procedure (TCLP) designed to determine the mobility of both organic and inorganic analytes present in liquid, solid and multiphasic wastes. The solid phase, separated from any liquid phase, is extracted in an extraction vessel. A zero headspace extraction vessel is required for TCLP of volatile analytes. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. Following extraction, the liquid extract, together with any initial liquid phase separated, are analysed for the target analytes (procedures not specified in Method 1311).
US EPA 3010[a]	Digestion procedure for the preparation of aqueous samples and wastes that contain suspended solids for the determination of total metals.
US EPA 3015[a]	Microwave assisted nitric acid digestion for the preparation of aqueous samples and wastes that contain suspended solids for metals analysis.
US EPA 3050[a]	Acid digestion of sediment, sludge and soil samples for metals analysis.
US EPA 3051[a]	Microwave assisted acid digestion of sediment, sludge, soil and oil samples for metals analysis.
US EPA 8020[a]	A gas chromatography method for determining volatile aromatic compounds, including BTEX, in water, soil and other media. The analytes are introduced into the GC using direct injection or purge-and-trap, with detection being achieved using a PID.
US EPA 8240[a]	GCMS method similar to US EPA 624, which uses capillary chromatography, and can be used for solid waste as well as water.

US EPA 8260[a]	Used to determine volatile organic compounds in a variety of solid waste matrices by purge-and-trap, capillary gas chromatography mass spectrometry. The method is applicable to nearly all types of samples regardless of water content, including groundwater, aqueous sludges, soils and sediments. Most volatile organic compounds that have boiling points below 200 °C can be quantified by this method. Method detection limits are dependent, in part, upon the purging efficiency of each compound.
US EPA 8270[a]	Capillary column method for solids and liquids. Samples are extracted with solvent and analysed by GCMS.

[a] Method belongs to the SW-846 series of test methods (US EPA, 1992).

Appendix 2

Safe handling of petroleum products

General

All petroleum products are hazardous. They can cause EXPLOSION or FIRE.

Most petroleum products are TOXIC when not used with due care.

Field investigators should determine the likely product to be investigated and consult the Material Safety Data Sheet (MSDS) for the product to ensure that appropriate precautions are taken.

Fire and Explosion

All petroleum products must be treated as being potentially explosive, even in small quantities.

Petrol, aviation gasoline and most solvents evaporate readily, producing an explosive mixture with air. Kerosene, jet fuel and the less volatile solvents can also produce explosive vapours, particularly in poorly ventilated areas. All products can accumulate static electricity which may trigger an explosion — kerosine type products are particularly susceptible.

Petroleum products can react violently if mixed with other chemicals. Always keep them isolated from other chemicals.

Automotive diesel, fuel oils and lubricating oils can produce explosive conditions if sprayed or heated, even over small areas.

Precautions Against Fire and Explosion

Keep all SOURCES OF IGNITION away from petroleum products and their vapours. Sources of ignition include:

x Matches, lighters and cigarettes, etc.

x Any flame, spark or static discharge.

x Any non-flameproof electrical equipment, including switches, hand torches, electric radiators, vacuum cleaners, power tools and radios.

x Welding sets, leads, connections and hand-pieces.

x Gas welding torches.

x Motor vehicles and all internal combustion engines.

x Tools that can cause a spark if dropped, etc.

x Grinders.

x Other chemicals.

Petroleum vapours are heavier than air and will readily collect in pits, drainage sumps, cellars, and any low areas. Small quantities of vapour can be quickly and safely dispersed by good and rapid ventilation.

- The presence or absence of petroleum vapours can be checked by a competent operator using an explosimeter.
- **Do not enter any tank or pit** that has contained or does contain petroleum products unless it has first been tested with an explosimeter and a safety certificate issued by a competent person.

- **Do not do any hot work** (e.g. welding, gas cutting, grinding, drilling or power wire brushing) on any tank or container that still contains any product or that has not been tested and certified gas free by a competent person.
- **Do not transfer or pour petroleum** products from one container to another, without ensuring that both containers are fully earthed, and that an effective earthing connection is made between hose nozzle and receiving container before any transfer is started, and is maintained as long as the transfer continues.

Toxic Hazards

Petroleum vapours can quickly asphyxiate. At lower concentrations, they irritate the eyes and lungs, and may cause nausea, headache and depression.

Petroleum products will irritate the eyes and skin and may cause dermatitis on prolonged or repeated contact.

In addition, aviation gasolines contain toxic lead compounds. Internal surfaces of gasoline tanks that have contained lead compounds will be contaminated and must be treated as highly toxic, even after all product has been removed.

Precautions Against Toxic Hazards

- Avoid splashing, or any contact with the eyes or skin.
- Wear PVC gloves and boots, and cotton overalls. Wear goggles or face shield if splashing is possible.
- If clothing becomes contaminated with product, remove under a running shower.
- If eye or skin contact occurs, flush thoroughly with clean water. For eyes, flush for 15 minutes.

Laboratory Safety

Laboratory staff should have the MSDSs for all compounds that they work with available in their workplace.

Care must be taken to avoid undue exposure to solvents and all containers should be kept capped or covered as much as possible. Where practicable, all procedures involving toxic solvents should be carried out in an efficient fume hood.

Distillation sludge and solvents should be disposed of via an appropriate waste disposal company.

