Schedule B (3)
Guideline on Laboratory Analysis of Potentially Contaminated Soils

NEPC

National Environment Protection
(Assessment of Site Contamination)
Measure 1999

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The following Guideline provides general guidance in relation to Laboratory Analysis of Potentially Contaminated Soils in the assessment of site contamination.

This Guideline 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.

The National Environment Protection Council acknowledges the contribution of the National Health and Medical Research Council to the development of this Measure.

PRECAUTIONARY CAVEAT

The methods of analysis specified or referred to herein may require the use of hazardous materials, operations and equipment. None of the methods specified or referred to purport to address all of the real or potential safety problems associated with their use. 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*, and to ensure that all personnel involved possess adequate training and experience, prior to performing any of the procedures herein or referred to.

CONTENTS

LABORATORY ANALYSIS OF POTENTIALLY CONTAMINATED SOIL

Page

1. GUIDELINE FOR THE LABORATORY ANALYSIS OF POTENTIALLY CONTAMINATED SOIL 1

2. DISCLAIMER 2

3. INTRODUCTION 2

3.1 Audience 2
3.2 Aim 2
3.3 Quality Control and Quality Assurance 2
3.4 Laboratory Analysis of Potentially Contaminated Soils 2
3.5 Use of Results 3
3.6 Scope 3
3.7 Philosophy of Methods Selected 4
3.8 Use of Alternative Specific Methods 5
3.9 Screening Tests 5
3.10 Methods for Inorganic Analysis 6
3.11 Methods for Organic Analysis 7
3.12 Determinative Methods 10
3.13 Validation Data 11
3.14 Methods for Assessing Physical Properties of Soil and Bioavailable Analytes 11
3.15 References 12

4. QUALITY ASSURANCE 13

4.1 Definitions 13
4.2 Recommended Minimum QC Procedures 14
4.3 Method Validation 17
4.4 Sample Control 20
4.5 Documentation 20
4.6 Analytical Report 20
4.7 Split Samples 21
4.8 Blind Replicate Samples 22
4.9 References 22

5. SAMPLE PREPARATION AND STORAGE 24

5.1 Sample Preparation 24
5.2 Sample Storage 28
5.3 Summary of Procedures for Sample Preparation 30
5.4 References 35

6. LEACHABLE INORGANICS AND SEMI-VOLATILE ORGANICS (METHOD 101) 37

6.1 Scope and Application 37

7. MOISTURE CONTENT (METHOD 102) 38

7.1 Scope and Application 38
7.2 Principle 38
7.3 Interferences 38
7.4 Apparatus 39
7.5 Procedure 39
7.6 Calculations 39
7.7 Use of Microwave Ovens 40
7.8 Method Performance 40
7.9 Reference 40

8. SOIL pH (METHOD 103) 41

8.1 Scope and Application 41
8.2 Principle 41
8.3 Apparatus 41
8.4 Reagents 41
8.5 Procedure 42
8.6 Method Performance 43
8.7 References 43

9. ELECTRICAL CONDUCTIVITY (METHOD 104) 44

9.1 Scope and Application 44
9.2 Principle 44
9.3 Apparatus 44
9.4 Reagents 44
9.5 Procedure 44
9.6 Conversion to Approximate Salt Content and Osmotic Pressure 45
9.7 Method Performance 45
9.8 References 45

10. ORGANIC CARBON (METHOD 105) 47

10.1 Scope and Application 47

10.2 Principle 47
10.3 Interferences 47
10.4 Apparatus 47
10.5 Reagents 47
10.6 Procedure 48
10.7 Calculations 49
10.8 Method Performance 50
10.9 References 50

11. AQUA REGIA DIGESTIBLE METALS (METHOD 201) 51

11.1 Scope and Application 51
11.2 Principle 51
11.3 Apparatus 51
11.4 Reagents 52
11.5 Procedure 52
11.6 Calculation 53
11.7 Method Performance 53
11.8 References 54

12. ACID DIGESTION OF SEDIMENTS, SLUDGES AND SOILS (METHOD 202) 55

12.1 Scope and Application 55
12.2 Principle 55
12.3 Analysis 56
12.4 Method Performance 56
12.5 References 56

13. MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS AND OILS (METHOD 203) 57

13.1 Scope and Application 57
13.2 Principle 58
13.3 Notes on Method 3051 58
13.4 Analysis 58
13.5 Method Performance 58
13.6 References 59

14. MERCURY (METHOD 204) 60

14.1 Scope and Application 60
14.2 Principle 60
14.3 Note on Method 7471A 60
14.4 Analysis 61
14.5 Method Performance 61

14.6 References 61

15. CATION EXCHANGE CAPACITY AND EXCHANGEABLE CATIONS (METHOD 301) 62

15.1 Scope and Application 62
15.2 Principle 63
15.3 Analysis 63
15.4 Method Performance 63
15.5 References 63

16. WATER-SOLUBLE CHLORIDE (METHOD 401) 64

16.1 Scope and Application 64
16.2 Principle 64
16.3 Interferences 64
16.4 Reagents (for Chloride Determination by Mohr's Titration) 64
16.5 Procedure 65
16.6 Calculations 65
16.7 Method Performance 66
16.8 References 66

17. BROMIDE (METHOD 402) 67

17.1 Scope and Application 67
17.2 Principle 67
17.3 Apparatus 67
17.4 Procedure 67
17.5 Calculation 67
17.6 Method Performance 68
17.7 References 68

18. TOTAL CYANIDE (METHOD 403) 69

18.1 Scope and Application 69
18.2 Principle 69
18.3 Apparatus 69
18.4 Reagents 70
18.5 Procedure 70
18.6 Calculation 72
18.7 Method Performance 73
18.8 References 73

19. FLUORIDE (METHOD 404) 74

19.1 Scope and Application 74
19.2 Principle 74

19.3 Apparatus 74
19.4 Reagents 74
19.5 Procedure 74
19.6 Calculation 75
19.7 Method Performance 75
19.8 References 75

20. TOTAL SULFUR 76

20.1 Scope and Application 76
20.2 Principle 76
20.3 Apparatus 76
20.4 Reagents 76
20.5 Procedure 76
20.6 Calculation 77
20.7 Method Performance 77
20.8 References 77

21. SULFATE (METHOD 406) 78

21.1 Scope and Application 78
21.2 Principle 78
21.3 Apparatus 78
21.4 Reagents 78
21.5 Procedure 78
21.6 Calculation 79
21.7 Method Performance 79
21.8 References 79

22. SULFIDE (METHOD 407) 80

22.1 Scope and Application 80
22.2 Principle 80
22.3 Analysis 80
22.4 Method Performance 80
22.5 Reference 80

23. VOLATILE ORGANICS (METHOD 501) 81

23.1 Volatile Alkanes and Monocyclic Aromatic Hydrocarbons (MAH) - 501.1 81
23.2 Volatile Halogenated Hydrocarbons - 501.2 82
23.3 Miscellaneous Volatile Organics - 501.3 84

24. POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) (METHOD 502) 86

24.1 Polycyclic Aromatic Hydrocarbons (PAHS) By Solvent Extraction - 502.1 86

24.2 Polycyclic Aromatic Hydrocarbons (PAHS) By Supercritical Fluid Extraction (SFE) - 502.2 88

25. CHLORINATED HYDROCARBONS (METHOD 503) 89

25.1 Sample Extraction 89
25.2 Sample Clean-Up 90
25.3 90
25.4 Extract Analysis 90

26. ORGANOCHLORINE INSECTICIDES (OCS) AND POLYCHLORINATED BIPHENYLS (PCBS) (METHOD 504) 91

26.1 Sample Extraction 91
26.2 Extract Clean-Up 92
26.3 Extract Analysis 92

27. ORGANOPHOSPHORUS PESTICIDES (METHOD 505) 93

27.1 Sample Extraction 93
27.2 Sample Clean-Up (Not Usually Necessary) 94
27.3 Sample Analysis 94
27.4 Reference 94

28. PETROLEUM HYDROCARBONS (PHCS) (METHOD 506) 95

28.1 Petroleum Hydrocarbons (PHCS) By Solvent Extraction - 506.1 95
28.2 Aliphatic Petroleum Hydrocarbons By Supercritical Fluid Extraction (SFE) - 506.2 99

29. PHENOLS (METHOD 507) 101

29.1 Sample Extraction 101
29.2 Extract Clean-Up 102
29.3 Extract Analysis 102

30. HERBICIDES (METHOD 508) 103

30.1 Sample Extraction 103
30.2 Sample Clean-Up 103
30.3 Extract Analysis 103

31. PHTHALATE ESTERS (METHOD 509) 104

31.1 Sample Extraction 104
31.2 Extract Clean-Up 105
31.3 Extract Analysis 105

APPENDIX 1 AUSTRALIAN STANDARDS FOR THE LABORATORY ANALYSIS OF CONTAMINATED SOIL 106

APPENDIX 2 ANALYSIS OF WATERS, WASTEWATERS AND GROUNDWATERS 107

1. GUIDELINE FOR THE LABORATORY ANALYSIS OF POTENTIALLY CONTAMINATED SOIL

This Guideline incorporates aspects of the ANZECC Guidelines for the Laboratory Analysis of Contaminated Soil 1996, which were prepared in response to a recognised need for consistent procedures of soil analysis for environmental assessment of contaminated land.

The Guideline covers several parts. It starts with a description of the philosophy behind the methods selected. It also comprises guidelines on the quality assurance procedures and techniques for sample preparation designed to provide greater confidence and comparability of the analytical results. The remaining parts describe methods for the analysis of physico-chemical properties, inorganics and organics in soil.

For most methods, only the procedures for the extraction are given. This is one of the areas of greatest inconsistency in the analysis of soils. Once extracted, the analytes can be determined by any one of the commonly accepted and easily available techniques. Suitable determinative techniques are recommended but where they are not given in detail, the analyst is referred to easily available methods. For some methods of inorganic analysis and all methods of organic analysis, outlines of the relevant recommended United States Environmental Protection Agency (USEPA) procedures are given but where available, selected alternative procedures are presented.

A few methods have been designed usually for agronomic reasons, to study the physical properties of the soil, the mobility and bioavailability of some metal ions and nutrients. These methods are highly specific to the soil type, chemical species, biota (usually plants) being studied, and have not been applied extensively to contaminated soils. It is therefore unclear how the results from such methods can be interpreted relative to highly contaminated soil. Further work is required to develop specific methods for assessing the mobility and bioavailability of chemicals to humans and biota exposed to highly contaminated soil. For these reasons, only a few of these methods are included or referred to in this guideline. These methods are however, applicable to soils expected to have relatively low concentrations of contaminants eg. background samples.

Expertise in the analysis of contaminated soil is still in the developmental stage in Australia. NEPC envisages that, in observing the methods outlined in this guideline, each participating jurisdiction will give consideration to the most current advice and best practices.

Contributions from individuals and organisations towards the development of these guidelines are gratefully acknowledged.

2. DISCLAIMER

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

3. INTRODUCTION

This Guideline should be followed for laboratory analysis of contaminated soils for the purpose of assessment of site contamination.

Characterisation of soil contaminants with a high degree of confidence will ensure valid assessments of site contamination. It is known among the scientific community that consistency in analysis can only be achieved if there is uniformity in procedures and nomenclature, beginning with sampling, sample storage, pre-treatment, extraction, analytical methodology through to data analysis. This document gives guidance on quality control, quality assurance, techniques for sample preparation, extraction and analytical methods.

3.1 AUDIENCE

This Guideline should be used by persons undertaking sampling and analysis of potentially contaminated soils.

3.2 AIM

This Guideline aims to ensure consistency in analytical results from laboratory analysis of potentially contaminated soils. It should be read in conjunction with Schedule B(2), of the Measure.

3.3 QUALITY CONTROL AND QUALITY ASSURANCE

Laboratories undertaking analysis of potentially contaminated soils for the purpose of assessment of site contamination should be accredited by the National Association of Testing Authorities (NATA) in the test methods and matrix for the analytes of concern.

3.4 LABORATORY ANALYSIS OF POTENTIALLY CONTAMINATED SOILS

These Guidelines for the laboratory analysis of contaminated soil provide guidance on quality assurance procedures and techniques for sample preparation, designed to

provide greater confidence and comparability of the analytical results. The remainder of the document describes analysis of physiochemical properties for inorganic and organic analytes in soil.

