National Environment Protection (Assessment of Site Contamination) Measure April 2011 National Environment Protection (Assessment of Site Contamination) Measure April 2011 National Environment Protection (Assessment of Site Contamination) Measure April 2011 National Environment Protection (Assessment of Site Contamination) Measure April 2011 National Environment Protection (Assessment of Site Contamination) Measure April 2011 National Environment Protection (Assessment of Site Contamination) Measure April 2011 National Environment Protection (Assessment of Site Contamination) Measure April 2011 National Environment Protection (Assessment of Site Contamination) Measure April 2011 National Environment Protection (Assessment of Site Contamination) Measure April 2011 National Environment Protection (Assessment of Site Contamination) Measure April 2011 National Environment Protection (Assessment of Site Contamination) Measure April

Schedule B3

GUIDELINE ON

Laboratory Analysis of Potentially Contaminated Soils

PRECAUTIONARY CAVEAT

This guideline refers to methods of analysis that may require the use of hazardous materials, operations and equipment. It does not, however, address all of the associated real or potential safety problems. It is the responsibility of the user of these guidelines to establish adequate health and safety practices such as those outlined in AS 2243 *Safety in laboratories,* Parts 1-10 as amended (available online at <http://www.standards.com.au>), and to ensure that any person involved in performing any relevant procedures is adequately trained and experienced.

DISCLAIMER

Any equipment or materials which meet stated specifications and result in satisfactory method performance may be used to carry out the methods referred to in this guideline. Mention of specific trade names, products or suppliers does not constitute endorsement by NEPC of those items, materials, or suppliers over other suitable products or sources. Rather, it is intended to provide users with examples of suitable products and information on those sources which are known to NEPC.

The following guideline provides general guidance in relation to laboratory analysis of potentially contaminated soils in the assessment of site contamination.

This Schedule forms part of the National Environment Protection (Assessment of Site Contamination) Measure as varied 2011 and should be read in conjunction with that document, which includes a policy framework and assessment of site contamination flowchart.

It aims to ensure consistency in analytical results from the laboratory analysis of potentially contaminated soils. It should be read in conjunction with Schedule B2 of the Measure.

This Schedule replaces Schedule B3 to the National Environment Protection (Assessment of Site Contamination) Measure 1999.

The National Environment Protection Council (NEPC) acknowledges the contribution of a number of individuals and organisations towards the development of these guidelines. In particular, these include Environment Protection Authority (EPA) Victoria (principal author), members of the Environmental Laboratories Industry Group (ELIG), other individual staff members of commercial and government laboratories, members of the Australian Contaminated Land Consultants Association (ACLCA) and individual contaminated site consultants, environmental auditors, officers of the NSW Department of Climate Change and Water (DECCW), and CRC CARE petroleum advisory group for guidance on TPH speciation and analysis.

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1 Guideline for the laboratory analysis of potentially contaminated soil

1.1 Introduction

This guideline is applicable to laboratory analysis of contaminated soils for assessment of site contamination and waste soil disposal. It also contains information on the collection of contaminated soil, including storage and handling considerations to enable valid analysis.

Rigorous characterisation and quantification of soil contaminants helps to ensure valid assessments of site contamination. Consistency in analysis and assessment can only be achieved if there is uniformity in procedures including sample collection, storage and handling, pre-treatment, extraction, analytical methodology and data analysis. This document gives guidance on quality control, quality assurance, and techniques for sample preparation, extraction and analytical methods.

1.2 Audience

This guideline should be used by people undertaking sampling and analysis of potentially contaminated soils. Its main audience includes but is not limited to:

- laboratory staff
- environmental consultants
- regulatory licence holders (e.g. for waste management or other statutory processes)
- custodians of waste /sites containing waste.

1.3 Exclusions

Groundwater analyses are beyond the scope of this Schedule.

1.4 Schedule structure

The Schedule will provide guidelines on laboratory analysis of potentially contaminated soils:

- the philosophy behind the methods selected
- guidance on quality assurance procedures
- techniques for sample preparation designed to provide confidence and comparability of analytical results.

The Schedule will provide analytical methods for potentially contaminated soils:

- a list of methods for analysis of physicochemical properties of inorganic and organic chemicals in soil.

2 Laboratory analysis of potentially contaminated soil

This Schedule provides guidance on analysis of physicochemical properties of soil, including inorganic and organic analytes commonly found in contaminated soils, and on procedures for sample preparation and for quality assurance.

Where possible, the Schedule adopts established 'standard methods' from recognised sources such as Standards Australia, United States Environmental Protection Agency (US EPA), American Public Health Association (APHA), American Society for Testing and Materials (ASTM) and the International Standards Organisation (ISO). When analysis is required for contaminants not included in this guideline, analysts should seek comparable established standard methods. Laboratories should ensure any such methods are validated prior to use.

2.1 Scope

Types of soil analyses for assessment of contaminated sites can fall into three broad categories:

- field measurements that can be performed on site when collecting samples
- laboratory-based screening tests to determine type of contamination present
- quantitative methods specific to known or expected soil contaminants.

This guideline provides detailed guidance for the third category only. The principal objective is to foster greater standardisation of the test methods most likely to be used in the final assessment of a site. General guidance on the first two categories listed above is available in section 3.1. Where field test procedures and screening tests are used, they should also undergo proper method validation against recognised quantitative methods and quality control tests, as described here for the specific test methods. Accreditation from the National Association of Testing Authorities (NATA) should be obtained for all analytical procedures wherever possible.

2.2 Philosophy of methods selected

Soil samples from contaminated sites may be submitted for analysis for various reasons including:

- potential risks to human and environmental health
- legal/financial risks to individuals and organisations.

These circumstances require high reliability of analyses.

In addition, large numbers of samples from a site may be required to be analysed within a short time; the sooner results are available, the sooner decisions can be made about the need for site remediation or protection of the public and environment from further contamination.

To meet these competing demands for speed and reliability, the extraction/digestion and analytical methods should ideally be:

1. Simple — procedures should be easy to follow and to perform, using equipment and reagents generally available in most environmental laboratories.
2. Rapid — ideally, extraction/digestion and analysis should be sufficiently rapid and non-labour-intensive to enable a large number of samples to be processed with acceptable turnaround time. This should not be at the expense of meaningful analytical results.
3. Accurate and precise — the test methods listed in these guidelines are regarded as 'reference' procedures, mostly derived from authoritative Australian references or internationally recognised authorities such as the US EPA or APHA.

They are considered to be sufficiently rigorous and reliable for the assessment of contaminated sites, by virtue of their measured accuracy and precision in validation studies and/or their usage and acceptance as rigorous techniques by the scientific community.

4. Capable of batch or automated analysis — samples should be able to be processed in large batches without being cumbersome; automated analyses are often preferred.
5. Capable of simultaneous analysis — procedures should allow a variety of chemical components to be analysed using aliquots of a single extract per sample. This minimises sample processing time and cost and maximises sample throughput.
6. Have an appropriate limit of reporting (LOR) — the selected method should have a limit of reporting no greater than 20% of the relevant maximum contaminant obtained in a similar matrix.
7. Safe — safety should never be compromised, especially when undertaking large batch processing and handling soils from contaminated sites.

The analytical methods in this guideline have been chosen to be, where possible, reliable, rapid, and to measure the 'non-residual' contaminants in soil (not total contaminant concentrations).

Analysis of these non-residual components (i.e. non-silicate and extractable) provides more useful information than a 'total' analysis which includes material bound in the silicate matrix; these residual components are usually less available and pose little threat to the environment. Therefore, the methods described in this guideline are directed towards the extraction or digestion of non-residual contaminants and not the total contaminant load in a soil.

2.3 Referenced methods and use of alternative methods

Analysis for regulatory or statutory purposes, or conducted under the principles of this Schedule, should be undertaken by either:

- the methods specified in this guideline (as updated over time)

or

- a method verified to be equivalent in outcome to the relevant referenced method.

NEPC acknowledges that other extraction and determinative methods may be at least as efficient, accurate and precise (as well as possibly faster and less expensive) than those recommended here, including specially designed commercial systems, for example, digestion units, distillation units and auto analysers. However, it is beyond the scope of this guideline to evaluate all possible alternatives.

Where such alternative methods are used, that is, any methods apart from those specified in this guideline, the user should ensure that the alternative method is at least as rigorous and reliable as the reference method and either that:

- it has been validated against an appropriate certified reference material (CRM). This requires adequate recovery of analytes using CRMs during method validation, as well as regular participation in national proficiency trials by bodies such as the National Measurement Institute (NMI) or Proficiency Testing Australia (PTA) or other accredited provider

and/or

- it has been verified against a laboratory that is NATA-accredited for the reference method.

3 Determinative methods

This guideline specifies procedures for extraction and digestion; the inclusion of determinative procedures for each analyte is outside its scope. Determinative methods are available for many analytes in a range of Standards Australia methods and international standards (US EPA SW-846, APHA 2005, ASTM 2008).

Where determinative methods are suggested, this does not preclude the use of alternative methods, provided they are validated by the laboratory for the matrix concerned. As previously mentioned, use of alternative methods requires method validation and/or demonstration of equivalence of rigour and outcome.

In selecting an appropriate method for a particular analyte, the analyst needs to consider the chemical characteristics of the final extract and analyte.

All methods require the use of quality control procedures.

3.1 Screening tests

Some screening tests in common usage — including laboratory screening tests and field tests, for example, field chemical test kits and field analysers — may be fast and cheap but, by their nature, are less rigorous and reliable than the analytical methods described here. They may be suitable for less exact tasks such as preliminary assessments, mapping pollutant distribution at known contaminated sites or monitoring the progress of site clean-up or remediation programs.

Data from 'screening' tests are not acceptable for detailed assessment of a contaminated site proposed to be used for a sensitive use or parks and open space, or for validating clean-up for a sensitive land use. These tasks require a high degree of accuracy and reliability, and data must be based upon results from one of the validated analytical tests referenced here, or other methods that have been shown to be at least as rigorous and reliable for the soil matrix in question.

The accuracy and precision of any analysis must be sufficient for the intended purpose. While there will be a compromise between speed of extraction/analysis and accuracy and precision, there should be a tolerance limit. Results from a screening (or semi-quantitative) method should be within ± 30% of:

- the mean value obtainable from multiple analyses using one of the reference methods from these guidelines (or an alternative quantitative method)

or

- the mean value for multiple analyses of an appropriate CRM.

Screening methods must also be validated for identification, repeatability and reproducibility.

3.2 Method validation

It is difficult to obtain complete validation data for all analytes covered in these guidelines due to large variations in soil types and physicochemical properties, and lack of suitable or reliable reference standard materials. For some analytes, for example, soil pH, conventional validation data has no bearing on method performance between one soil sample and the next; for such analyses, better performance indicators may be obtained through inter-laboratory comparisons.

This guideline recommends certain extraction procedures or complete methods; however, each laboratory should fully validate each method used (from extraction through to the determinative step) following the principles for quality assurance and method validation described in this section and other relevant references (US EPA SW-846, APHA 2005-1040B method validation, NATA Technical note 23, NATA Technical note 17). Validation should be performed on the range of soil types most likely to be analysed.

3.2.1 Confirmation of organic compounds (for non-specific techniques)

Where non-specific analytical techniques are used, for example, gas chromatography (GC) or high performance liquid chromatography (HPLC), the identity of organic compounds should be confirmed by one of the methods in the NATA Field Application Document ISO/IEC17025 FAD (NATA 2007); these include mass spectrometric detection, variation of the test procedure (e.g. different column stationary phase), another test procedure (e.g. alternative detector) or conversion of the analyte to another compound (e.g. derivatisation technique).

A GC/MS or HPLC/MS spectral library match alone is only sufficient for tentative identification. Confirmation is achieved (i.e. no additional confirmatory analysis is required) if GC/MS or HPLC/MS methods are employed *and* standards of the compound are analysed under identical conditions (US EPA SW-846, Method 8000B). A compound identity is then confirmed if *all* of the following criteria (US EPA SW-846, Method 8270D) are met:

- the intensities of the characteristic ions of the compound in the sample must maximise in the same scan, or within one scan, as that of the reference compound
- the relative retention time (RRT) of the sample component is within ±0.06 of the RRT of the standard component
- the relative intensities of the characteristic ions (see Note immediately below) in the sample all agree within 30% of the relative intensities of these ions on the reference compound spectrum.

  Note: The characteristic ions are defined as the three ions of greatest intensity in the reference compound spectrum.

3.3 Assessing analyte leachability and bioavailability

Some methods for assessing mobility and availability of soil chemicals are based on methods designed for agronomic studies and land surveys and hence are only applicable to soils expected to have relatively low contaminant concentrations, for example, background samples or natural soil.

Such methods should be used with caution on contaminated soils, as the high concentrations of analytes in contaminated soil may exhaust the exchangeable capacity of the reagents and lead to false results. These tests have not yet been shown to apply to contaminated soils, and meaningful results can only be obtained from natural soils or background samples.

Leachability of contaminants is a more useful parameter for assessing site contamination. This Schedule describes two leachability methods for assessing the mobility of common metal contaminants. Other methods available to study mobility of metal ions and nutrients for agronomic reasons are highly specific to the soil type, chemical species, and biota (usually plants) being studied, and are not recommended for generic studies of contaminated soils.

3.4 Use of results

Effective site assessment is dependent on a partnership between the site assessor and the laboratory, to ensure that:

- samples are collected and transported in a condition suitable for analysis
- the laboratory understands the information required by the site assessor
- the analyst communicates all relevant information to the site assessor
- the assessor appreciates the uncertainties and limitations associated with the analytical data.

When using the results of laboratory analysis, the site assessor should be aware of the relationship between the property measured by the method (e.g. total or leachable concentrations), the measurement uncertainty, and the basis for the derivation of any investigation level or response level with which it is compared.

4 Quality assurance

4.1 Definitions

The terms 'quality assurance' and 'quality control' are often misinterpreted. This guideline defines them as follows (ISO 8402–1994):

Quality assurance (QA) is 'all the planned and systematic activities implemented within the quality system and demonstrated as needed to provide adequate confidence that an entity will fulfil requirements for quality'.

This encompasses all actions, procedures, checks and decisions undertaken to ensure the accuracy and reliability of analysis results. It includes routine procedures to ensure proper sample control, data transfer, instrument calibration, the decisions required to select and properly train staff, select equipment and analytical methods, and the day-to-day judgements resulting from regular scrutiny and maintenance of the laboratory system.

Quality control (QC) is 'the operational techniques and activities that are used to fulfil the requirements for quality'.

These are the QA components that serve to monitor and measure the effectiveness of other QA procedures by comparing them with previously decided objectives. They include measurement of reagent quality, apparatus cleanliness, accuracy and precision of methods and instrumentation, and reliability of all of these factors as implemented in a given laboratory from day to day.

A complete discussion of either of these terms or the steps for implementing them is beyond the scope of this guideline; suffice to say, sound laboratory QA and QC procedures are essential. In brief, laboratories should incorporate quality laboratory management systems, and participate in accreditation and/or self-audit systems, to ensure reliable results are produced by trained analysts, using validated methods and suitably calibrated equipment, and to maintain proper sample management and recordkeeping systems. For more information on good laboratory practice and QA procedures, refer to guidance from NATA (Cook 2002, NATA Technical note 23, NATA 2007) and Standards Australia (AS 2830.1-1985).

4.2 Recommended minimum QC procedures

The laboratory should adopt, at a minimum, the minimum QC concepts and procedures described below and be able to demonstrate:

- method proficiency within the laboratory
- conformance to the performance characteristics expected of the method
- confidence in the results produced.

Recommended QC procedures for all soil analyses are described in US EPA SW-846 (in that document, see Chapter 1: 'Quality control')

4.2.1 Process batch

For the purposes of QC requirements, a process batch is deemed to consist of up to 20 samples which are similar in terms of sampling and testing procedures and are processed as a unit for QC purposes. If more than 20 samples are being processed, this should be considered as more than one batch.

4.2.2 Analysis blank

This refers to the component of the analytical signal which is not derived from the sample but from reagents, glassware, etc. It can be determined by processing solvents and reagents in exactly the same manner as for samples. Where laboratories are required to report analysis blanks, the uncorrected result and the method blank should be reported in the same units of measurement.

There should be at least one analysis blank per process batch.

4.2.3 Duplicate analysis

This is the analysis of a duplicate sample from the same process batch. If possible, the sample selected for duplicate analysis should have an easily measurable analyte concentration. The variation between duplicate analyses should be recorded for each process batch to provide an estimate of the method precision.

The number of duplicate analyses should be the smaller of one per process batch or one per 10 samples.

4.2.4 Laboratory control sample

A laboratory control sample (LCS) comprises either a standard reference material or a control matrix spiked with analytes representative of the analyte class. Representative samples of either material should be spiked at concentrations which are easily quantified and within the range of concentrations expected for real samples.

There should be at least one LCS per process batch.

4.2.5 Matrix spikes

A matrix is the component or substrate (e.g. water, soil) which contains the analyte of interest. A matrix spike is an aliquot of sample spiked with a known concentration of target analyte. A matrix spike documents the effect (bias) of matrix on method performance (US EPA SW-846, Chapter 1).