Solid wastes containing small amounts of residual solvent can usually be disposed of into a waste bin along with left over samples. Note that, depending on the number of samples, and the levels of contamination in them processed by a laboratory, it may be necessary to develop specific procedures for storing and disposing of solid samples.

All refrigerators and freezers used for storing samples and standards should be certified for flammable solvent storage (i.e. any electrical contacts that may cause a spark must be moved to the outside of the cabinet).

Notes for Physician

See specific ‘Notes to Physicians’ in the MSDSs.

Appendix 3

Total Petroleum Hydrocarbons: Petroleum Hydrocarbons by Gas Chromatography

1 Introduction

1.1 Scope

The standard method for use in screening contaminated sites for hydrocarbon contamination has historically been Freon Extraction/Infrared Spectroscopy as defined by US EPA Method 418.1 and APHA 5520C. The manufacture of Freon 112 has now been banned and these methods will no longer be able to be carried out.

The method described in this Appendix is aimed as a replacement for the above methods for use in the investigation of contaminated sites, particularly those which may be contaminated with petrol, diesel, other petroleum fuels, and petroleum based solvents. Very volatile (e.g. pentanes) or heavy petroleum products will not be determined using this method.

The method is written as a 'performance-based' method, and is designed to be rapid and economical to carry out. It will provide a guide to the relative levels of hydrocarbon contamination as well as information as to the likely source of the hydrocarbons and the extent of their degradation.

The incorporation of standard reporting procedures will mean that it will be possible to meaningfully compare data produced by different laboratories using this method.

The method must be carried out under the supervision of an analyst experienced in the interpretation of capillary gas chromatograms.

1.2 Limitations

This method is designed to provide quantitative data for the carbon ranges from C_{10}-C_{36} that can be used in a risk assessment in line with the document *Draft Guidelines for Assessing and Managing Petroleum Hydrocarbon Contaminated Sites in New Zealand*. The method cannot be used to provide quantitative data for the C_6-C_9 hydrocarbon range for use in a risk assessment. Quantitative analyses for lower hydrocarbons MUST be carried out by Purge & Trap GCMS (which may give results for BTEX as well as C_6-C_9 hydrocarbons less the BTEX component). Laboratories may choose to report to higher carbon numbers but this is not a mandatory part of this method.

The method is not designed to produce data which can be used in risk assessment calculations for the C_6-C_9 hydrocarbons, or for other specific PAH analytes (such as benzo[a]pyrene). Data for C_6-C_9 hydrocarbons should be reported from this TPH method, but only to indicate the presence of VOCs.

Specific methods should be used if risk assessment calculations are to be carried out for C_6-C_9 hydrocarbons (such as Purge and Trap GCMS [US EPA Method 8240]) or for PAHs (US EPA Method 8270).

Most of the proposed methods for sample preparation will give rise to the loss of the most volatile components in the sample, mainly during the weighing and chemical drying steps.

1.3 Interferences

1.3.1 Any organic compounds which are soluble in the extracting solvent and which elute from the GC under the conditions used will interfere. These may include vegetable and animal oils and fats, chlorinated and other solvents, plasticisers, etc. The use of silica to adsorb polar compounds may reduce these interferences.

1.3.2 Impurities in the extracting solvent, drying agents and silica will interfere. The use of high purity (but expensive) solvents will reduce this. Laboratory blanks must be analysed along with each batch of samples.

1.3.3 Carryover from previous highly contaminated samples extracted in the same glassware may cause spurious elevated results. Efficient cleaning of all glassware, syringes, etc, is essential to minimise this.

2 Method summary

The sample is extracted into a suitable solvent, the extract cleaned up using anhydrous sodium sulphate and (if required) silica, and then analysed using GC-FID. The results are reported as amount of hydrocarbon in various carbon bands.

The solvent used may be dichloromethane, or any other suitable solvent (such as dichloromethane/acetone) that will meet the performance specifications of this method.

The method is based on American Petroleum Institute (API) “Method for Characterisation of Petroleum Hydrocarbons in Soil” and is similar to Washington States WTPH-HCID (Washington TPH - Hydrocarbon Identification) method. Other documents used in the development of this method were: API, 1991; ASTM, 1991; DoE, 1987; US EPA, 1992.

3 Definitions

The term ‘TPH:Petroleum Hydrocarbons: by Gas Chromatography’ (PHGC) should be used when referring to data generated using this test method if there is any possibility of comparisons being made with historical data generated using the IR method. If not, this may be shortened to TPH.

PHGC	**Petroleum Hydrocarbons by Gas Chromatography:** Those compounds which are extractable into the solvent and which elute from a GC column under the conditions specified in the test method.
ASE	**Accelerated Solvent Extractor.**
DCM	**Dichloromethane**, also called methylene chloride.
DM	**Dry matter** i.e. Weight of Total Sample - Weight of water. Expressed as a percentage of the Total.
FID	**Flame Ionisation Detector** (used with GC). The FID is a non-specific detector which responds to almost all organic compounds.
GC	**Gas Chromatography.**
GCMS	**Gas chromatography using a mass selective detector or a mass spectrometer**. Allows (almost) unequivocal identification and quantitation of many organic compounds**.**
HC	Hydrocarbon(s).
P & T	**Purge and Trap.** A method for stripping volatiles from soil or water samples by passing a stream of helium through the sample. The volatiles are trapped and analysed, usually by GCMS.
SFE	**Supercritical Fluid Extraction.** Extraction using carbon dioxide under conditions of temperature and pressure such that the CO_2 acts as a supercritical fluid.
SPE	**Solid Phase Extraction**. Extraction of hydrocarbons onto discs or cartridges, followed by elution with solvent.
TPH	**Total Petroleum Hydrocarbons**. A generic term that can be used when referring to data generated using the PHGC method.