When analysis of soil samples for contaminants not included in the methods presented in this Guideline or appropriate Australian Standards is required, reference should be made to standard methods from recognised sources including the American Public Health Association (APHA) and the USEPA. Each laboratory should ensure such methods are appropriately validated prior to use.

3.5 USE OF RESULTS

Effective site assessment is dependent on a partnership between the site assessor and the analytical laboratory ensuring:

- samples arrive at the laboratory in a condition suitable for analysis;
- the information required by the site assessor is understood by the laboratory;
- the site assessor appreciates the uncertainties and limitations associated with the analytical data; and
- all relevant information obtained by the analyst is communicated to the site assessor. For example, chromatographs generated as part of analyses should be reviewed by an experienced analytical chemist noting, and where possible identifying, unusual peaks. In some cases, subsequent analysis by an alternate method may be warranted to confirm the identity of such peaks.

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

3.6 SCOPE

Analyses of soils are often undertaken for assessment of contaminated sites. Test methods fall into the following three broad categories:

- Field measurements that can be performed on the site where the sample was collected;
- Laboratory based broad screening methods used to determine the type of contamination present; and
- Methods specific for contaminants that are known or expected to be present.

This document provides detailed guidelines for just the last of these classes, the principal objective being to foster greater standardisation of the test methods most likely to be used in the final assessment of a site for a particular land use. However, the needs for proper method validation and quality control, as described here for

specific test methods, are equally important for field test procedures and screening tests. Performance of such tests must be validated against recognised quantitative methods.

Accreditation from the National Association of Testing Authorities (NATA) should normally be obtained for all tests.

3.7 PHILOSOPHY OF METHODS SELECTED

For assessment of contaminated soils, recognition should be given to the analysis of non-silicate and extractable (non-residual) components. This is because they provide more useful information than a "total" analysis which includes material bound in the silicate matrix. Residual components are usually less available and therefore pose little threat to the environment. Therefore, the inorganic methods described in this manual are directed towards the extraction or digestion of non-residual contaminants and not the total content in the soil.

Numerous constraints may be placed on the analysis of samples from contaminated sites. Potential risks to human and environmental health, and the financial risks to individuals and organisations make reliability of analysis a top priority. The number of samples collected from a site can be quite large and analytical results are usually required within a short period after sample collection. The sooner these results are available, the quicker decisions can be made with respect to site remediation or protection of the public and environment from further contamination. To meet these demands, the extraction/digestion and analytical methods should be:

1. **Simple**

Procedures should be easy to follow and not tedious. Equipment and reagents should be available in most environmental laboratories.

2. **Rapid**

Extraction/digestion and analysis should preferably be sufficiently rapid and non-labour intensive to allow large numbers of samples to be processed with acceptable turnaround time. This however, should not be at the expense of achieving meaningful analytical results.

3. **Capable of batch or automated analysis**

Processing of samples in large batches should be possible without being too cumbersome (automated analysis is preferred).

4. **Capable of simultaneous analysis**

As far as possible, extraction/digestion procedures should be selected such that a variety of chemical components can be analysed using aliquots of a single extract per

sample. This not only minimises sample processing (turnaround) time and cost but also maximises sample throughput.

5. **Safety**

Safety in the use of the method should never be compromised. This is especially pertinent because of the circumstances surrounding large batch processing and the handling of soils from contaminated sites containing unknown and potentially hazardous substances.

6. **Accurate and precise**

The test methods listed in these guidelines are regarded as "reference" procedures, mostly derived from authoritative references or internationally recognised authorities such as the USEPA [1] or APHA [2]. 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 or their very common usage and acceptance as rigorous techniques by the scientific community.

7. **Limit of reporting**

The method should be selected such that the LR is not greater than 20% of the relevant maximum contaminant obtained.

3.8 USE OF ALTERNATIVE SPECIFIC METHODS

It is recognised that there are other extraction and determinative methods which are at least as efficient, accurate, precise, and possibly less tedious, than those recommended here. These include specially designed commercial systems eg. digestion units, distillation units and autoanalysers. However, it is beyond the scope of these guidelines to evaluate all possible alternatives. For these alternative methods, the following condition will apply:

- Alternative methods may be used provided they can be demonstrated by the user to be at least as rigorous and reliable as those recommended in these guidelines, or have been validated by the user against an appropriate certified reference material.

3.9 SCREENING TESTS

Screening tests are procedures which may be in common usage but are widely regarded as possibly less reliable or rigorous for some soil types in terms of analyte extraction. For example, whereas the "reference" procedure provided in these guidelines for extraction of semi-volatile organics is a 16-24 hour soxhlet extraction, a "screening" test would perhaps utilise a fast shake extraction.

Screening tests may be suitable for less exacting tasks such as mapping pollutant distribution at known contaminated sites, or for monitoring the progress of site

clean-up or remediation programs. They include both laboratory screening tests and those used in the field eg. field chemical test kits and field analysers.

For use of screening methods, the following condition will apply:

- Data from "screening" tests would not be acceptable for validating the clean-up of a contaminated site for a sensitive land use. This is a task which requires a high degree of accuracy and reliability. Data for such tasks must be based upon results from one of the "reference" tests outlined here, or other procedures which have been shown to be at least as rigorous and reliable for the soil matrix in question.

The accuracy and precision of any analysis must be sufficient for the intended purpose. For practical reasons, there needs to be a compromise between speed of extraction/ analysis, and the accuracy and precision of the analytical method. However, there should be a tolerance limit. A recommended margin is that results from a screening (or semi-quantitative) method will generally be within ± 30% of:

(i) the mean value obtainable from multiple analyses using one of the reference methods from these guidelines (or an alternative quantitative method – see Section 3.8), or
(ii) the mean value for multiple analyses of an appropriate certified reference material.

Screening methods must also be validated for identification, repeatability and reproducibility (see Section 4.3).

3.10 METHODS FOR INORGANIC ANALYSIS

The methods of analysis given for inorganic constituents, some of which are written in full in this manual, have been selected to satisfy, as far as possible, all of the criteria listed in Section 3.7. The procedures are based on methods commonly used and found to be acceptable by various government organisations and researchers in the field of soil analysis.

An appropriate technique for preliminary assessment of the spatial extent of contamination is X-Ray Fluorescence (XRF), provided there is sufficient elemental sensitivity. It may also indicate which elements should be quantified by more rigorous methods. However, XRF analysis indicates the total quantity of the element in the sample. Therefore, use of this technique and interpretation of the results should be undertaken with consideration given to the mobility and bioavailability of the element and its associated chemical forms. XRF methods may be used to provide guidance and elemental values only. Because of the highly specific procedures required for this technique and since it is not a standard instrument in most laboratories, details of XRF analysis are not described in this manual.

3.11 METHODS FOR ORGANIC ANALYSIS

The majority of methods of organic analysis referred to in this manual are obtained from the following source:

Test Methods for Evaluating Solid Waste
Publication SW-846, Third Edition, Final Update III, 1996
United States Environmental Protection Agency

This reference is available as a multi-volume loose-leaf set, or on CD ROM. It is hereafter in this guideline referred to simply as "USEPA SW-846". The following sources of the manual are known:

1. Standards and Technical Publications
   PO Box 1019, UNLEY SA 5061
   Phone: (08) 8373 1540 Fax: (08) 8373 1051

2. A.F.R. Info-Line
   Overseas Document Section
   GPO Box 506, SYDNEY NSW 2001
   Phone: (02) 9282 1614 Fax: (02) 9282 3656

3. Accents Publications Service Inc.
   Suite 203, 721 Ellsworth Drive
   SILVER SPRING, MARYLAND 20910, USA
   Fax: 0011-1-301-588-5249

4. Superintendent of Documents
   U.S. Government Printing Office
   PO Box 371954, PITTSBURGH PA 15250-7954, USA

3.11.1 List of Methods Referenced (Organics)

In these guidelines, the USEPA SW-846 methods referenced for organics analysis are listed in Table 3-A below.

Table 3-A

List of USEPA SW-846 Methods Referenced

Code	Method Title
3540 C	Soxhlet Extraction
3545	Accelerated Solvent Extraction
3550 B	Ultrasonic Extraction
3610 B	Alumina Clean-up
3611 B	Alumina Column Clean-up and Separation of Petroleum Wastes
3620B	Florisil Column 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
3810	Headspace
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
8015B	Non-halogenated Volatile Organics by Gas Chromatography
8020A	Aromatic Volatile Organics by Gas Chromatography
8021B	Halogenated Volatiles by Gas Chromatography Using Photoionisation and Electrolytic Conductivity Detectors in Series: Capillary Column Technique
8040A	Phenols by Gas Chromatography
8041	Phenols by Gas Chromatography: Capillary Column Technique
8060	Phthalate Esters
8061A	Phthalate Esters by Capillary Gas Chromatography with Electron Capture Detection
8080A	Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography
8081A	Organochlorine Pesticides and PCBs as Aroclors by Gas Chromatography: Capillary Column Technique
8082	Polychlorinated Biphenyls (PCBs) by Gas Chromatography

Code	Method Title
8100	Polynuclear Aromatic Hydrocarbons
8120A	Chlorinated Hydrocarbons by Gas Chromatography
8121	Chlorinated Hydrocarbons by Gas Chromatography: Capillary Column Technique
8140	Organophosphorus Pesticides
8141A	Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique
8150B	Chlorinated Herbicides by Gas Chromatography
8151A	Chlorinated Herbicides by GC using Methylation or Pentafluorobenzylation Derivatisation : Capillary Column Technique
8240B	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (Packed Column Technique)
8250A	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry
8260B	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry: Capillary Column Technique
8270C	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry: Capillary Column Technique
8310	Polynuclear Aromatic Hydrocarbons by HPLC
8440	Total Recoverable Petroleum Hydrocarbons by Infrared Spectrophotometry

3.11.2 Definitions of Sample Analysis Terms

Table 3-B below lists some of the definitions of sample analysis terms used in these guidelines.

Table 3-B

Definitions of Sample Analysis Terms Used

Term	Definition
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 Spectroscopy
GC/PID	GC/Photo Ionisation Detector

GC/NPD	GC/Nitrogen-Phosphorus (Thermionic) Detector
HPLC	High Performance Liquid Chromatography
HPLC/ECD	HPLC/Electrochemical Detector
HPLC/F	HPLC/Fluorescence Detector
HPLC/UV	HPLC/Ultraviolet Detector
KD	Kuderna Danish evaporator

3.11.3 Notes on 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. In each case a "preferred" technique is nominated by notation with a (P). Preferred techniques, which usually incorporate mass-selective detection, are chosen because they are less likely, by virtue of detector selectivity or clean-up steps employed, 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.

3.12 DETERMINATIVE METHODS

For most of the methods in this manual, only the extraction and digestion procedures are described. The inclusion of determinative procedures for each individual analyte is beyond the scope of this manual.

Determinative methods are available for many analytes in a range of Standards Australia methods and in the following documents:

1. Test Methods for Evaluating Solid Waste
   Publication SW-846, Third Edition, Final Update III, 1996
   United States Environmental Protection Agency (USEPA)
   (details on obtaining this are given in Section 3.8 above)

2. Standard Methods for the Examination of Water and Wastewater
   American Public Health Association
   Greenberg, A.E., Clesceri, L.S. and Eaton, A.D. (eds.), 19th Edition, 1995
   (or latest edition)

3. American Society for Testing and Materials
   Water and Environmental Technology,
   Volumes 11.01 to 11.04
   ASTM, Philadelphia, PA 19103 (Latest edition)

In some cases however, one or more suitable determinative method is suggested. This does not preclude the use of alternative methods, provided they are validated by the laboratory for the matrix concerned (see Section 4.3).

In deciding an appropriate method for the particular analyte, the analyst needs to consider the chemical characteristics of the final extract and analyte. To this end, quality control procedures should always be implemented as described in Section 4.

3.13 VALIDATION DATA

Due to the large variation in physico-chemical properties and soil types, it is difficult to obtain complete validation data for all analytes covered in these guidelines. The lack of suitable or reliable reference standard materials also adds to the problem. For some analytes eg. soil pH, conventional validation data has no bearing on the method's performance between one soil sample and the next. For such analyses, better performance indicators may be better obtained through interlaboratory comparisons. However, where available, validation data are provided in these guidelines for some analytes. Where the methods are derived from published methods eg. USEPA SW-846 [1] or APHA [2], the reader is referred to the validation data in those publications.