The matrix spike enables determination of any matrix interferences. If the recovery of the matrix spike is below the expected analytical method performance, it may be necessary to use other internal calibration methods, a modification of the analytical method or alternative analytical methods to accurately measure the analyte concentration in the extract.

Matrix spikes should be added to the analysis portion before extraction or digestion, and in most cases added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than half the regulatory level, the spike concentration may be as low as half the analyte concentration but not less than the limit of reporting (LOR).

To avoid differences in matrix effects, the matrix spikes must be added to the same nominal amount/quantity of sample as that which was analysed for the unspiked sample. There should be one matrix spike per soil type per process batch.

4.2.6 Surrogate spikes

Surrogate spikes are known additions to each sample, blank, matrix spike or reference sample, of compounds which are similar to the analytes of interest in terms of:

- extraction
- recovery through clean-up procedures
- response to chromatography or other determination

but which:

- are not expected to be found in real samples
- will not interfere with quantification of any analyte of interest
- may be separately and independently quantified by virtue of, for example, chromatographic separation or production of different mass ions in a GC/MS system.

Surrogates can provide a means of checking that no gross errors have occurred at any stage of the procedure and which may cause significant analyte losses.

Surrogate spikes are only appropriate for analyses of organics, for example, chromatographic analyses. Where they are used, they should be added to all samples being analysed and are added to the analysis portion before extraction. Surrogate spike compounds may be deuterated, alkylated or halogenated analogues, or structural isomers of analyte compounds.

4.2.7 Internal standards (where appropriate)

Use of internal standards is highly recommended for chromatographic analysis of organics and some inorganic analyses, to check the consistency of the analytical step (e.g. injection volumes, instrument sensitivity and retention times for chromatographic systems) and to provide a reference against which results may be adjusted in case of variation (for organics analysis only).

Internal standards are added to each final extract solution, after all extraction, clean-up and concentration steps. The addition is a constant amount of one or more compounds with qualities like those listed above.

Adjustments for variations in injection volume and instrument sensitivity are made by calibrating against the ratio of:

(peak height or area for analyte/s) : (peak height or area for internal standard/s).

Such adjustment should only occur where variation in internal standard signal is within pre-defined limits.

Note: Chromatograms for final extracts may contain both internal and surrogate standards. The compounds used for these standards may be similar but their addition at different analytical stages provides different information.

Results of QC procedures should be recorded and maintained for a sufficient time to establish method reliability, confidence intervals for analysis results and trends in precision and accuracy over time or with variation of equipment or analyst.

4.3 Method validation

This is the process of obtaining data on a method in order to determine its characteristic performance and to establish confidence that use of that method provides reliable results. Method validation needs to be performed for each laboratory before being adopted and applied to the analysis of actual samples.

All validation steps pertaining to the method should be recorded and retained while the method is being used.

Method performance should be based on extraction of a CRM and/or spiked samples (NATA, Technical note 17) or compared with a more rigorous method (such as Soxhlet extraction for organic analytes).

The minimum validation data required are:

- accuracy
- precision
- per cent recovery
- limits of detection and reporting.

4.3.1 Accuracy

Accuracy is a measure of the closeness of the analytical result to the 'true' value (NATA, Technical note 17). The levels of accuracy generally achievable from a reference method should be within ± 30 % of:

- the expected value of a certified reference material of similar matrix

  or

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

Note: Deviations from the expected result are likely to be higher with low analyte concentrations; for example, less than 10 times the minimum detectable concentration. Apparent lower recoveries than those specified will occasionally be obtained for CRMs which have been assessed by more rigorous methods involving matrix dissolution. The specific analyte cited in the CRM certificate should match that being determined under this Schedule. For example, if the certified reference values are obtained using aqua regia digest, only the aqua regia method should be applied to this CRM. Otherwise, an alternative CRM should be used. Further information may be obtained from 'General requirements for the competence of testing and calibration laboratories' (ISO 17025, 2005) and 'Uncertainty of measurement -- Part 3: Guide to the expression of uncertainty in measurement' (ISO/IEC Guide 98-3:2008).

4.3.2 Precision

Precision is a measure of the variation in the method results. It is a combination of two components, repeatability and reproducibility, and is expressed in terms of standard deviation (SD) or relative standard deviation (RSD) of replicate results (APHA 2005).

4.3.2.1 Repeatability

This is a measure of the variation in the method results produced by the same analyst in the same laboratory using the same equipment under similar conditions and within a short time interval (Eaton et al. 2005).

4.3.2.2 Confidence limit and confidence interval

When results are qualified with standard deviations or their multiples, for example, ± SD, these are taken to be their confidence limits. This means that a result of 10±4 mg/kg would have confidence limits of 6 and 14 mg/kg and a *confidence interval* from 6 to 14 mg/kg (APHA 2005). In a normal distribution, 95% of results are found within approximately twice the standard deviation of the mean. Further clarification of these terms may be found in any reputable statistics text.

4.3.2.3 Reproducibility

This is a measure of the variation in the method results for the same split sample(s) produced by different analysts in different laboratories under different conditions and using different equipment. It measures the 'ruggedness' of the method. Reproducibility data should be obtained as part of the validation procedure, and are best obtained through inter-laboratory comparisons and proficiency studies.

4.3.3 Percent recovery

This is the most realistic and useful component of the daily quality control performance (APHA 2005), and describes the capability of the method to recover a known amount of analyte added to a sample.

The sample is spiked with a known quantity of the analyte, such that the total of the suspected natural concentration of the analyte plus the spike is within the working range of the method. For compliance monitoring, the spike level should be at or below the regulatory limit or in the range of 1-5 times the background concentration. If the background concentration is not known, the spike level may be at the same concentration as the reference sample, near the middle of the calibration range, or approximately 10 times the LOR in the matrix of interest (US EPA SW-846, Method 3500C). The longer the spiked analyte can remain in the sample before extraction or digestion, the closer is the simulation to recovering the analyte from the natural sample (except for volatile organics). Percent recovery is calculated as follows:

$$\text{Per cent recovery} = \frac{c - a}{b} \times 100$$

where:

a = measured concentration of the unspiked sample aliquot

b = nominal (theoretical) concentration increase that results from spiking the sample

c = measured concentration of the spiked sample aliquot

Note: If a is known beforehand, b should be approximately equal to a and c should be approximately twice that of a for 100% recovery.

In general, at least 70% recovery should be achievable from a reference method, although some standard methods state that recoveries for validated methods can be lower. Lower recoveries may be expected for low concentrations of analytes.

4.3.4 Limits of detection and reporting

4.3.4.1 Method detection level

The method detection level (MDL) is the concentration of analyte which, when the sample is processed through the complete method, produces a response with a 99% probability that it is different from the blank (APHA 2005). It is derived by:

- analysing at least 7 replicates of a sample with a concentration close to the estimated MDL over a period of at least 3 days and determining the standard deviation
- calculating the MDL as follows

MDL = t * Std Deviation, using a one-sided t distribution

where, for 7 replicates t= 3.14 for 99% confidence levels

4.3.4.2 *Practical quantitation limit*

The practical quantitation limit (PQL) is the limit of reporting (LOR), also known as the limit of quantitation (LOQ), and is the lowest concentration of an analyte that can be determined with acceptable precision (repeatability) and accuracy under the stated conditions of a test (NATA Technical Note 17). It is usually calculated as follows (APHA 2005):

LOR = LOQ = PQL = 5 X MDL

4.4 Sample control

The laboratory should maintain rigorous procedures in sample control from the time the sample is received. This includes the entire process from registration of the sample through to pre-treatment and sample analysis, sample storage and disposal. Unique identification of each and all portions of every sample is mandatory. Sample integrity should be maintained as far as possible, even after completion of analysis.

4.5 Documentation

All validation steps pertaining to the method should be recorded and retained while the method is being used.

After analysis completion, all documentation relating to the sample and its analysis (including raw data and data validation) should be retained for at least three years (APHA 2005) so that all relevant information may be easily retrieved. This helps establish chain of custody of the sample and traceability of all data, and enables reviewing the analysis during an audit or investigation of a dubious result.

This applies to both hard copy data and data in electronic formats. Laboratories should ensure adequate electronic data storage and backup to ensure data and documentation relating to analyses can be retained.

4.6 Analytical report

The analytical report should describe all information and data relevant to the analysis of the sample. This includes:

Requirements for NATA-endorsed documents (AS ISO/IEC 17025 – 2005):

- a title
- the name and address of the analytical laboratory (including NATA accreditation no.)
- the analytical report number (a unique identification)
- sample identification (a unique identification for each sample)
- the identity of the test method and any deviations from it
- analytical results
- a statement of uncertainty where relevant to the validity or application of results or where uncertainty affects compliance to a specification limit, or where requested by the client. (The statement of uncertainty may be implicit in the results presented, e.g. a result may be rounded to the nearest 100 or 1000 indicating an uncertainty of ±50 or ±500 respectively)
- any other information specified by the test method or statutory regulation
- a statement of conditions pertaining to reproduction of the report
- the signature of an approved NATA signatory
- the date of analytical report issue.

Other valuable information for inclusion on analysis reports is:

- the date the sample was received
- the name of person receiving the sample
- a description of the sample
- whether the sample was received in good order (where appropriate) , for example, note any broken or leaking containers, incorrect storage condition during transit, sample temperature container for the analyte (where appropriate)
- brief description of analytical method and equipment used, including pre-treatment procedures and test conditions where appropriate
- confidence interval, QC data and LOR
- any bias noted during the analysis or information on the analysis which may affect the interpretation of the result
- the date on which sample analysis commenced.

Where laboratories are required to report analysis blanks, the uncorrected result and the method blank should be reported.

The analytical report should be checked for transcription errors, accuracy n the calculation and expression of results, description of the sample, and whether the QC data meets the acceptable limits for the method. These are all components of the laboratory QA processes.

4.7 Split samples

This is a field QC process implemented by the client rather than laboratory QC; however, laboratories and sample collectors should both be aware of its requirements and purpose.

Split samples provide a check on the analytical performance of the laboratory. At least 1 in 20 samples from a site should be homogenised and split, with one duplicate sample set submitted to a secondary laboratory (an independent laboratory run by a different organisation or company) and the remaining samples to the primary laboratory. The client must stipulate that each laboratory analyses the split samples for the same analytes using, as far as possible, the same methods recommended in these guidelines. For comparability of data, there should be minimal delay in sample submission to each laboratory to allow minimum time difference between analyses, especially for analysis of volatile analytes.

The difference in the results between the split samples should, in general, be within 30% of the mean concentration determined by both laboratories. However, higher variation can be expected for organic analyses compared to inorganic analyses and for samples with low analyte concentrations.

4.8 Blind replicate samples

Blind replicate samples provide a check of the repeatability of a laboratory's analysis. At least 5% of samples should include a larger than normal quantity of soil collected from the same sampling point, removed from the ground in a single action if possible, and mixed as thoroughly as practicable and divided into two vessels. These samples should be submitted to the laboratory as two individual samples without any indication to the laboratory of their common source.

A similar test of analysis repeatability is provided by re-submission of previously analysed samples, provided the stability of analyte is adequate under the storage conditions used between the two submission dates.

5 Sample preparation and storage

5.1 Sample preparation

To obtain reproducible results it is essential that laboratories use standardised procedures when preparing samples. These procedures will not necessarily be the same for each sample but will comprise various combinations of the following treatments:

- separation and removal of extraneous components
- homogenising
- drying
- hand grinding
- sieving
- partitioning (to obtain representative portions).

The combination of treatments applied to any sample will depend primarily on the nature of the analytes of interest. These can be split into three broad categories:

1. Non-volatile compounds (including most metals, inorganics and some heavy organics)
2. Semi-volatile compounds (many organics, some metals and other inorganics subject to evaporative losses)
3. Volatile compounds (such as organic solvents and inorganic gases).

The following sections discuss the individual steps in sample preparation for these three categories.

Throughout the sample preparation step, the analyst should be aware of the potential for any bias to be introduced, and report any bias noted in the results.

WARNING: Handling potentially contaminated soil and fine dust may present a health hazard. All preparations described in this section should be performed in a fume cupboard, wearing appropriate gloves and respiratory protection conforming to Australian Standards (AS/NZS 2243.1-2005).

5.1.1 Separation and removal of extraneous (non-soil) components – non-volatiles and semi-volatiles

Prior to grinding or mixing the sample, vegetation and other non-soil material (including rocks, gravel, concrete, particles naturally greater than 5 mm) should normally be removed by hand or sieving, except for samples to be analysed for volatile components, since this process may lead to significant analyte losses. The analyst should also confirm with the client whether any fraction of the removed material is to be analysed.

As stated above, the contaminants or analytes of concern should be the 'available' contaminants which reside on the surface of the soil particles. It is likely that larger particles and rocks will contain, on a weight basis, considerably less contaminant than the smaller particles. In certain circumstances, however, it will be prudent to also analyse the larger particles, preferably separately. The reverse will be true if, for instance, contamination of a site has arisen by importation of contaminated screenings or other large particles.

Any material removed should be weighed so that its proportion relative to the entire sample, and its description, are recorded. If required, this mass and the description may be included in the analytical report. The significance of the analyte concentration in the soil or fraction of removed material can then be assessed relative to the entire sample composition.

The removed material (including the materials retained on the sieve) should be labelled and retained for possible future analysis.

5.1.2 Homogenising (for non-volatile constituents)

Samples for analysis of volatile contaminants should not be homogenised by stirring, grinding or sieving. Procedures applicable to volatile analytes are described below.

To minimise the amount of reagents used and waste produced, most analytical methods require analysis of only a portion of the sample, sufficient to provide a quantifiable response. The amount of sample received by the laboratory is usually larger than required for a single determination and any additional analyses for QA purposes.

Depending on the analyses required (excluding volatile analysis), a homogeneous test sample is prepared from either the field-moist (i.e. 'as received') or dried sample. The analysis portions are then taken from this test sample.

The sub-sample taken should comprise at least 25% by weight or 200 g of the sample received by the laboratory (laboratory sample), whichever is the smaller. It must be thoroughly disaggregated and mixed using a mortar and pestle or other appropriate apparatus. The entire sample may be homogenised but only if no test requiring the original, untreated sample will be needed. Further, it is advisable to keep a portion in the 'as received' state to check, if necessary, that no contamination has occurred during the homogenising process. Described below are the pre-treatment procedures to obtain homogenised field-moist and dry analysis portions.

5.1.3 Preparation of field-moist ('as received') analysis portions

In general, soils to be tested for organic analytes, especially rapidly degradable or otherwise labile contaminants, should not be dried but should be analysed in a field-moist state. Where an excessive amount of moisture can affect the extraction efficiency, the sample may be 'dried' by mixing the analysis portion with anhydrous sodium sulfate or magnesium sulfate prior to extraction (US EPA SW-846, Method 3540C).

Field-moist samples will often not be amenable to mechanical grinding or sieving. For those samples which are amenable to this, and for which non-volatile analytes are to be determined, at least 25% by weight or 200 g of the laboratory sample, whichever is the smaller, should be thoroughly ground and mixed by hand, in a mortar and pestle, to obtain a homogeneous sub-sample.

For most metals and inorganics, better analytical reproducibility is obtained using air-dried soil. However, if the sample is to be analysed for these analytes in the field-moist state and if it is amenable to sieving, for example, sandy loam, it should also be passed through a 2 mm plastic sieve. Ensure that there are no solid particles distinctly different from the soil; for example, fragments of metal or coloured particles of an unusual nature. If this is the case, the sample must be analysed in the air-dried state and pre-treated as described below.

Store the treated sample in a suitable container.

All equipment must be cleaned in a way to minimise sample cross-contamination; this can be confirmed by analysing equipment rinsates and/or control samples.

5.1.4 Preparation of dry analysis portions (non-volatiles only)

Air-drying helps to give a representative analysis portion by producing samples amenable to grinding, sieving and splitting. However, air-drying may modify the chemical form of some species and hence affect the results obtained (Adam et al. 1983, Bartlett et al. 1980, Harry et al. 1981, Khan et al. 1978, Leggett et al. 1985, Specklin et al. 1989).

The effect of drying temperature on analyte modification is not completely understood, but in some cases it seems to change the bioavailability or extractability of the analyte. The impact of air-drying on analysis may be more pronounced in certain soil types and in sediments. Therefore, air-drying is only applicable to some methods of soil analysis.

It is generally accepted that soils for most metals and some inorganic analytes can be air-dried, followed by grinding and sieving. However, the procedure described below is not applicable to analysis of volatile constituents or where analytical methods specifically forbid such preparation (e.g. certain leaching tests). Samples for volatile metallics, for example, methyl mercury or tetraethyl lead, must be homogenised and sub-sampled in the field-moist state.

Note: Grinding samples will increase surface area and may give higher results.

5.1.4.1 Sample drying

Dry at least 25% by weight or 200 g of the sample, whichever is the smaller, by spreading the soil on a shallow tray of a suitable non-contaminating material, such as plastic or stainless steel. If necessary, break up large clods with a spatula to speed up the drying process. Allow the soils to dry in the air (at <40°C), ideally with the trays placed in a clean air chamber, or a non-contaminating oven at 40 ± 3°C. The relative humidity should be less than 70% to achieve drying within a reasonable time. The sample is dry when the loss in mass of the soil is not greater than 5% per 24 hours (AS 4479.1-1997).

