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Schedule B3

GUIDELINE ON

Laboratory Analysis of Potentially Contaminated Soils

Federal Register of Legislative Instruments F2013L00768

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 that 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 that are known to NEPC.

Explanatory note

The following guideline provides general guidance in relation to investigation levels for soil, soil vapour and groundwater in the assessment of site contamination.

This Schedule forms part of the National Environment Protection (Assessment of Site Contamination) Measure 1999 and should be read in conjunction with that document, which includes a policy framework and assessment of site contamination flowchart.

It aims to ensure accuracy and precision in analytical results from the laboratory analysis of potentially contaminated soils. It should be read in conjunction with Schedule B2 of the NEPM.

The original Schedule B3 to the National Environment Protection (Assessment of Site Contamination) Measure 1999 has been repealed and replaced by this document.

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 Environment Protection Authority and CRC CARE.

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Laboratory analysis of contaminated soil

1 Introduction

This guideline is applicable to laboratory analysis of contaminated soils for assessment of site contamination and disposal of contaminated soil. 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.

1.1 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, site assessors
- regulatory licence holders (e.g. for waste management or other statutory processes)
- custodians of waste/sites containing waste.

1.2 Exclusions

Groundwater analyses are beyond the scope of this Schedule.

1.3 Schedule structure

The Schedule provides guidelines on laboratory analysis of potentially contaminated soils, including:

- 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 provides analytical methods for potentially contaminated soils and, in particular, 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, the United States Environmental Protection Agency (US EPA), the American Public Health Association (APHA), the 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 2.5.

Whenever possible, accreditation to ISO 17025 should be obtained for all analytical procedures and matrices for the analytes of concern, from the National Association of Testing Authorities (NATA) or one of its mutual recognition agreement partners.

2.2 Determinative methods

This guideline specifies procedures for extraction and digestion of common contaminants. The inclusion of determinative procedures for identification and quantification of contaminant concentrations in sample extracts and digests for every analyte is outside the scope.

Descriptions of determinative methods are available for analytes in a range of reference documents including Standards Australia and International standards (US EPA SW-846, APHA 2005, ASTM 2008). In selecting an appropriate method for a particular analyte, the analyst needs to consider the chemical characteristics of the final extract and analyte, and the specificity of the detector.

2.3 Philosophy of methods selected

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

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

These circumstances require highly reliable analyses, with analytical data representative of site condition.

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:

1. be simple—procedures should be easy to follow and to perform, using equipment and reagents generally available in most environmental laboratories.
2. be rapid ideally, extraction/digestion and analysis should be sufficiently rapid and non-labour-intensive to enable a large number of samples to be processed within acceptable turnaround times. This should not be at the expense of meaningful analytical results.
3. be 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 US EPA or APHA.
4. 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.
5. be capable of batch or automated analysis—samples should be able to be processed in large batches without being cumbersome; automated analyses are often preferred.
6. be 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.
7. have an appropriate limit of reporting (LOR)—the selected method should have a limit of reporting, where practicable, no greater than 20% of the relevant soil criteria and validated for a variety of soil matrices, including sand, clay and loams.
8. be safe—safety should never be compromised, especially when undertaking large batch processing and handling soils from contaminated sites.

The analytical methods referenced in this guideline have been selected on the basis of having reliability and where possible, ease of use and efficient data turnaround. The methods primarily measure the potentially mobile or bioavailable fraction of contaminants in soil (not necessarily the total residual contaminant concentrations) because many such residual components (for example, those bound to a silicate matrix) pose little immediate threat to human health or the environment.

2.4 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.

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) on the range of soil types and concentrations most likely to be analysed. 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 quantitative data generated by a laboratory that is accredited for the reference method to ISO 17025 by NATA or one of its mutual recognition agreement partners.

The laboratory should document the method performance verification and make the data available for independent audit.

See Section 3.2 for more guidance on method validation.

2.5 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 contaminant distribution at known contaminated sites or monitoring the progress of site clean-up or remediation programs (refer Schedule B2, Section 7.4).

Data from screening tests is not suitable for detailed assessment of contaminated sites or for validating clean-up. These tasks require a high degree of accuracy and reliability and data should 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 should be sufficient for the intended purpose. Therefore screening methods should be evaluated for appropriate analyte specificity, repeatability and reproducibility prior to use.

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

Where non-specific analytical techniques are used, (e.g. gas chromatography (GC) or high performance liquid chromatography (HPLC)), the identity of organic compounds should be confirmed by one of the methods detailed in the NATA Field Application Document ISO/IEC 17025 (NATA 2011). 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. derivation technique).

A mass 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 8260B, Method 8270D) are met:

- the intensities of the characteristic ions of the compound in the sample should maximise in the same scan, or within one scan, as that of the reference calibration check standard
- the relative retention time (RRT) of the sample component is within ±0.06 of the RRT of the reference calibration check standard
- the relative intensities of the characteristic ions (see note immediately below) in the sample check standard.

Note: The characteristic ions are generally defined as the three ions of greatest intensity in the preceding calibration check standard.

2.7 Leachability and bioavailability

Some methods for assessing mobility and availability of soil constituents are based on methods designed for agronomic studies and land surveys (e.g. metal availability, as part of soil nutrient assessment) and hence are only applicable to soils expected to have relatively low contaminant concentrations (e.g. 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.

This Schedule describes two leachability methods for assessing the mobility of common metal contaminants in contaminated site assessments. 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.

See Section 12 for more discussion of methods to assess leachability of soil contaminants.

2.8 Use of laboratory results

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

- samples are collected, transported and received by the laboratory 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 in a timely manner
- 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.

3 Quality assurance and quality control

3.1 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 the application of routine documented procedures to ensure proper sample control, data transfer, instrument calibration, the decisions required to select and properly train all staff, select and maintain equipment, select analytical methods, and the regular scrutiny of all laboratory systems and corrective actions applied forthwith.

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 systems 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) and Standards Australia (AS 2830.1–1985).

3.2 Method validation

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

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 (e.g. 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, in some cases, complete methods—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, or on the most complex soil type likely to be analysed (e.g. clay instead of sand).

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.

The minimum validation data required are:

- Accuracy Precision
- Limit of detection (LOD)and limit of reporting (LOR)
- Linearity (range over which accurate quantification is expected)
- Uncertainty of measurement (MU).

3.2.1 Accuracy

Accuracy is a measure of the closeness of the analytical result to the 'true' value (NATA Technical note 17). When low analyte concentrations are present the results of a reference method may differ by as much as ±30 % of:

- the expected value of a certified reference material (CRM) of similar matrix; or
- the value obtained by another currently-accepted and separately validated quantitative method for the sample matrix.

This is a particular issue when analyte concentrations are less than 10 times the minimum detectable concentration. Apparent lower recoveries than those specified for the method 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 for comparison with this CRM. Otherwise, an alternative CRM should be used.

3.2.1.1 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 (in the form of either a laboratory control sample (LCS), matrix spike or surrogate compound spike).

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 near 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 equivalent concentration to the midpoint 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, then ‘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; some standard methods state that recoveries for *validated* methods can be lower.

’Recovery of the analyte need not be 100%, but the extent of the recovery of the analyte and internal standard should be consistent, precise, and reproducible’ (FDA 2001).

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).

3.2.2 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).