In these guidelines, extraction procedures or complete methods are provided. **Each laboratory should however, still fully validate each method used** (from the extraction through to the determinative step), following the principles for quality assurance and method validation as described in Section 4 or other references [3-7]. The validation should be performed on the range of soil types most likely to be analysed. It is also necessary that where non-specific techniques of analysis are used eg. GC or HPLC, the identities of the organic compounds are confirmed. This can be achieved through one of several methods recommended in Technical Note 25 [8].

3.14 METHODS FOR ASSESSING PHYSICAL PROPERTIES OF SOIL AND BIOAVAILABLE ANALYTES

Methods designed for agronomic studies and land surveys eg. Method 301: Cation exchange capacity and exchangeable cations, need to be applied with care. This is because the high concentrations of analytes in the contaminated soil may exhaust the exchangeable capacity of the reagents, leading to false low results [9]. Before applying these tests for contaminated site assessments, it is also important to note that the extractable analytes will have separate effects on different biota. Specific tests are sometimes necessary for determining the bioavailability of analytes to different plants and animals [9].

These tests have not yet been demonstrated to be applicable to contaminated soils. Currently, meaningful results can only be obtained from natural soils or background samples collected to provide supporting information during the site investigation.

3.15 REFERENCES

1. Test Methods for Evaluating Solid Waste, 1986, USEPA Publication SW-846, Third edition.

2. Standard Methods for the Examination of Water and Wastewater, 1995, 19th Ed., Greenberg, A.E., Clesceri, L.S. and Eaton, A.D. (eds), American Public Health Association.

3. Test Methods for Evaluating Solid Waste, 1986, USEPA Publication SW-846, Third edition, Chapter 1: Quality Control.

4. Standard Methods for the Examination of Water and Wastewater, 1995, 19th Ed., 1040B Method Validation, Greenberg, A.E., Clesceri, L.S. and Eaton, A.D. (eds), American Public Health Association.

5. Guidelines for Quality Control in the Analytical Laboratory, 1995, Technical Note 23, National Association of Testing Authorities, Australia.

6. Requirements for the Format and Content of Test Methods and Recommended Procedures for the Validation of Chemical Test Methods, April, 1994, Technical Note 17, National Association of Testing Authorities, Australia.

7. Criteria for Assessing Conformance to USEPA Testing Methods, 1994, Technical Note 22, National Association of Testing Authorities, Australia.

8. Guidelines on the Methods of Positive Identification of Trace Amounts of Organic Compounds, 1996, Technical Note 25, National Association of Testing Authorities, Australia.

9. L. Plues, 1995, Director Laboratories, Environment Protection Authority, New South Wales, personal communication.

4. QUALITY ASSURANCE

4.1 DEFINITIONS

The terms "quality assurance" and "quality control" are often confused. With respect to laboratory analysis activities, these terms are defined in these guidelines as follows:

Quality Assurance (QA) : "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."

- ISO 8402-1994 [1]

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

Quality Control (QC) : "The operational techniques and activities that are used to fulfil the requirements for quality."

- ISO 8402-1994 [1]

These are the components of QA which serve to monitor and measure the effectiveness of other QA procedures by comparison with previously decided objectives. They include measurement of the quality of reagents, cleanliness of apparatus, 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 manual. It is widely recognised, however, that adoption of sound laboratory QA and QC procedures is essential and readers are referred to documentation available from the National Association of Testing Authorities (NATA).

The analytical laboratory should also incorporate quality laboratory management systems to ensure reliable results are produced by trained analysts, using validated methods and suitably calibrated equipment. It includes proper sample management and record maintenance as well. To this end, it is strongly recommended that procedures as described in Guidelines for Quality Control in the Analytical Laboratory [2] and AS2830.1-1985: Good Laboratory Practice - Chemical Analysis [3], and participation in an accreditation and/or self-audit system be adopted.

4.2 RECOMMENDED MINIMUM QC PROCEDURES

Through the QC procedures adopted, the laboratory should be able to demonstrate:

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

It is recommended that the QC procedures described in Chapter 1: Quality Control in "Test Methods for Evaluating Solid Waste", USEPA Publication SW-846 [4], be adopted in all soil analysis.

Many of the organic analysis methods recommended in this manual are derived from USEPA SW-846, and the QC procedures referred to above form a part of those methods. These procedures or variations of them, can be incorporated into almost any analytical method. When using these USEPA methods, the analyst should consider the criteria for conformance to QA/QC requirements as discussed in "Criteria for Assessing Conformance to USEPA Testing Methods" [5].

In particular, it is expected that laboratories would incorporate the following QC procedures:

4.2.1 Analysis Blank (at least one per process batch)

The component of the analytical signal which is not derived from the sample but from reagents, glassware, etc. can be determined by processing solvents and reagents in exactly the same manner as for samples. If below the maximum acceptable method blank, this contribution is subtracted from the gross analytical signal for each analysis before calculating the sample analyte concentration (established during the method validation and not exceeding 20% of the PQL). Where laboratories are required to report analysis blanks, the uncorrected result and the method blank should be reported in the same units of measure.

4.2.2 Duplicate Analysis (at least one per process batch or one per ten samples, whichever is the smaller)

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

4.2.3 Laboratory Control Sample (at least one laboratory control sample per process batch)

This comprises either a standard reference material or a control matrix fortified with analytes representative of the analyte class. Recovery check portions should be

fortified at concentrations which are easily quantified but within the range of concentrations expected for real samples.

4.2.4 Matrix spikes (one matrix spike for each soil type)

The purpose of the matrix spike is to monitor the performance of the analytical methods used, and to determine whether matrix interferences exist. When the recovery of the matrix spike is below the expected analytical method performance, it may be necessary to use other internal calibration methods, a modification of the analytical method or alternative analytical methods to accurately measure the analyte concentration in the extract.

In most cases, matrix spikes should be added at a concentration equivalent to the corresponding regulatory level. If the analyte concentration is less than one half the regulatory level, the spike concentration may be as low as one half of the analyte concentration, but may be not less than five times the method detection limit. In order to avoid differences in matrix effects, the matrix spikes must be added to the same nominal amount/quantity of sample as that which was analysed for the unspiked sample.

Matrix spikes should be performed when validating a method by addition to the analysis portion before extraction or digestion..

4.2.5 Surrogate Spikes (where appropriate)

For determinations where it is appropriate eg. chromatographic analysis of organics, surrogate spikes should be added to all analyses. Surrogate spikes are known additions to each sample, blank and matrix spike or reference sample analysis, of compounds which are similar to the analytes of interest in terms of:

(i) extraction;
(ii) recovery through clean-up procedures; and
(iii) response to chromatography or other determination;

but which:

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

Surrogate spikes are added to the analysis portion **before extraction**. The purpose of surrogates is to provide a means of checking, for every analysis, that no gross errors have occurred at any stage of the procedure leading to significant analyte losses.

In the case of organic analyses the surrogate spike compounds may be deuterated, alkylated or halogenated analogues, or structural isomers of analyte compounds.

4.2.6 Internal Standards (where appropriate)

Use of internal standards is highly recommended for chromatographic analysis of organics and some inorganic analyses. Internal standards are added, after all extraction, clean-up and concentration steps, to each final extract solution. The addition is a constant amount of one or more compounds with similar qualities to 4.2.5 (iv), (v), and (vi) above.

The purpose of internal standards is to check the consistency of the analytical step (eg. injection volumes, instrument sensitivity and retention times for chromatographic systems) and provide a reference against which results may be adjusted in case of variation (for organics analysis only).

Injection volume and instrument sensitivity variations are usually adjusted for by calibration using the RATIO of peak height or area for analytes compared with that for the internal standard(s). Such adjustment should only occur where variation in internal standard signal is within predefined limits.

Note: The chromatograms for final extracts may then contain both internal and surrogate standards. The compounds used for these standards may be similar but the different stage of analysis at which they are added allows them to provide different information.

4.2.7 Confirmation of Organic Compounds (for non-specific techniques)

As far as possible, where non-specific techniques of analysis are used eg. GC or HPLC, the identities of the organic compounds should be confirmed. This can be achieved through one of several methods recommended in Technical Note 25[6]. These include using a mass spectrometric detector , a variant of the test procedure (eg. different column stationary phase), another test procedure (eg. alternative detector) or conversion of the analyte to another compound (eg. derivatisation technique) [6].

A GC/MS or HPLC/MS spectral library match alone is only sufficient for tentative identification. Confirmation is achieved (i.e. no additional confirmatory analysis is required) if GC/MS and HPLC/MS methods are employed and standards of the compound are analysed under identical conditions[12]. A compound identity is then confirmed if all of the following criteria [13] are met:

- The intensities of the characteristic ions of the compound in the sample must maximise in the same scan, or within one scan, of that for the reference compound;
- The relative retention time of the sample component is with 0.06 RRT units of that of the standard component; and

- The relative intensities of the characteristic ions in the sample all agree within 30% of the relative intensities of these ions on the reference compound spectrum.

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

Records of results of QC procedures should be maintained to provide a means of establishing method reliability, confidence intervals for analysis results and trends in precision and accuracy which occur over time or with variation of equipment or analyst.

4.3 METHOD VALIDATION

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

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

4.3.1 Accuracy

Accuracy is a measure of the closeness of the analytical result obtained by a method to the 'true' value [7]. The following levels of accuracy should generally be achievable from a screening or reference method.

- screening method: within ± 30 % of:
  - (a) the expected value of a certified reference material of similar matrix; or
  - (b) the value obtained by a separately validated and recognised quantitative method for the sample matrix.
- reference method: within ± 15 % of:
  - (a) the expected value of a certified reference material of similar matrix; or
  - (b) the value obtained by a separately validated and recognised quantitative method for the sample matrix.

It is recognised, however, that coefficients of variation for a procedure can be expected to be higher for low concentrations of analytes, e.g. those below ten times the minimum detectable concentration. Apparent lower recoveries than those specified will occasionally be obtained for CRMs which have been assessed by more rigorous methods involving matrix dissolution. The methods for CRM characterisation should be considered. The specific analyte cited in the CRM

certificate should match that being determined under the Schedule B(3) method. If, for example, the Certified Reference values are obtained using aqua regia digest, only the aqua regia method should be applied to this CRM. Otherwise, an alternative CRM should be used. The methods described in this document may not satisfy crieria for compliance with section 10 of the *National Measurements Act 1960*. Therefore, they may only be systems of measurement for comparison against results obtained for CRMs. Further information may be obtained from *Assessment of Uncertainties of Measurement for Calibration and Testing Laboratories*, Ron Cook, CSIRO, and *ISO Guide to the Expression of Uncertainty in Measurement*.

4.3.2 Precision

Precision is a measure of the variation in the method's results. It is a combination of two components, repeatability and reproducibility.

4.3.2.1 Repeatability

This is the precision that measures the variation in the method's results produced by the same analyst under conditions which are as close as possible using the same equipment in the one laboratory and within a short interval of time [7]. Repeatability is expressed as a standard deviation [8]. The smaller the standard deviation the better the repeatability. Determine the standard deviation as follows:

- Perform at least 7 replicate analysis of each sample type expected to be analysed routinely. This should be repeated over at least three different analyte concentrations, across the range normally expected. From these results, calculate the standard deviation, s, for each concentration, c, as follows:

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

where: x_i = concentration of analyte of *i*th replicate

x' = mean concentration of n replicate analytes

n = number of replicate analyses for that concentration

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

4.3.2.2 Confidence limit and confidence interval

When the results are assigned to the ± sc multiples, they are the confidence limits eg. 10±4 mg/kg indicates the confidence limits are 6 and 14, while values from 6 to 14 represent the confidence interval [9].

4.3.2.3 Reproducibility

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

4.3.3 Percent Recovery

Percent recovery describes the capability of the method to recover a known amount of analyte added to a sample. This is the most realistic and useful term to be applied to the daily quality control of the analytical performance [10]. Spike the sample with a known quantity of the analyte such that the combined added and suspected natural concentration of the analyte is within the working range of the method. The longer the residence time of the spiked analyte before extraction or digestion, the closer is the simulation in recovering the analyte from the natural sample. Calculate the percent recovery as follows.

$$\% \text{ Recovery} = \frac{c - a}{b} \times 100$$

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

b = concentration of analyte added to the sample

c = concentration of analyte determined in the spiked sample.

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

In general, at least 85 % recovery should be achievable from a reference method. Lower recoveries may be expected for low concentrations of analytes.