5.1.4.2 Grinding of dry sample

The dry sample should be crushed in a mortar and pestle of appropriate material (glass, agate or porcelain) or other suitable grinding apparatus to achieve a particle size appropriate to the analysis. The sample should be mixed as thoroughly as possible.

Extreme care should be taken to avoid contamination during the grinding process. Equipment should be suitably cleaned before grinding each sample to prevent cross-contamination. Cleaning procedures will vary according to the analyte/s being determined. Generally, detergent washing followed by deionised water rinsing and oven drying will suffice. For trace metal analysis it may be necessary to incorporate soaking in dilute acid followed by deionised water rinsing. For analysis of organics, equipment will normally need solvent rinsing followed by air-drying, prior to homogenising samples. For quality control, the final washing should be sampled and analysed to evaluate the decontamination efficiency (Barth et al. 1984): one final wash sample per process batch or 1 in every 10 samples ground, whichever is the smaller. Alternatively, treat a well-characterised control soil sample similarly. If there is significant carry-over due to the grinding process, the results from that process batch may have to be rejected.

5.1.4.3 Sieving

Unless impracticable or required by a specific method, the sample portion for analysis must be of a size to pass a 2.0 mm aperture sieve. This can typically be achieved by grinding. If another particle size is chosen, this should be consistently used within an analysis regime and reported with analytical results.

WARNING: Grinding of soils can produce fine dust particles which may present a health hazard, and should be performed in a fume cupboard wearing gloves and respiratory protection conforming to Australian Standards (AS/NZS 2243.1-2005).

5.1.4.4 Partitioning of dry samples to obtain representative analysis portions

The analysis portion of the dry sample must be a representative sample. For sufficiently dry samples, use of a chute splitter (riffler) is recommended, or the entire sample should be thoroughly mixed and divided using the 'cone-and-quarter' technique or by any other suitable sampling apparatus. This equipment should be made of appropriate material (i.e. stainless steel) to avoid contamination.

Repeat partitioning to obtain the desired amount of analysis portion (including any replicate analyses and extra portions required for quality assurance purposes). Store the remaining homogenised dry sample separately in a glass screw-cap jar or other appropriate vessel.

Note: Mechanical grinding of dry soil, for example, in a ring mill, will mix the sample, but use of the cone-and-quarter technique or a mechanical sample divider is preferred, to avoid sub-sampling only the larger particles.

5.2 Summary – non-volatiles and semi-volatiles

5.2.1 Preparation of dried samples (e.g. non-volatiles):

1. Remove vegetation and large stones and other particles (> 5 mm) unless they are to be included for bulk analysis. Record proportion by weight with a description of each fraction of material removed.
2. Air-dry at least 25% by weight or 200 g of the laboratory sample, whichever is the smaller, including sufficient amounts for repeat analyses or other analysis on this same sample including moisture content (using field-moist sample).
3. Samples may also be oven dried at 40 ± 3°C. Sample is dry when the loss in soil mass is not greater than 5% per 24 hours. (Note caveats in 5.1.4.)
4. Grind to disaggregate the soil particles, using a clean mortar and pestle.
5. Pass through a 2 mm mesh sieve.
6. Weigh and set aside the particles >2 mm diameter for later analysis if required (and to examine for large particles of solid contaminant if necessary).
7. Partition the fraction <2 mm diameter by hand, with sample divider or alternate comparable method -

   by hand:

   a. Spread soil into a thin even layer.
   b. Divide soil into four quadrants.
   c. Combine and mix the soil from two opposite quadrants.
8. Repeat steps (a) to (c) until the required quantity of soil is obtained for analysis or for further size reduction:
   - using mechanical sample divider
   - in accordance with the manufacturer's instructions.
9. If small analysis portions (<10 g) are to be taken or smaller sieve sizes are required, grind at least 10 g of the <2 mm fraction to pass through smaller mesh sieves (0.15, 0.5 or 1.0 mm sieve size for sample sizes of <1 g, <2 g and 2-9 g respectively).

Note: Analysis of volatile contaminants such as C6-C10 fractions should be undertaken prior to any other analysis required from that sample. Sampling and sub-sampling for volatiles should be undertaken as described in section 5.3 below.

5.2.2 Preparation of field-moist samples (e.g. semi-volatiles, analytes for which drying may lead to losses):

1. Remove vegetation and large stones and other particles (> 5 mm) unless they are to be included for bulk analysis. Record proportion by weight with a description of each fraction of material removed.
2. Select at least 25% by weight or 200 g of the laboratory sample, whichever is smaller, to be used for analysis, including sufficient amounts for repeat analyses or other analysis on this same sample including moisture content.
3. Grind in a clean mortar and pestle to disaggregate soil particles and to produce a homogeneous test sample.
4. Note: Soils to be analysed for metals or other inorganics or non-volatiles in the field-moist state and which are amenable to sieving, for example, sandy loam, should then be passed through a 2 mm plastic sieve. Ensure there are no solid particles distinctly different from the soil, otherwise the sample must be analysed in the air-dried state.
5. Dry a separate weighed portion of the laboratory sample to determine moisture content (see Analytical Methods section in this Schedule). Report the moisture content with the analytical result so that analyte concentrations may be estimated on a 'dry-weight' basis.

5.3 Volatile analytes – sample collection and preparation

These guidelines generally do not include instructions for sample collection, except for volatile analytes, as the sampling method has a direct bearing on the choice of analysis method and reliability of the results. The site assessor may request the laboratory to advise on relevant collection techniques or to supply appropriate equipment.

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

5.3.1 Sample collection

Samples should be collected with minimal sample disturbance to avoid evaporative losses as detailed in AS 4482.2-1999. Typically, sampling is carried out using a coring device. However, if this is not available, an alternative device, for example, a trowel, may be used, ensuring the sample remains intact and the container is filled as full as possible to ensure minimal headspace and evaporation potential. In many cases, duplicate sampling is recommended for sample re-analysis if required (e.g. if contaminant levels are over range).

Since volatiles are easily lost from the ground's surface, sampling soil for volatile analysis should not be carried out from this surface layer unless a very recent chemical spill is being investigated.

Where the sample container must be subsequently opened to obtain a sub-sample for analysis, the dimensions of the original core taken should be such as to leave a minimum of void space (headspace, and between core and container walls) in the vessel. However, in situations where the whole sample is to be purged or extracted without prior opening, this need not apply.

If soils are granular and easily sampled, place sample cores immediately into:

- two or more pre-weighed 40 mL glass volatile organic analysis (VOA) vials with PTFE—lined pierce-able silicone septum caps

or

- one or more 125 mL wide mouth glass jars with PTFE lined lid (see Table 4-1 , Chapter 4 in SW-846 revision 4, 2007), and sub-sample according to the procedures given below.

If soils are difficult to sample, for example, highly compacted or hard clays, it is recommended that a minimum of three core samples be placed into pre-weighed 40 mL glass VOA vials marked at a level corresponding to the required sample weight for analysis. One sample should be used for preliminary screening analysis if desired, the others for analysis by purge and trap analysis.

Note 1: The 40 mL VOA vials are particularly effective in conjunction with modified closures (US EPA SW-846, Method 5035), or suitably designed purge and trap instruments, which allow the vial to function as a sparge vessel for purge and trap analysis. This means there may be no need to open the vial to prepare an analysis sample.

Note 2: Using larger containers may be more convenient and possibly result in fewer analyte losses where removal of test sub-samples is required (Ilias et al. 1993).

Note 3: While immersion of samples into methanol in the field has been shown to be effective in preserving volatile organics (Lewis et al. 1991), such a practice may not be practicable or permissible according to local laws. Handling volatile chemicals in the field, and transporting them, can have occupational health and safety implications, and is not generally recommended unless so advised by the analyst to meet a specific requirement.

Once samples are taken, ensure that vial closures are free of soil particles before capping. Samples should be sealed and transported under suitable cooling aids (for example, ice bricks, refrigerated container) to ensure sample starts cooling as soon as possible, and should be stored in a refrigerator (< 6°C) until analysis.

Note 4: For suspected acid sulphate soils or asbestos contamination, consult *Analysis of acid sulfate soil-dried samples-methods of test* (AS 4969.0-14-2008/2009) or the *Method for the qualitative identification of asbestos in bulk samples*, (AS 4964-2004) for guidance on sampling and handling.

5.3.2 Preliminary screening analysis

Some laboratories perform a preliminary screening analysis of soils to prevent contamination of purge and trap equipment by samples with a high contaminant load. This is done by:

- methanol extraction of a core sample in a 40 mL VOA vial. (Methanol is added with a syringe through the septum cap. A portion of the methanol extract is analysed by purge and trap or other method.)

  or

- headspace analysis (US EPA SW-846, Method 5021)

  or

- hexadecane extraction (US EPA SW-846, Method 3820)

  or

- rapidly removing a core sample from a chilled 125 mL jar sample and transferring to a vial for analysis as in methanol extraction or headspace analysis above.

After taking a sub-sample from a 125 mL jar, immediately re-seal and return to refrigerator storage (≤6°C). If analysing whole 40 mL vial samples, re-weigh beforehand and subtract vial weight to determine sample mass.

If screening results indicate a low analyte level suitable for purge and trap analysis, perform this using a second 40 mL vial sample (preferably using instrumentation which employs the original vial as the sparge vessel), or take one or more fresh core samples from a 125 mL jar sample.

If screening results indicate a high analyte level, accurate analysis of the original screening sample is sufficient if the sample weight is known and suitable extraction protocols followed. Otherwise, take a second analysis portion.

5.4 Sample storage

To maintain sample integrity, samples must be collected and kept in a container which will not increase or reduce the analyte concentration in the sample. Also note that the shorter the time the sample is stored, the more closely the analytical result will reflect the condition of the sample at the time of sampling.

Table 1 below lists the containers, maximum holding times and condition of the soil for the analytes included in these guidelines. State regulatory agencies may specify different holding times or container types. In the event of a discrepancy between such requirements and those in Table 1, the most conservative approach should be followed.

Storing field-moist samples has the disadvantage that it will allow faster degradation of analytes via microbial activity, particularly if samples are stored at ambient temperatures. Moist samples should be stored at low temperature (<6°C) and the analysis carried out as quickly as possible.

Air-dried or oven-dried samples easily absorb moisture. Immediately after grinding, homogenising and partitioning, the prepared samples should be transferred into clearly labelled and sealed containers to be stored under dry, relatively cool (<18°C) and low light conditions while awaiting analysis.

All unanalysed portions of the sample should be retained for a reasonable amount of time after the dispatch of the analytical report (i.e. at least two months) or until agreed to or advised by the client that they may be discarded.

Table 1. Sample containers, holding times and condition of soil for analysis[a].

Analyte	Container[b]	Maximum holding time	Sample condition
Leachable metals and semi-volatile organics	As for analyte of interest	As for analyte of interest	As for analyte of interest
Moisture Content - moisture content only - moisture correction	P, PTFE or G As for analyte of interest	14 days Same day as sample extraction for analyte	Field-moist Field-moist
pH	P, PTFE or G	24 hours recommended. 7 days allowed	Air-dry or field-moist, depending on analyte of interest
Electrical conductivity	P or G	7 days	Air-dry
Organic carbon	G with PTFE lined cap [c]	28 days	Air-dry
Metals (except mercury and chromium VI)	P, PTFE or G	6 months	Air-dry or field-moist
Mercury and chromium VI	P (AW) [c]	28 days (For chromium , 7 days after extraction)	Field-moist
Cation exchange capacity and exchangeable cations	P (AW)	28 days	Air-dry
Chloride (water-soluble)	P or G	28 days	Field-moist or air-dry
Bromide (water-soluble)	P or G	28 days	Air-dry
Cyanide	P, PTFE or G[c]	14 days	Field-moist
Fluoride	P	28 days ISO 5667-3: 2003	Field-moist or air-dry
Sulfur – total	P, PTFE or G	7 days	Field-moist or air-dry
Sulfate	P, PTFE or G	28 days	Field-moist or air-dry
Sulfide	P or G [d]	7 days	Field-moist
Volatile organics	G with PTFE lined lid/septum [e]	14 days, except for vinyl chloride, styrene, or 2-chloroethyl vinyl ether (7 days)	Field-moist
Semi-volatile organics - PAH - Chlorinated hydrocarbons - OC Insecticides and PCB - OP Pesticides - Total Recoverable hydrocarbons - Phenols - Herbicides - Phthalate esters - Dioxins & furans	G with PTFE lined lid/septum[f]	14 days, except for PCBs (28 days) & dioxins & furans (30 days)	Field-moist

a Sourced from various references including US EPA SW-846 and Australian and international standards
b Minimum volume of 250 mL; P = Plastic; G = Glass; PTFE=polytetrafluoroethylene AW = Acid-washed; SR = Solvent rinsed.
c Store in the dark.
d Add sufficient 2M zinc acetate to fully cover surface of solid with minimal headspace; refrigerate (≤ 6°C) (see SW-846 Method 5021, Method 9030B)
eThe vials and septa should be washed with soap and water and rinsed with distilled deionized water. After thoroughly cleaning the vials and septa, they should be placed in an oven and dried at 100 °C for approximately one hour.
f Containers used to collect samples for the determination of semivolatile organic compounds should be soap and water washed followed by methanol (or isopropanol) rinsing(see US EPA SW846 Chapter 4 Sec. 4.1.4 for specific instructions on glassware cleaning)

6 Analytical methods

This section describes the methods recommended to analyse soil from a contaminated site.

It sets out methods for:

- physicochemical analyses
- soil moisture
- pH
- electrical conductivity
- cation exchange capacity
- water soluble chloride
- organic carbon
- inorganic contaminants:

metals – including separate methods for mercury, chromium (hexavalent)

- halides – bromides, fluoride
- non-metals – cyanide, sulfur compounds
- organic contaminants:

volatile organics – including MAHs, VHCs, and vTRHs

semi-volatile organics — including PAHs, OCPs, PCBs, OPPs, TRH and TRH (silica), phenols, chlorinated herbicides, phthalate esters, dioxins and furans

- leachability.

6.1 Method selection

For some analyte groups, two or more alternative procedures are suggested which differ in extraction method, clean-up (or lack of), the final determinative step, or a combination of these. The preferred technique will incorporate mass-selective detection and will have more favourable detector selectivity or clean-up steps employed. These methods are less likely to be subject to errors due to interference from co-extracted, non-target compounds. The alternative techniques are known to be useful but would normally require additional independent verification of analyte identity and concentration.

The preferred method is denoted by 'P'.

7 Physicochemical analyses

7.1 Soil moisture content

7.1.1 Scope and application

This method (AS 1289.2.1.1-2005) measures the amount of water lost after oven drying (105-110 ^{o}C) a soil sample (field-moist or air-dried) to constant mass. For chemical analyses, this allows a correction factor to be obtained to then express chemical concentrations on a dry weight basis.

This drying method will not remove all the water of crystallisation that may be associated with minerals.

The oven-dried moisture content is always determined on a separate representative sub-sample of the soil when several tests are to be performed. The oven-dried sample should not be used for other chemical or physical tests as the drying step may affect results of other tests.

7.2 Soil pH

7.2.1 Scope and application

This method (AS 1289.4.3.1-1997) measures the hydrogen-ion concentration in a soil-water or soil-aqueous calcium chloride suspension and is expressed in pH units.

The soil pH may have a profound effect on the form and behaviour of other chemicals in the soil. It is therefore recommended that soil pH be measured whenever other chemical constituents, particularly metals, are to be evaluated.

The use of 0.01 M calcium chloride extract is recommended where the soil salt content may influence the pH value (Rayment et al. 1992, p. 15). Generally, the pH of the calcium chloride extract is about 0.5 to 1.0 pH units lower than the water extract and gives more accurate values.

The same 1:5 soil-water suspension for electrical conductivity determination may be used for measuring pH but to avoid contamination of the suspension from KCl in the pH probe, electrical conductivity must be analysed first.

For acid sulphate soils, 'Analysis of acid sulfate soil - dried samples - methods of test - determination of pH_{KCl} and titratable actual acidity (TAA) (AS 4969.2-2008), and 'Analysis of acid sulfate soil - dried samples - methods of test - determination of peroxide pH (pH_{OX}), titratable peroxide acidity (TPA) and excess acid neutralising capacity (ANCE)' (AS 4969.3-2008) should be consulted for detailed procedures of their pH and acidity determinations.

7.2.2 Principle

Soil pH is measured electrometrically on a 1:5 soil-water suspension at 25°C. A 1:5 soil-calcium chloride extract is also provided as an option. The analytical report should state which method was used.

7.3 Electrical conductivity

7.3.1 Scope and application

This method measures the electrical conductivity of a 1:5 soil-water suspension. Electrical conductivity of the soil is sometimes used to estimate the soluble salt content of a sample (Rayment et al. 1992, p.17). A high soluble salt content may have physical detrimental effects on a soil, compromising its agronomic and structural attributes, for example, potential for corrosion of below ground structures.