3.2.2.1 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).

3.2.2.2 Reproducibility

This is a measure of the variation in the method results for the same 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 method validation procedure, and are best obtained through inter-laboratory comparisons and proficiency studies.

3.2.2.3 Confidence limit and confidence interval

When results are qualified with standard deviations (SD) or their multiples (for example, ‘x ± SD‘), these are taken to be their confidence limits. This means that a result of 10±4 mg/kg would have confidence limits (CLs) of 6 and 14 mg/kg and a confidence interval (CI) 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 (e.g. ‘95% CI = x ± 2SD‘). Further clarification of these terms may be found in standard statistics texts.

3.2.3 Limits of detection and reporting

3.2.3.1 Method detection limit

The method detection limit (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 (NATA Technical Note 17). It is derived by:

- analysing at least 7 replicates of a sample with a concentration close to the estimated MDL, 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.

3.2.3.2 Limit of Reporting

The limit of reporting (LOR) is the practical quantification limit (PQL), 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 calculated as follows (APHA 2005):

LOR = PQL = 5 x MDL

The LOR should be at or below the relevant HIL, HSL or EIL and should be equal to the lowest calibration standard (as expressed in units of mg/kg of soil sample).

3.3 Laboratory Batch QC procedures

The laboratory should adopt, at a minimum, the 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 Chapter 1: 'Quality Control'.

3.3.1 Process batch and QC interval

For the purposes of QC requirements and QC monitoring intervals, a laboratory process batch is deemed to consist of up to 20 samples that are similar in terms of matrix and test procedure, and are processed as one unit for QC purposes. If more than 20 samples are being processed, they are considered as more than one batch.

3.3.2 Method blank

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

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

Method blank data is reported with the primary sample data, thus enabling the site assessor to assess potential method bias for the relevant analytes.

3.3.3 Laboratory 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 and sample heterogeneity.

Samples reasonably perceived to contain target analytes should be chosen for the duplicate analyses, though samples with obviously high concentrations of interferents—which will likely require subsequent dilution of sample extracts and raised LORs—should not be used for duplicate analysis. There should be at least one duplicate per process batch, or two duplicates if the process batch exceeds 10 samples.

If results show greater than 30% difference, the analyst should review the appropriateness of the method being used.

Duplicate analysis data is reported with the primary sample data, thus enabling the site assessor to assess method precision for the relevant analytes.

3.3.4 Laboratory control sample

A laboratory control sample (LCS) comprises a standard reference material, or a matrix of proven known concentration or a control matrix spiked with all analytes representative of the analyte class. Representative samples of either material should be spiked at concentrations equivalent to the midpoint of the preceding linear calibration or continuing calibration check, upon which sample quantification will be based. Thus the concentrations should be easily quantified and be within the range of concentrations expected for real samples.

The LCS should be from an independent source to the calibration standard, unless an ICV (independent calibration verification) is used to confirm the validity of the primary calibration.

There should be at least one LCS per process batch.

LCS percent recovery data is reported with the primary sample data, thus enabling the site assessor to assess method accuracy for all targeted analytes, as distinct from method accuracy for site-specific soil samples (see Section 3.3.5 Matrix spikes below). The laboratory should use statistically derived quality control limits from ongoing LCS percent recovery data, for all target analytes, and report such QC limits with the sample data.

3.3.5 Matrix spikes

A matrix is the component or substrate (e.g. water, soil) that 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.

Matrix spikes should be added to the analysis portion before extraction or digestion and, in most cases, added at a concentration as close as practicable to the corresponding regulatory level (e.g. the relevant HIL or EIL). 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 LOR.

To avoid differences in matrix effects between sample and spiked sample, the matrix spikes should be added to the same nominal mass of soil sample as that which was analysed for the unspiked sample.

There should be one matrix spike per soil type per process batch.

If the percent recovery of the matrix spike is below the expected analytical method performance, the laboratory should investigate the likely cause and, where a suitable amount of soil mass remains, re-extract and analyse another spiked soil. It may be necessary to use other internal calibration methods (for example, isotope dilution, a modification of the analytical method or alternative analytical methods) to accurately measure the analyte concentration in the extract.

If, after investigation, the matrix spike percent recovery is still below method QC limits then this failed recovery should be reported to the client with an explanation to show the limitations of the method for that particular matrix. An acceptable LCS result may indicate that it is the matrix, not the method, that may be the issue but it is not acceptable to assign poor recovery to matrix effects, without a reasonable investigation.

3.3.6 Surrogate spikes (where appropriate)

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

- extraction efficiency
- recovery through clean-up procedures

- response to chromatography or other determination
- instrumental detector response

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, e.g. chromatographic separation or production of different mass ions in a GC/MS system.

Surrogates 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 organic analyses, for example, chromatographic methods. 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. Surrogate compounds used in analytical methods, normally three per method, should be chosen to monitor the variable method performance of the entire target analyte list.

3.3.7 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, detector response and retention times for chromatographic systems). Internal standards provide a reference against which quantitative data may be corrected for sample-specific variation in instrumental response (for organics analysis only).

For organics analysis, internal standards are normally synthetic deuterated compounds (isotopic analogues) of target compounds. 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 for surrogates, i.e. a similar instrumental response to that of the target compounds, etc.

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

(peak height or area for analyte) : (peak height or area for the referenced internal standard) X (a response factor determined from a preceding calibration standard)

Methods should define specific QC criteria for internal standard response and procedures for analyte quantification where response is observed outside of predefined limits.

3.4 Documentation of validation and QC procedures

All method validation steps (including raw data and data validation assessment) should be recorded and retained while the method is in use. Results of validation procedures should be retained to enable monitoring of method reliability, confidence intervals for analysis results and trends in precision and accuracy over time, or with variation of equipment, source of calibration or analyst.

After completion of analysis of each sample process batch, all documentation relating to the samples and their analysis (including raw data and supporting QC data) should be retained for at least three years (NATA 2011, Section 4.13) 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 questionable result.

This data retention requirement 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.

3.5 Field duplicate and secondary duplicate (split) samples

These field QC processes are implemented by the site assessor rather than the laboratory though laboratories and sample collectors should both be aware of the requirement and purpose.

3.5.1 Field duplicate

Field Duplicate: a blind field replicate sample submitted to the laboratory to provide a check of the precision (repeatability) of the laboratory‘s analysis.

At least 5% of samples (i.e. 1 in 20 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 and coded separately to avoid identification 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.

Data for primary and duplicate is collated and reported as a relative percent difference (RPD) of the mean concentration of both samples. If results show greater than 30% difference, a review should be conducted of the cause (e.g. instrument calibration, extraction efficiency, appropriateness of the method used, etc.).

3.5.2 Secondary duplicate

Secondary Duplicate: a blind field replicate sample submitted to a secondary laboratory (inter-laboratory check sample) to provide a check of the analytical performance of the primary laboratory and specifically, the reproducibility of primary laboratory data.

At least 5% of samples from a site should be homogenised and split, with one duplicate sample set submitted to a secondary laboratory (independently accredited for ISO 17025, by NATA or one of its mutual recognition agreement partners) and the remaining samples submitted to the primary laboratory. The duplicate sample should be submitted independently and coded to avoid identity as a duplicate sample. The client should 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. It is best practice to submit the secondary duplicate (‘check sample‘) directly to the secondary laboratory to minimise time in transit.