4.3.4 Limits of Detection and Reporting

4.3.4.1 Lower Limit of Detection (LLD)

This is the concentration of analyte which, when the sample is processed through the complete method, produces a response with a 95 % probability that it is different from the blank [9]. Determine the standard deviation, S_{LD}, of at least 7 replicates of the sample with a concentration close to the estimated detection limit. The LLD is then calculated as follows:

LLD = 2 x t x Std Deviation (APHA 19th. ed. as per reference in Schedule B(3)), using a one sided t distribution

Where, for 7 replicates t= 3.14 for 99% confidence

4.3.4.2 Practical Quantitation limit (PQL)

The PQL, also known as the limit of quantitation, 'is the lowest concentration of an analyte that can be determined with acceptable precision (repeatability) and accuracy under the stated conditions of the test' [7]. The limit of reporting is usually calculated as follows:

PQL = 5 X LLD (not 10) when the LLD is determined according to APHA guidelines[9].

Records of all validation steps pertaining to the method should be retained while the method is being used. All raw data for the results should be retained for at least three years after completion of the analysis [11].

4.4 SAMPLE CONTROL

The laboratory should maintain rigid procedures in sample control immediately after the sample is received. This includes the entire process beginning with the registration of the sample through to pre-treatment and sample analysis, sample storage and disposal (see Section 5). Unique identification of every and all portions of each sample is mandatory. Sample integrity should also be maintained as far as possible, even after completion of the analysis.

4.5 DOCUMENTATION

All documentation with respect to the sample and its analysis (including raw data, data validation) should be retained such that all relevant information on the sample may be easily retrieved. This is particularly important in establishing chain-of-custody of the sample and traceability of all data. It also enables reviewing of the analysis during an audit or investigation of a dubious result.

4.6 ANALYTICAL REPORT

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

NATA Endorsed documents must contain:

- a title;
- name and address of the analytical laboratory;(and NATA registration No.)
- analytical report number (has to be a unique identification);

- sample identification (has to be a unique identification for each sample);
- the identity of the test method and any deviations from it;
- analytical results, accompanied by a statement of uncertainty (note that the statement of uncertainty may be implicit in the results presented. For example, 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;
- the signature of an approved NATA signatory; and
- date of analytical report issue.

Other valuable information for inclusion on analysis reports is:

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

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

The data validation processes include checking the analytical report for transcription errors, correctness in the calculation and expression of results, sample description and that the QC data meets the acceptable limits for the method.

4.7 SPLIT SAMPLES

(This is a Field QC implemented by the client rather than a Laboratory QC but laboratories should be aware of its purpose.)

These samples provide a check on the analytical performance of the laboratory. At least 1 in 20 samples from a site should be homogenised under laboratory conditions and split. One of the duplicate samples from each split set is submitted by the client to a secondary laboratory (an independent laboratory run by a different organisation or company) and the remaining samples to the primary laboratory. The client shall ensure that each laboratory analyses the split samples for the same analytes of interest using, as far as possible, the same methods recommended in these

guidelines. For comparability of data, it is important that there is little delay in the sample submission to allow minimum time difference between commencement of analysis by both laboratories. This is particularly important with the analysis of volatile analytes.

The difference in the results between the split samples should, in general, be within 30 percent of the mean concentration determined by both laboratories. However, this variation can be expected to be higher for organic analysis than for inorganics, and for low concentrations of analytes.

4.8 BLIND REPLICATE SAMPLES

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

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

4.9 REFERENCES

1. ISO 8402-1994 : Quality management and quality assurance.

2. Guidelines for Quality Control in the Analytical Laboratory, 1995, Technical Note 23, National Association of Testing Authorities, Australia.

3. AS 2830.1, 1985, Good Laboratory Practice Part 1: Chemical Analysis, Standards Australia.

4. Test Methods for Evaluating Solid Waste, 1986, USEPA Publication SW-846, Third edition, Chapter 1: Quality Control.

5. Criteria for Assessing Conformance to USEPA Testing Methods, 1994, Technical Note #22, National Association of Testing Authorities, Australia.

6. Guidelines on the Methods of Positive Identification of Trace Amounts of Organic Compounds, 1996, Technical Note 25, National Association of Testing Authorities, Australia

7. Requirements for the Format and Content of Test Methods and Recommended Procedures for the Validation of Chemical Test Methods, April, 1994, Technical Note #17, National Association of Testing Authorities, Australia.

8. Quality Management in the Laboratory, 1988, National Association of Testing Authorities, Australia.

9. Standard Methods for the Examination of Water and Wastewater, 1995, 19th Ed., 1030 E Method Detection Limit, Greenberg, A.E., Clesceri, L.S. and Eaton, A.D. (eds), American Public Health Association.

10. Annual Book of ASTM Standards, 1988, Volume 11.01 Water (I), ASTM, Philadelphia.

11. General Requirements for Registration, 1992, National Association of Testing Authorities, Australia, p8.

12. Test Methods for Evaluating Solid Waste, 1986, USEPA Publication SW-846, Third edition, Final Update 3, December 1996. Method 8000B.

13. Test Methods for Evaluating Solid Waste, 1986, USEPA Publication SW-846, Third edition, Final Update 3, December 1996. Method 8270C.

5. SAMPLE PREPARATION AND STORAGE

5.1 SAMPLE PREPARATION

To obtain reproducible results it is essential that laboratories use standardised procedures for the preparation of 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; and
- 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-volatiles compounds (many organics, some metals and other inorganics subject to evaporative losses); and

3. Volatile compounds (such as organic solvents and inorganic gases).

The following sections discuss the individual steps in sample preparation, followed by a summary of the recommended protocols for the three analyte classes.

Throughout the sample preparation step, the analyst needs to be aware of any bias introduced. Any bias noted should be reported with the analytical result.

WARNING: Potentially contaminated soil and fine dust may present a health hazard when handled. The preparation should be performed in a fume cupboard. Appropriate gloves and respiratory protection conforming to Australian Standards should be worn.

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

Vegetation and other non-soil material (including rocks, gravel, concrete, particles naturally greater than 5 mm) should normally be removed by hand or sieving prior to grinding or mixing the sample, except for samples to be analysed for volatile components since this process may lead to significant analyte losses. The analyst

should confirm with the client whether any fraction of the removed materials is to be analysed.

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

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

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

5.1.2 Homogenising

(Samples for analysis of volatile contaminants should not be homogenised by stirring, grinding or sieving. For procedures applicable to volatile analytes, see Section 5.3.3).

In order to minimise the cost of reagents used and waste disposal, most analytical methods require the 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 quality assurance purposes.

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

The sub-sample taken should comprise at least 50 percent by weight or 200 g of the sample received by the laboratory (laboratory sample), whichever is the smaller. It must be thoroughly disaggregated and mixed using a mortar and pestle or any other appropriate apparatus. The entire sample may be homogenised but only if no test requiring the original, untreated sample will be needed. Further, it is advisable to keep a portion in the "as received" state to check, if necessary, that no contamination has occurred during the homogenising process. Sections 5.1.3 and 5.1.4 below describe the pre-treatment procedures to obtain homogenised field-moist and dry analysis portions.

5.1.3 Preparation of Field-Moist Analysis Portions

In general, soils to be tested for organic analytes, especially rapidly degradable or otherwise labile contaminants, should not be dried but should be analysed in a field-moist state. Where an excessive amount of moisture can affect the extraction efficiency, the sample may be 'dried' by mixing the analysis portion with anhydrous sodium sulfate or magnesium sulfate prior to extraction[1].

Field moist samples will often not be amenable to machine grinding or sieving. For non-volatile analytes, at least 50 percent by weight or 200 g of the laboratory sample, whichever is the smaller, should be thoroughly ground and mixed in a mortar and pestle to obtain a homogeneous sub-sample.

Recent studies have indicated that for metals analysis, there is little difference in results between air-dried and field-moist soils if the latter is mixed thoroughly and sieved (if it is amenable to sieving) [2]. Even so, for better reproducibility in most cases, air-dried soil is preferred for the analysis of metals and some inorganics. However for these analytes, if the sample is to be analysed in the field-moist state and if it is amenable to sieving eg. sandy loam, it should also be passed through a 2mm plastic sieve. Ensure that there are no solid particles distinctly different from the soil e.g. fragments of metal or coloured particles of an unusual nature. If this is the case, the sample has to be analysed in the air-dried state and pre-treated according to Section 5.1.4.

Store the treated sample in a glass screw cap jar.

Prior to use, all equipment used for this procedure must be cleaned (eg. by solvent rinsing) in a way which ensures minimum contamination of the sample. If samples are to be analysed for organics, final solvent rinses should be kept for examination as a check of cleanliness (one final solvent rinse per process batch or one in every 10 samples homogenised; alternatively treat a well-characterised control soil sample similarly). If there is significant carry-over due to the homogenising process, the results from that process batch may have to be rejected.

5.1.4 Preparation of Dry Analysis Portions

Until recently, air-drying was considered to be applicable for most types of analyses. It aids in obtaining a representative analysis portion by producing samples amenable to grinding, sieving and splitting. It is now recognised, however, that even air-drying may modify the chemical form of some species (especially Mn and Fe) and hence, affect the results obtained [3-8]. The effect of drying temperatures on analyte modification is not completely understood. The impact of air-drying on analysis may be more pronounced in certain soil types and in sediments. Therefore, air-drying is only applicable to some methods of soil analysis. It is generally accepted that soils for metals and some inorganic analytes can be air-dried, followed by grinding and sieving.

The procedure described below is not applicable to the analysis of soils for volatile constituents or where analytical methods specifically forbid such preparation (eg. certain leaching tests). Samples for volatile metallics eg. methyl mercury or tetraethyl lead, must be homogenised and sub-sampled in the field-moist state.

5.1.4.1 Sample Drying

Dry at least 50 percent 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 (less than 35°C), ideally with the trays placed in a clean air chamber or a non-contaminating oven at 35 ± 3°C [9]. 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 percent per 24 hours [9]

5.1.4.2 Grinding of Dry Sample

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

Extreme care should be taken to avoid contamination during the grinding process. Equipment used should be suitably cleaned before grinding each sample to prevent cross-contamination. Cleaning procedures will vary according to the analytes being determined. Generally detergent washing, followed by deionised water rinsing and oven drying will suffice. For trace metal analysis it may be necessary to incorporate soaking in dilute acid followed by deionised water rinsing. Solvent rinsing followed by air-drying the equipment will normally be required prior to homogenising samples for organics analysis. For quality control, the final washing should be sampled and analysed to evaluate the decontamination efficiency [10]. For this purpose, the sampling frequency should be one final wash per process batch or one in every 10 samples ground, whichever is the smaller; alternatively, treat a well-characterised control soil sample similarly. If there is significant carry-over due to the grinding process, the results from that process batch may have to be rejected.

5.1.4.3 Sieving

Unless impracticable or required by a method, the analysis portion must be at least pass a 2.0 mm aperture sieve. For analyses requiring a small sample size (eg. 1 g), even a 2.0 mm sieve size would not be small enough to be representative. Gy suggested that in order to obtain acceptably representative portions of 1.5 g and 10 g of a sample of average mineralogy, the maximum particle dimensions should be less than 0.15 mm and 0.3 mm respectively [11].

As a compromise, where a method does not specify sample particle dimensions, it is recommended that the analysis portions be taken from homogenised test samples, or sub-samples of same which have been ground to pass the following sieves:

Mass of sample required for a single analysis (g)	Sieve size recommended (mm)
less than 1	0.15
less than 2	0.5
2 to 9	1.0
10 or greater	2.0

For reducing to less than 2 mm particle size, it is sufficient to grind a sub-sample of at least 10 g of a 2 mm sieved sample.

WARNING: Grinding of soils to fine dimensions may produce dust particles which present a health hazard. Preparation should be performed in a fume cupboard. Appropriate gloves and respiratory protection conforming to Australian Standards should be worn.

5.1.4.4 Partitioning to Obtain Representative Analysis Portions of Dry Samples

The analysis portion of the dry sample must be taken in a representative fashion. Use of a chute splitter (riffler) is recommended for sufficiently dry samples; or the entire sample thoroughly mixed and divided using the "cone-and-quarter" technique (see Section 5.3) or by any suitable sampling apparatus. These equipment should be made of appropriate material (ie. stainless steel) to avoid contamination.

Repeat the partitioning to obtain the desired amount of analysis portion (including any replicate analyses and extra portions required for quality assurance purposes). Store the remaining homogenised dry sample separately in a glass screw-cap jar or other appropriate vessel (see Section 5.2 below on Sample Storage).