The same 1:5 soil-water suspension for pH determination may be used for measuring the electrical conductivity but to avoid contamination, electrical conductivity must be analysed first.

7.3.2 Principle

The electrical conductivity is measured on the aqueous extract of a 1:5 soil-water suspension and recorded in dS/m at 25°C.

7.4 Cation exchange capacity and exchangeable cations

7.4.1 Scope and application

Methods in the following table measure the CEC of major exchangeable cations/'bases' (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) of near-neutral and alkaline soils.

Soil type	pH	Extractant	Salt content*	Method *	Comments
non-calcareous & non-gypsiferous soils	7.0	1M ammonium chloride	EC< 0.3 dS/m EC> 0.3 dS/m * Based on electrical conductivity (EC) determined on a 1:5 soil/water extract.	15B1 15B2 15B3 * Soil Chemical Methods	No pre-treatment for soluble salts Pre-treatment: soluble salts are removed using aqueous ethanol and aqueous glycerol. Adjustment: corrected for soluble Na^{+} when NaCl is the dominant soluble salt.

Limitation: These methods are designed to assess the ion-exchange characteristics of soils for land surveys or soil fertility studies, not contaminated soil. Soils heavily contaminated with soluble metals may 'saturate' an extractant's exchangeable sites and may not, without further tests, provide a true indication of the soil's exchangeable capacity. These methods should only be used with natural soils or background samples to give supporting information about the extent of contamination. In other samples the methods are qualitative and the results will be indicators only.

The US EPA method (US EPA SW-846, Method 9081) can be used on most soils (calcareous and non-calcareous) to measure the total amount of displaced ions from exchangeable sites in soil, compared with the summation of individual ions to express soil's CEC.

7.4.2 Principle

The soil is shaken with an appropriate extractant under certain conditions to exchange cations in the soil with the chosen extracting ions. The processed extract is then analysed for exchangeable cations including Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} or total CEC.

7.5 Water-soluble chloride

7.5.1 Scope and application

This method measures water-soluble chloride in soil water extracts (1:5 soil/water) (Rayment et al. 1992, p.24-25).

7.5.2 Principle

Chloride in soil is extracted in deionised water and the chloride concentration determined by colorimetric analysis or potentiometric titration.

7.5.3 Interferences

Water-soluble colour in the soil may mask the colour change at the endpoint of the titration. If this occurs, the colour can be removed by adding an aluminium hydroxide suspension (APHA Method 4500-Cl). Alternatively, chloride in the water extract can be determined using an ion-selective electrode or ion-chromatography.

7.6 Organic carbon

7.6.1 Scope and application

This determination (Rayment et al. 1992, p. 29), known also as the Walkley & Black method, measures the oxidisable organic carbon content of soils and may also be used to estimate their total organic carbon (TOC) content.

Soil organic carbon comprises a variety of carbonaceous materials including humus, plant and animal residues, micro-organisms, coal, charcoal and graphite. It does not include carbonate minerals such as calcite or dolomite. Australian soils generally contain less than 5% organic carbon, with higher levels common in surface soils (Rayment et al. 1992, p. 29 and p. 32).

The first method listed in Rayment gives poor recoveries of carbonised materials such as graphite, coal, coke and similar coal derivatives. If such materials make up the bulk of the carbon in the sample or if the total organic carbon content is required, an alternative method which makes use of an external heat source is recommended (Rayment et al. 1992, p. 32).

For acid sulphate soils, consult the Australian standard for the *Analysis of acid sulfate soil - dried samples - methods of test - introduction and definitions, symbols and acronyms*, (AS 4969.0-2008) for relevant definitions and recommended analytical procedures.

7.6.2 Interferences

Overestimation of organic carbon may occur due to large amounts of chloride or metallic or ferrous iron in the sample. Underestimation may result when large amounts of higher oxides of manganese are present. These interferences are common in Australian soils. The potential interferences should be taken into account particularly when analysing some types of poorly aerated soils.

Since the first method recovers variable proportions of organic carbon actually present in a soil sample (recoveries typically in the range of 65 - 85%), a correction factor is usually needed. In the absence of a specific correction factor for the soil being tested, a correction factor of 1.3 is commonly used such that:

Total organic carbon (per cent) = Oxidisable organic carbon (per cent) x 1.3.

8 Metals

8.1 Aqua regia digestible metals

8.1.1 Scope and application

This method AS 4479.2-1997 may be used to obtain extracts from soils for the analysis of most metals and metalloids. Extracts obtained here are not suitable for speciation studies, and analysis of the extracts does not necessarily result in total or bio-available heavy metal levels in a soil.

Metals extractable by this digestion include metallic components adsorbed on soil particles, complexed by and adsorbed on organic matter, and soluble metal salts. Complete decomposition of the soil is not possible using aqua regia. Therefore, metals bound within part or most of the silicate matrix may not be fully recovered by this method.

Samples extracted by this method can be analysed for metals by a suitable spectrophotometric method while accounting for likely interferences, for example, chlorides.

US EPA Method 3050B (microwave digestion) or Method 200.2 may be used as alternatives to this method.

8.1.2 Principle

Boiling aqua regia (3:1 hydrochloric/nitric acid) is used to extract metals from soil. This concentrated acid mixture can extract inorganic metals as well as those bound in organic or sulfide forms.

8.2 Acid digestible metals in sediments, sludges and soils

8.2.1 Scope and application

This method (US EPA SW-846, Method 3050B) may be used to prepare extracts from sediments, sludges and soils for the analysis of metals by various common spectrophotometric techniques.

It can be used to determine the following extracted metals:

FAAS/ICP-AES		GFAAS/ICP-MS
Aluminium	Magnesium	Arsenic
Antimony	Manganese	Beryllium
Barium	Molybdenum	Cadmium
Beryllium	Nickel	Chromium
Cadmium	Potassium	Cobalt
Calcium	Silver	Iron
Chromium	Sodium	Lead
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		

FAAS = Flame atomic absorption spectroscopy
GFAAS = Graphite furnace atomic absorption spectroscopy
ICP-AES = Inductively coupled plasma atomic emission spectroscopy
ICP-MS = Inductively coupled plasma mass spectrometry

8.2.2 Principle

Two separate digestion procedures, whose extracts are not interchangeable for each other's determinations, are provided for determination of the above elements.

8.2.2.1 For FAAS and ICP-AES

The field-moist or dry sample is digested at 95°C in nitric acid and hydrogen peroxide until the volume is reduced, or heated for two hours. Hydrochloric acid is then added and the mixture digested further at heat.

For improved solubility and recovery of antimony, barium, lead and silver, an optional nitric acid/hydrochloric acid digestion step may be used when necessary.

8.2.2.2 For GFAAS and ICP-MS

The field-moist or dry sample is digested at 95°C in nitric acid and hydrogen peroxide until the volume is reduced, or heated for two hours.

8.3 Metals by microwave assisted acid digestion of sediments, sludges, soils and oils

8.3.1 Scope and application

This method (US EPA SW-846, Method 3051A) describes a rapid acid assisted microwave procedure for digesting sediments, sludges, soils and oils for the analysis of most metals, some metalloids and some non-metals, including (but not limited to):

Aluminium	Cadmium	Iron	Molybdenum	Sodium
Antimony	Calcium	Lead	Nickel	Strontium
Arsenic	Chromium	Magnesium	Potassium	Thallium
Barium	Cobalt	Manganese	Selenium	Vanadium
Boron	Copper	Mercury	Silver	Zinc
Beryllium				

8.3.2 Principle

The sample is digested in concentrated nitric acid, or a mixture of nitric and hydrochloric acids, using microwave heating in a sealed Teflon vessel at elevated temperature and pressure. The final digest can be analysed for the element by various common spectrophotometric methods, as described in US EPA Method 3051A.

8.4 Mercury

8.4.1 Scope and application

This method (US EPA SW-846, Method 7471B) may be used as an alternative to methods described in this Schedule for mercury. It uses strong acid digestion (aqua regia) to determine total mercury (inorganic and organic) in soils, sediments, bottom deposits and sludge type materials.

8.4.2 Principle

Mercury is digested with aqua regia (1:3 nitric acid, hydrochloric acid) at 95°C in the presence of a strong oxidant (potassium permanganate). The digest is then analysed by cold-vapour atomic absorption spectrometry.

CAUTION: Mercury vapour is highly toxic. Use appropriate safety precautions ensuring the mercury vapour is vented into an appropriate exhaust hood or preferably, trapped in an absorbing medium (e.g. potassium permanganate/sulfuric acid solution).

Note: US EPA, Method 1630 may be used for methyl mercury.

8.5 Hexavalent chromium

8.5.1 Scope and application

This method (US EPA SW-846, Method 3060A) is an alkaline digestion procedure for extracting hexavalent chromium [Cr (VI)] from soluble, adsorbed and precipitated forms of chromium compounds in soils, sludges, sediments and similar waste materials.

8.5.2 Principle

This method uses an alkaline digestion to solublise both water-soluble and water-insoluble Cr(VI) compounds. The pH must be carefully monitored during digestion to prevent reduction of Cr(VI) or oxidation of native Cr(III).

Cr(VI) in the digest can then be determined colourimetrically by UV visible spectrophotometry (US EPA SW-846, Method 7196), ion chromatography(US EPA SW-846, Method 7199) or other suitable validated methods.

CAUTION: Cr(VI) is highly toxic. Use appropriate safety precautions when handling and disposing of waste.

9 Halides

9.1 Bromide

9.1.1 Scope and application

This method (Adriano et al. 1982, p. 449) is applicable to the determination of water-soluble bromides in soils, sediments and other solids.

9.1.2 Principle

Most bromides in soils are considerably soluble and can be readily leached using water. In this method, bromide in the sample is extracted into water with a suitable soil:water ratio, which will depend on the bromide species and concentration present. Determination is by suitable APHA methods (APHA Methods 4500-Br and 4110).

9.2 Fluoride

9.2.1 Scope and application

This method is applicable to the determination of total fluoride in plants, soils, sediments and other solids (ASTM D3269-96 [2001], McQuaker et al. 1977, ASTM D3270-00 [2006]).

9.2.2 Principle

The sample is fused with sodium hydroxide at 600°C and a solution of the melt is analysed for fluoride.

Note 1: To avoid fluoride losses, do not use glassware to hold sample extracts for long periods; use plasticware as far as possible.

Note 2: This method is not appropriate for samples with high aluminium concentrations, which can cause negative interferences.

10 Non-metals (cyanide and sulphur)

10.1 Total cyanide

10.1.1 Scope and application

This method is applicable to the determination of inorganic cyanides in soils, sediments and other solids, with the exception of cyano-complexes of some transition metals like cobalt, silver, gold, platinum and palladium (APHA Method 4500-CN, US EPA SW-846, Method 9013).

10.1.2 Principle

Extractable or soluble cyanide in the soil is extracted into an alkaline solution; the high pH will enable the cyanide complexes, such as iron cyanide complexes, to be decomposed and dissolved (US EPA SW-846, Method 9013). The cyanide extract is then distilled after adding a strong acid by reflux distillation (> 1 hour), yielding hydrogen cyanide and collection in a strong alkali solution (APHA Method 4500-CN, US EPA SW-846, Method 9010C, US EPA SW-846, Method 9012B).

Total or amenable cyanide is determined by reflux distillation under strong acidic conditions (US EPA SW-846, Method 9012B).

Cyanide in the distillate can then be determined colourimetrically, titrimetrically, using an ion-selective electrode or other validated method.

10.2 Total sulfur

10.2.1 Scope and application

This method (Tabatabai et al. 1988, Tabatabai 1982) is applicable to the determination of total sulfur in soil, sediment, plants and other solids.

10.2.2 Principle

Sulfur is oxidised to the sulfate form by fusion. The sample is ignited with sodium bicarbonate and silver oxide at 550°C for three hours and the melt is dissolved in acetic acid. The resultant solution is analysed for total sulfur as sulfate (SO_4^{2-}) using a validated method, for example, ion chromatography (APHA Method 4110).

Other decomposition methods for total sulfur analysis, for example, high temperature furnace combustion method, may be used if they can be demonstrated to be at least as rigorous as this method or validated against a CRM (Peverill et al. 2001). For example:

- nitric / perchloric acid digestion (Tabatabai & Bremner 1970)
- sodium hypobromide digestion (Tabatabai & Bremner 1970)
- sodium carbonate/sodium peroxide fusion (AOAC 1980).

10.3 Sulfate

10.3.1 Scope and application

These methods are applicable to the determination of soluble and adsorbed inorganic sulfate in soils, sediments and other solids (AS 1289.4.2.1-1997, Rayment & Higginson 1992, ASTM C1580-09 [2009[, Tabatabai 1982).

10.3.2 Principle

The sample is shaken in a 1:5 soil:water extract, or in some cases a calcium phosphate solution (Tabatabai 1982) (500 mg phosphorus/L) and the resulting extractant subsequently analysed (APHA Method 4110). In the latter, phosphate ions displace adsorbed sulfate while calcium ions depress extraction of soil organic matter and thus eliminate interference from extractable organic sulphur.

10.4 Sulfide

10.4.1 Scope and application

This method (US EPA SW-846, Method 9030B) is suitable for soil samples containing 0.2 mg/kg–50 mg/kg of sulfide. It measures 'total' sulphide, usually defined as acid-soluble sulfide. For soils with significant metal sulfides, total sulfide is defined as both the acid-soluble and acid-insoluble fractions, and both procedures must be employed.

10.4.2 Principle

For acid-soluble sulfides, sulfide is separated out by adding sulfuric acid to a heated sample. For acid-insoluble sulfides (for example, metal sulfides such as CuS, SnS_2) sulfide is separated by suspending the sample in concentrated hydrochloric acid with vigorous agitation.

11 Organics

The table below lists the US EPA SW-846 methods specified for organics analysis.

Code	Method Title
3540 C	Soxhlet extraction
3541	Soxhlet extraction (automated)
3545 A	Pressurised fluid extraction (accelerated solvent extraction)
3546	Microwave extraction
3550 C	Ultrasonic extraction
3561	Supercritical fluid extraction (of PAHs)
3620C	Florisil clean-up
3630 C	Silica gel clean-up
3640A	Gel-permeation clean-up
3650B	Acid-base partition clean-up
3660B	Sulfur clean-up
3665A	Sulfuric acid/ permanganate clean-up
3820	Hexadecane extraction and screening for purgeable organics
5021	Volatile organic compounds in soils and other solid matrices using equilibrium headspace
5030B	purge and trap
5035	Closed -system purge-and-trap and extraction for volatile organics in soil and solid wastes
8015C	Non-halogenated organics by GC
8021B	Aromatic and halogenated volatiles by GC using photoionisation and electrolytic conductivity detectors
8041A	Phenols by GC
8061A	Phthalate esters by GC with electron capture detection
8081B	Organochlorine pesticides by GC
8082A	Polychlorinated biphenyls (PCBs) by GC
8121	Chlorinated hydrocarbons by GC: capillary column technique
8141B	Organophosphorus compounds by GC
8151A	Chlorinated herbicides by GC using methylation or pentafluorobenzylation derivatisation
8260B	Volatile organic compounds by GC/MS
8270 D	Semi-volatile organic compounds by GC/MS
8280 B	Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by high-res GC/low-res MS
8290 A	PCDDs and PCDFs by high-res GC/MS
8310	Polynuclear aromatic hydrocarbons (HPLC)
8440	TRPs by infrared spectrophotometry

11.1 Volatile organics

11.1.1 Scope and application

Unless indicated otherwise, the methods described in this section are contained in SW-846. This section lists methods for the following classes of volatile compounds:

- MAH
- VHC
- miscellaneous volatile organic compounds
- volatile TRH.

11.2 Monocyclic aromatic hydrocarbons (MAH)

This method is applicable to most volatile compounds with boiling points less than 200°C and which are insoluble or only slightly soluble in water, including (but not limited to):

Benzene	Ethyl benzene
Toluene	Xylenes
Styrene (vinyl benzene, ethenyl benzene)	Propyl benzene
Trimethylbenzenes	Cumene

11.2.1 Preliminary screening

Preliminary screening by headspace analysis (Method 5021) or hexadecane extraction (Method 3820) is appropriate for samples which may contain high concentrations.

Note: Headspace analysis may not be as rigorous or reliable as purge and trap (Method 5035); however, it is suitable as a 'screening analysis'.

11.2.2 Sample extraction

Low concentration: (individual compounds approx < 200µg/kg)

- purge and trap technique (Method 5035, Method 5030B)

Analysts should determine an appropriate concentration limit and ensure that quantitative results are based on sample concentrations that do not exceed the instrumental range.

High concentration: (individual compounds ≥ 200µg/kg)

- methanol extraction followed by purge and trap technique (Method 5035 or 5030B).

11.2.3 Sample clean-up

Not applicable.

11.2.4 Sample analysis

The table below lists the US EPA SW-846 methods specified for MAHs.

8021B	GC/ PID
8260B	GC/MS

Note: Flame ionisation detection (FID) may be substituted for MS or PI detection, for screening purposes but FID is more susceptible to interference and erroneous quantification due to its non-specific response. Accordingly, residues should be confirmed by chromatography on a stationary phase of different polarity or by measurement using MS or PI detector.