Data for primary and duplicate is collated as a relative percent difference (RPD) of the mean concentration determined by both laboratories. Higher variations can be expected for organic analyses compared to inorganic analyses, and for samples with low analyte concentrations or non-homogeneous samples.

If results show greater than 30% difference, a review should be conducted of both laboratories and of the appropriateness of the methods being used.

3.5.3 Replicates for volatile organic compound analysis

For analysis of volatile organic compounds (VOCs), field duplicate and secondary duplicate samples should be created as rapidly as possible by halving the sample and placing each half in a smaller container, compacting and topping up to achieve zero headspace in each, attempting to minimise volatile losses. They should be submitted as soon as possible to the laboratory/ies to prevent loss while in storage or transit.

4 Sample control, preparation and storage

The laboratory should maintain rigorous procedures and documentation for 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; samples should be stored in controlled refrigeration for at least two weeks after issue of analytical data, to enable repeat analysis in case any anomalous results are observed by the laboratory or the site assessor, subsequent to reporting analytical data.

4.1 Sample preparation – general principles

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 accordance with work health and safety requirements.*

Asbestos or acid sulfate soils: This Section does not apply to the sampling and handling of soil containing asbestos or acid sulfate materials. For guidance consult *Analysis of acid sulfate soil—dried samples—methods of test* (AS 4969.0-14-2008/2009) and the *Method for the qualitative identification of asbestos in bulk samples* (AS 4964-2004).

4.2 Sample preparation: non-volatiles and semi-volatiles

4.2.1 Separation and removal of extraneous (non-soil) components

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

Also take a separate weighed portion of the sample to determine moisture content (see Analytical Methods, Section 5 in this Schedule). Report moisture content with the analytical result so that analyte concentrations may be estimated on a 'dry-weight' basis.

As stated previously, the analytes of concern should be the 'available' contaminants, which generally 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 likely if contamination of a site has arisen by importation of contaminated screenings or other large particles.

Any material removed for analysis should be weighed and its proportion relative to the entire sample, and its description, 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.

4.2.2 Homogenising (for non-volatile constituents)

Note: This section only applies to non-volatile samples; samples of volatile contaminants should not be homogenised by stirring, grinding or sieving. Procedures for volatile analytes are described in Section 4.3 below.

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, or some other sub-sample that can provide a well-mixed portion representative of the whole sample. It should be thoroughly disaggregated and mixed using a mortar and pestle, or other appropriate method. If no test requiring the original untreated sample will be needed in future, the entire sample may be homogenised; however, 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.

4.2.3 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. If an excess of moisture would 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 that are suitable, the process involves taking at least 25% by weight or 200 g of the laboratory sample, whichever is the smaller (or other sub-sample that can provide a well-mixed portion representative of the whole sample), and thoroughly grinding and mixing by hand in a mortar and pestle, or using other

appropriate techniques, to obtain a homogeneous sub-sample. Equipment should be thoroughly cleaned between samples, or other systems put in place to ensure no cross-contamination.

For most metals and inorganics, better analytical reproducibility is obtained using air-dried soil (see Section 4.2.4 below). 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 be passed through a 2 mm plastic sieve to remove large soil particles and other extraneous particles—ensure that the sample contains no solid particles distinctly different from the soil, such as fragments of metal or other unusual particles.

Note: Do not grind samples being analysed for metal contaminants, as this can release natural metals from the interior of soil grains that are not normally available.
Store the treated sample in a suitable container.

Clean all equipment to minimise sample cross-contamination; this can be confirmed by analysing equipment rinsates and/or control samples.

4.2.4 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 & Anderson 1983, Bartlett & James 1980, Harry & Alston 1981, Khan & Soltanpour 1978, Leggett & Argyle 1985, Specklin & Baliteau 1989).

The effect of air-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.

Soils for most metals and some other inorganic analytes can be air-dried, and then sieved. However, the procedure described below is not applicable to analysis of volatile constituents—including volatile metallics such as metallic mercury, methyl mercury or tetraethyl lead—or where analytical methods specifically forbid such preparation (e.g. certain leaching tests). Samples for volatile metallics should be homogenised and sub-sampled in the field-moist state.

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

4.2.4.1 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).

4.2.4.2 Grinding of dry sample

Note: Grinding increases the surface area and can give higher results.

Grinding is not recommended for analysing ‘available‘ metal contaminants, as it can release natural metals inside the soil particles that are not normally available.

Where necessary, crush the dry sample 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. Mix the sample as thoroughly as possible.

Take care to avoid contamination during the grinding process, and clean equipment between each sample to prevent cross-contamination. See below. To evaluate decontamination efficiency, the final wash solution should be sampled and analysed (Barth & Mason 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.

WARNING: *Grinding of soils can produce fine dust particles that may present a health hazard if inhaled. Sample grinding, and subsequent handling, should be performed in accordance with work health and safety requirements.*

4.2.4.3 Sieving

Unless impracticable or not recommended for a specific method, the sample portion for analysis should be of a size to pass a 2.0 mm aperture sieve. This may be achieved by grinding, if appropriate.

If small analysis portions (<10 g) are required, or smaller sieve sizes, 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).

If another particle size is chosen, this should be consistently used within an analysis regime and reported with analytical results.

4.2.4.4 Partitioning of dry samples to obtain representative analysis portions

The analysis portion of the dry sample should 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 (e.g. stainless steel) to avoid contamination.

Cone and quarter technique:

a. Spread soil into thin even layer
b. Divide into four quadrants
c. Combine and mix soil from two opposite quadrants.

Repeat steps a. to c. until required quantity of soil is obtained for analysis (including any replicate analyses and extra portions required for quality assurance purposes).

If using mechanical sample divider, use in accord with the manufacturer's instructions.
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.

4.2.4.5 Equipment cleaning during sample preparation (including grinding, sieving and homogenising procedures)

Cleaning procedures will vary according to the analyte/s being determined. Minimum procedures include detergent washing followed by rinsing with deionised water and then oven drying. 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 wash solution should be sampled and analysed to evaluate the decontamination efficiency (Barth & Mason 1984); one final wash sample per process batch or 1 in every 10 samples ground/sieved/processed, whichever is the smaller. Alternatively, treat a well-characterised control soil sample similarly. If there is significant carry-over due to the grinding/sieving process, the results from that process batch may have to be rejected.

4.2.5 Sample Preparation Summary – Non-volatiles and semi-volatiles

Note: Analysis of volatile contaminants such as C_6–C_{10} 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 4.3 below.

All samples (non-volatile and semi-volatile)

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 the smaller, including sufficient amounts for repeat analyses or other analysis on this same sample including moisture content (using field-moist sample).