Note: Mechanical grinding of the dry soil eg. in a ringmill, will mix the sample but to avoid subsampling only the larger particles, the cone-and-quarter technique or the use of a mechanical sample divider is preferred.

5.2 SAMPLE STORAGE

To maintain sample integrity, it is necessary that it is collected and kept in a container which will not add to or reduce the analyte concentration in the sample. It is also important to note that the less time the sample is stored, the more accurate the analytical result is likely to be. Table 5-A lists the containers, maximum holding times and condition of the soil for the analytes included in these guidelines.

Storing of field moist samples has the disadvantage that it will allow faster degradation of analytes via microbial activity, particularly if samples are stored at ambient temperatures. Moist samples should therefore be stored at low temperature (4°C or below) and the analysis carried out within a reasonable time.

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

All portions of the sample not analysed should be retained until agreed to or advised by the client that they may be discarded, or retained for a reasonable amount of time after the dispatch of the analytical report (eg. two months).

Table 5-A

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

Analyte	Method No.	Container[b]	Maximum Holding Time	Sample Condition
Leachable metals and semi-volatile organics	101	As for analyte of interest	As for analyte of interest	As for analyte of interest
Moisture Content - moisture content only - moisture correction	102	P or G As for analyte of interest	7 days Same day as sample extraction for analyte	Field-moist Field-moist
pH	103	P or G	7 days	Air-dry
Electrical conductivity	104	P or G	7 days	Air-dry
Organic carbon	105	G [c]	7 days	Air-dry
Metals (except mercury)	201, 202 203	P (AW)	6 months	Field-moist or air-dry
Mercury	204	P (AW) [c]	28 days	Field-moist
Cation exchange capacity and exchangeable cations	301	P (AW)	6 months	Air-dry
Chloride (water-soluble)	401	P or G	7 days	Field-moist or air-dry
Bromide (water-soluble)	402	P or G	7 days	Air-dry
Cyanide	403	P or Gc	7 days	Field-moist
Fluoride	404	P	7 days	Field-moist or air-dry
Sulfur - total	405	P or G	7 days	Field-moist or

Analyte	Method No.	Container[b]	Maximum Holding Time	Sample Condition
				air-dry
Sulfate	406	P or G	7 days	Field-moist or air-dry
Sulfide	407	P or G d	7 days	Field-moist
Volatile organics - MAH - Halogenated HC - Miscellaneous	 501.1 501.2 501.3	G (SR) [c]	14 days	Field-moist
Semi-volatile organics - PAH - Chlorinated hydrocarbons - OC Insecticides and PCB - OP Pesticides - Petroleum hydrocarbons - Phenols - Herbicides - Phthalate esters	 502.1,502.2 503 504 505 506.1,506.2 507 508 509	G (SR) [c]	14 days	Field-moist

a Adapted from USEPA SW846[1] and Draft Australian Standard 95140 [12].
b Minimum volume of 250 mL; P = Plastic; G = Glass; AW = Acid-washed; SR (Solvent rinsed).
c Store in the dark.
d Add sufficient 2M zinc acetate to fully cover surface of solid with minimal headspace; store at 4°C (see Reference 1, Method 9030A).

5.3 SUMMARY OF PROCEDURES FOR SAMPLE PREPARATION

The recommended sample preparations described in Section 5.1, which differ according to analyte volatility, are summarised below. In all cases, all preparation steps are to be recorded and included in the analytical report. No portion of the sample should be discarded until advice is obtained from the client.

WARNING: Potentially contaminated soil and fine dust may present a health hazard when handled. The preparation should be performed in a fume cupboard. Appropriate gloves and respiratory protection conforming to Australian Standards should be worn.

5.3.1 Analytes for which air-drying of sample is appropriate eg. non-volatiles:

1. Remove large stones (obviously > 5 mm) and vegetation unless they are to be included for bulk analysis. Record the proportion by weight with a description of each fraction of material removed.

2. Air-dry 50 percent by weight or 200 g of the laboratory sample, whichever is the smaller, taking into consideration amounts required for repeat analyses, other analysis to be carried out on this same sample including moisture content (determined using field-moist sample).

   Samples may also be dried in an oven at 35 ± 3°C. The sample is dry when the loss in mass of the soil is not greater than 5% per 24 hours.

3. Grind to disaggregate the soil particles.

4. Pass through a 2 mm mesh sieve.

5. Weigh and set aside the particles >2 mm diameter for later analysis if required (and to examine for large particles of solid contaminant if necessary).

6. Partition the fraction <2 mm diameter either by hand or using a mechanical sample divider.

   By hand:

   (a) Spread the soil into a thin even layer.

   (b) Divide the soil into four quadrants.

   (c) Combine and mix the soil from two opposite quadrants.

   (d) Repeat Steps (a)to (c) until the required quantity of soil is obtained for analysis or for further size reduction.

   Using mechanical sample dividers:

   In accordance with the manufacturer's instructions.

   If small analysis portions (<10 g) are to be taken or smaller sieve sizes are required, grind at least 10 g of the <2 mm fraction to pass 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).

7. Analysis of volatile contaminants such as C_6-C_9 should be undertaken prior to any other analysis required from that sample. Sampling and sub-sampling shall be undertaken in accordance with Section 5.3.3.

5.3.2 Analytes for which drying may lead to losses eg. semi-volatiles, or preparation of field-moist sample:

1. Remove large stones (obviously > 5 mm) and vegetation (unless they are to be included for bulk analysis). Record the proportion by weight with a description of each fraction of material removed.

2. Grind 50 percent by weight or 200 g of the laboratory sample, whichever is smaller, in a clean mortar and pestle to disaggregate soil particles and to produce a homogeneous test sample (consider amounts required for repeat analyses, other analysis to be carried out on this same sample including moisture content).

   Note: Soils to be analysed for metals or some inorganics in the field-moist state and which are amenable to sieving eg. sandy loam, should also be passed through a 2mm plastic sieve. Ensure that there are no solid particles distinctly different from the soil eg. fragments of metal or coloured particles of an unusual nature. If this is the case, the sample has to be analysed in the air-dried state and pre-treated accordingly.

3. Dry a separate, weighed portion of the laboratory sample to determine the moisture content (see Method 102 of this manual). Report the moisture content with the analytical result so that analyte concentrations may be estimated on a "dry-weight" basis.

5.3.3 Volatile analytes

In general, these guidelines do not include instructions for sample collection. An exception is made here for volatile analytes, however, as the choice of the analysis method and reliability of the results are both related to the sampling method.

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

5.3.3.1 Sample collection

Collection of samples should be accomplished with minimal sample disturbance, using a coring device.

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

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

- two or more pre-weighed 40 mL glass "VOA" vials with PTFE lined, pierceable silicone septum caps, or
- one or more 125 mL wide mouth glass jars with PTFE lined lid[13] and sub-sample according to the procedures given below.

For soils which are difficult to sample, eg 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 which are marked at a level corresponding to the required sample weight for analysis. The vials should have PTFE lined, pierceable silicone septum caps. One sample should be used for preliminary screening analysis if desired (see below), the others for analysis by purge and trap analysis.

Note 1: The 40 mL VOA vials have been shown to be particularly effective in conjunction with modified closures[15], 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 (eg. see USEPA Method 5035

: Closed-system Purge-and-trap and Extraction for Volatile Organics and Solid Wastes [16]).

Note 2: The use of 125 mL containers may be more convenient, and possibly result in fewer analyte losses where removal of a test sub-samples is required [14]. Field immersion into methanol has also been shown effective in preserving volatile organics.[15]

Laboratory personnel should always be consulted regarding the most appropriate of the sampling procedures above.

Once the samples are taken, ensure that vial closures are free of soil particles before capping. Immediately store vials and jars on ice, or in a refrigerator at 4°C, for transport to the laboratory.

5.3.3.2 Sub-sampling and analysis

Where a sub-sample is taken from the vial for analysis, the sample should be chilled and the operation performed rapidly, with minimal disturbance of the sample, by using a corer.

Preferably, the entire sample should be extracted by purge and trap or methanol immersion.

Note 1: The representativeness of analysis portions should be demonstrated by analysis of multiple portions, rather than attempting to homogenise, and risking analyte losses.

Note 2: The presence of large particles (obviously > 5 mm) and vegetation, may prohibit sampling with a coring device. If so, a sample should be taken by other means, but rapidly and with minimum disturbance so as to reduce the risk of significant analyte losses. For these samples it is recommended that, after measurement of volatiles in the analysis sample, the analyst should determine and record the proportion by weight of each type of material in the analysis sample.

Note 3: Dry a separate, weighed portion of the original sample to determine the moisture content (see Method 102 of this manual). Report the moisture content with the analytical result so that analyte concentrations may be estimated on a "dry-weight" basis.

5.3.3.3 Preliminary screening analysis

Some laboratories perform a preliminary screening analysis of soils to prevent contamination of purge and trap equipment by high level samples. This should be done by:

1. 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.

2. Headspace analysis (eg. USEPA method 3810 or 5021), or

3. Hexadecane extraction (USEPA 3820)

4. Rapidly removing a core sample from a chilled 125 mL jar sample and transferring to a vial for analysis as in 1 or 2 above.

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

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

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

5.4 REFERENCES

1. Test Methods for Evaluating Solid Waste, 1986, Methods 3540C and 3550B, USEPA Publication SW-846, Third edition, Vol. 1B Part B.

2. Louie, H., Soo, S.Y., Tam, J. and Wu, M.G., 1996, Evaluation of Methods in Sample Preparation and Digestion of Environmental Samples for the Determination of Metals by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS), Australian Government Analytical Laboratories, Sydney, New South Wales (Draft).

3. Adam, A.J. and Anderson, W.B., 1983, Soil Moisture Influence on Micronutrients Cation Availability Under Aerobic Conditions, Plant and Soil, 72, 77-83.

4. Bartlett, R. and James, B., 1980, Studying Dried, Stored Soil Samples-Some Pitfalls, Soil Sci-Soc Am. J., 44, 721-724.

5. Harry, S.P. and Alston, A.M., 1981, Effect of Temperature on EDTA-Extractable Copper in Soils, Soil Sci. Soc. Plant Anal., 12(7), 661-668.

6. Khan, A. and Soltanpour, P.N., 1978, Effect of Wetting and Drying on DPTA-Extract-able Fe, Zn, Mn, and Cu in Soils, Commun. in Soil Sci. Plant Anal., 9(3), 193-202.

7. Legget, G.E. and Argyle, D.P., 1985, The DTPA-extractable Iron, Manganese, Copper and Zinc from Neutral and Calcareous Soils Dried Under Different Conditions, Soil Sci. Am. J., 47, 518-522.

8. Specklin, G. and Baliteau, J.Y., 1989, Influence des conditions de preparation des echantillons de terre sur les teneurs en oligo-elements: 19-37, In "P. DUC Ed. Les obligo-elements et le sol" Editions Frontieres.

9. Soil Quality-Pretreatment of Soil Samples for the Analysis of Heavy Metals, Arsenic, Antimony and Selenium (Draft), 1995, Standards Australia, DR95363.

10. Barth, D.S. and Mason, B.J., 1984, Soil Sampling Quality Assurance and the Importance of an Exploratory Study: 97-104, In "G.E. Scheitzer and J.A. Santolucito Eds. Environmental Sampling for Hazardous Waste", Am. Chem. Soc.

11. Gy, P., 1956, "Nomogramme d'Echantillonage", Societe de Minerais et Metaux, Paris.

12. Wastes, Sediments and Contaminated Soils, Part 3: Preparation of Leachates-Bottle Leaching Procedure, 1995, Standards Australia, DR95140.

13. Test Methods for Evaluating Solid Waste, 1986, USEPA Publication SW-846, Third edition, Chapter Four, Vol. 1B Part B, Revision 2 Sept. 1994, Section 4.1.2 and Table 4-1.

14. Ilias, A. M. and Jaeger, C., 1993, Evaluation of Sampling Techniques for Analysis of Volatiles and Total Recoverable Petroleum Hydrocarbons (TRPH) by IR, GC and GC/MS Methods" in Hydrocarbon Contaminated Soils, Lewis Publishers.

15. Lewis, T.E, Crockett, A. B., Siegrist, R. L. and Zarrabi, K., 1991, Soil Sampling and Analysis for Volatile Compounds". USEPA Office of Solid Waste and Emergency Response, Publication EPA/540/4-91/001.