11.3 Volatile halogenated compounds

This method (Method 5035) is applicable but not limited to analysis of the following volatile halogenated hydrocarbons.

Allyl chloride	Chloromethane	Epichlorhydrin
Benzyl chloride	Chloroprene	Ethylene dibromide
Bis(2-chloroethy)sulphide	1,2-Dibromo-3-chloropropane	Hexachlorobutadiene
Bromoacetone	1,2-Dibromomethane	Hexachloroethane
Bromochloromethane	Dibromomethane	Iodomethane
Bromodichloromethane	Dichlorobenzenes	Pentachloroethane
Bromoform	1,4-Dichloro-2-butene	Tetrachloroethane
Bromomethane	Dichlorodifluoromethane	Tetrachloroethene
Carbon tetrachloride	Dichlorethane	Trichlorobenzene
Chlorobenzene	Dichlorethene	Trichloroethane
Chlorodibromomethane	Dichloromethane (methylene chloride)	Trichloroethene
Chloroethane	1,2-Dichloropropane	Trichlorofluoromethane
2-Chloroethanol	1,3-Dichloro-2-propanol	Trichloropropane
2-Chloroethyl vinyl ether	1,3-Dichloropropene	Vinyl chloride
Chloroform		

11.3.1 Sample extraction

Low concentration (individual compounds <200µg /kg):

- purge and trap technique (Method 5035, Method 5030B)

Analysts should determine an appropriate concentration limit and ensure that results are based on sample concentrations that do not exceed the instrument range.

High concentration (individual compounds ≥200µg/kg):

- methanol extraction followed by purge and trap technique (Method 5035 or 5030B).

11.3.2 Sample clean-up

Not applicable.

11.3.3 Sample analysis

The table below lists the US EPA SW-846 methods specified for volatile halogenated compounds.

	8021B	GC/ELCD
(P)	**8260B**	GC/MS

Note: Preliminary screening by headspace analysis (Method 5035) or hexadecane extraction (Method 8021B) is appropriate for samples which may contain high concentrations.

11.4 Miscellaneous volatile organic compounds

The following volatile compounds do not fall into the aromatic or chlorinated categories detailed in the sections above, and may be analysed using the methods below.

Analysis of other volatile organics by these methods is not precluded. These methods could also be appropriate for volatile petroleum products (hydrocarbon fuels and solvents).

Acetone	Ethyl methacrylate
Acetonitrile	2-Hexanone
Acrolein	2-Hydroxypropionitrile
Acrylonitrile	Isobutyl alcohol
Allyl alcohol	Light alkanes (e.g. as in petrol)
2-Butanone (MEK)	Malononitrile
t-Butyl alcohol	Methacrylonitrile
Carbon disulfide	Methyl methacrylate
Chloral hydrate	4-Methyl-2-pentanone (MIBK)
bis-(2-Chloroethyl) sulphide	2-Picoline
2-Chloroethyl vinyl ether	Propargyl alcohol
1,2:3,4-Diepoxybutane	b-Propiolactone
Diethyl ether	Propionitrile
1,4-Dioxane	n-Propylamine
Ethanol	Pyridine
Ethylene oxide	Vinyl acetate

11.4.1 Sample extraction

Low concentration (individual compounds < 200µg /kg):

- purge and trap technique (Method 5035)
- analysts should determine an appropriate concentration limit and ensure that results are based on sample concentrations that do not exceed the instrumental range.

High concentration (individual compounds ≥ 200 µg/kg):

- methanol extraction followed by purge and trap technique.

11.4.2 Sample clean-up

Not applicable.

11.4.3 Sample analysis

The table below lists the specified US EPA SW-846 method.

8260B	GC/MS

11.5 Volatile total recoverable hydrocarbons (vTRH)

The term 'TRH' (total recoverable hydrocarbons) is equivalent to the previously used term 'TPH' (total petroleum hydrocarbons), and represents extracted biogenic and petrogenic (petroleum) hydrocarbons by selected solvents. The new terminology has been chosen to avoid confusion with past practices.

TRH fractions are based on newly derived health screening levels (HSL) for petroleum hydrocarbon products.

The vTRH method is applicable but not limited to analysis of hydrocarbons which may be constituents or residues present in or from materials such as the following:

- petrol
- dry cleaning liquids
- industrial solvents
- paints, thinners and strippers.

11.6 Volatile total recoverable hydrocarbons (vTRH) by purge and trap analysis

11.6.1 Scope

This method, which is a modified version of the 'closed-system purge and trap and extraction for volatile organics in soil and waste samples method' (Method 5035), is applicable to hydrocarbons eluting between nC_6 and nC_{10}. A clean-up procedure is not applicable here since only the volatile components are being investigated.

11.6.2 Sample extraction

The table below lists the specified US EPA SW-846 method.

5035	Purge and trap extraction using methanol.

11.6.3 Extract clean-Up

Not required/applicable.

11.6.4 Extract analysis

The table below lists the specified US EPA SW-846 method.

8260B	GC/MS or GC/FID. Volatile TRH fraction is specified as nC6-nC10. Details of GC conditions, standards , and procedure for quantification of fractions as suggested by CRC Care are listed in Appendix 1.

11.7 Semi-volatile organics

11.7.1 Scope and application

This section lists methods for the following classes of non-volatile compounds:

- non-volatile chlorinated hydrocarbons
- PAHs by solvent extraction
- PAHs by supercritical fluid extraction
- organochlorine pesticides (OCPs) and PCBs
- OPPs
- total recoverable hydrocarbons – non-volatile
- phenols
- chlorinated herbicides
- phthalate esters
- dioxins and furans.

Note: Many of these methods use ultrasonic extraction. When this method is used, ensure samples don't overheat; consider putting ice packs into ultrasonic bath.

This method must not be used for volatile contaminants.

11.8 Semi-volatile chlorinated hydrocarbons

This method is applicable but not limited to the analysis of the following semi-volatile chlorinated hydrocarbons.

Benzal chloride	Benzotrichloride
Benzyl chloride	2-Chloronaphthalene
Dichlorobenzenes	Trichlorobenzenes
Tetrachlorobenzenes	Pentachlorobenzenes
Hexachlorobenzene	Hexachlorobutadiene
Hexachlorcyclopentadiene	Hexachloroethane
α-Hexachlorocyclohexane (α -HCH)	β-Hexachlorocyclohexane (β--HCH)
γ-Hexachlorocyclohexane (gamma-HCH or Lindane)	δ–Hexachlorocyclohexane (delta-HCH)

11.8.1 Sample extraction

The table below lists the specified US EPA SW-846 methods.

3540C	Soxhlet extraction using: • acetone/hexane (1:1) or • dichloromethane/acetone (1:1)
3550C	Ultrasonic extraction* using: **a.** for low concentration (individual compounds <20 mg/kg): • dichloromethane or • dichloromethane/acetone (1:1) or • hexane/acetone (1:1) or • methyl tertiary-butyl ether or • methyl tertiary-butyl ether/methanol (2:1). The solvent system chosen must be shown to give optimum, reproducible recovery of analytes spiked into the particular matrix (soil type) under test. Analysts should determine an appropriate concentration limit and ensure that quantitative results are based on sample concentrations that do not exceed the instrument range. **b.** for high concentration (individual compounds >20 mg/kg): • dichloromethane or • hexane

* Ensure samples don't overheat; consider putting ice packs into ultrasonic bath.

3545A **CRC Technical Note 10**	Pressurised fluid extraction. End-over-end tumbling/shaking.

11.8.2 Extract clean-up

3620C	Florisil column clean-up or
3640A	Gel permeation column clean-up and
3660B	Sulfur clean-up if necessary.

11.8.3 Extract analysis

	8121	GC/ECD
(P)	**8270D**	GC/MS

11.9 Polycyclic aromatic hydrocarbons by solvent extraction

This method is applicable but not limited to analysis of the following polycyclic aromatic hydrocarbons (PAHs):

Naphthalene	Anthracene	Benzo(k) fluoranthene
Acenaphthylene	Fluoranthene	Benzo(a) pyrene
Acenaphthene	Pyrene	Dibenz (a,h)anthracene
Fluorene	Benzo(a) anthracene	Benzo(ghi) perylene
Phenanthrene	Chrysene	Indeno(123-cd) pyrene
	Benzo(b) fluoranthene	

11.9.1 Sample extraction

The tables below list the specified US EPA SW-846 methods.

3540 C	Soxhlet extraction using: • acetone/hexane (1:1) or • dichloromethane/acetone (1:1)
3550 C	Ultrasonic extraction* using: **a.** for low concentration (individual compounds <20 mg/kg): • dichloromethane or • dichloromethane/acetone (1:1) or • hexane/acetone (1:1) or • methyl tertiary-butyl ether or • methyl tertiary-butyl ether/methanol (2:1). The solvent system chosen must be shown to give satisfactory, reproducible recovery of analytes spiked into the particular matrix (soil type) under test. Analysts should determine an appropriate concentration limit and ensure that results are based on sample concentrations that do not exceed the instrument range. b. for high concentration (individual compounds >20 mg/kg): • dichloromethane.

* Ensure samples don't overheat; consider putting ice packs into ultrasonic bath.

3545A	Pressurised fluid extraction using dichloromethane/acetone (1:1).
CRC TECHNICAL NOTE 10	End-over-end tumbling/shaking.

11.9.2 Sample clean-up

3630C	Silica gel column clean-up.

The extract must be concentrated using a Kuderna Danish (KD) evaporator and solvent exchanged to cyclohexane, prior to clean-up.

11.9.3 Extract analysis

(P)	**8270D**	GC/MS (capillary column)
	8310	HPLC with UV* and fluorescence* detectors

*Due to the high probability of interferences using these less specific detectors, clean-up of extracts using Method 3630C will normally be necessary. Protocols for verification of analyte identities should be developed when Method 8310 is used.

11.10 Polycyclic aromatic hydrocarbons by supercritical fluid extraction

PAHs / supercritical fluid extraction (SFE)

3561	SFE of PAHs

11.10.1 Sample extraction

The tables below list the specified US EPA SW-846 methods.

The extraction is a three-step process using:

- supercritical CO_2
- supercritical CO_2 plus water and methanol modifiers
- supercritical CO_2 (to purge system of modifiers).

Collection of SFE extract:

either

- octadecylsilyl (ODS) trap with elution of trap using:
  - **a.** acetonitrile / tetrahydrofuran (50/50) for HPLC determination, or
  - **b.** DCM (dichloromethane)/isooctane (75/27)

or

- solvent trapping in solvent system (a) or (b) above, or another system validated by the laboratory.

11.10.2 Extract clean-up

The table below lists the specified US EPA SW-846 methods.

3620C	Florisil column clean-up or
3640A	gel permeation column clean-up and
3660B	sulfur clean-up if necessary.

11.10.3 Extract analysis

The table below lists the specified US EPA SW-846 methods.

(P)	**8270D**	GC/MS
	8310	HPLC with UV and Fluorescence detectors

11.11 Organochlorine pesticides and polychlorinated biphenyls

This method is applicable but not limited to analysis of the following organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs).

Aldrin	Endrin
HCB	Endosulfan (alpha-, beta- and sulfate)
alpha-HCH, beta-HCH	Heptachlor, Heptachlor epoxide
gamma-HCH (lindane), delta-HCH	Mirex
Chlordane (alpha, beta chlordane, and oxychlordane)	Methoxychlor
DDD, DDE, DDT	Toxaphene
Dieldrin	PCB (Aroclor 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262)

11.11.1 Sample extraction

The table below lists the specified US EPA SW-846 methods.

3540C	Soxhlet extraction using: • acetone/hexane (1:1) or • dichloromethane/acetone (1:1).

(see over)

3550C	Ultrasonic extraction* using: **a.** for low concentration (individual compounds <20 mg/kg): • dichloromethane or • dichloromethane/acetone (1:1) or • hexane/acetone (1:1) or • methyl tertiary-butyl ether or • methyl tertiary-butyl ether/methanol (2:1). The solvent system must be chosen to give optimum reproducible recovery of analytes spiked into the matrix (soil type) under test. Analysts should determine an appropriate concentration limit and ensure that quantitative results are based on sample concentrations that do not exceed the instrumental range. **b.** for high concentration (individual compounds >20 mg/kg): • dichloromethane or • hexane.
CRC TECHNICAL NOTE 10	End-over-end tumbling/shaking.

* Ensure samples don't overheat; consider putting ice packs into ultrasonic bath.

Note: Extract clean-up. Methods for the clean-up of some co-extracts/analytes are suggested below. The tables below list the specified US EPA SW-846 methods.

For samples of biological origin or containing high molecular weight materials:

3640A	Gel permeation column clean-up.

If only PCBs are to be determined:

3665A	sulfuric acid/permanganate clean-up followed by:
3620C	florisil column clean-up or
3630C	silica gel fractionation.

If both PCBs and pesticides are to be measured:

3630C	silica gel fractionation.

If only pesticides are to be determined:

3620C	florisil column clean-up and
3660B	sulfur clean-up.

Elemental sulfur may interfere with determination of pesticide and PCBs. This should be removed using Method 3660B: sulfur clean-up, which utilises reaction with reactive copper.

11.11.2 Extract analysis

The table below lists the specified US EPA SW-846 methods.

8081B	GC/ECD (capillary column)
8082A	GC/ECD or GC/ ELCD
8270D	GC/MS (capillary column)

11.12 Organophosphorus pesticides

This method is applicable but not limited to the analysis of the following organophosphorus pesticides (OPPs).

Atrazine	EPN	Parathion ethyl
Azinphos methyl	Ethoprop	Parathion methyl
Bolstar (Sulprophos)	Fensulfothion	Phorate
Chlorpyriphos	Fenthion	Ronnel
Coumaphos	Malathion	Sulfotep
Demeton, O and S	Merphos	TEPP
Diazinon	Mevinphos	Stirophos (Tetrachlorvinphos)
Dichlorvos	Monocrotophos	Tokuthion (Protothiophos)
Dimethoate	Naled	Trichloronate
Disulfoton		

11.12.1 Sample extraction

The table below lists the specified US EPA SW-846 methods.

3540C	• Soxhlet extraction using: • acetone/hexane (1:1) or • dichloromethane/acetone (1:1).

3550C	Ultrasonic extraction* using: **a.** for low concentration (individual compounds <20 mg/kg): • dichloromethane or • dichloromethane/acetone (1:1) or • hexane/acetone (1:1) or • methyl tertiary-butyl ether or • methyl tertiary-butyl ether/methanol (2:1). The solvent system chosen must be shown to give satisfactory, reproducible recovery of analytes spiked into the particular matrix (soil type) under test. Analysts should determine an appropriate concentration limit and ensure that quantitative results are based on sample concentrations that do not exceed the instrumental range. **b.** for high concentration (individual compounds >20 mg/kg): • dichloromethane or • hexane.
CRC TECHNICAL NOTE 10	End-over-end tumbling/shaking.

* Ensure samples don't overheat; consider putting ice packs into ultrasonic bath.

11.12.2 Extract clean-up (not usually necessary)

The tables below list the specified US EPA SW-846 methods.

3620C	Florisil column clean-up. (Analyst should verify the use of this step for the pesticide of interest, as low recoveries have been reported for certain OPPs).
3660B	Sulfur clean-up.

11.12.3 Sample Analysis

8141B	GC/ FPD or GC/ NPD
8270D	GC/MS

11.13 Total recoverable hydrocarbons - non volatile

The term total recoverable hydrocarbons (TRH) is equivalent to the previously used total petroleum hydrocarbons (TPH), and represents extracted biogenic (biological) and petrogenic (petroleum) hydrocarbons by selected solvents. It has been chosen to avoid confusion with past practices. A silica gel clean-up is recommended where significant levels of non petroleum hydrocarbon interferences are suspected. Where such a clean-up is done it must be clearly stated with any relevant interpretation of the chromatogram on the analyst's report.

When soil contains high levels of non petroleum based hydrocarbons (e.g. from heavy manure, compost additions or polymeric materials), inspection of the chromatogram may reveal that the silica gel clean-up was not sufficient to remove the non petroleum based hydrocarbons from the sample and resolve interferences. This can result in false positive results for petroleum based hydrocarbon determination. In these cases it is recommended that GC-MS — or other appropriate analytical method, e.g. NMR (nuclear magnetic resonance) — is applied to the extract or a silica gel cleaned sample to improve accuracy. It is important that a report and interpretation of the result is prepared by the analyst.

Where it can be determined that compounds in the sample are of non petroleum origin, the results should be adjusted as far as practicable to finalise the level of petroleum based hydrocarbon in the sample.

TRH fractions are based on those used to derive Health Screening Levels (HSLs) for petroleum hydrocarbon products (CRC CARE, Technical note 10).

The TRH method is applicable but not limited to the analysis of hydrocarbons which may be constituents or residues present in or from materials such as the following:

- kerosene
- diesel
- aviation fuel
- lubricating oil
- heating oil/marine fuel
- dry cleaning liquids
- tars
- gasworks wastes
- industrial solvents
- paints, thinners and strippers.