Field-moist sample analysis e.g. semi-volatiles, analytes for which drying may lead to losses (*Details in S.4.2.3)*	**Dried sample analysis** non-volatiles (*Details in S.4.2.4)*
3. (Intentionally left blank)	3. Dry in oven or air chamber (40±3°C) Sample is dry when the loss in soil mass is not greater than 5% per 24 hours.
4. Grind in clean mortar and pestle to disaggregate soil particles and to produce a homogeneous test sample. *– Where suitable (e.g. for non-volatiles)*	4. Where appropriate *(usually organics, not metals)*, grind to disaggregate the soil particles, using a clean mortar and pestle or using other appropriate techniques, to obtain a homogeneous sub-sample.
5. For 'field-moist'metal samples or other inorganics or non-volatiles that are amenable to sieving (e.g. sandy loam), pass through a 2 mm plastic sieve. Ensure no extraneous particles in sample, otherwise analyse in air dried state.	5. Pass through a mesh sieve (2 mm).
6. Dry a separate sub-sample to determine moisture content (see method in Section 6). Report moisture content with analytical result so that analyte concentrations may be estimated on a 'dry-weight' basis.	6. Weigh the particles >2 mm diameter and set aside for later analysis if required (and to examine for large particles of solid contaminant if necessary).
	7. Partition the (<2 mm diameter) fraction with sample divider (e.g. riffler) or 'cone & quarter' or alternate comparable method. Ensure sufficient soil is obtained to cover all analyses, including repeats and QA. *(See S 4.2.4.4)*
	8. If small analysis portions (<10 g) are required, or smaller sieve sizes, 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).

4.3 Volatile analytes – sample collection and preparation

These guidelines generally do not include instructions for sample collection, with the exception of samples collected for volatile analytes, as the sampling method has a direct bearing on the 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.

For samples requiring analysis of volatiles as well as non-volatiles and/or semi-volatiles, it is recommended that additional, separate samples are taken for the various types of analysis, to allow for volatile analysis to be completed and repeated if necessary on samples which have not been homogenised or otherwise inappropriately treated.

4.3.1 Sample collection

Samples should be collected with minimal sample disturbance and handling to avoid evaporative losses, as detailed in AS 4482.2-1999. Ideally, sampling is carried out using a coring device; however if this is not available, an alternative device such as a trowel may be used. In all cases, the sample-taker should ensure that the sample remains intact and the container is filled as full as possible to ensure minimal headspace and void space and evaporation potential. In many cases, taking duplicate samples is recommended to allow 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 the surface layer unless a very recent chemical spill is being investigated.

Where the sample container will be subsequently opened to obtain a sub-sample for analysis, the dimensions of the original sample core taken should be such as to leave a minimum of void space (headspace, and between core and container walls) in the vessel. 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 pierceable silicone septum caps

or

- one or more wide-mouth glass jars (usually 125 mL or 250 mL) 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 may be used for preliminary screening analysis if desired, the others for analysis by purge and trap.

Once samples are taken, ensure that jar or vial closures are free of soil particles before capping. Samples should be sealed and transported to the laboratory as soon as practicable, under suitable cooling aids (preferably ice bricks or in a refrigerated container) to ensure samples start cooling as soon as possible, and they should be stored in a refrigerator (≤6°C) until 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 & Jaeger 1993).

Note 3: While immersion of samples into methanol on-site is 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 work health and safety implications and is not generally recommended unless so advised by the analyst to meet a specific requirement.

4.3.2 Preliminary screening analysis

Laboratories may perform a preliminary screen 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/250 mL jar sample and transferring to a vial for analysis as in methanol extraction or headspace analysis above.

After sub-sampling, immediately reseal jar and return to refrigerator storage (≤6ºC).

If analysing whole 40 mL vial samples, note pre-sample weight 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 the sample vial as the sparge vessel), or take one or more fresh core samples from the larger jar sample.

If screening results indicate a high analyte level, use the data to predict the required sample mass or methanolic extract dilution needed to achieve sample extract concentration at or near the midpoint of the method calibration range. Note that high concentrations, far exceeding the linear range of the method will normally underestimate true sample concentration.

4.4 Sample storage

To maintain sample integrity, samples should be collected and kept in a container that will not increase or reduce the analyte concentration in the sample (i.e. will not add contaminants or leach them). The sooner the sample is analysed after collection, the more closely the analytical result will reflect the condition of the sample at the time of sampling.

Table 1 below lists the recommended containers, maximum holding times and soil conditions for the analytes included in these guidelines. State regulatory agencies may specify different holding times or container types; in which case the jurisdictional requirements should be followed.

Long-term storage of field-moist samples has the disadvantage of allowing 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 analysed as quickly as possible.

Air-dried or oven-dried samples can easily absorb moisture in storage. Immediately after homogenising and partitioning, the prepared samples should be transferred into clearly labelled and sealed containers and 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.

4.4.1 Holding Times

The holding times in Table 1 are the recommended maximum times before sample extraction. They are taken from a number of sources, and are a guideline only; the integrity of the sample and reliability of results will depend not only on the length of time the sample has been stored, but also on the conditions of sample handling and storage. The effects of storage on sample integrity will be based on the concentration of analyte in the sample, sample temperature, reactions with other compounds that may be present, degradation by microbiological factors, etc. Analytes such as metals and some semi-volatile organics (including PCBs, PAHs) are persistent in the environment and are not likely to change significantly after sampling; analysis slightly outside of these holding times is not likely to cause significant variation in results if samples have been handled and stored correctly. However, all tests should be carried out as soon as practicable after sampling, and according to any jurisdictional requirements.

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

Analyte	Container[c]	Maximum holding time	Sample condition
Moisture content - Moisture content only - Moisture correction	 - P, PTFE or G - As for analyte of interest	 - 14 days - As for analyte of interest	 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 or field-moist
Organic carbon	G with PTFE-lined cap[d]	28 days	Air-dry or field-moist
Metals (except Mercury & Chromium VI)	P, PTFE or G	6 months	Air-dry or field-moist
Mercury & Chromium VI	P (AW)[d]	28 days. For Cr VI, can hold up to 7 days *post-extraction*	Field-moist
Cation exchange capacity, exchangeable cations	P (AW)	28 days	Air-dry or field-moist
Chloride (water-soluble)	P, PTFE or G	28 days	Air-dry or field-moist
Bromide (water-soluble)	P, PTFE or G	28 days	Air-dry or field-moist
Cyanide	P, PTFE or G[d]	14 days	Field-moist
Fluoride	P or G	28 days	Air-dry or field-moist
Sulfur – total	P, PTFE or G	7 days	Air-dry or field-moist
Sulfate	P, PTFE or G	28 days	Air-dry or field-moist
Sulfide	P or G[e]	7 days	Field-moist
Volatile Organics, except for vinyl chloride, styrene, or 2-chloroethyl vinyl ether	G with PTFE-lined lid/septum[f]	14 days	Field-moist
Vinyl chloride, styrene, 2-chloroethyl vinyl ether	G with PTFE-lined lid/septum[f]	7 days	
Semi-volatile organics, except PCBs, dioxins & furans	G with PTFE-lined lid/septum[g]	14 days[h]	Field-moist
PCBs, dioxins & furans	G with PTFE-lined lid/septum[g]	28 days[h]	Field-moist

Notes

a – Recommended maximum time until sample extraction.

b – Sourced from various references including US EPA SW-846 and Australian and international standards

c – Minimum volume of 250 mL. Containers should be free from contamination, either washed as appropriate or use clean food-grade containers.