16. Test Methods for Evaluating Solid Waste, 1986, Method 5035, USEPA Publication SW-846, Third edition, Final Update, 1996. Vol. 1B Part B

6. LEACHABLE INORGANICS AND SEMI-VOLATILE ORGANICS (METHOD 101)

6.1 SCOPE AND APPLICATION

Leachable organics (volatile and semi-volatile), metals and anions (except cyanide) may be determined using the Toxicity Characteristic Leaching Procedure (TCLP), which is method 1311 in SW-846 (USEPA, 1997).

Alternatively, Australian Standard 4439.2 (Standards Australia, 1997b) can be used for volatile organics, and Australian Standard 4439.3 (Standards Australia, 1997c) can be used for semi-volatile organics, metals and anions.

The methods in the Australian Standards are different from the USEPA method in that a wider range of leaching reagents is allowed. All methods are designed to simulate leaching conditions in the environment to determine available pollutants. The choice of leach reagent should be based on the environmental conditions to which the wastes are, or will be, exposed .

Leachable cyanide may be determined by Method 1312, the Synthetic Precipitation Leaching Procedure using deionised water leach fluid (USEPA, 1997) or by leaching with distilled or de-ionised water only, using the methods in Australian Standard 4439.2 (Standards Australia, 1997b).

7. MOISTURE CONTENT (METHOD 102)

7.1 SCOPE AND APPLICATION

This method measures the mass of water in a field-moist or air-dried soil sample. For most chemical analyses, the moisture content is usually determined to obtain a correction factor to express chemical concentrations on a dry weight basis. For this purpose, regardless of whether the soil is analysed in a field-moist state or after air-drying, moisture determination should be carried out on a portion of the sample as analysed.

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

When a number of tests are to be performed on a soil sample, 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 drying the sample may affect the results of other tests.

7.2 PRINCIPLE

Water in the field-moist or air-dried sample is evaporated at 105 ± 5°C. The loss in moisture is expressed as a percentage of the mass of soil prior to oven-drying ie. the field-moist or air-dried mass.

Note: This method differs from AS 1289.2.1-1992 (Testing of Soils for Engineering Purposes: Determination of Moisture Content Using the Oven-drying Method) [1]. The major difference between the two methods is that the Australian Standard procedure requires a substantially larger mass of sample.

7.3 INTERFERENCES

Oven-drying at 105 ± 5°C does not result in reliable moisture content values for soils containing gypsum or other minerals having loosely bound water of hydration or for certain soils containing significant quantities of organic material (eg. peats). These soils may oxidise or undergo decomposition at the drying temperature used in this test. Weight losses observed, therefore, may not be due entirely to removal of water. If gypsum is suspected to be present in the sample, use a drying temperature of 80°C instead of 105°C [1].

7.4 APPARATUS

- Drying oven, continuously thermostatically controlled at 105 ± 5°C
- Desiccator with active desiccant
- Balance, accurate to 0.01 g

7.5 PROCEDURE

1. Weigh a clean dry beaker (or aluminium dish) to the nearest 0.01 g (W_1).

2. Add approximately 10 g of the homogenised soil to the beaker and weigh to the nearest 0.01 g again (W_2). For coarse textured soils a larger sample mass should be used to ensure a representative sample is taken.

3. Place the beaker with moist (or air-dried) sample in a drying oven maintained at a temperature of 105 ± 5°C for about two hours (or the expected time for all the moisture to evaporate off).

   Note: This time is indicative only and will vary with the amount of moisture and type of soil.

4. Remove the sample from the oven and place it in a desiccator to cool.

5. Weigh the sample and beaker again (W_3). Repeat steps (3) to (5) until constant weight is achieved ie. the moisture loss is not more than 1 percent of the previous weight. Drying overnight is usually sufficient to achieve constant weight.

6. Report the moisture content (or corrected analyte concentration), and the oven temperature if it was other than 105°C.

7.6 CALCULATIONS

1. Oven-dried moisture content, mass basis

$$M \text{ (percent)} = \frac{\text{weight of water (g)} \times 100}{\text{weight of field-moist or air-dried soil (g)}}$$

$$= \frac{[W_2\,(g) - W_3\,(g)] \times 100}{W_2\,(g) - W_1\,(g)}$$

where: M = moisture content (%)
W_1 = weight of beaker (g)

W_2 = weight of beaker and field-moist or air-dried soil (g)

W_3 = weight of beaker and oven-dried soil (g)

2. Correction of field-moist or air-dried analyte concentration to oven-dried basis

$$C_{dry} = \frac{100}{(100 - M)} \times C_{moist}$$

where: C_{dry} = concentration of analyte in a sample expressed as oven-dried basis

C_{moist} = concentration of analyte in a sample expressed as field-moist or air-dried basis

M = moisture content (%)

7.7 USE OF MICROWAVE OVENS

The use of microwave oven drying for the determination of soil moisture content is not currently recommended, as it has not been demonstrated that the water driven off in microwave drying is equal to that removed in conventional oven drying.

7.8 METHOD PERFORMANCE

No validation data are available for this method.

7.9 REFERENCE

1. AS 1289.2.1.1-1992, Testing of Soils for Engineering Purposes: Determination of Moisture Content Using the Oven-drying Method, Standards Australia.

8. SOIL PH (METHOD 103)

8.1 SCOPE AND APPLICATION

This method measures the hydrogen-ion concentration in a soil-water or soil-calcium chloride suspension and is expressed in pH units.

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

The use of 0.01 M calcium chloride extract is recommended where the salt content may have an influence on the pH value [1-3]. Generally, the pH of the calcium chloride extract is about 0.5 to 1.0 pH unit lower than the water extract and gives more precise values [4-6]. For comparability of the pH values of different soils collected at different times, it may be useful to determine the pH of both extracts.

The same 1:5 soil-water suspension for electrical conductivity determination (Method 104) may be used for measuring pH but to avoid contamination, electrical conductivity should be analysed first.

8.2 PRINCIPLE

Soil pH is measured electrometrically on a 1:5 soil-water suspension (or its equivalent, using field-moist soil) at 25°C. A 1:5 soil-calcium chloride extract is also provided as an option.

8.3 APPARATUS

- Magnetic stirrer with magnetic stirring bar
  (for processing large numbers of samples, it is more efficient to agitate the Erlenmeyer flasks on an orbital platform shaker)
- Digital pH meter, sensitive to 0.01 pH unit
- pH electrode (glass and saturated calomel reference electrodes, or combination electrode)

8.4 REAGENTS

All reagents used should be of recognised analytical reagent grade.

- Buffer solutions:
  Three buffer solutions which bracket the expected soil pH values, for calibrating the pH meter (eg. pH 4.00, 7.00 and 10.00).
- Calcium chloride, 1 M (for water and $CaCl_2$ extracts); or
  0.01 M (if only calcium chloride extract is required).

8.5 PROCEDURE

1. Weigh 20.0 g (± 0.1 g) of air-dried soil(<2 mm) into a beaker. Alternatively, weigh an equivalent mass of field-moist soil (<2 mm) calculated after determining moisture content in accordance with Method 102. (The mass correction should only be applied if >30% moisture is suspected).

2. Add 100 mL deionised water (or 0.01 M calcium chloride if electrical conductivity (EC) of the water extract is not required to be measured).

3. Place the beaker containing the soil on an agitator (preferably a mechanical flask shaker or orbital platform shaker; otherwise on a stirring mantle with a magnetic bar placed inside the flask). Agitate the solution for one hour. Monitor the temperature of the solution. Precautions should be taken, if necessary, to ensure that heat generated by the stirrer motor does not affect the temperature of the test suspension.

4. Calibrate the pH meter while the soil is being stirred, preferably as close as possible to the end of the stirring period.

   Perform a two-point calibration of the pH meter, if this facility is available, using the pH 7 (or similar) buffer and one other which brackets the majority of soil pH expected (soils in Victoria are mainly acidic [4]). Check the calibration using the third buffer. Where two-point calibration is not provided, calibrate the meter with the pH 7 (or similar) buffer and check with two other buffers.

   All measurements should be made at 25°C or corrected for any substantial deviations of the testing temperature from 25°C. The manufacturer's instructions on the use and calibration of the pH meter should be followed.

5. After an hour of stirring, switch off the stirrer and allow the solution to stand for one minute. Insert the pH electrode and a thermometer, and take the reading after a further minute has elapsed but while the solids are still settling. If the sample batch is large, the solution may need to be re-agitated manually for a few seconds, about a minute prior to taking the reading.

   Note: If the sample temperature differs from the buffer temperature by more than 2°C, the measured pH value must be corrected to 25°C. Alternatively, measure the pH in a constant temperature environment set at 25°C eg. in water bath.

6. If the pH value is constant at the end of this period (difference of not more than 0.05 pH units), record the pH to the nearest 0.1 pH units. Otherwise, take further readings at approximately 1 minute intervals until the pH value stabilises.

7. If the pH of both water and calcium chloride extracts are required, add 1 mL of 1 M calcium chloride to the water extract and stir the solution to mix. Record the reading when the pH value stabilises.

8. Remove the electrode from the solution and rinse with deionised water.

9. The pH 7 (or similar) buffer should be used to check the meter at least every twenty samples in any one batch.

10. Report the pH value, the temperature at which the reading was taken and the extractant used.

8.6 METHOD PERFORMANCE

No validation data are available for this method.

8.7 REFERENCES

1. Chang, M.L. and Thomas, G.W., 1963, Soil Sci. Am. Proc. 27, 281-283.

2. Coleman, N.T. and Thomas, G.W., 1964, Soil Sci. Am. Proc. 28, 187-190.

3. Coleman, N.T. and Thomas, G.W., 1967, The Basic Chemistry of Soil Acidity, In R.W. Pearson and F. Adams (ed.), Soil Acidity and Liming, Agronomy 12:1, Am. Soc. of Agron., Inc., Madison, Wisconsin

4. Greenhill, N., June 1994, personal communication, State Chemistry Laboratory, Department of Agriculture, Energy and Minerals (Victoria).

5. Conyers, M.K. and Davey, B.G., 1988, Observations on Some Routine Methods for Soil pH Determination, Soil Sci. 145, 29-36.

6. Rayment, G.E. and Higginson, F.R., 1992, Soil pH in Australian Laboratory Handbook of Soil and Water Chemical Methods, Inkata Press, Melbourne, p19.

9. ELECTRICAL CONDUCTIVITY (METHOD 104)

9.1 SCOPE AND APPLICATION

This method measures the electrical conductivity of a 1:5 soil-water suspension. Electrical conductivity of the soil is sometimes used to estimate the soluble salt content of a sample [1]. The soluble salt content may affect the suitability of the soil as a plant growth medium or the potential for corrosion of below ground structures.

The same 1:5 soil-water suspension for pH determination (Method 103) may be used for measuring the electrical conductivity but to avoid contamination, electrical conductivity should be analysed first.

9.2 PRINCIPLE

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

9.3 APPARATUS

- Conductivity meter, preferably with readout in dS/m.
- Conductivity cell with automatic temperature compensation, or conductivity probe.
- Magnetic stirrer, with magnetic stirring bar.
  (for processing large numbers of samples, it is more efficient to agitate the Erlenmeyer flasks on an orbital platform shaker).

9.4 REAGENTS

All reagents used should be of recognised analytical reagent grade.

- Conductivity water:
  Deionised water having a conductivity of less than 0.001 dS/m (1 µS/cm).
- Standard potassium chloride solutions, 0.010 M and 0.100 M:
  At 25°C, these solutions should have conductivities of 1.412 dS/m and 12.900 dS/m respectively.

9.5 PROCEDURE

1. Weigh 20.0 g (± 0.1 g) air-dried soil (<1 mm) into a beaker.

2. Add 100 mL conductivity water to the soil.

3. Place the beaker containing the soil on an agitator (preferably a mechanical flask shaker or orbital platform shaker; otherwise on a stirring mantle with a magnetic bar placed inside the flask). Agitate the solution for one hour. Monitor the

temperature of the solution, maintaining it at 25.0 ± 0.1°C. Precautions should be taken, if necessary, to ensure that heat generated by the stirrer motor does not affect the temperature of the test suspension.

4. Towards the end of the stirring period, calibrate the conductivity meter using the standard potassium chloride solutions and in accordance with the manufacturer's instructions. Rinse the conductivity cell or probe with deionised water, shaking off any excess water that might otherwise dilute the sample before testing the soil-water suspension.

5. Switch off the magnetic stirrer and allow the solution to stand for one minute. Decant the supernatant solution into the conductivity cell (or into a clean dry glass beaker if using a conductivity probe) and take a reading after another minute has elapsed.