11.13.1 Total recoverable hydrocarbons by solvent extraction

11.13.1.1 Scope

This method is for the determination of semi-volatile TRH in soil by gas chromatography applicable to hydrocarbons eluting between $>nC_{10}$ and nC_{40}. The method extracts major hydrocarbons such as aliphatic linear, branched and cyclic hydrocarbons, PAHs, and other compounds in the boiling point range up to nC_{40}. If PAHs are suspected of being present in a sample, target analysis techniques are preferred for risk assessments.

Hydrocarbons with boiling points less than nC_{10} (volatiles) or greater than nC_{40} (heavy petroleum products) will not be quantitatively determined using this method.

TRH can be defined as all chromatographic peaks extractable by specified solvent and detectable by GC/FID in specified ranges. Hydrocarbon interferences such as vegetable and animal oils and greases, organic acids, chlorinated hydrocarbons, phenols and phthalate esters will also be measured. The presence of petroleum hydrocarbons in TRH may be confirmed by clean-up of extract with silica gel. However silica gel clean-up may not completely remove non petroleum hydrocarbon interferences of biological origin.

11.13.1.2 Sample Extraction

The table below lists the specified US EPA SW-846 methods.

3540C	Soxhlet extraction using: • dichloromethane/acetone (1:1).
3550C	Ultrasonic extraction* using: • dichloromethane/acetone (1:1)
3545A	Pressurised fluid extraction (PFE) using: • dichloromethane/acetone (1:1) or • hexane/acetone (1:1)
CRC TECHNICAL NOTE 10	End-over-end tumbling/shaking using: • dichloromethane/acetone (1:1) This procedure, specified for TRH, has evolved from work carried out by the CRC CARE working group. Although all components of it are in common use, no validation data are currently available for the entire method.

* Ensure samples don't overheat; consider putting ice packs into ultrasonic bath

The solvent system chosen must be shown to give optimum, reproducible recovery of analytes spiked into the particular matrix (soil type) under test.

11.13.1.3 Extract clean-up

(Recommended when there is significant amount of non petroleum hydrocarbon interferences, to avoid reporting false positive results.)

The table below lists the specified US EPA SW-846 methods.

3630C	Silica gel clean-up.
	Clean-up is necessary if the extract contains interfering quantities of polar non petroleum compounds evidenced by a GC/FID profile or GC/MS analysis, uncharacteristic of petroleum hydrocarbons. Clean-up may be achieved after solvent exchange to hexane or other suitable solvent. Clean-up can be either carried out using a silica gel column or by shaking a solvent extract with loose silica gel. Silica gel activity may have to be adjusted by water addition for optimum retention of PAHs and TRH in extract. US EPA Method 3630C gives conditions for silica gel clean-up of PAHs.

11.13.1.4 Extract Analysis

The table below lists the specified US EPA SW-846 methods.

8015B	Specifies GC/FID conditions up to nC_{28} alkanes
8270D	GC/FID conditions for $>nC_{28}$ alkanes can be obtained here or in Appendix 1 (CRC CARE method). Due to the non-specific response of GC/FID, identities of unusual mixtures and predominant individual compounds should be confirmed using GC/MS. TRH fractions are specified as $>C_{10}$-C_{16}, $>C_{16}$-C_{34} and $>C_{34}$-C_{40}. Details of GC conditions, standards, and procedure for quantification of fractions are listed in Appendix 1. Where clean-up with silica gel has occurred it must be clearly stated on the report. The result will be reported as TRH (silica).

11.14 Phenols

This method is applicable but not limited to the analysis of the following phenolic compounds:

Phenols

Chlorophenols, Dichlorophenols, Trichlorophenols

Tetrachlorophenols, Pentachorophenol

Cresols (methyl phenols)

Nitrophenols, Dinitrophenols

11.14.1 Sample extraction

The table below lists the specified US EPA SW-846 methods.

3540C	Soxhlet extraction using: • acetone/hexane (1:1) or • dichloromethane/acetone (1:1) plus • exchange solvent (2-propanol).
3545A **3550C**	Pressurised fluid extraction (PFE) Ultrasonic extraction* using: **a.** for low concentration (individual compounds <20 mg/kg): • dichloromethane or • dichloromethane/acetone (1:1) or • hexane/acetone (1:1) or • methyl tertiary-butyl ether or • methyl tertiary-butyl ether/methanol (2:1) and • exchange solvent (2-propanol). The solvent system chosen must be shown to give satisfactory, reproducible recovery of analytes spiked into the particular matrix (soil type) under test. Analysts should determine an appropriate concentration limit and ensure that quantitative results are based on sample concentrations that do not exceed the instrumental range. **b.** for high concentration (individual compounds >20 mg/kg): • dichloromethane.

* Ensure samples don't overheat; consider putting ice packs into ultrasonic bath.

CRC TECHNICAL NOTE 10	End-over-end tumbling/shaking.

11.14.2 Extract clean-up

The tables below list the specified US EPA SW-846 methods.

3630C	Silica gel column clean-up (for samples derivatised for GC/ ECD determination).
3640A	Gel permeation clean-up.
3650B	Acid/base partition extraction (it is recommended that all extracts undergo this clean-up): • pentafluorobenzyl bromide derivatisation (for GC/ECD analysis) • phenols by GC/capillary column technique.

11.14.3 Extract Analysis

	8041A	GC/FID GC/ECD (after derivatisation, if interferences prohibit proper analysis by GC/FID)
(P)	**8270D**	GC/MS

Note: GC analysis of some underivatised phenols is difficult (e.g. chlorinated and nitro compounds). The GC injector port must be clean and adequately silanised.

11.15 Chlorinated herbicides

The method described below for chlorinated herbicides (by gas chromatography) is applicable but not limited to the determination of:

2,4-D	DCPA diacid	MCPA
2,4-DB	Dalapon	MCPP (mecoprop)
2,4,5-T	Dicamba	4-Nitrophenol
2,4,5-TP (Silvex)	3,5-Dichlorobenzoic acid	Pentachlorophenol
Acifluoren	Dichlorprop	Picloram
Bentazon	Dinoseb	
Chloramben	5-Hydroxydicamba	

11.15.1 Sample extraction

The tables below list the specified US EPA SW-846 methods.

8151A	The soil is extracted and may be derivatised with diazomethane or 2,3,4,5,6-pentafluorobenzyl bromide.
3545A	Pressurised fluid extraction (PFE)

11.15.2 Extract clean-up

3650B	Acid/base partitioning step if required.

11.15.3 Extract analysis

8151A	GC/ECD
8270D	GC/MS

11.16 Phthalate esters

This method is applicable but not limited to analysis of the following phthalate esters:

Bis (2-n-butoxyethyl) phthalate
Bis (2-ethoxyethyl) phthalate
Bis (2-ethylhexyl) phthalate
Bis (2-methoxyethyl) phthalate
Bis (4-methyl-2-pentyl) phthalate
Butyl benzyl phthalate
Diamyl phthalate
Di-n-butyl phthalate
Dicyclohexyl phthalate
Diethyl phthalate
Dihexyl phthalate
Diisobutyl phthalate
Dimethyl phthalate
Dinonyl phthalate
Di-n-octyl phthalate
Hexyl 2-ethylhexyl phthalate

11.16.1 Sample extraction

The table below lists the specified US EPA SW-846 methods.

3545A	Pressurised fluid extraction (PFE)
3540C	• Soxhlet extraction using: • acetone/hexane (1:1) or • dichloromethane/acetone (1:1).

3550C	Ultrasonic extraction* using: **a.** for low concentration (individual compounds <20 mg/kg): • dichloromethane or • dichloromethane/acetone (1:1) or • hexane/acetone (1:1) or • methyl tertiary-butyl ether or • methyl tertiary-butyl ether/methanol (2:1). The solvent system chosen must be shown to give satisfactory, reproducible recovery of analytes spiked into the particular matrix (soil type) under test. Analysts should determine an appropriate concentration limit and ensure that results are based on sample concentrations that do not exceed the instrumental range. **b.** for high concentration (individual compounds >20 mg/kg): • dichloromethane or • hexane.

* Ensure samples don't overheat; consider putting ice packs into ultrasonic bath.

CRC TECHNICAL NOTE 10	End-over-end tumbling/shaking.

11.16.2 Extract clean-up

Note: The analyst should verify that quantitative recovery of phthalates is achieved for whichever clean-up procedure used.

The tables below list the specified US EPA SW-846 methods.

3620C	Florisil column clean-up
3640A	Gel-permeation clean-up

11.16.3 Extract analysis

8061A	GC/ECD
8270D	GC/MS

11.17 Dioxins and furans

11.17.1 Scope and application

This method is applicable but not limited to the analysis of the following PCDDs and PCDFs by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS), or HRGC/high resolution mass spectrometry (HRMS):

- 2,3,7,8 tetrachloro dibenzo-p-dioxin
- 2,3,7,8 tetrachloro dibenzofuran.

11.17.2 Sample extraction

The tables below list the specified US EPA SW-846 methods.

3545A	Pressurised fluid extraction (PFE)
3546	Microwave extraction using hexane: acetone (1:1)
8290A	• Soxhlet and Dean-Stark separator extraction using toluene (a) for low concentration (individual compounds (<1 µ g/kg): - toluene
8280B	• Soxhlet and Dean-Stark separator extraction using toluene (b) for high concentration (individual compounds (>1 µg/kg): - toluene

11.17.3 Extract clean-up

Methods for the clean-up of some co-extracts/analytes are suggested below.

8280B	Acid/base clean-up followed by: • silica gel column clean-up • alumina clean-up • carbon clean-up.

Note: Acid base clean-up may not be necessary for uncoloured extracts.

11.17.4 Extract analysis

8280B	PCDDs and PCDFs by HRGC/LRMS. This method applies to reporting of total concentration of TCDD/PCDF in a given level of chlorination. Complete chromatographic separation of all 210 isomers is not possible under stated instrumental conditions. Quantitation limits are greater than 1 µ g/kg of solid (parts per billion).

8290A	PCDDs and PCDFs by HRGC/HRMS. This method applies to reporting individual concentration of tetra through to octachlorinated TCDD/PCDF homologues. Quantitation limits are less than 1 µ g/kg of solid (parts per billion). Sensitivity of method is dependent on level of interference in matrix.
1613B	Isotope dilution. High resolution GC/MS.

12 Leachable contaminants

12.1 Scope and application

The leachability characteristics of a contaminant can be used to help predict the likely impact it will have whether the soil is left on site, proposed for re-use or intended for disposal.

Contaminants in soil can leach into groundwater under certain conditions, depending on the local chemistry and geology of a site; leachability is particularly affected by soil pH, contaminant solubility and redox conditions. These parameters are not controlled in leaching tests but should be recorded from field tests, and other laboratory tests, to ensure that leachability test results can be compared accordingly.

A variety of leaching tests are available, and it is important to specifically test leachability in soil under conditions approximating those found in the field or the proposed end-use environment.

Leachability testing can be of two types:

- batch leaching (or static extraction tests): equilibrium based
- dynamic leaching: column and diffusion tests.

Generally, batch tests have a much shorter duration than dynamic tests; however, the latter may give a better representation of contaminant leaching. Batch extraction protocols assume that a steady state condition is achieved by the end of the test.

All methods are designed to simulate leaching conditions in the environment and thus estimate the likely availability of pollutants. The choice of leaching reagent should be based on the environmental conditions to which the soil or wastes are likely to be exposed — ideally using actual surface and groundwater from the relevant site.

The two most relevant leaching tests for Australian conditions are:

- Australian standard leaching procedure (ASLP) as per Australian standards 4439.1 (AS 4439.1-1999), 4439.2 (AS 4439.2-1997) and 4439.3 (AS 4439.3-1997)
- toxicity characteristic leaching procedure (TCLP) as per US EPA method 1311, (US EPA SW-846, Method 1311).

The ASLP allows a wide range of leaching reagents to be used and is generally the most appropriate leach test to cover a range of conditions encountered in contaminated site management in Australia, whether soil is to remain on site or be moved.

The exception is where contaminated soil is to be disposed of at a municipal landfill and mixed with municipal solid waste (MSW), in which case TCLP is more appropriate.

The TCLP was designed to simulate conditions in a MSW landfill. It is not suitable for soil that is NOT intended to be mixed with MSW.

Leachable organics (volatile and semi-volatile), metals and anions (except cyanide) may be determined using ASLP (or TCLP if permitted by local regulatory guidelines). The zero headspace methods for ASLP (AS 4439.2-1997) and TCLP (US EPA SW-846, Method 1311) list the volatile compounds of concern. The ASLP procedure lists an 'informative' group of volatile compounds, but does not preclude others. The TCLP (US EPA SW-846, Method 1311) lists benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, methyl ethyl ketone, tetrachloroethylene and vinyl chloride as toxicity characteristic constituents at a contaminated site.

Leachable cyanide may be determined by the synthetic precipitation leaching procedure (US EPA SW-846, Method 1312) using de-ionised water leach fluid or by the ASLP methods described in AS 4439.2-1997, also using distilled or de-ionised water as the leach fluid.

Leachates collected from the leaching procedures should be analysed using methods listed for waters and wastewaters.

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or on CD ROM from:

National Technical Information Service (NTIS), US Dept of Commerce
5285 Port Royal Rd, SPRINGFIELD, VA 22161, USA
Tel 703-605-6000 (outside continental US).

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14 Appendix 1: CRC Care Technical Report Nº 10 - Health screening levels for petroleum hydrocarbons in soil and groundwater (Summary Report)

14.1 Introduction

14.1.1 Project background

The Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) research program includes Subprogram 1.4 – Risk Characterisation and Communication. This subprogram includes the objective of preparing health screening levels (HSLs) for hydrocarbons in soil and groundwater. This summary presents the derived petroleum HSLs for Australian assessments. The tables in Schedule B1 contain a summary of the derived HSLs for petroleum hydrocarbons for different land uses and media (soil vapour, groundwater and soil). The accompanying text in this document and table notes must be read in conjunction with the HSLs which highlight the key limitations of the HSLs. The assumptions and methodology used to derive the HSLs are the outcome of extensive discussion within the Australian regulator, industry and consultant community. Further information is provided in Section 2 on the application of the HSLs.

14.1.2 References

The detailed methodologies and assumptions used in the development and application of HSLs for petroleum hydrocarbons are presented in the following documents:

- Friebel, E & Nadebaum, P 2010, Health screening levels for petroleum hydrocarbons in soil and groundwater. Part 1: Technical development document (DRAFT), Technical Report no. 10, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.
- Friebel, E & Nadebaum, P 2010, Health screening levels for petroleum hydrocarbons in soil and groundwater. Part 2: Application document (DRAFT), Technical Report no. 10, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

It is recommended that these documents be referred to for technical details on the key assumptions and limitations of the derived screening levels and on their application and use. Section 2 is a summary of the key considerations in the application of the HSLs.

Additional references important to the application of the HSLs are:

- Friebel, E & Nadebaum, P 2010, Health screening levels for petroleum hydrocarbons in soil and groundwater. Part 3: Sensitivity assessment (DRAFT), Technical Report no. 10, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.
- Friebel, E & Nadebaum, P (in preparation), Health screening levels for petroleum hydrocarbons in soil and groundwater. Part 4: Extension model, Technical Report no. 10, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.
- Davis, GB, Patterson, BM & Trefry, MG 2009, Biodegradation of petroleum *hydrocarbon vapours*, Technical Report no. 12, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.
- Davis, GB, Wright, J & Patterson, BM 2009, Field assessment of vapours, Technical Report no. 13, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia

14.2 Application of HSLs

HSLs have been derived for soil vapour, groundwater and soil for petroleum hydrocarbons (attached). The approach taken in the development of the HSLs has sought to set a combination of assumptions and parameters that correspond to the reasonable maximum exposure that can be expected, to be protective of human health for a range of scenarios. Users of the screening levels should consider whether their site situation falls within the range of conditions that has been assumed; if this is not the case the HSLs may not be protective and a more detailed consideration of the site-specific situation should be carried out.

The HSLs should only be directly applied to petroleum contamination sources and not to pure compound solvents, as solubility limits incorporated into the HSLs were derived based on typical compositions of petrol and diesel. The HSLs may be applied to other fuel types (e.g. kerosene, aviation fuel and fuel oil); however, confirmation of aliphatic/aromatic speciation (80:20) is required to confirm their applicability.

There are a number of important considerations when applying the HSLs; some are discussed in this section. The HSL application document (Friebel & Nadebaum 2010 – Part 2) should be referred to for detailed information.

Maximum soil vapour from soil and groundwater sources

- HSLs for vapour intrusion from soil (see Table 1A(3). HSLs soil (mg/kg) in Schedule B1) and groundwater (see Table 1A(4). HSLs groundwater (mg/L) in Schedule B1) sources are limited by estimates of chemical solubilities from petroleum mixtures. Soil and groundwater HSLs have been based on the three-phase equilibrium theory, and the soil vapour is limited by the maximum solubility limit of the chemical in the pore water phase or groundwater. The soil saturation concentration (Csat) is the calculated bulk soil concentration where pore water is at the solubility limit and soil vapour is at its maximum. Where it is determined that a soil concentration greater than Csat (or a groundwater concentration greater than solubility limit) is the calculated HSL, this means that the soil vapour in the soil or above groundwater cannot result in an unacceptable vapour risk for that given scenario, and hence no HSL is presented. In Tables 2 and 3, this is denoted by 'NL'.
- For soil vapour HSLs (see Table 1A(5). HSLs soil gas (mg/m^3) in Schedule B1) maximum soil vapour concentrations have been based on vapour pressures of individual chemicals, and the ideal gas law. Soil vapour HSLs that exceed the maximums cannot result in an unacceptable vapour risk for that given scenario, and hence no HSL is presented. In Table 1, this is denoted by 'NL'.