P = Plastic G = Glass PTFE= polytetrafluoroethylene AW = Acid-washed SR = Solvent rinsed.

d – Store in the dark.

e – Add sufficient 2M zinc acetate to fully cover surface of solid with minimal headspace; refrigerate (<6°C) (see SW-846 Method 5021, Method 9030B).

f – The vials and septa should be washed with soap and water and rinsed with distilled deionised water. After thoroughly cleaning the vials and septa, they should be placed in an oven and dried at 100°C for approximately one hour. Food-grade containers may also be used without the need for cleaning. Containers should be free from contamination.

g – Containers used to collect samples for the determination of semi-volatile organic compounds should be washed with soap and water then rinsed with methanol (or isopropanol) (see US EPA SW846 Chapter 4 Section 4.1.4 for specific instructions on glassware cleaning). Food-grade containers may also be used without the need for cleaning. Containers should be free from contamination.
h – Once the SVOC is extracted, the extract can be held for 40 days.

4.5 Documentation and reporting

4.5.1 Sample receipt report

Upon receipt of sample, laboratories should issue a Sample Receipt Report detailing the condition of samples, including temperature upon receipt (recorded and reported per individual sample delivery container) and sample preservation status, and chain-of-custody details. As well as commencing a record for the future analytical report, this provides an opportunity for the analyst and sample submitter/site investigator to confirm their requirements.

4.5.2 Analytical report

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

(a) Requirements for AS ISO/IEC 17025–2005:

- a title
- the name and address of the analytical laboratory (including accreditation details from NATA or one of its mutual recognition agreement partners)
- 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 name(s), function(s) and signature(s) or equivalent identification of person(s) authorising the test report
- the date of analytical report issue.

Plus

(b) Other relevant information including:

- the date the sample was received
- the name of the person receiving the sample
- a description of the sample
- the sample condition upon receipt; including temperature upon receipt, any broken or leaking containers, inappropriate containers for the analyte, incorrect storage conditions during transit (e.g. sample temperature control)

- brief description of analytical method and equipment used, including pre-treatment procedures and test conditions where appropriate (e.g. whether the sample was homogenised, ground or sieved)
- confidence interval, QC data and LOR
- any bias noted during the analysis or information on the analysis that may affect the interpretation of the result
- the date/s on which sample analysis was commenced and finalised, and whether extraction and/or analysis was conducted within relevant holding times
- information on all laboratories performing analyses (identify any subcontracted samples).

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 in 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.

5 Analytical methods

The following Sections describe 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 VI
halides – bromides, fluoride
non-metals – cyanide, sulfur compounds

organic contaminants:
volatile organics – including MAHs, VHCs, and vTRHs
semi-volatile organics – including PAHs, PCBs, pesticides (OPPs, OCPs, chlorinated herbicides), phenols, phthalate esters, dioxins and furans, TRH and TRH – silica.

leachability

5.1 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‘.

6 Physicochemical analyses

6.1 Soil moisture content

6.1.1 Scope and application

This method (AS 1289.2.1.1-2005) measures the amount of water lost after drying a soil sample (field-moist or air-dried) in an oven (105–110ºC) to constant mass. 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; the oven-dried sample should not be used for other chemical or physical tests as the drying step may affect results of other tests.

6.2 Soil pH

6.2.1 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.

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

The use of 0.01 M calcium chloride extract is recommended where the soil salt content may influence the pH value (Rayment & Higginson 1992, p. 17). 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 should be analysed first.

When assessing acid sulfate soils, consult *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 (pHOX), titratable peroxide acidity (TPA) and excess acid neutralising capacity (ANCE)* (AS 4969.3-2008).

6.2.2 Principle

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

6.3 Electrical conductivity

6.3.1 Scope and application

This method measures the electrical conductivity (EC) 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 & Higginson 1992, p.17). A high soluble salt content may have physical detrimental effects on a soil, compromising its agronomic and structural attributes, for example, increasing 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 should be analysed first.

6.3.2 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.

6.4 Cation exchange capacity and exchangeable cations

6.4.1 Scope and application

Methods in the following table measure the cation exchange capacity (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 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; they 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. Soils heavily contaminated with soluble metals may saturate an extractant's exchangeable sites and may not, by itself, provide a true indication of the soil's exchangeable capacity.

US EPA Method 9081 (US EPA SW-846) 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 the soil's CEC.

6.4.2 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.

6.5 Water-soluble chloride

6.5.1 Scope and application

This method measures water-soluble chloride in soil water extracts (1:5 soil–water) (Rayment & Higginson 1992, p.24–25).

6.5.2 Principle

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

6.5.3 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.

6.6 Organic carbon

6.6.1 Scope and application

This determination (Rayment & Higginson 1992, p. 29), also known 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, microorganisms, 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 & Higginson 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 & Higginson 1992, p. 32).

For organic carbon analysis in acid sulfate 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.

6.6.2 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 (%) = Oxidisable organic carbon (%) x 1.3

7 Metals

7.1 Aqua regia digestible metals

7.1.1 Scope and application

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 bioavailable 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 SW-846 Method 3050B, SW-846 Method 3051A (microwave-assisted digestion) or Method 200.2 may be used as alternatives to this method.

7.1.2 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.

7.2 Acid digestible metals in sediments, sludges and soils

7.2.1 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

7.2.2 Principle

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

7.2.2.1 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.

7.2.2.2 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.

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

7.3.1 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				

7.3.2 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.

7.4 Mercury

7.4.1 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.

7.4.2 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.

7.5 Hexavalent Chromium

7.5.1 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.

7.5.2 Principle

The method uses an alkaline digestion to solubilise both water-soluble and water-insoluble Cr(VI) compounds. The pH should 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.

8 Halides

8.1 Bromide

8.1.1 Scope and application

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

8.1.2 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).

8.2 Fluoride

8.2.1 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 & Gurney 1977, ASTM D3270-00 (2006)).

8.2.2 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.

9 Non-metals (cyanide and sulfur)

9.1 Cyanide (weak acid dissociable)

9.1.1 Scope and application

Free cyanide (defined as the cyanide ion (CN^-) or hydrogen cyanide (HCN)) is only formed in environments that are dominated by weak cyanide–metal complexes (for example, silver cyanide) and dissolved cyanide complexes. The presence of free cyanide in soil and the potential for formation of HCN is complex and depends on the soil pH, ionic strength and complexation.

The HIL has been derived on the basis of free cyanide and it is recognised that the measurement of free cyanide in soil is difficult, due to instability of free cyanide and also the instability of cyanide metal complexes that can produce free cyanide. A cautious approach, (Department of Resources, Energy and Tourism 2008 and ICMI 2009), is to measure not only the free cyanide but also to measure several other dissociable cyanide species that could furnish free cyanide either by dilution or by other natural processes (refer to US EPA method 9016).

The US EPA Weak Acid Dissociable Cyanide (WAD) method is a surrogate (and conservative) measure of free cyanide, due to the difficulty in measuring free CN.

9.1.2 Principle

The US EPA Weak Acid Dissociable Cyanide (WAD) method measures free cyanide plus the cyanide associated with most unstable metal cyanide complexes. The WAD cyanide refers to any species where cyanide is liberated at pH of 4.5. Such species include HCN (aq) and CN^-, the majority of Cu, Cd, Ni, Zn and Ag complexes. If the WAD result conforms to the HIL then the free cyanide level is also in compliance with the HIL.

9.2 Total sulfur

9.2.1 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.

9.2.2 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). Examples include nitric/perchloric acid digestion (Tabatabai & Bremner 1970), sodium hypobromide digestion (Tabatabai & Bremner 1970) and sodium carbonate/sodium peroxide fusion (AOAC 1980).