4 Safety issues

4.1 Dichloromethane

Dichloromethane (DCM) is a suspected toxic compound. It may affect the body through the lungs, ingestion or by direct absorption through the skin.

Care must be taken to avoid undue exposure to DCM and all containers should be kept capped or covered as much as possible. Where practicable, all procedures involving DCM should be carried out in an efficient fume hood.

4.2 Hydrocarbons

Hydrocarbon solvents such as pentane and hexane are neurotoxic and very flammable. An efficient fume hood should be used and care taken to prevent the build-up of vapours in areas where the flash point may be exceeded e.g. ovens.

Petrol and diesel both contain potentially toxic compounds such as benzene, toluene and polycyclic aromatic hydrocarbons. Unnecessary exposure should be avoided.

Petrol and other hydrocarbons are flammable and must be kept clear of all potential sources of ignition.

4.3 MSDS

Staff should have the Material Safety Data Sheets (MSDS) for all compounds with which they work available in their workplace.

4.4 Handling of wastes

Residual solvent should be collected into waste containers (e.g. glass winchesters) and can be redistilled in a fume hood. **Redistilled solvents can be reused only after their purity has been checked by GC-FID.**

Distillation sludge, and solvent which is not going to be redistilled, should be disposed of via an appropriate waste disposal company.

Solid wastes which contain small amounts of residual solvent can usually be disposed of into a waste bin along with left over samples. Note that, depending on the number of samples, and the levels of contamination in them, processed by a particular laboratory it may be necessary to develop specific procedures for storing and disposing of solid samples.

4.5 Storage facilities

All refrigerators and freezers used for storing samples and standards should be certified for flammable solvent storage (i.e. any electrical contacts which may cause a spark must be moved to the outside of the cabinet).

5 Apparatus

Extraction apparatus suitable for the method chosen.

GC-FID instrument. Use of a bonded phase capillary column is strongly recommended.

Integrator or computer and integration software.

Volumetric pipettes and glassware. These should all be regularly calibrated and a calibration record maintained.

Glassware. All glassware used should be thoroughly cleaned e.g. with a hot Decon wash followed by rinsing with tap water. Solvent rinsing with acetone (**Care!**) is also recommended. Oven baking (except for volumetric glassware) is useful.

6 Reagents and standards

6.1 Reagents

Dichloromethane (DCM) CAS 75-09-2

The DCM used should be of high purity and should be checked by GC-FID analysis prior to use. DCM can be purified for re-use by distillation and each batch should have its purity checked before use. Adequate records of purity checking should be kept.

Other solvents

Other solvents may be used, provided they satisfy the performance criteria for this method. Special attention should be paid to any safety aspects of alternative solvents.

Anhydrous sodium sulphate

This can contain plasticisers leached from plastic storage containers and each batch should be checked before use. One possible cleanup method is as follows. The sodium sulphate should be spread in a metal tray to a depth of less than 2 cm and ignited in a muffle furnace at 600°C for 1 hour, cooled and stored in a tightly closed metal or glass container.

Silica

(e.g. Merck, Silica Gel 60, 70-230 mesh)

Deactivated with 2% water as per ASTM Method D3921. Weigh silica gel into a container having an aluminium or Teflon-lined lid. Add solvent to make a slurry and mix well. Allow gel to settle, pour off free solvent, heat - CARE -to remove remainder of solvent. Then heat at 150°C for at least 2 hours. Remove from oven and immediately seal. Allow to cool in a dry environment. When cool add water equal to 2% of the weight of the gel, recap, shake well and store for several hours to reach equilibrium. Do not expose the gel to the atmosphere more than necessary when removing portions for use.

6.2 Calibration standards

The exact preparation of calibration standards may vary between laboratories, and these are suggested procedures only. All storage vials should have the date of preparation and the batch number written on the label.

Freshly made calibration standards should be checked by GC-FID against the calibration standards currently being used in the TPH method as a check for any gross error in their preparation.

6.2.1 Hydrocarbon standards

Stock Hydrocarbon Standard (500 mg/L) [maximum holding time 6 months]

This standard mix is used to quantify the hydrocarbons falling into each "carbon band" and is also useful if single components need quantifying e.g. toluene, styrene.

Includes n-nonane (C_9), n-undecane (C_{11}), n-tetradecane (C_{14}), n-eicosane (C_{20}), n-pentacosane (C_{25}),and n-triacontane (C_{30}), n-hexatriacontane (C_{36}) and n-tetratetracontane (C_{44}) along with n-heptane (C_7) or the first n-alkane which can be reliably separated from the solvent front under the GC conditions used. These are obtainable in sufficient purity from chemical suppliers such as Sigma/Aldrich, Supelco or Alltech.

Because of the low solubility of the higher hydrocarbons in the usual solvents, the maximum stock standard concentration which is practical is 500 mg/L.