Appropriate sampling

- When considering the appropriate media for sampling, consideration needs to be given to accuracy and representativeness of the measurement, and needs to be considered on a site-by-site basis.
- Soil vapour measurements may be considered to be a more accurate assessment of vapour risks than measurements from bulk soil or groundwater. However measurement of soil vapour is not always appropriate or possible, such as during validation of excavation pits prior to backfilling.
- Other issues may arise for soil vapour measurements in redevelopment sites where the proposed building does not exist and the source in question is near surface where soil vapour measurements may be subject to atmospheric and meteorological influence.

Appropriate land use and exposure scenarios

- The selected land use must be considered. For example, HSLs derived for commercial/industrial land use (HSL-D) assume adults are exposed during the work day, and cannot be applied to land use settings where there may be prolonged exposure to more sensitive receptors, such as children in schools or childcare centres, inpatients or residents in health care facilities, nursing homes or hospitals or other similar land use that may be permitted under a commercial or industrial zoning.
- Residential use has been subdivided into low-density (HSL-A, access to soils) and high-density (HSL-B, limited access to soils). Where there is access to surface soils, HSLs for direct contact in addition to HSLs based on vapour need to be considered (see Table 1A(6). HSLs direct soil contact (mg/kg))
- Where access to soils is unlikely, such as soils at depth, only HSLs based on vapour intrusion need be considered.
- Land use setting for vapour intrusion into high density residential building is based on occupation of ground floor. If residents occupy ground floor apartments, HSL-B should be used. If ground floor consists of commercial properties, HSL-D should be used. If building contains basement car park, commercial use (HSL-D) should be applied.
- The HSLs only consider direct contact with soils and vapour intrusion. Consideration has not been given to health risk associated with extraction and use of groundwater. If a groundwater bore is impacted by a petroleum source, the HSLs do not consider the contribution of risk from this exposure route and a sitespecific risk assessment on the combined risk scenario should be considered.

Appropriate soil type

- The HSLs assume a homogeneous soil type. The dominating soil type should be used when assessing contaminated sites. The sand/silt/clay content, as well as moisture content and air porosity, needs to be assessed and the appropriate soil type category carefully selected. The categories for soil are:

  Sand (sand, sandy clay, sandy clay loam, sandy loam, loamy sand, loam, sandy silt and silty sand)

  Silt (silt, silty clay and silty clay loam)

  Clay (clay, clay loam and silt loam)
- If the soil type varies with depth or location, then this needs to be considered. For example, the backfill associated with underground storage tanks (USTs) that have been removed and cleaned up can contain backfill material different to the in-situ soil.

Contamination sources

- As previously mentioned, soil and groundwater HSLs for vapour intrusion have been developed based on typical petroleum mixtures and consider the solubility limits of petroleum mixtures. HSLs cannot be applied to non-petroleum sources such as pure solvents or gasworks wastes, where solubility limits are much higher. To assess chemicals from non-petroleum sources the appropriate method is described in the application document (Friebel & Nadebaum 2010 – Part 2).
- The 95% upper confidence limit (UCL) of the mean soil concentration may be used (or other appropriate statistical method) to compare with the HSLs; however, the sample concentrations used for the calculation of the mean must be relevant to the area of the property where the exposure is likely to occur. This is particularly important for large commercial sites, such as industrial/commercial complexes, where an individual may only be exposed in a small section of land (such as a small shop).

The same situation applies for large site redevelopments, which result in subdivision into residential lots. In this case the statistical mean based on sitewide data may not be representative and concentrations representative of localised areas relevant to potential exposure should be considered.

- When comparing groundwater monitoring results to HSLs consideration should be given to the maximum reported concentration, or a concentration that represents the likely exposure for a given receptor. Limited number of groundwater wells makes statistical analysis unsuitable. Consideration of groundwater trends is also important, i.e. is the concentration increasing or decreasing.
- Soil vapour HSLs should be compared to measurements of vapour sources and soil vapour above sources, and hence measurements should be taken as laterally close as possible to the soil or groundwater source. Soil vapour measurements require consideration of where the sample is taken, the current state of the site and the future state of the site. Shallow soil-gas measurements (less than 1 m) in open space areas may be subject to influence of their surroundings such as weather conditions and moisture. Nested soil vapour samples of varying depths can be useful to assess the source and show the change of soil vapour concentration with depth, potentially highlighting where degradation of vapours is occurring.
- Groundwater and soil vapour HSLs have been derived assuming a non-depleting source (i.e. infinite source). Soil HSLs for vapour intrusion have been based on a finite source model with an initial contamination layer thickness of 2 m.

Shallow groundwater

- Groundwater HSLs have not been derived for shallow groundwater (i.e. shallower than 2m) where direct contact with contaminated water is possible through shallow excavations. For vapour intrusion into a building, sub-slab soil vapour measurements may be used as a preferred option.

Mixtures

- The HSLs for TPH fractions are based on a composition typical of petrol for lighter chain hydrocarbons and diesel fuel for heavier chain hydrocarbons.
- If carcinogenic PAHs including benzo(a)pyrene are identified at a site, these concentrations should be compared with the appropriate health investigation levels (HIL) presented in the NEPM.
- Fuel additives such as MTBE have not been included in the derivation of HSLs. If such chemicals are identified in the site contamination assessment, then a sitespecific assessment should be carried out.
- HSLs have been derived for indicator chemicals and TPH fractions assuming that the contamination comprises petroleum hydrocarbons and is derived from petrol and diesel fuels. If non-petroleum contaminants are identified at the site, then the potential for cumulative effects of chemicals should be considered. The effect of ethanol concentration greater than 10% in the fuels on the HSLs is currently unclear.

Application depths

- The applicable depth range for the sample should be chosen based on the sample location, whether it is soil or groundwater. For soil vapour, if the measurement is taken from groundwater headspace (i.e. vapour from within the groundwater well in equilibrium with the groundwater), then the applicable depth should be the groundwater table depth.
- For vapour intrusion into buildings the depth to contamination should be considered relative to the underside of the building slab. Therefore when considering basements, 0 m is the location directly under the basement floor. The location considered should be where the soil touches the underside of the concrete slab, not the footings.

- Soil HSLs for direct contact (see Table 1A(6). HSLs direct soil contact (mg/kg) in Schedule B1) should be applied where direct contact is deemed likely, such as surface soil (i.e. surface to 1 m). At uncontrolled sites (e.g. low-density residential) where there may be bulk soil movement, such as excavation associated with building works, a swimming pool or a cellar, contaminated soil at depth may be relocated to the surface of the site. For such sites, consideration may be given to use of HSLs for direct contact and HSLs for vapour intrusion from 0 to <1m, for deeper soils.

Adjustment to reflect field observations

- Soil HSLs for vapour intrusion (see Table 1A(3). HSLs soil (mg/kg) in Schedule B1) incorporate an adjustment factor of 10 to the vapour phase partitioning to reflect the differences observed between theoretical estimates of soil vapour partitioning and field measurements (refer to Friebel & Nadebaum 2010 – Part 1 for further information). This does not apply to soil HSLs for direct contact(see Table 1A(6). HSLs direct soil contact (mg/kg) in Schedule B1)).

Vapour biodegradation

- Vapour biodegradation has not been included as a default assumption in the derivation of HSLs for soil (see Table 1A(3). HSLs soil (mg/kg) in Schedule B1), groundwater (see Table 1A(4). HSLs groundwater (mg/L) in Schedule B1) or soil vapour (see Table 1A(5). HSLs soil gas (mg/m^3) in Schedule B1).
- Davis, Patterson & Trefry (2009) (CRC CARE Technical Report no. 12) report that for petroleum hydrocarbons, emission reduction factors may be applied to vapour HSLs due to vapour degradation under specific circumstances. This may involve a reduction factor of 10 or 100 for sites where the slab area is small and the presence of oxygen in soil is indicated. For further details refer to Section 7.4 of the technical development document (Friebel & Nadebaum 2010 – Part 1). Guidance on the field assessment of vapours is presented in Davis, Wright & Patterson (2009) (CRC CARE Technical Report no. 13). This document outlines the advantages and disadvantages of a range of vapour sampling and analysis approaches. It is recommended that these reports be referred to before applying adjustments for vapour biodegradation.

Other considerations

- Even though vapour risks may be acceptable when the HSL exceeds the soil saturation limit, consideration should be given to the potential for other effects such as the contamination forming a source of unacceptable groundwater pollution. Local regulatory agencies can have specific requirements for the management and clean up of separate phase or mobile hydrocarbons.
- Accepted techniques for sampling and analysis of chemicals (BTEX, TPH and naphthalene) must be applied when determining the concentrations that are to be compared with the soil, groundwater and soil vapour HSLs.
- When HSLs are exceeded it does not automatically indicate an unacceptable risk, and therefore should not automatically be viewed as clean-up criteria, but rather a trigger for further investigation or evaluation of management options.
- Where possible, a multiple lines of evidence approach should be considered when assessing the vapour intrusion pathway.
- If the assumptions underlying the derivation of HSLs are not valid for a specific site then a site specific, higher tier, assessment of vapour intrusion may need to be undertaken. Such a higher tier assessment may include different assumptions and/or different parameter values as long as these are adequately justified based on site-specific data (refer to the application document (Friebel & Nadebaum 2010 – Part 2)).

15 Appendix 2: Determination of total recoverable hydrocarbons (TRH) in soil

This material has been adapted from procedures developed by the TPH Working Group convened by CRC CARE in 2009. References used include:

- CRC CARE 2009, *Health screening levels for petroleum hydrocarbons in soil and groundwater*, Technical note 10, Cooperative Research Centre for Contamination Assessment & Remediation of Environment, Adelaide, Australia.
- US EPA, Method 1664: n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGTHEM; Non-polar Material) by Extraction and Gravimetry, Revision A, 1999, US EPA Office of Water.

15.1 Volatile (C_6 – C_{10}) and semi-volatile (>C_{10} - C_{40}) TRH

These methods can be used to determine TRHs in soil by gas chromatography with an appropriate detector. The term 'TRH' is equivalent to the historically reported 'TPH'.

Method A1 can determine volatile TRH (vTRH) and can be used to investigate sites contaminated with petrol, other light fuels and petroleum-based solvents.

Method A2 can determine semi-volatile TRH and can be used to investigate sites contaminated with diesel, other petroleum fuels, mineral oil and petroleum-based solvents.

The methods are performance-based and designed to be rapid and economical. To obtain consistent and reliable results they must be carried out by experienced analysts trained in the operation, maintenance and troubleshooting of GC instrumentation and in interpretation of gas chromatograms.

This section describes the general principles common to both methods, including quality control and method validation procedures.

15.1.1 Definitions and shortened forms

ASE© Accelerated solvent extraction (pressurised fluid extraction)

BTEX Benzene, toluene, ethylbenzene & xylenes

DCM Dichloromethane, also called methylene chloride

DW Dry weight i.e. (weight of dried sample) / (weight of total sample). Expressed as a percentage (%) of the total weight.

FID Flame ionisation detector (used with GC). The FID is a non-specific detector which responds to almost all organic compounds

GC Gas chromatography

HC Hydrocarbon(s)

Internal standard Internal standards are added to each final extract solution, after all extraction, clean-up and concentration steps. 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.

MS Mass spectrometer

nC Normal alkane carbon

PAH Polycyclic aromatic hydrocarbons

PID Photo ionisation detector

Purge and trap gas chromatography A gas chromatography procedure in which analytes are purged from the sample by a stream of inert gas and subsequently concentrated onto a suitable absorbent. The components are desorbed then analysed by gas chromatography.

SPC Solid phase cartridge

Surrogate Surrogate spikes are known additions to each sample, blank and matrix spike or reference sample analysis, of compounds which are similar to the analytes of interest in terms of extraction, recovery through clean-up procedures and response to chromatography or other determination. A surrogate is not expected to be found in real samples; will not interfere with quantification of any analyte of interest and may be separately and independently quantified by virtue of, for example, chromatographic separation or production of different mass ions in a GC/MS system.

TPH Total petroleum hydrocarbons

TRH Total recoverable hydrocarbons**.** Those compounds which are extractable into the solvent and elute from a GC column under the conditions specified in the test method. The term 'TRH: total recoverable hydrocarbons' should be used when referring to data generated using this test method where no clean-up is employed.

If silica cleanup is employed, the results must be qualified as 'TRH - silica'.

vTRH Volatile TRH

15.1.2 Quality control considerations

Standard NEPM quality controls are required to ensure the correct performance of these methods. Additional quality control measures are a calibration verification standard (CVS) - consisting of a hydrocarbon product mix - and a laboratory control sample (LCS) - consisting of a suitable hydrocarbon product mix. Ideally, the LCS should be spiked with hydrocarbons that test all fractions reported.

- Calibration verification standard (CVS) – A known quantity of hydrocarbon product(s) is/are dissolved in extraction solvent. This standard must contain hydrocarbons covering the required hydrocarbon fractions being analysed and serve as a check on the GC system and quantification procedure. This calibration verification standard should be between 80 and 120% of the expected concentration in the sample. This can be run once per sequence or 24 hour period.
- Laboratory control sample (LCS) - As a minimum, a laboratory control sample must be run with each batch of 20 samples. This quality control sample must be processed through the entire analytical method and reported with the data. The LCS is a clean soil fortified with the same hydrocarbon product mix as used for the CVS, or a reference sample with a consensus hydrocarbon value. Recovery of product should be checked by analysing either ethanol-free petrol or any other suitable product with predominant hydrocarbons in the nC_6 – nC_{10} range. The calculated LCS concentration should be between 70 and 130% of the expected concentration or a recovery range established by ongoing quality control charts.

15.1.3 Method validation

The methods must be validated by each laboratory using them, in accord with this NEPM Schedule. Some method validation parameters require particular attention:

15.1.3.1 Hydrocarbon product linearity

Establish linearity of the detector response using hydrocarbon products that cover the particular hydrocarbon fraction (for example, ethanol-free petrol for Method A1 (analysis of volatiles), or a mix of diesel and motor oil for Method A2, analysis of semi-volatiles). Linearity must be within 15% in each of the calibrated carbon ranges. As a general principle, the peak height of the largest product component in a fraction should not exceed the peak height of the single n-alkane in the highest level calibration standard.

15.1.3.2 Product standard reference materials

A reference hydrocarbon product(s) must be prepared and analysed. The products(s) must cover the range of hydrocarbon fractions specified in this method. The product or products should be well characterised such that the quantitative composition of the relevant fractions is known. This allows the assignment of a portion of a known quantity of this product to a particular fraction. This solution can then be ideally used as the CVS for ongoing quality control.

Accuracy of the method must be established by obtaining acceptable recoveries for hydrocarbons from a certified reference material (i.e. soil contaminated with hydrocarbons).

15.1.3.3 Proficiency studies

Ongoing participation in relevant proficiency studies is required to validate this method.

15.2 Method A1: Determination of volatile TRH: TRH C_6 – C_{10}

15.2.1 Scope and application

This method is applicable to the determination of hydrocarbons eluting between nC6 and nC10 alkanes, inclusive of BTEX. Target compound analysis can occur simultaneously when running this method, provided that suitable specific detectors are employed, e.g. PID for aromatic compounds, or MS.

NB: Semi-volatile hydrocarbons with higher boiling points must be analysed by the TRH semi-volatile method (see Method A2 below (Section 13.3)and Section 11.13).

15.2.1.1 Limitations

- This method does not distinguish between petrogenic and biogenic compounds or synthetic compounds, such as chlorinated solvents; it measures the *total* recoverable hydrocarbons present, hence it is designated TRH.
- Excess moisture in sample: the method requires extraction of the sample with methanol which is soluble in water. Excess moisture can dilute the extraction solvent, increasing the solvent volume thus diluting the extract.
- High organic carbon content in sample: methanol is a relatively weak solvent for non-polar compounds. Volatile analytes may be retained by matrices containing high organic carbon levels. Surrogates added to extractions may preferably partition onto the carbon matrix.

15.2.1.2 Interferences

The method is subject to certain interferences including:

- highly contaminated samples may cause a carry-over on the instrument
- laboratory background including ambient air, carry-over and contaminated soils.

15.2.1.3 Principle

A soil sample (≥ 5 g) is extracted with a sufficient volume of methanol, then the methanol is separated from the soil and added to a purging vessel or other equivalent apparatus for determination of volatile compounds, using FID or MS in scan mode.

15.2.2 Method

15.2.2.1 Apparatus

- A gas chromatograph with appropriate detector for hydrocarbon determination.
- Columns suitable for volatiles, as specified in US EPA Method 8260B (latest version).