6. Report the electrical conductivity at 25°C or corrected to 25°C.

9.6 Conversion to Approximate Salt Content and Osmotic Pressure

The following equations are commonly used to estimate soluble salt content of the soil-water suspension [2-4]. Note that these relationships are approximate only and will vary, depending upon the nature of the soluble salts in the sample.

1. Total cation (or anion) concentration ($mmol_{c(or\ a)}/L$) ≈ 10 x EC (dS/m)

2. Salt concentration (mg/L) ≈ EC (dS/m) x 640

   where EC, expressed as dS/m, is the electrical conductivity of a 1:5 soil-water suspension, corrected to 25°C.

   Note: The conductivity unit, Siemen (S), is numerically equivalent to the conductivity unit, mho. mhos are reciprocal ohms, so conductivity measurements may be converted to resistivity units by a simple calculation.

9.7 Method Performance

No validation data are available for this method.

9.8 References

1. Rhoades, J.D., 1982, Soluble Salts in Methods of Soil Analysis, Part 2, Page, A.L., Miller, R.H. and Keeney, D.R. (eds.), Agronomy Monograph No. 9, 2nd. Ed., American Soil Science Society, Madison WI, 168.

2. Ibid., 173

3. Jurinak, J.J., 1990, The chemistry of Salt-affected Soils and Waters in Agricultural Salinity Assessment and Management, K.K. Tanji (ed.), American Society of Civil Engineers, New York.

4. Sumner, M.E., Rengasamy, P. and Naidu, R., In Press, Chapter 1 Sodic Soils: A Reappraisal in Sodic Soils: Distribution, Processes, Management and Environmental Consequences, Sumner, M.E. and Naidu, R. (eds.), Oxford University Press, New York.

10. ORGANIC CARBON (METHOD 105)

10.1 SCOPE AND APPLICATION

This determination, based on the Walkley-Black Method [1], measures the oxidisable organic carbon content of soils. The results of the determination may be used to estimate the "total organic carbon" content of soil, although this conversion is rarely recommended for use in the investigation of contaminated soils.

Soil organic carbon comprises a variety of carbonaceous materials including humus, soil micro-organisms, plant and animal residues, coal, charcoal, coke, and graphite. It does not include carbonate minerals such as calcite or dolomite. Australian soils generally contain less than 5 percent of organic carbon but higher levels are common in surface soils [2].

This method is known to give poor recoveries of carbonised materials such as graphite, coal, coke and similar coal derivatives. If these materials are likely to make up a large part of the carbon present in the soil sample or when total organic carbon content is required, an alternative method which makes use of an external heat source is recommended [2,3].

10.2 PRINCIPLE

The organic material in the soil sample is oxidised with chromic acid in the presence of excess sulfuric acid without external heat being applied. The excess dichromate ion is determined by titration with standard ammonium iron (II) sulfate solution and the amount of oxidised material is calculated from the quantity of dichromate reduced.

10.3 INTERFERENCES

Over-estimation of organic carbon may occur due to the presence of large amounts of chloride or metallic or ferrous iron in the soil sample. Underestimation of the organic carbon content may result when higher oxides of manganese are present in substantial quantities. The possible effects of these interferences should be taken into account in the analysis of some types of poorly aerated soils.

10.4 APPARATUS

- Glass fibre filters (pre-washed with 1% (v/v) nitric acid)

10.5 REAGENTS

All reagents used should be of recognised analytical reagent grade.

- Potassium dichromate solution, 0.1667 M

CAUTION: Strong oxidising agent. Cr (VI) compounds are also toxic. Avoid skin contact and inhaling the chemical. Prepare this in a fumehood.

- Sulfuric acid, concentrated

  CAUTION: Corrosive liquid. Handle with extreme care using acid-resistant gloves and eye-protection.

- Phenanthroline iron (II) sulfate indicator solution (Ferroin indicator):

  Dissolve 1.48 g of 1,10-(ortho)-phenanthroline monohydrate and 0.70 g of $FeSO_4.7H_2O$ in 100 mL of deionised water.

  (This indicator is also available commercially as "Ferroin Indicator").
- Silver sulfate crystals (required only if chloride interference is likely to be present)
- Ammonium iron (II) sulfate, 0.5 M

10.6 PROCEDURE

1. Dry the soil at 35°C and grind to pass a 0.15 mm mesh sieve. A non-ferrous mill or mortar should be used to reduce the possibility of sample contamination by metallic iron.

2. Accurately weigh an appropriate quantity (± 0.01 g) of the sieved soil into a 500 mL Erlenmeyer flask (refer table below).

Soil Type	Appropriate amount of soil [4]
Organic horizon*	0.1-0.2 g
Surface soils	0.5 g
Subsoils	2.0 g

* surface layer of decomposing material not significantly mixed with the mineral soil

3. Pipette 10.00 mL standard dichromate solution into the flask and gently swirl to mix.

4. If chloride interference is anticipated, add Ag_2SO_4 to some concentrated sulfuric acid at a rate of 15 g/litre of acid.

5. Cautiously add 20 mL the concentrated sulfuric acid to the flask with the soil and again gently swirl for about 30 seconds.

6. Allow the flask to cool.

7. Carefully add about 200 mL deionised water. Allow the solution to cool by standing it on a white tile or sink for about 30 minutes. The end-point of the titration is more easily determined with a cold mixture.

Note: The heat transfer affects the extent and rate of reaction. Therefore, it is crucial that the flask is cooled prior to the titration in order to obtain uniformity of results.

8. Filter the suspension through an acid-washed glass fibre filter.

9. Add 3 to 4 drops of the indicator solution to the filtrate and titrate the excess dichromate with the 0.5 M ammonium iron (II) sulfate solution. The colour change at the end-point will be sharp, changing from a blue-green to a reddish hue.

10. Make a blank determination in the same manner but without soil to standardise the ammonium iron (II) sulfate solution.

11. Repeat the determination with less soil if more than 75 percent of the dichromate is reduced.

10.7 CALCULATIONS

1. Standardisation of ammonium iron (II) sulfate:

$$M_A = \frac{6 \times 10 \times C}{V}$$

where: M_A = concentration of ammonium iron (II) sulfate (M)
C = concentration of potassium dichromate (M)
V = volume of ammonium iron (II) sulfate titrated against 10.00 mL of potassium dichromate (mL)

2. Percent oxidisable organic carbon (OC):

$$OC = \frac{[(B - A) \times 0.3 \times M_A]}{W}$$

where: OC = per cent oxidisable organic carbon
B = blank titre (mL)
A = sample titre (mL)
M_A = concentration of ammonium iron (II) sulfate (M)
W = weight of dried soil (g)

3. Correction for total organic carbon:

The method described above recovers variable proportions of the organic carbon actually present in a soil sample. Typical recoveries vary from less than 65% to more than 85%. In the absence of a correction factor derived specifically for the soil being tested, the use of 1.3 as a correction factor is commonly recommended. The total organic carbon content would therefore be:

Total organic carbon (percent) = Oxidisable organic carbon (percent) x 1.3

10.8 METHOD PERFORMANCE

No validation data are available for this method.

10.9 REFERENCES

1. Walkley, A and Black, I.A., 1934, Soil Sci. 37, 29-38.

2. Rayment, G.E. and Higginson, F.R., 1992, Organic Carbon in Australian Laboratory Handbook of Soil and Water Chemical Methods, Inkata Press, Melbourne, p29.

3. Heanes, D.L., 1984, Determination of total organic-C in soils by an improved chromic acid digestion and spectrophotometric procedure, Commun. Soil Sci. Pl. Anal. 15, 1191-1213.

4. Organic carbon by modified Walkley-Black method, Method 014, 1987, State Chemistry Laboratory, Victorian Department of Agriculture.

11. AQUA REGIA DIGESTIBLE METALS (METHOD 201)

11.1 SCOPE AND APPLICATION

This method[1] may be used to obtain extracts from soils or solids for the analysis of all metals except antimony, arsenic, selenium, volatile organo-metals and mercury (for these analyses, see Method 202, Method 203 and Method 204). Metals extractable by this digestion include the metallic components adsorbed on soil particles, complexed by and adsorbed on organic matter, and in the form of soluble 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.

Extracts of this method can be analysed for metals by flame atomic absorption spectrometry, graphite atomic absorption spectrometry or inductively coupled plasma atomic emission spectrophotometry (ICP-AES). Interference from the high chloride content in the extract makes it unsuitable for analysis by inductively coupled plasma mass spectrophotometry (ICP-MS) [2-3].

This method is not applicable to the determination of volatile organo-metallic compounds eg. tetramethyl-lead or tetraethyl-lead in samples from service stations [4]. These samples and those with a high content of oil should be analysed by USEPA Method 3050B (nitric acid/ hydrogen peroxide digestion at 95°C; see Method 202)[5], where greater decomposition of organics is achieved by the addition of the hydrogen peroxide. The lower digestion temperature also minimises loss of the volatile metals.

USEPA Method 3050B may be used as an alternative to this method (see Method 202). It gives comparable and even slightly better extraction efficiencies for some metals compared with the aqua regia method[6]. Laboratory trials at EPA (Victoria) have however, shown that the digestion time for Method 3050B is longer and requires greater control of the digestion temperature to obtain uniformity of results.

Microwave digestion of soils for metals analysis can also be used as an alternative to this method (see Method 203). Other alternatives eg. digestion in tubes, may be used if it can be demonstrated that comparable results can be obtained.

11.2 PRINCIPLE

Boiling aqua regia (3:1 hydrochloric/nitric acid) is used to extract the metals from the soil. The strong and concentrated acid mixture is capable of extracting inorganic metals as well as those bound in organic or sulfide forms.

11.3 APPARATUS

- Filter paper (Whatman 541 or equivalent), prewashed with 1% (v/v) nitric acid and deionised water.

Note: Some filter papers have been shown to contain residual metals, particularly zinc. It is therefore necessary to wash filters thoroughly with 1% nitric acid and water, or to use alternative filters. Whatman 541 filters (hardened ashless filter papers) have been shown to be satisfactory.

11.4 REAGENTS

All reagents should be of recognised analytical reagent grade.

CAUTION: Handle concentrated acids with extreme care. Wear protective clothing, safety glasses and acid-resistant gloves.

- Hydrochloric acid, concentrated
- Nitric acid, concentrated
- Nitric acid, 1% (v/v)

11.5 PROCEDURE

A reagent blank with no soil should be included with each process batch of samples.

1. Accurately weigh 1 g (± 0.02 g) of air-dried soil (<2 mm) (or an amount approximately equal to 1 g of soil when dried), into a 150 mL Erlenmeyer flask.

   Note: For better reproducibility of results, air-dried soil is preferred. However, if the field-moist sample is used, ensure that the entire sample is homogenised by thoroughly mixing and sieving (if amenable to sieving), according to 5.1.3, and that there are no solid particles distinctly different from the soil eg. fragments of metal or coloured particles of an unusual nature.

2. Moisten the soil with a little deionised water.

3. Cautiously add 18 mL of concentrated HCl and 6 mL of concentrated HNO_3 to the soil in the flask.

4. Place the flask on a hot plate and cover with a watch glass or funnel.

5. Gently boil the acid until about 5 to 10 mL of extract remains in the flask while ensuring the sample is covered with solution.

6. Remove the flask from the hot plate and allow to cool for about 15 min.

7. Add another 18 mL of concentrated HCl and 6 mL of concentrated HNO_3 to the flask.

8. Repeat boiling off the aqua regia till about 5 to 10 mL of extract remains.

9. Remove the flask from the hot plate and allow it to cool to room temperature.

10. Carefully add about 20 mL of deionised water to the flask, rinsing the inner walls of the flask in this step.

11. Quantitatively transfer and filter the extract through an acid-washed filter paper into a 50 mL volumetric flask (use about two 10 mL portions of deionised water to wash the residue and inner walls of the flask).

12. After the volumetric flask has cooled, make up to the mark.

13. Analyse for the analytes of interest by atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) or other suitable validated method.

11.6 CALCULATION

Calculate the concentration of the metal as follows:

$$M \text{ (air-dried basis)} = \frac{(C - B) \times 50}{W}$$

where: M = concentration of metal in the soil, air-dried basis (mg/kg)
C = concentration of metal in the digest (mg/L)
B = concentration of metal in the blank (mg/L)
W = weight of air-dried soil sample digested (g)

11.7 METHOD PERFORMANCE

The following recoveries were obtained by Environment Protection Authority (Victoria)[7] from standard reference soils or sediment using Method 201.