Standard Preparation Procedure

Accurately weigh about 50 mg (record the actual weight) of each of the hydrocarbons, except the lowest n-alkane, into a 100 mL beaker, starting with the highest carbon number and going down to C_9. Warm gently to melt the solids then add 50 mL solvent.

Transfer to a 100 mL volumetric flask. Add 75 µL n-hexane (density 0.66, so 75 µL = 50 mg) or the appropriate volume of the other lowest n-alkane if used, and make to the mark with solvent.

Store in 10 mL vials labelled with the exact concentrations of each hydrocarbon.

Working Hydrocarbon Standards (2.5, 5, 25, 50, 250 mg/L) [maximum holding time 1 month]

Half fill five labelled 10 mL volumetric flasks with solvent.

Pipette 50 µL, 100 µL, 500 µL, 1 mL and 5 mL of the stock standard into respective flasks.

Make to the mark with solvent.

Either store in 10 mL vials in the freezer, or aliquot into GC autosampler vials and store in racks in the freezer. A new aliquot should be used each 24 hours for GC analysis.

As a full five-point calibration only has to be done occasionally, it is useful to make up extra vials of the linearity check standard (usually 25 mg/L) at the same time as the above.

7 Sample collection, preservation, storage and transport

7.1 Sample collection

Samples should be collected using representative sampling methods (see Sections 2.5 and 3.6, main document). Note that the laboratory will only be using 2-20g of the sample for extraction for hydrocarbon analysis.

7.2 Sample containers

Samples for TPH (C_{10}-C_{36} range) should be collected into appropriate clean glass jars (see Sections 2.5 and 3.6, main document).

For volatile constituents (C_6-C_9 range) a separate sample for volatile analysis must be collected if the data is to be used for risk assessment purposes. If samples are being collected for volatile analysis by Purge and Trap methods (see Section 5, main document), then glass jars with Teflon-lined caps must be used for soil samples, and VOC pottles with Teflon-coated septa must be used for water samples (see Section 6.1, main document). Samples collected for volatile analytes must have no headspace.

7.3 Sample storage and transport

Samples should be cooled to <4°C as soon as possible after collection. This will reduce loss of volatile hydrocarbons and inhibit microbial action in the soil which may lead to hydrocarbon breakdown. Details on containers, preservatives and holding time are given in Section 6.1 of the main document.

The glass jars should be protected by plastic bubble wrap or similar to prevent breakage. Samples should be transported to the laboratory in a chilled condition.

7.4 Chain of custody

It is essential that sufficient information is recorded on the Chain of Custody which must be supplied to the laboratory to enable accurate analysis of the samples to be carried out (see Section 4.7 of the main document). An example of a typical Chain of Custody is given in Appendix 4.

8 Quality control

Standard laboratory quality assurance procedures are outlined in Section 7 of the main document.

Two types of QC samples can be used to track quality in the laboratory.

The first is a sample containing a known quantity of diesel dissolved in the extraction solvent. This should be analysed with every batch of samples and serves as a check on the GC system and quantification procedures.

The second is a simulated 'real' sample which is taken through the full extraction and analysis, giving a check on the entire procedure. Experience has shown that it is not easy, maybe impossible, to prepare enough of a homogeneous real sample to act as a QC sample which will last for a reasonable length of time.

8.1 QC sample preparation

Because of the volatility of petrol, it is not feasible to prepare a QC sample containing petrol. The stability/useability of the QC standard should be determined by the laboratory. It is likely to be no more than 3-6 months.

8.1.1 Fuel standards

QC samples of diesel could be prepared using the following procedure. Note that solvents are volatile and a weight loss will occur during exposure to the atmosphere so these steps should be completed as rapidly as possible. Only fresh fuels should be used for preparing QC samples.

Stock QC Fuel Samples (10000 mg/L)

Weigh 0.500g fuel into a tared 50 mL volumetric flask on a balance. Immediately add about 20 mL solvent (acetone is best for diesel).

Make to the mark with solvent.

Aliquot into 10 mL storage vials and store in a suitable freezer. Label vials with date of preparation. Warm to room temperature before use.

Working QC Fuel Samples (50, 100, 500, 1000, 5000 mg/L)

Half fill five labelled 10 mL volumetric flasks with solvent.

Pipette 50 µL, 100 µL, 500 µL, 1 mL and 5 mL of the stock standard into respective flasks. Make to the mark with solvent.

Either store in 10 mL vials in the freezer, or aliquot into GC autosampler vials and store in racks in the freezer. The latter is preferable, and allows each calibration vial to be replaced easily once it is reduced to half it's starting volume.

A vial with a punctured liner should not be used for more than one week.

8.1.2 A Diesel Soil QC sample

1. Dry a representative soil sample (35°C, overnight in a forced air oven) and grind to pass a 2 mm sieve.
2. Prepare a solution of fresh diesel fuel in acetone by weighing about 2.5 g (note the exact weight) diesel into a 10 mL volumetric flask and making to the mark with solvent.
3. Add 1000 g of the soil to a large glass jar (a quart size Agee preserving jar with a screw lid is suitable).
4. Add 100 mL deionised water, screw the lid on and mix by rotation or shaking for 1 hour. An end-over-end TCLP mixer works very well. This will hydrate the soil to 90% dry weight.
5. Add 2 mL of the diesel in acetone solution and mix again for a minimum of overnight.