15.2.2.2 Reagents and standards

Reagents

Unless otherwise specified, all reagents shall be of analytical grade (AR) and all solvents of chromatography grade. Chromatography grade methanol and organic-free water are recommended, and ultra pure carrier gas for gas chromatography.

Standards

Internal standard

This solution comprises a suitable compound dissolved in methanol to a suggested concentration of 10 mg/L and should be stored at 4°C. Suitable compounds are specified in US EPA Method 8260B.

Surrogate standard

This standard comprises a methanol solution containing at least one surrogate compound. Suitable compounds include 4-bromofluorobenzene, dibromofluoromethane, toluene-d_8. It should be stored at 4°C.

Calibration standard solutions

nC6 – nC10 TRH Standard (standards for mass selective detector or flame ionisation detector).

Owing to the differential responses of mass spectrometric detectors towards aliphatic and aromatic compounds, it is essential that the standard contain representatives of both groups.

This standard should therefore consist of about **40% aromatic and 60% aliphatic target analytes, to be representative of a typical Australian fuel**. The aromatic compounds shall comprise the components of BTEX. The aliphatics shall comprise equal proportions of all n-alkanes in the C6 to C10 range.

These solutions are stable for 6 months when stored at <6°C with minimum headspace and away from all possible sources of contamination.

Note:

- If a client requests a different fraction split, the relevant compounds shall be represented in the calibration standard solution.
- While it may be possible to store and use the stock solutions for longer than 12 months after preparation, the laboratory should assure itself of the stability of the solution by carrying out regular checks of the concentration of the analyte. The laboratory should retain records to confirm the stability of the solutions.

Calibration verification standard solution

Calibration performance should be assessed against ethanol-free petrol or any other suitable product with predominant hydrocarbons in the nC_6 –nC_{10} range used to check validity of the calibration curve.

The product should be well characterised such that the quantitative composition of the relevant fractions is known. This allows the assignment of a portion of a known quantity of this product to a particular fraction.

Calibration standards

Initial calibration

This involves analysis of at least five different concentrations covering the working range of the instrument used. Extrapolation of response curve above the highest calibration level is not recommended. Initial calibration is run at the beginning of each analytical sequence.

Procedure

1. Open the sample jar quickly, scrape off top 1 cm sample and discard. Remove all extraneous material (grass, pebbles, etc) from the sample. Obtain subsample by driving an inert coring device (PTFE or stainless steel spatula) into the sample and rapidly transfer a minimum of 5 grams into a tared extraction vessel. Record the weight (W).
2. Add methanol (at a minimum ratio of 1:2 sample:solvent) and appropriate amount of surrogate standard solution in order to produce final surrogate concentration at about mid-point of the calibration range, taking further dilutions into consideration.
3. Shake extract about 30 minutes using end-over-end tumbler, orbital shaker or ultrasonic bath. Allow to settle. Clay samples must be completely disintegrated before an aliquot is taken for analysis.
4. Analyse an aliquot of methanol extract using an appropriate instrument for hydrocarbon analysis. If an internal standard is used, it should be included with the methanol extract transfer. Alternatively, the internal standard may be added automatically by instruments having this capability.

15.2.3 GC Analysis

15.2.3.1 Calibration

At least five calibration standards should be prepared from the relevant calibration standard solution.

- Calibration curve should have a linear regression of >0.99.
- At a minimum, run a daily check of the *lowest calibration standard* and the *midpoint calibration standard* to confirm stability of the calibration curve. Rerun the calibration curve if the low standard deviates by more than 30% from the curve or if the midpoint calibration standard deviates by more than 20% from the curve.
- A CVS is run to check the validity of the calibration curve against a characterised hydrocarbon product.

15.2.3.2 Measurement of test sample

After calibration, carry out the determination on the test samples (field or laboratory methanol extracts). Where the analyst has some prior knowledge regarding the relative concentration of analytes in the samples, the run should be arranged in order of increasing concentration. In the absence of such information and if samples with high concentration of analytes occur in the middle of a run, the analyst must examine the analytical run for possible carry-over, and re-analyse affected samples, if required.

15.2.4 Calculations

15.2.4.1 Integration of peaks

All peaks in a chromatogram must be integrated and included in the calculation of results. Total area contributed to by the surrogate and internal standards must be excluded from the calculation of the final result.

15.2.4.2 Calculation of vTRH (C_6 – C_{10}) content

Integrate the appropriate chromatogram.

C_6 - C_{10} fraction is integrated from the peak start of the n-C_6 peak to the time corresponding to end of n-C_{10} peak.

The vTRH content is calculated according to the following formula:

$$C = \frac{\text{Area of C in sample}}{1_{SAM}} \times \frac{I_{STD}}{\text{Area of standard}} \times \text{conc. of standard} \times \frac{VF}{MA} \times \frac{ME}{W} \times \frac{100}{100\text{-}\% \text{ moisture}}$$

Where:

C	=	*vTRH in soil (mg/kg)*
VF	=	*Volume of water-methanol extract as analysed by purge and trap.*
MA	=	*Volume of methanol extract transferred into reagent water*
ME	=	*Volume of methanol added to soil/sediment*
W	=	*Weight of soil/sediment analysed*
I_{STD}	=	*Peak area or height produced by internal standard in calibration chromatogram*
I_{SAM}	=	*Peak area or height produced by internal standard in sample chromatogram*
% Moisture	=	*Moisture content of original soil/sediment expressed as %w/w*

The method blank should contain no detectable levels of analytes of interest and results of the method blank should not be subtracted from sample results.

15.3 Method A2 : Determination of semi-volatile TRH: TRH >C10 – C40

15.3.1 Scope and application

The method is applicable to the determination of hydrocarbons eluting between >nC10 and nC40 alkanes. The method extracts target component hydrocarbons such as PAHs. If the presence of PAHs is suspected, target analysis techniques are preferred for risk assessments. Volatile hydrocarbons with lower boiling points than nC10 or heavy petroleum products (boiling points >nC40) will not be quantitatively determined using this method.

Where significant levels of non-TPH interferences are suspected, a silica gel clean-up procedure is included as an optional but recommended clean-up step.

15.3.1.1 Limitations

The method cannot be used to provide quantitative data for the nC6 to nC10 hydrocarbon range, as it allows loss of the most volatile components in the sample mainly during the weighing and chemical drying steps. For quantitative analysis of nC6 to nC10 hydrocarbons, refer to Method A1 and this Schedule.

15.3.1.2 Interferences

- Interferences may be caused by any organic compounds that are soluble in the extracting solvent and that elute from the GC under the conditions used. 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.
- Impurities in the extracting solvent, drying agents and silica will interfere, and can be reduced by the use of high purity solvents. Laboratory blanks must be analysed along with each batch of samples.
- Carry-over from previous highly contaminated samples extracted in the same glassware may cause spurious elevated results, which can be minimised through efficient cleaning of all glassware, syringes, etc.

15.3.1.3 Principle

A soil sample ($\geq$ 10 g) is treated with anhydrous sodium sulphate then extracted into a minimum of 20 mL 1:1 DCM:acetone. The sample is extracted by mechanical end-over-end shaking for a minimum of 1 hour or other suitably validated extraction techniques (ASE©, horn probe ultrasonication, mechanical wrist action shaker or soxhlet extraction). Where non-TPH interferences are suspected, a silica gel treatment step is recommended.

The extract is analysed with a phenyl polymethylsiloxane phase column containing up to 5% polymethylsiloxane using a GC equipped with an FID. The results are reported as amount of hydrocarbon in three defined fractions – >nC10 to nC16, >nC16 to nC34 and >nC34 to nC40.

15.3.2 Method

15.3.2.1 Apparatus

- Gas chromatograph with FID.
- Column: non-polar or semi-polar bonded phase capillary column is strongly recommended (polymethylsiloxane up to 5% phenyl polymethylsiloxane).
- Integrator or computer and integration software.
- Volumetric pipettes and glassware: they should all be regularly calibrated and a calibration record maintained.

15.3.2.2 Reagents and standards

Reagents

All reagents used in this method should be reagent grade or higher.

Dichloromethane (DCM) & acetone should be high purity and give no interference peaks by GC-FID.

Anhydrous sodium sulphate may contain plasticisers leached from plastic storage containers; each batch should be checked before use. A suggested clean-up method is as follows:

1. Spread the sodium sulphate on a metal tray to a depth of less than 2 cm.
2. Ignite in a muffle furnace at 600°C for 1 hour.
3. Cool and store in a sealed metal or glass container.

Silica (e.g. Merck, Silica Gel 60, 70-230 mesh, methods may require a specific mesh size)

Must be appropriately activated to meet the performance requirements of the method. For example, dry at 200–250°C for 24 h minimum and store in a desiccator or tightly sealed container. Deactivate by adding an appropriate weight of reagent grade water and mix thoroughly.

Note: degree of deactivation depends on the constitution of the solvent extract to be cleaned up.

Calibration standards

- The fraction definition standards for this method – and the calibration standards used to quantify the fractions - are nC10, nC16, nC34 & nC40.
- A calibration verification standard consists of hydrocarbon product dissolved in extraction solvent. Products used as calibration verification mixes must cover the applicable carbon ranges of the method.
- Freshly made calibration standards should be checked by GC-FID against the calibration standards currently being used in the TRH method as a check for any gross error in their preparation.

Procedure

- Weigh a minimum of 10 g of sample into a tared vessel.
- Add sufficient amount of anhydrous sodium sulphate to permit drying of sample.
- Add a minimum of 20 mL DCM:acetone (1:1) and extract by end-over-end tumbler for a minimum of 1 hour. Alternative extraction solvent mixes or extraction procedure can be used if results meet method performance criteria.

15.3.2.3 Silica gel clean-up

Quantities of silica gel used will vary with the volume of extract and the suspected concentration of polar substances. The choice of solvent and suitably deactivated silica gel should demonstrate a quantitative recovery of aliphatic and aromatic hydrocarbons between 70 and 130%. When validating a particular procedure, this must be demonstrated to quantitatively remove a typical surrogate polar compound, for example, palmitic or stearic acid.

The procedure described below is for a dispersive sorbent clean-up. Mini-columns or commercial silica solid phase cartridges (SPC) may also be used if comparable method performance criteria can be met.

- Exchange an aliquot of sample extract into a suitable solvent for clean-up. For example, a 1:1 DCM:acetone extract should be exchanged into a solvent other than acetone, to allow for removal of polar substances.
- To the solvent-exchanged extract add an appropriate weight of silica gel. If an empirical determination of bulk density has been made, the weight may be replaced with an appropriate volume.

Mix the extract and silica gel thoroughly (e.g. with vortex mixer) and allow the sorbent to settle before removing a portion of the extract for analysis.

US EPA 3630 C silica clean-up method gives information about clean-up of PAHs, PCBs, OCs and phenols but not specifically for hydrocarbons. On the other hand, US EPA Method 1664 gives silica gel clean-up information specifically for hydrocarbons.

Limitations:

1. Silica gel has a capacity to adsorb polar compounds, at approximately 30 mg per gram of material. Silica may become overloaded if too much polar material is present beyond capacity of silica gel used. In such cases, multiple clean-up steps may be required.
2. Waste sludges containing paint can give anomalous results due to clean-up procedures unable to remove all such unwanted material. Such non polar polymeric materials remaining in a solvent extract can then degrade in the high temperature GC injector producing smaller hydrocarbon molecules recorded as petroleum hydrocarbons. In such situations, alternate clean-up procedures should be investigated, for example, gel permeation chromatography (GPC).
3. Soils high in organic matter may also give false positive results.

15.3.3 GC analysis

The sample should be analysed using a gas chromatograph fitted with a FID.

15.3.3.1 GC conditions

The exact conditions used will vary from laboratory to laboratory.

Injector: a split/splitless injector at >250°C is recommended. The injection liner should be checked and replaced regularly.

Oven: the oven ramp should be a single linear ramp. The final temperature of the oven program should be as high as possible to ensure maximum removal of the higher molecular weight hydrocarbons from the column prior to the next analysis.

Column: the capillary column must be a non-polar to semipolar phase – such as a bonded phase of polydimethylsiloxane containing up to 5% phenyl polydimethylsiloxane.

15.3.3.2 Chromatographic integration

Sample sequence should have adequate solvent blanks run to monitor baseline drift. Samples are integrated by taking a horizontal line from a baseline point after the elution of nC10. The fraction areas are calculated by the software and concentrations determined according to the 'Calculations' section below.

15.3.3.3 GC calibration

Perform calibration and retention time marking for the nC10 to nC40 hydrocarbons using approximately equal weights of nC10, nC16, nC34 and nC40 hydrocarbons dissolved in hexane (toluene can be added to assist dissolution).

- At a minimum, run a 5-point calibration curve using the nC14, nC24 and nC36 hydrocarbons and a blank before analysis begins. Linearity should have a linear regression of >0.99.
- At a minimum, run a daily check of the *lowest calibration standard* and the *midpoint calibration standard* to confirm stability of the calibration curve. Rerun the calibration curve if the low standard deviates by more than 30% from the curve or if the midpoint calibration standard deviates by more than 20% from the curve.

15.3.4 Calculations

Calculation of TRH fractions in a sample:

$$>C_{10} - C_{16} \text{ hydrocarbons (mg/kg)} = \frac{A_{>C_{10}-C_{16}}}{A_{C_{14}}} \times C_{14} \text{ conc} \times \frac{Vol_{ext}}{W} \times F \times \frac{100}{\%DW}$$

$$>C_{16} - C_{34} \text{ hydrocarbons (mg/kg)} = \frac{A_{>C_{16}-C_{34}}}{A_{C_{24}}} \times C_{24} \text{ conc} \times \frac{Vol_{ext}}{W} \times F \times \frac{100}{\%DW}$$

$$>C_{34} - C_{40} \text{ hydrocarbons (mg/kg)} = \frac{A_{>C_{34}-C_{40}}}{A_{C_{36}}} \times C_{36} \text{ conc} \times \frac{Vol_{ext}}{W} \times F \times \frac{100}{\%DW}$$

Where:

$A_{>C10-C16}$	=	*the integration of all area counts from the end of the nC_{10} to the end of the nC_{16} peak*
$A_{>C16-C34}$	=	*the integration of all area counts from the end of the nC_{16} to the end of the nC_{34} peak*
$A_{>C34-C40}$	=	*the integration of all area counts from the end of the nC_{34} to the end of the nC_{40} peak*
C_{14}	=	*concentration of C_{14} standard (mg/litre)*
C_{24}	=	*concentration of C_{24} standard (mg/litre)*
C_{36}	=	*concentration of C_{36} standard (mg/litre)*
Vol_{ext}	=	*Final volume of sample extract (litre)*
F	=	*Dilution factor applied to bring the samples and standards into appropriate peak height range*
W	=	*weight of sample taken (kg)*
% DW	=	*% Dry weight*

16 Shortened forms

ANCE	excess acid neutralizing capacity
ASE©	accelerated solvent extractor
ASLP	Australian standard leaching procedure
APHA	American Public Health Association
ASTM	American Society for Testing & Materials
CRC CARE	Cooperative Research Council for Contamination Assessment and Remediation of the Environment
CRM	certified reference materials
CVS	calibration verification standard
GC	gas chromatography
GC/ECD	GC/electron capture detector
GC/ELCD	GC/ electrolytic conductivity detector
GC/FID	GC/flame-ionisation detector
GC/FPD	GC/flame photometric detector
GC/MCD	GC/microcoulometric detector
GC/MS	GC/mass spectrometry
GC/PID	GC/photo-ionisation detector
GC/NPD	GC/nitrogen-phosphorus (thermionic) detector
HEM	n-Hexane extractable material
HPLC	high-performance liquid chromatography
HPLC/ECD	HPLC/electrochemical detector
HPLC/F	HPLC/fluorescence detector
HPLC/UV	HPLC/ultraviolet detector
HRGC/HRMS	high-resolution gas chromatography/high-resolution mass spectrometry
HRGC/LRMS	high-resolution gas chromatography/low-resolution mass spectrometry
HSL	health screening level
ISO	International Standards Organisation (<www.isostandard.com>)
KD	Kuderna-Danish evaporator
LOD	limit of detection
LOR	limit of reporting
MAH	monocyclic aromatic hydrocarbon
MDL	method detection limit
MS	mass spectrometry
MSW	municipal solid waste

NMI	National Measurement Institute
NATA	National Association of Testing Authorities, Australia
PCBs	polychlorinated biphenyl compounds
pHOX	peroxide pH
PTA	Proficiency Testing Australia
PQL	practical quantitation limit
QA	quality assurance
QC	quality control
RT	retention time
RRT	relative retention time
RSD	relative standard deviation
SD	standard deviation
SGT-HEM	silica gel treated n-hexane extractable material
SPC	solid phase cartridge
SRM	standard reference material
TAA	titratable actual acidity
TPA	titratable peroxide acidity
TCLP	toxicity characteristic leaching procedure
TRH	total recoverable hydrocarbons
US EPA	United States Environmental Protection Agency
VOA	volatile organic analysis
vTRH	volatile total recoverable hydrocarbons