9.3 Sulfate

9.3.1 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, Tabatabai 1982).

9.3.2 Principle

The sample is shaken in a 1:5 soil:water extract, or in some cases a calcium phosphate solution (500 mg phosphorus/L) (Tabatabai 1982) 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 sulfur.

9.4 Sulfide

9.4.1 Scope and application

This method (US EPA SW-846, Method 9030B) is suitable for soil samples containing 0.2–50 mg/kg of sulfide. It measures 'total' sulfide, 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 should be employed.

9.4.2 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.

10 Organics

The table below lists the US EPA SW-846 methods specified for organics analysis. Use the current or most recent version of the method.

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 photo-ionisation 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	Organophosphorous compounds by GC
8151A	Chlorinated herbicides by GC using methylation or pentafluorobenzylation derivation
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

10.1 Volatile organics

10.1.1 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.

10.1.2 Monocyclic aromatic hydrocarbons

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, ethenylbenzene)	propyl benzene
trimethylbenzenes	cumene

10.1.2.1 Preliminary screening

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

Note 1: Headspace analysis may not be as rigorous or reliable as purge and trap (Method 5035) though it is suitable as a 'screening analysis'.

Note 2: 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.

10.1.2.2 Sample extraction

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

- 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: (≥200 µg/kg, for individual compounds)

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

10.1.2.3 Sample clean-up

Not applicable.

10.1.2.4 Sample analysis

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

8021B	GC/PID
8260B	GC/MS

10.1.3 Volatile halogenated compounds (VHC)

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	Tetrachloroethanes

Bromomethane	Dichlorodifluoromethane	Tetrachloroethene
Carbon tetrachloride	Dichlorethanes	Trichlorobenzenes
Chlorobenzene	Dichlorethene	Trichloroethanes
Chlorodibromomethane	Dichloromethane (methylene chloride)	Trichloroethene
Chloroethane	1,2-Dichloropropane	Trichlorofluoromethane
2-Chloroethanol	1,3-Dichloro-2-propanol	Trichloropropanes
2-Chloroethyl vinyl ether	1,3-Dichloropropene	Vinyl chloride
Chloroform		

10.1.3.1 Sample extraction

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

- 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 (≥200 µg/kg, for individual compounds):

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

10.1.3.2 Sample clean-up

Not applicable.

10.1.3.3 Sample analysis

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

8021B	GC/ELCD
8260B	GC/MS

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

10.1.4 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.

10.1.4.1 Scope

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

10.1.4.2 Sample extraction

Low concentration (<200 µg /kg, for individual compounds):
- 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 (≥200 µg/kg, individual compounds):
- methanol extraction followed by purge and trap technique.

10.1.4.3 Sample clean-up

Not applicable.

10.1.4.4 Sample analysis

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

8260B	GC/MS

10.1.5 Total recoverable hydrocarbons - volatile

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 volatile 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.

10.1.5.1 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.

10.1.5.2 Sample extraction

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

5035	Purge and trap extraction using methanol

10.1.5.3 Extract clean-up

Not required/applicable.

10.1.5.4 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 nC_6–nC_{10}. Details of GC conditions, standards, and procedure for quantification of fractions as suggested by CRC CARE are listed in Appendix 1.

10.2 Semi-volatile organics

10.2.1 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 do not overheat; consider putting ice packs into the ultrasonic bath.

This method should not be used for volatile contaminants.

10.2.2 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
Hexachlorocyclohexane (alpha-HCH)	Hexachlorocyclohexane (beta-HCH)
Hexachlorocyclohexane (gamma-HCH or Lindane)	Hexachlorocyclohexane (delta-HCH)

10.2.2.1 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 should 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 do not overheat.

3545A	Pressurised fluid extraction
CRC CARE TPH TECHNICAL WORKING GROUP	End-over-end tumbling/shaking

10.2.2.2 Extract clean-up

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

10.2.2.3 Extract analysis

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

10.2.3 Polycyclic aromatic hydrocarbons by solvent extraction

10.2.3.1 Scope and application

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		

10.2.3.2 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 should 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 do not overheat.

3545A	Pressurised fluid extraction using dichloromethane/acetone (1:1).
CRC CARE TPH TECHNICAL WORKING GROUP	End-over-end tumbling/shaking

10.2.3.3 Sample clean-up

3630C	Silica gel column clean-up

The extract should be concentrated using a Kuderna Danish (KD) evaporator or other suitable method and solvent exchanged to cyclohexane, prior to clean-up.

10.2.3.4 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.

10.2.4 Polycyclic aromatic hydrocarbons by supercritical fluid extraction

PAHs / supercritical fluid extraction (SFE)

3561	SFE of PAHs

10.2.4.1 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 (75/25)

or

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

10.2.4.2 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

10.2.4.3 Extract analysis

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

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

10.2.5 Organochlorine pesticides and polychlorinated biphenyls

10.2.5.1 Scope and application

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	PCBs (Aroclor 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262).

10.2.5.2 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 should 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 CARE TPH TECHNICAL WORKING GROUP	End-over-end tumbling/shaking

* Ensure samples do not overheat.

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 uses reaction with reactive copper.

10.2.5.3 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)

10.2.6 Organophosphorus pesticides

10.2.6.1 Scope and application

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.		

10.2.6.2 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 should 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 CARE TPH TECHNICAL WORKING GROUP	End-over-end tumbling/shaking

* Ensure samples do not overheat

10.2.6.3 Extract clean-up

This step is 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

10.2.6.4 Sample Analysis

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

10.2.7 Total recoverable hydrocarbons

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. The term has been chosen to avoid confusion with past practices. Where significant levels of non-petroleum hydrocarbon interferences are suspected, a silica gel clean-up is recommended, in which case the analytical report should include a clear statement about this and any relevant interpretation of the chromatogram; the analysis should be referred to as 'TRH–silica'. See Section 11.2.8.1.

When soil contains high levels of non-petroleum-based hydrocarbons (e.g. from heavy manure, compost additions or polymeric materials), inspection of the TRH–silica 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. nuclear magnetic resonance (NMR)—is applied to the extract or a silica gel cleaned sample to improve accuracy.

The analyst should discuss any unusual profiles—and the possibility of interferences from high biogenic hydrocarbon—with the site assessor, before issuing the report.

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 the Health Screening Levels (HSLs) for petroleum hydrocarbon compounds (See Schedule B1).

The TRH method is applicable but not limited to the analysis of hydrocarbons that 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.

10.2.8 Total recoverable hydrocarbons by solvent extraction

10.2.8.1 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 compounds) will not be quantitatively determined using this method.

TRH can be defined as those compounds that are extractable into the solvent and elute from a GC column under the conditions specified in the test method. 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 the extract with silica gel. However, silica gel clean-up may not completely remove non-petroleum hydrocarbon interferences of biological origin.

10.2.8.2 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 CARE TPH TECHNICAL WORKING GROUP	End-over-end tumbling/shaking using: dichloromethane/acetone (1:1) This procedure, specified for TRH, has evolved from work carried out by CRC CARE (2009). Although all components of it are in common use, no validation data are currently available for the entire method.

* Ensure samples do not overheat.

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

10.2.8.3 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 the extract. US EPA Method 3630C gives conditions for silica gel clean-up of PAHs.