This will give a QC sample with a hydrocarbon concentration of approximately 500 mg/kg dry weight. This concentration is of the same order as the soil acceptance criteria for residential land use for the C_{10}-C_{14} hydrocarbons (MfE, 1999).

8.1.3 Contaminated Soil QC

A contaminated soil, or homogeneous mixture of contaminated soils, could be used as a QC. Note that it is extremely difficult to prepare a homogeneous sample from very contaminated soils as it tends to form clumps during mixing. Cryogenic preparation may help.

8.1.4 QC Storage

The QC sample should be subdivided into smaller glass containers with Teflon-lined lids (40 mL IChem VOC vials are suitable), each containing about 50 g. These should be stored in a freezer.

8.1.5 QC Limits

The QC sample should be analysed a number of times (minimum = 9) over several days or weeks to establish warning and action limits.

8.2 Extraction

Each extraction batch should contain, at minimum, one blank (i.e. laboratory reagent blank) and one replicate which are carried through the whole extraction process.

QC and spiked samples should be run at least once every 20 samples analysed.

8.3 Analysis

Every analytical run should contain a standard hydrocarbon mix (for determining retention time limits for the carbon bands) and 100 and 500 ppm diesel standards. The hydrocarbon mix and 500 ppm diesel standard should be re-analysed at least once every 20 samples.

9 Method performance data

This method has been written to allow for flexibility in introducing new solvents or procedures for extraction. These will be acceptable provided the following method performance standards can be attained.

The raw data used to determine the following should be available from the laboratory on request. Note that this is the data required for IANZ Certification of the test method for the laboratory.

The QCs, replicates and spiked samples, and the reagent blank should be analysed at the frequency specified in Section 7 of the main document, and the precision and recovery monitored to ensure compliance.

9.1 Soils

9.1.1 Precision

A real sample containing 500-1,000 mg/kg dry wt of diesel or similar hydrocarbon should be analysed in triplicate on three occasions over at least a two week period.

The 95% confidence limit (i.e. the mean ± 2 standard deviations) should be better than 30%. An example of a template that can be used to aid determination of precision data is given in Appendix 4.

9.1.2 Recovery

The recovery of diesel and lubricating oil spiked at 500-1,000 mg/kg dry wt onto soil, sand or Celite should be in the range of 80-120%.

9.1.3 Method Detection Limit (MDL).

The MDL should be 40 mg/kg dry weight or better. See Section 11.

9.1.4 Interlaboratory comparison study

The laboratory should participate in an interlaboratory comparison study for soils contaminated with C_{10}-C_{36} range hydrocarbons.

9.2 Waters

9.2.1 Precision

A sample containing 5-50 mg/L of diesel or similar hydrocarbon should be analysed in triplicate on three occasions over at least a two week period.

The 95% confidence limit (i.e. the mean ± 2 standard deviations) should be better than 30%. An example of a template that can be used to aid determination of precision data is given in Appendix 4.

9.2.2 Recovery

The recovery of diesel and lubricating oil spiked into water at 1-10 mg/L should be in the range of 80-120%.

9.2.3 Method Detection Limit (MDL)

The MDL should be 0.2 mg/L or better. See Section 11.

9.2.4 Interlaboratory comparison study

The laboratory should participate in an interlaboratory comparison study for waters contaminated with C_{10}-C_{36} range hydrocarbons.

10 Procedure

10.1 Soil sub-sampling

Many of the samples collected from oil industry sites will be heterogeneous in nature and it is important that these be properly processed and sub-sampled prior to analysis. The TPH method is undertaken on a sub-sample of the sample collected in the field. Most laboratory methods extract only approximately 5-20 g of sample and great care must be exercised to ensure that the sub-sample removed for analysis is representative of the sample as a whole. In addition, the sample processing and sub-sampling must be carried out as rapidly as possible to minimise loss of volatiles.

For reasonable homogeneous samples, where possible, mix thoroughly in the cold container using a spatula.

For non-homogeneous samples e.g. several different soil types present, or a wide range of particle sizes, the sample should be spread out on a cold aluminium tray, any aggregates or lumps broken down using a spatula and the sample well mixed.

Samples that contain a wide range of particle sizes (e.g. gravel, sand and silt) may need to be separated into fractions using sieving (e.g. 10 and 2 mm sieves), keeping a note of the weight ratio. The results for the <2 mm diameter fraction should be reported, along with the percentage of each fraction in the sample.

Further details on the preparation of soil samples are given in Section 6.2.1 of the main document.

10.2 Soil dry weight determination

10.2.1 Principles of test

The soil samples are weighed, air dried at 105±5°C to constant weight, and re-weighed. The loss of weight is used to calculate the Dry Matter %.

Care must be exercised in drying samples containing high levels of volatile hydrocarbons as this may be a fire hazard. Preliminary “drying” in a fume hood may reduce the hazard. Note also that the loss of weight due to loss of hydrocarbon will give an erroneous result for Dry Matter % which may need to be accounted for in highly contaminated samples.

10.2.2 Procedure

1 Weigh a clean aluminium drying tray (e.g. pie dish) and record weight (W_1).

2 Re-weigh and record this weight (weight of tray plus wet sample) (W_2).

3 Place the drying tray in the oven at 105±5°C overnight to dry.

4 Next day cool the sample in a desiccator and re-weigh the tray plus dried sample (W_3).

10.2.3 Calculation

$$\%\ \text{dry matter} = \frac{(W_3 - W_1)}{(W_2 - W_1)} * 100$$

Where W_1 = weight (g) of tray

W_2 = weight (g) of wet sample plus weight of tray

W_3 = weight (g) of dried sample plus weight of tray

10.3 Extraction

Any extraction method which can be demonstrated to meet the performance criteria is acceptable.

10.3.1 Soils

Possible procedures include:

10.3.1a Accelerated Solvent Extraction

10.3.1b Supercritical Fluid Extraction

10.3.1c Ultrasonic Extraction

10.3.1d Microwave Extraction

10.3.2 Waters

The extraction procedures used for waters may depend on the hydrocarbon fraction required. For example, in groundwaters the dissolved (soluble) hydrocarbon is of most interest as this is what is being carried in the groundwater flow. Sampling from groundwater bores sometimes includes sediment in the sample bottle and extraction of the "Total" sample may reflect more the hydrocarbon associated with the sediment than with the water. For stormwaters or leachates which are discharging to a surface water body (e.g. a stream or lake) the "Total hydrocarbon" concentration will be of more interest (see Section 6.2.2, main document).

Possible extraction procedures for "dissolved" hydrocarbon include (after settling or centrifugation of the sample, and decanting the aqueous layer);

10.3.2a Solid phase extraction

10.3.2b Liquid-liquid extraction in separating funnel

10.3.2c Continuous liquid-liquid extraction

Possible extraction procedures for "Total" hydrocarbon include;

10.3.2a Solid phase extraction [Only suitable if little or no sediment present]

10.3.2b Liquid-liquid extraction in separating funnel

10.3.2c Continuous liquid-liquid extraction

10.4 Treatment of extract

Note: Quantities used will vary with the volume of extract**.** The procedures described are an example and other methods of treating the extract with sodium sulphate and silica gel may be used.

1. Add a 1 g scoop of anhydrous sodium sulphate and mix.
2. Add a 1 g scoop of silica and mix. If residual colour is still apparent in the extract supernatant then add a further 1 g scoop of silica and mix.
3. Allow the silica to settle (10-15 minutes) then remove a 1 mL aliquot to a pre-labelled GC vial.

Clean-up with silica gel is optional, and depending upon the amount of co-extracted contaminants or impurities present in the extract (as indicated by its colour), silica gel clean-up may not be required for every sample.

11 GC Analysis

Analysis should be supervised by someone familiar with the operation, maintenance and troubleshooting of GC instrumentation and with the interpretation of chromatograms.

The sample should be analysed using a gas chromatograph fitted with a flame ionisation detector (FID).

11.1 GC conditions

The exact conditions used will vary from laboratory to laboratory.

A split/splitless injector at 330°C is recommended. The injection liner should be checked and replaced regularly.

The final temperature of the oven programme should be as high as possible to ensure maximum removal of the higher molecular weight hydrocarbons from the column.

11.2 Proof of linearity

The calibration standards should be analysed at all concentrations and the log(area response) plotted against log(concentration). Visual inspection will reveal any obvious non-linearity.

A linear regression analysis of the log values should give a regression coefficient >0.9950.

Once the linear range has been determined, it is only necessary to carry out a full five-point calibration every month. It should also be repeated if the column is changed or if there are any major repairs carried out to the GC system.

A one point calibration using a mid-range standard is suitable provided that the area response for this standard is logged and warning (±2 standard deviations) and action (±3 standard deviations) limits determined. If the one point calibration falls outside the warning limits then the full five point calibration should be repeated.

11.3 Detection Limits and Method Validation

The major problem in this area is in determining a detection limit for carbon band reporting. An individual component can have a DL of, say, 1 unit. If there are 20 individual peaks between, say C_{12} and C_{14}, and each is present at 0.8 which is below the DL of the individual peak then there may be 16 units of Total Hydrocarbon in the band but this is 'undetectable'. If, however, one compound is present at 5 units, it is clearly there and should be reported as such.

There are considerable variations in ways of determining "detection limits" for hydrocarbons.

An Instrument Detection Limit (IDL) gives information about the performance of the instrumental part of the analysis only. It is useful to determine this during method development/validation as it gives an indication of the best possible DL which may be achieved.

A Method Detection Limit (MDL) covers all steps in the analytical process (but not sampling), including extraction, cleanup and analysis. A MDL is almost invariably higher than an IDL. It is also useful to determine MDL during method validation.

It is recommended that Section 11.3.1c (Instrument Detection Limit for carbon bands) be adopted as the Detection Limit to be reported by laboratories, as this seems to be the method already in use by the laboratories.

The DL described in sections 11.3.1a, 11.3.1b and 11.3.1d should all be determined during method validation, and on a regular (annual, or depending on changes in equipment or procedures) basis thereafter.

11.3.1 Instrument detection limit (IDL) for diesel fuel

From the calibration curve and a knowledge of the noise and minimum peak area settings, make an estimate of the likely detection limit.

Prepare a standard diesel in acetone solution at 5 x the estimated detection limit and analyse it in triplicate on three separate days.

Determine the mean concentration and standard deviation (SD).