10.2.8.4 Extract Analysis

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

8015B	Specifies GC/FID conditions up to nC28 alkanes
	GC/FID conditions for >nC28 alkanes can be obtained from 8270D 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 should be clearly stated on the report. The result will be reported as TRH–silica.

10.2.9 Phenols

10.2.9.1 Scope and application

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

10.2.9.2 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 should 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 do not overheat.

CRC CARE TPH TECHNICAL WORKING GROUP	End-over-end tumbling/shaking.

10.2.9.3 Extract clean-up

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

3630C	Silica gel column clean-up (for samples derived 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

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 un-derived phenols is difficult (e.g. chlorinated and nitro compounds). The GC injector port should be clean and adequately silanised.

10.2.10 Chlorinated herbicides

10.2.10.1 Scope and application

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

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

10.2.10.2 Sample extraction

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

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

10.2.10.3 Extract clean-up

3650B	Acid/base partitioning step if required

10.2.10.4 Extract analysis

8151A	GC/ECD
8270D	GC/MS

10.2.10.5 Extract analysis

8151A	GC/ECD
8270D	GC/MS

10.2.11 Phthalate esters

10.2.11.1 Scope and application

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

10.2.11.2 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 should 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 do not overheat.

CRC CARE TPH TECHNICAL WORKING GROUP	End-over-end tumbling/shaking

10.2.11.3 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

10.2.11.4 Extract analysis

8061A	GC/ECD
8270D	GC/MS

10.2.12 Dioxins and furans

10.2.12.1 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.

10.2.12.2 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 µg/kg): toluene
8280B	Soxhlet and Dean-Stark separator extraction using toluene **(b)** for high concentration (individual compounds (>1µg/kg): toluene

10.2.12.3 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.

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

11 Leachable contaminants

11.1 Scope and application

The leachability characteristics of a contaminant can be used to help predict the likely impact it will have if 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 evaluated 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 though 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 contaminants. 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 (AS4439.1-1999), 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 SW846, 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 deionised water leach fluid or by the ASLP methods described in AS 4439.2-1997, also using distilled or deionised 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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US EPA 2007, SW-846, Method 8081B, *Organochlorine pesticides by* GC, Revision 2, United States Environment Protection Authority.

US EPA 2007, SW-846, Method 8082A, *Polychlorinated biphenyls (PCBs) by GC*, Revision 1, United States Environment Protection Authority.

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US EPA 2007, SW-846, Method 8141B, *Organophosphorus compounds by gas chromatography*, Revision 2, United States Environment Protection Authority.

US EPA 1996, SW-846, 8151A, *Chlorinated herbicides by GC using methylation or pentafluorobenzylation derivatisation*, Revision 1, United States Environment Protection Authority.

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US EPA 2007, SW-846, Method 8270D, *Semivolatile organic compounds by gas chromatography/mass spectrometry (GC/MS)*, Revision 4, United States Environment Protection Authority.

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resolution mass spectrometry (HRGC/HRMS), Revision 1, United States Environment Protection Authority.

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US EPA 1986, SW-846, Method 9081, *Cation-exchange-capacity of soils (sodium acetate)*, Revision 0, United States Environment Protection Authority.

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US EPA 2004, SW-846, Method 9012B, *Total and amenable cyanide (colorimetric, automated UV)*, Revision 2, United States Environment Protection Authority.

US EPA 1992, SW-846, Method 9013 (Appendix to Method 9010), *Cyanide extraction procedure for solids and oils*, Revision 0, United States Environment Protection Authority.

US EPA 2010,SW-846, Method 9016, *Free Cyanide In Water, Soils And Solid Wastes By Microdiffusion*, Revision 0, United States Environment Protection Authority.

13 Appendix 1: Determination of total recoverable hydrocarbons (TRH) in soil

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

- CRC CARE 2009, *Health screening levels for petroleum hydrocarbons in soil and groundwater*, CRC CARE TPH Technical Working Group, Cooperative Research Centre for Contamination Assessment & Remediation of Environment, Adelaide, Australia.
- US EPA 1999, 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, US EPA Office of Water, United States Environment Protection Authority.

13.1 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 should 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.

The term 'TRH–total recoverable hydrocarbons' should be used when referring to data generated using these test methods where no clean-up is employed.

If silica clean-up is employed, the results should be qualified as 'TRH–silica'.

13.1.1 Quality control considerations

Standard quality controls are required to ensure the correct performance of these methods (see Section 4). Quality control measures should include 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 should contain hydrocarbons covering the required hydrocarbon fractions being analysed and serves as a check on the GC system and quantification procedure. The CVS 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 should be run with each batch of 20 samples. This quality control sample should 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.

13.1.2 Method validation

The methods should be validated by each laboratory using them, in accord with this Schedule. Some method validation parameters require particular attention, as below.

13.1.2.1 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 should 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.

13.1.2.2 Product standard reference materials

A reference hydrocarbon product(s) should be prepared and analysed. The products(s) should 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 should be established by obtaining acceptable recoveries for hydrocarbons from a certified reference material (i.e. soil contaminated with hydrocarbons).

13.1.2.3 Proficiency studies

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

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

13.2.1 Scope and application

This method is applicable to the determination of hydrocarbons eluting between nC_6 and nC_{10} 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.

Note: Semi-volatile hydrocarbons with higher boiling points should be analysed by the TRH semi-volatile method (see Method A2 below (Section 14.3) and Section 11.13).

13.2.2 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.

13.2.3 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.

13.2.4 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.

13.2.5 Method

13.2.5.1 Apparatus

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

13.2.5.2 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

nC_6–nC_{10} 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 contains representatives of both groups.

This standard should therefore consist of about 40% aromatic and 60% aliphatic target analytes, in order 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 C_6–C_{10} 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 different fraction split is requested, 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 the response curve above the highest calibration level is not recommended. Initial calibration is run at the beginning of each analytical sequence.

13.2.5.3 Procedure

1. Open the sample jar quickly, scrape off the top 1 cm of sample and discard. Remove all extraneous material (grass, pebbles, etc.) from the sample. Obtain the subsample by driving an inert coring device (PTFE or stainless steel spatula) into the sample and rapidly transfer a minimum of 5 g into a tared extraction vessel. Record the weight.
2. Add methanol (at a minimum ratio of 1:2 sample:solvent) and an appropriate amount of surrogate standard solution in order to produce a final surrogate concentration at about the midpoint of the calibration range, taking further dilutions into consideration.
3. Shake extract for about 30 minutes using end-over-end tumbler, orbital shaker or ultrasonic bath. Allow to settle. Clay samples should be completely disintegrated before an aliquot is taken for analysis. Samples should be maintained in a cool environment to ensure they do not overheat.
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.

13.2.6 GC Analysis

13.2.6.1 Calibration

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

- The 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.

13.2.6.2 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 should examine the analytical run for possible carry-over, and re-analyse affected samples, if required.

13.2.7 Calculations

13.2.7.1 Integration of peaks

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

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

Integrate the appropriate chromatogram.

The C_6–C_{10} fraction is integrated from the peak start of the nC_6 peak to the time corresponding to the end of the nC_{10} peak.

The vTRH content is calculated according to the following formula:

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

where:

C	=	*vTRH in soil (mg/kg)*
VF	=	*Volume of water–methanol extract as analysed by purge and trap (L)*
MA	=	*Volume of methanol extract transferred into reagent water (L)*
ME	=	*Volume of methanol added to soil/sediment (L)*
W	=	*Weight of soil/sediment analysed (kg)*
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.

13.3 Method A2: Determination of semi-volatile TRH: TRH >C_{10} – C_{40}

13.3.1 Scope and application

The method is applicable to the determination of hydrocarbons eluting between >nC_{10} and nC_{40} 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 nC_{10} or heavy petroleum products (boiling points >nC_{40}) 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 (with the results qualified as 'TRH-silica').

13.3.2 Limitations

The method cannot be used to provide quantitative data for the nC_6 to nC_{10} 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 nC_6 to nC_{10} hydrocarbons, refer to Method A1 in this Schedule.

13.3.3 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 should be analysed 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.

13.3.4 Principle

A soil sample (>10 g) is treated with anhydrous sodium sulfate 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 the amount of hydrocarbon in three defined fractions – $>nC_{10}–nC_{16}$, $>nC_{16}–nC_{34}$ and $>nC_{34}–nC_{40}$.

13.3.5 Method

13.3.5.1 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.

13.3.5.2 Reagents and standards

Reagents

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

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

Anhydrous sodium sulfate 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 sulfate on a metal tray to a depth of <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)

Should be appropriately activated to meet the performance requirements of the method. For example, dry at 200–250ºC for 24 hours 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 nC_{10}, nC_{16}, nC_{34} and nC_{40}.
- A calibration verification standard consists of hydrocarbon product dissolved in extraction solvent. Products used as calibration verification mixes should 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.

13.3.5.3 Procedure

- Weigh a minimum of 10 g of sample into a tared vessel.
- Add sufficient amount of anhydrous sodium sulfate 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 procedures can be used if results meet method performance criteria.

13.3.5.4 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 of between 70 and 130%. When validating a particular procedure, this should 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. witha vortex mixer) and allow the sorbent to settle before removing a portion of the extract for analysis.

US EPA 3630C 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 the 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 being 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.

13.3.6 GC analysis

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

13.3.6.1 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 should be a non-polar to semipolar phase—such as a bonded phase of polydimethylsiloxane containing up to 5% phenyl polydimethylsiloxane.

13.3.6.2 Chromatographic integration

The 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 nC_{10}. The fraction areas are calculated by the software and concentrations determined according to the 'Calculations' section below.

13.3.6.3 GC calibration

Perform calibration and retention time marking for the nC_{10} to nC_{40} hydrocarbons using approximately equal weights of nC_{10}, nC_{16}, nC_{34} and nC_{40} hydrocarbons dissolved in hexane (toluene can be added to assist dissolution).

- At a minimum, run a 5-point calibration curve using the nC_{14}, nC_{24} and nC_{36} 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.

13.3.7 Calculations

Calculation of TRH fractions in a sample:

$$>C_{10}–C_{16}\ \text{hydrocarbons (mg/kg)} = A_{>C10\text{-}C16} \times \frac{C_{14\ conc} \times Vol_{ext} \times F \times 100}{A_{C14} \quad W \quad \%DW}$$

$$>C_{16}–C_{34}\ \text{hydrocarbons (mg/kg)} = A_{>C16\text{-}C34} \times \frac{C_{24\ conc} \times Vol_{ext} \times F \times 100}{A_{C24} \quad W \quad \%DW}$$

$$>C_{34}–C_{40}\ \text{hydrocarbons (mg/kg)} = A_{>C34\text{-}C40} \times \frac{C_{36\ conc} \times Vol_{ext} \times F \times 100}{A_{C36} \quad W \quad \%DW}$$

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*

14 Shortened forms

ABC	ambient background concentration
ACL	added contaminant limits
ADWG	*Australian drinking water guidelines*
AM	arithmetic mean
ANCE	excess acid neutralizing capacity
APHA	American Public Health Association
AS	Australian Standard
ASE©	accelerated solvent extractor
ASLP	Australian standard leaching procedure
ASTM	American Society for Testing & Materials
AWQG	*Australian and New Zealand guidelines for fresh and marine water quality*
BTEX	benzene, toluene, ethylbenzene and xylenes
CEC	cation exchange capacity
CI	confidence interval
CL	confidence limit
CRC CARE	Cooperative Research Centre for Contamination Assessment and Remediation of the Environment
CRM	certified reference material
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CVS	calibration verification standard
CWS PHC	*Canada Wide Standard for Petroleum Hydrocarbons (PHCs) in Soil*
DQO	data quality objective
EIL	ecological investigation level
ESL	ecological screening level
FA	fibrous asbestos
FID	flame ionisation detector
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/NPD	GC/nitrogen-phosphorus (thermionic) detector
GC/PID	GC/photo-ionisation detector
GIL	groundwater investigation level
GM	geometric mean
GMRRW	*Guidelines for managing risk in recreational water*
HEM	n-Hexane extractable material
HIL	health investigation level
HPLC	high-performance liquid chromatography
HPLC/ECD	HPLC/electrochemical detector
HPLC/F	HPLC/fluorescence detector
HPLC/MS	HPLC/mass spectrometry
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
ICV	independent calibration verification
IEUBK	Integrated exposure uptake biokinetic model (for lead)
ISO	International Standards Organisation
ISQG	*Interim sediment quality guideline*
KD	Kuderna-Danish evaporator
LCS	Laboratory Control Sample
LNAPL	light non-aqueous phase liquid
LOD	limit of detection
LOEC	lowest observed effect concentration
LOR	limit of reporting
MAH	monocyclic aromatic hydrocarbon
MDL	method detection limit
MS	mass spectrometry
MSW	municipal solid waste
MU	Uncertainty of Measurement
NATA	National Association of Testing Authorities, Australia
NL	non limiting
NMI	National Measurement Institute
NMR	nuclear magnetic resonance
OCP	organochlorine pesticides
OPP	organophosphorus pesticides
(P)	preferred method
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyl compounds
PFE	pressurised fluid extraction
pHox	peroxide pH
PID	photo ionisation detector
PQL	practical quantification limit
PTA	Proficiency Testing Australia
PTFE	polytetrafluoroethylene
QA	quality assurance
QC	quality control
RPD	relative percent difference
RRT	relative retention time
RSD	relative standard deviation
RT	retention time
SD	standard deviation
SFE	supercritical fluid extraction
SGT-HEM	silica gel treated n-hexane extractable material
SPC	solid phase cartridge
SRM	standard reference material
SVOC	semi-volatile organic compounds
TAA	titratable actual acidity
TCLP	toxicity characteristic leaching procedure
TDS	total dissolved solids
TEF	toxicity equivalence factor
TEQ	toxicity equivalent quotient

TOC	total organic carbon
TPA	titratable peroxide acidity
TPH	total petroleum hydrocarbons
TRH	total recoverable hydrocarbons
TRH-silica	total recoverable hydrocarbons - silica gel clean-up employed
UCL	upper confidence limit
US EPA	United States Environmental Protection Agency
VHC	volatile hydrocarbons
VOA	volatile organic analysis
VOCC	volatile organic chlorinated compound
vTRH	volatile total recoverable hydrocarbons
WAD	weak acid dissociable cyanide
WHO	World Health Organization