Calculate the Instrument Detection Limit using the following formula (US EPA, 1982):

MDL = SD x t

where t = Students' t values at 99% Confidence Level depending on the number of replicates (see Table)

Number of Replicates (n)	Degrees of Freedom (n-1)	t value
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.764
16	15	2.602
21	20	2.528
infinite	infinite	2.326

11.3.2 Method detection limit for diesel.

Prepare a spiked diesel soil sample (Section 8.1.2) at close to the estimated DL.

Analyse this sample in triplicate on at least three different days and calculate the DL as shown above.

As this sample is processed through the entire extraction and analysis procedure, it will provide a "Method Detection Limit" (MDL) which is more meaningful than the IDL.

11.3.3 Instrument detection limit for carbon bands.

Prepare a hydrocarbon standard which contains the first hydrocarbon in each band (i.e. n-heptane, n-decane and n-pentadecane) at close to the estimated detection limit for each.

Analyse in triplicate on at least three days.

Calculate the DL for each hydrocarbon as shown in section 11.3.1a. This gives an IDL for each individual hydrocarbon.

As each band can contain a number of hydrocarbons, the DL for each band can then be estimated by calculating the number of fully resolved peaks which will fit between the first and last standard in the band (the Trennzahl number) and multiplying this by the DL for the first standard in the band.

$$\text{Band DL} = \text{DL}_x \text{ x } \left[\frac{(t_y - t_x)}{0.5(w_x + w_y)} - 1\right]$$

Where DL_x = Detection limit for the first hydrocarbon in the band

t_x, t_y = Retention times for the first and last hydrocarbon in the band

w_x, w_y = Peak widths for the first and last hydrocarbon in the band.

For example. Suppose C_{10} has a retention time of 5 min, a peak width of 0.1 min and a DL of 0.2. C_{14} has t = 9 min and w = 0.3 min. The DL for the C10-C14 band is given by;

$$C_{10} - C_{14} \text{ DL} = 0.2 \text{ x } \left[\frac{(9 - 5)}{0.5(0.1 + 0.3)} - 1\right]$$

$$= 0.2 \text{ x } [(4 / 0.2) - 1]$$

$$= 3.8$$

This would usually be rounded to 4.

Note that high efficiency capillary GC columns will lead to higher and narrower peaks for individual components, increasing the signal to noise ratio and improving the detection limits for individual components. Hydrocarbons eluting later in the chromatogram will be broader, giving a poorer DL for these compounds.

11.3.4 Method detection limit for carbon bands.

As for Section 11.3.1c but the standards should be spiked into a clean soil matrix and the spiked sample carried through the whole extraction and analysis procedure.

As this sample is processed through the entire extraction and analysis procedure, it will provide a "Method Detection Limit" (MDL) which is more meaningful than the IDL.

11.4 Quantitation

11.4.1 Quantitation against hydrocarbon standards.

This is the most widely used method in New Zealand. [Preferences have been shown for having results reported in two slightly different ways as shown below]

The retention time (RT) and peak width (PW) of each hydrocarbon standard must be determined.

Integration groups are then set up to sum the area of all peaks in a group as follows.

11.4.1.1 Condensed Reporting.

Reports for the Oil Industry Environmental Working Group should be provided using this condensed reporting format.

Group	**Start Integration** (see note 2)	**End Integration** (see note 2)
C_7-C_9 (see note 1)	RT C_7 - 0.5*PW C_7	RT C_9 + 0.5*PW C_9
C_{10}-C_{14}	RT C_9 + 0.5*PW C_9	RT C_{14} + 0.5*PW C_{14}
C_{15}-C_{36}	RT C_{14} + 0.5*PW C_{14}	RT C_{36} + 0.5*PW C_{36}

Note 1. Use C_6 instead of C_7 only if the chromatographic conditions allow baseline separation of C_6 from the solvent peak. The compounds in the C_7-C_9 group must be quantified by a Purge and Trap method for risk assessment purposes.

Note 2. The times are set as shown because the branched chain alkanes will elute BEFORE the n-alkane with the same number of carbons. For instance, with the C_{10}-C_{11} band, isomeric C_{10} compounds will elute between C_9 and C_{10}. Thus all peaks from just after C_9 and up to, and including, $C_{11}$are included in this range.

The concentration of hydrocarbon in each band (for soils) is then calculated from

Carbon band = Area sample/area 1st HC std x std conc. x vol. extracting soln/W x 100/DM% (mg/kg DM or mg/L)

where 'W' = weight of soil OR volume of water extracted.

i.e. the peak area for all peaks in a band are summed and quantified using the first hydrocarbon standard for that group.

11.4.1.2 Full Reporting.

Preferred by some environmental consultants and industry sectors because of the extra information provided.

Group	**Start Integration**	**End Integration**
C_7-C_9 (see note 1)	RT C_7 - 0.5*PW C_7	RT C_9 + 0.5*PW C_9
C_{10}-C_{11}	RT C_9 + 0.5*PW C_9	RT C_{11} + 0.5*PW C_{11}
C_{12}-C_{14}	RT C_{11} + 0.5*PW C_{11}	RT C_{14} + 0.5*PW C_{14}
C_{15}-C_{20}	RT C_{14} + 0.5*PW C_{14}	RT C_{20} + 0.5*PW C_{20}
C_{21}-C_{25}	RT C_{20} + 0.5*PW C_{20}	RT C_{25} + 0.5*PW C_{25}
C_{26}-C_{36}	RT C_{25} + 0.5*PW C_{25}	RT C_{36}+ 0.5*PW C_{36}
C_{37}-C_{44}	RT C_{36} + 0.5*PW C_{36}	RT C_{40} + 0.5*PW C_{40}

Note 1. Use C_6 instead of C_7 only if the chromatographic conditions allow baseline separation of C_6 from the solvent peak. The compounds in the C_7-C_9 group must be quantified by a Purge and Trap method for risk assessment purposes.

Results equivalent to those obtained using the condensed reporting format can be obtained by summing the appropriate groups e.g. (C_{10}-C_{11}+C_{12}-C_{14}) = C_{10}-C_{14}

12 Reporting

All soil results should be reported on a dry weight basis in the soil i.e. mg/kg dry weight. All water results should be reported as mg/L.

The percentage of dry matter in the soil should be reported.

Results should be reported for carbon bands as shown in the table below. Note that some carbon banding groups are options for this method depending on the particular reporting requirements for the work (i.e. condensed reporting or full reporting as outlined in Sections 11.4.1.1 and 11.4.1.2 respectively).

Carbon Band	**Hydrocarbon (mg/L)**	**Hydrocarbon (mg/kg dry wt)**	**Options**
C_7-C_9			C_7-C_9 (See Note 1)
C_{10}-C_{14}			C_{10}-C_{11}
			C_{12}-C_{14}
C_{15}-C_{36}			C_{15}-C_{20}
			C_{21}-C_{25}
			C_{26}-C_{36}
			C_{37}-C_{44} (See Note 2)
			TPH C_x-C_y (See Note 3)

Note 1 The lower carbon number will be determined by the GC column used by the laboratory and must be specified in the laboratory's validation data.

Note 2 The highest attainable carbon number will be governed by the GC column used by the laboratory and must be specified in the laboratory's validation data. It has been found that only about 60% of heavy lubricating oil will elute from a 30m x 0.25 mm DB5ms column at 350°C.

Note 3 See definitions section. The actual C range must be shown. Very volatile compounds may be lost during extraction. Very high carbon number compounds either will not extract or will not elute from the GC.

13 References

API, 1991. IAL Rhodes, RZ Olvera, JA Leon, EM Hinojosa, Determination of Total Petroleum Hydrocarbons by Capillary GC, in *Sampling and Analysis of Gasoline Range Organics in Soil*, API Publication 4516, American Petroleum Institute.

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US EPA, 1982. *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater*, PB83-20178, United States Environmental Protection Agency.

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Appendix 4

Example Chain of Custody, example template for precision determinations

Please fax this form as soon as possible:

To: ______________________ Attention:

Fax: Phone:

Sample Receipt Advice

Please complete and fax to the sender as soon as samples are received at the laboratory.

Receiving Laboratory

Date sent: ______________

Sender's Reference: ____________________

Attention: ____________________________

Despatched by: ____________________________
(Print Name!)

Laboratory Quote #: ________________

Samples sent are as follows (full details are on the attached Chain-of-Custody):

	Number and Type								
Ref #'s	Ground Water	Surface Water	Effluent	Leachate	Sewage	Soil	Sludge	Other	Marine

Please confirm

All samples received in good order with appropriate documentation ☐

The laboratory job number for these samples is ____________

Estimated completion date ____________

Comments (e.g. details of missing or damaged samples, incomplete documentation, etc)

Signed by laboratory representative: ______________________ Date: ____________

Print name legibly!: ______________________

Chain-of-Custody Form (Must be accompanied by a Sample Receipt Advice Form)

From:

Phone:
Fax::

To: ______________________________
____
____

Sender (Legible!) ____________________

Our Reference: __________

Laboratory Quote:__________

Attention: ____________________

#	Sample ID	Type See Note 1	Field pH	Field EC /salinity	Tests required (Use “See Quote” if appropriate)
Total number of samples =			EC Units		*{ Use a continuation form if necessary }*

Notes: The information requested about the samples will make it easier for the laboratory by reducing the number of dilutions which may have to be done and allowing anticipation of matrix effects which may affect certain tests. This will help to reduce turnaround time.

1. Enter the Type of Sample e.g. SW(Surface Water), GW (Ground Water), E (Effluent), L (Leachate), Sew (Sewage), Soil, Sl (Sludge), O (Other). Blanks may be identified if wished but this is not necessary.

Received at ____________________________ on _____________ by (Print) ________________________ Signed ___________

Precision Data Determination

Test Code:

Detection Limit:

Units:

This sheet is designed for summarising data for precision determinations.
This should be repeated approximately annually for each test.

Method.

Select three samples which have levels of analyte about 5x the detection limit, 25-50% and 80-100% of the calibration range ensuring that there is sufficient sample for at least 9 replicate determinations. The analyses should be carried out as triplicate determinations on separate days spread over at least two weeks.

Calibration Stds:

	5x DL	***25-50% of calibration***	***80-100% of calibration***
# Analyses			
Mean			
Std Dev			
% Std Dev (COV)			
CL(95%) +/-			
Upper 95% Limit			
Lower 95% Limit			

Job #			
Sample #			
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			