Metal	SRM 2710 Montana Soil				SRM 1646 Estuarine Sediment			
	n	Nominal value (mg/kg)	Recovery (%)	Coeff. Var. (%)	n	Nominal value	Recovery (%)	Coeff. Var. (%)
Iron	6	3.38%	86	3.8	2	3.35%	97	10
Lead	6	5532	97	5.5	3	28.2	73	16
Zinc	6	6952	90	3.4	3	138	81	5.2
Copper	6	2950	91	6.8	3	18	85	3.8

Metal	SRM 2710 Montana Soil				SRM 1646 Estuarine Sediment			
Cadmium	4	21.8	83	7.8	b	0.36	-	-
Chromium	a	-	-	-	3	76	69	8.8
Nickel	4	14.3	59	28	3	32	78	6.9

n= number of samples; a = Not Certified; b = Not Analysed; Coeff. Var. = Coefficient of Variation

Metal	CRM 277 Trace Elements in Estuarine Sediment				CRM 146 Trace Elements in Sewerage Sludge of Mainly Industrial Origin			
	n	Nominal value (mg/kg)	Recovery (%)	Coeff. Var. (%)	n	Nominal value	Recovery (%)	Coeff. Var. (%)
Lead	14	146	86	5.1	4	1270	96	1.2
Zinc	12	547	102	9.2	3	4059	96	3.1
Copper	12	101.7	88	4.5	4	934	92	7.4
Cadmium	9	11.9	84	10	2	77.7	89	3.1
Chromium	11	192	85	5.8	c	-	-	-
Nickel	10	43.4	95	12	2	280	93	6.2

n= number of samples; c = Not Analysed; Coeff. Var. = Coefficient of Variation

11.8 REFERENCES

1. Agemian, H. and Chau, A.S.Y., 1976, Evaluation of Extraction Techniques for the Determination of Metals in Aquatic Sediments, The Analyst 101, 761.

2. Ms L. Plues, 1995, Director Laboratories, Environment Protection Authority, Bankstown, New South Wales, personal communication.

3. Dr H. Louie, 1996, Australian Government Analytical Laboratory, Sydney, New South Wales, personal communication.

4. Dr R. Mooney, 1996, AMDEL, Sydney, New South Wales, personal communication.

5. Test Methods for Evaluating Solid Waste, 1986, Method 3050B, Acid Digestion of Sediments, Sludges and Soils, USEPA Publication SW-846, Third edition.

6. Shelley, B., 1995, personal communication, State Chemistry Laboratory, Department of Agriculture, Energy and Minerals (Victoria).

7. Environment Protection Authority, 1992, Method 2100: Aqua Regia Digestible Metals, Victoria.

12. ACID DIGESTION OF SEDIMENTS, SLUDGES AND SOILS (METHOD 202)

Source: USEPA, SW-846 Method 3050B [1]

12.1 SCOPE AND APPLICATION

USEPA Method 3050B may be used to obtain extracts from sediments, sludges and soils for the analysis of metals by flame atomic absorption spectroscopy (FAAS), graphite furnace atomic absorption spectroscopy (GFAAS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS). It is applicable to the determination of the following elements:

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		Vanadium

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

This method is also applicable to the analysis of volatile organo-metallic compounds eg. tetramethyl-lead or tetramethyl-lead in samples from service stations, and samples with a high content of oil [2]. The low digestion temperature (95°C) minimises the loss of volatile metals and the hydrogen peroxide enhances the decomposition of the organics.

12.2 PRINCIPLE

Two separate digestion procedures are provided for determination of the above elements:

12.2.1 For FAAS and ICP-AES:

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

12.2.2 For GFAAS and ICP-MS:

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

For the analysis of antimony, barium, lead and silver, an optional nitric acid/hydrochloric acid digestion step is included to improve the solubilities and recoveries of these analytes.

Note: USEPA Method 3050B does not include arsenic in the above list with the optional step. It has however been shown that arsenic recovery is improved when the optional step is included [3]. As a result of the addition of HCl in the optional step, the extract may be unsuitable for analysis by GFAAS or ICP-MS. FAAS or ICP-AES may be used instead.

12.3 ANALYSIS

The procedure as described in USEPA SW-846 Method 3050B should be adhered to strictly, without any changes to the method.

12.4 METHOD PERFORMANCE

Refer USEPA Method 3050B and Reference 3.

12.5 REFERENCES

1. Test Methods for Evaluating Solid Waste, 1986, Method 3050B, Acid Digestion of Sediments, Sludges and Soils, USEPA Publication SW-846, Third edition.

2. Dr R. Mooney, 1996, AMDEL, Sydney, New South Wales, personal communication.

3. Kimbrough, D.E. and Wakakuwa, J.R., 1989, Acid Digestion for Sediments, Sludges, Soils and Solid Waste. A Proposed Alternative to EPA SW 846 Method 3050, Environ. Sci. Technol. 23, 898.

13. MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS AND OILS (METHOD 203)

Source: USEPA, SW-846 Method 3051 [1]

13.1 SCOPE AND APPLICATION

This method, USEPA Method 3051, "Microwave assisted digestion of sediments, sludges, soils and oils" [1,2] describes a rapid procedure for digesting sediments, sludges, soils and oils for the analysis of most metals, some metalloids and some nonmetals. The elements that can be determined by this method are:

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

This method can be used as an alternative to the aqua regia method (see Method 201) or the nitric acid/ hydrogen peroxide method (see Method 202 - USEPA Method 3050B).

A typical working range for cadmium, chromium, copper, iron, lead, nickel and zinc in soils by this method is given below [3].

Metal	**Working range * (mg/kg)**
Cadmium	4 - 400
Chromium	20 - 2000
Copper	10 - 1000
Iron	20 - 2000
Lead	40 - 4000
Nickel	20 - 2000
Zinc	2 - 200

* Working range for 0.5 g sample and final volume of 100 mL

Note: Samples with values higher than these can be diluted during analysis.

The advantages of the microwave digestion technique include reduced digestion time (from several hours by conventional hotplate method, to 10 minutes) and uniformity of digestion conditions. The final digest can be analysed for the element by flame atomic absorption (FAAS), graphite furnace atomic absorption (GFAAS), inductively coupled plasma emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS).

Although the digestion step is rapid, sample throughput is limited to the number of slots available in the microwave turntable and the time required for cooling and cleaning the vessels between batches of digestions. Therefore, the aqua regia digestion (see Method 201) or nitric acid/ hydrogen peroxide digestion (see Method 202) may be more suitable for large numbers of samples.

13.2 PRINCIPLE

The sample is digested in concentrated nitric acid using microwave heating in a sealed Teflon vessel at elevated temperature and pressure. The extract can then be analysed by FAAS, GFAAS, ICP-ES or ICP-MS.

13.3 NOTES ON METHOD 3051

- This digestion involves the use of concentrated acid at elevated temperature (180°C) and pressure (700 kPa). It is important that extra safety precautions eg. acid vapour venting procedure, are in place to ensure the safe handling of the extracts and proper operation of the microwave unit.
- Due to the small quantity of sample required for this method (0.5 g or less), it is important that the sample is well homogenised. Although field-moist samples can be used for this method, a more representative sample can be obtained by subsampling the dried and well-mixed sample.

13.4 ANALYSIS

The procedure as described in USEPA SW-846 Method 3051 should be adhered to strictly, without any changes to the method.

13.5 METHOD PERFORMANCE

The following recoveries were obtained by Environment Protection Authority (Victoria)[3] using this method.

Metal	SRM 2704 Buffalo River Sediment			
	n	Nominal value (mg/kg)	Recovery (%)	Coeff.Var.(%)
Iron	3	4.11%	72	10
Lead	5	161	85	16
Zinc	4	438	81	7.4
Copper	4	98.6	84	11
Cadmium	3	3.45	70	15
Chromium	4	135	61	14
Nickel	3	44.1	67	28

Coeff. Var. = Coefficient of Variation

More validation data are available from USEPA Method 3051 and Reference 2.

13.6 REFERENCES

1. Method 3051, Microwave Assisted Acid Digestion of Sediments, Sludges, Soils and Oils, 1986, Test Methods for Evaluating Solid Waste, USEPA Publication SW-846, Third edition.

2. Binstock, D.A., Grohse, P.M. and Gaskill, A., Jnr., 1991, Development and Validation of a Method for Determining Elements in Solid Waste Using Microwave Digestion, J. Assoc. Off. Anal. Chem. 74 (2), 360-366.

3. Environment Protection Authority, 1992, Method 2101: Microwave Assisted Acid Digestion of Sediments, Soils and Oils, Victoria.

14. MERCURY (METHOD 204)

Source: USEPA SW-846 Method 7471A [1]

14.1 SCOPE AND APPLICATION

This method is applicable to the determination of total mercury (inorganic and organic) released by strong acid digestion (aqua regia) of soils, sediments, bottom deposits and sludge type materials [1].

This method describes a closed system for the determination of mercury by cold-vapour atomic absorption spectrometry. Although no guidance is given, it allows the use of open systems and commercial instruments designed specifically for determining mercury by the cold-vapour technique.

Note: Open systems are more widely used in Australia. Laboratories which use such systems should demonstrate that reliable results can be obtained from them.

The typical instrument detection limit for this method is 0.0002 mg/L[1].

Method 203 (USEPA Method 3051) may be used as an alternative to this method.

14.2 PRINCIPLE

Inorganic and organic forms of mercury are digested with aqua regia (1:3 nitric acid, hydrochloric acid) at 95°C and in the presence of a strong oxidant (potassium permanganate). Mercury in the digest is then analysed by cold-vapour atomic absorption spectrometry at 253.7 nm. The soil is analysed as received and the result reported on a dry weight basis after correcting for moisture content (see Method 102).

CAUTION: Avoid inhaling the highly toxic mercury vapour. Ensure the mercury vapour is vented into an appropriate exhaust hood or preferably, trapped in an absorbing medium eg. $KMnO_4/H_2SO_4$ solution.

14.3 NOTE ON METHOD 7471A

- As this method uses only a small quantity (0.2 g) of the field-moist sample, it is very important that the sample is well-mixed before removing an aliquot for analysis.

14.4 ANALYSIS

The procedure as described in USEPA SW-846 Method 7471A should be adhered to strictly, without any changes to the method.

14.5 METHOD PERFORMANCE

The following recoveries were obtained from two spiked samples [2].

Spiked Mercury Concentration (ug/g)	Recovery (% of True Value)	Standard Deviation (ug/g)
0.30	97	0.02
0.87	94	0.03

Two laboratory trials at Environment Protection Authority (Victoria) for 5 replicate analysis of two standard reference soils, CRM 277 Trace Element in Estuarine Sediment (expected Hg = 1770 µg/kg) and SRM 1645 Buffalo River Sediment (expected Hg = 1100 µg/kg) , gave recoveries of 120 and 99 percent respectively. The mercury was determined using the borohydride cold-vapour generation system (open system) [3].

14.6 REFERENCES

1. Method 7471A, Mercury in Solid or Semisolid Waste (Manual Cold Vapour Technique), 1994, Test Methods for Evaluating Solid Waste, USEPA Publication SW-846, Third edition.

2. Guidance Manual on Sampling, Analysis and Data Management for Contaminated Sites, Volume II: Analytical Method Summaries, 1993, The National Contaminated Sites Remediation Program, Canadian Council of Ministers of the Environment, Report CCME EPC-NCS66E, 150-151.

3. VGA-76 Vapour Generation Accessory, 1989, Operation Manual, Varian Techtron.

15. CATION EXCHANGE CAPACITY AND EXCHANGEABLE CATIONS (METHOD 301)

(Calcium, Magnesium, Potassium and Sodium)

Source: Rayment & Higginson (1992), Methods 15B1, 15B2, 15B3, 15C1 [1]

15.1 SCOPE AND APPLICATION

These methods measure the cation exchange capacity (CEC) and exchangeable cations (Ca^{2+}, Mg^{2+}, Na^{+} and K^{+}) of near-neutral and alkaline soils [1] (reference 1 refers to the exchangeable cations as "exchangeable bases"). They are applicable to the analysis of the following types of soils:

Soil Type	pH	Extractant	Salt content*	Method No. 1	Comments
non-calcareous; non-gypsiferous; near-neutral; soils dominated by minerals with constant surface charge	7.0	0.1M ammonium chloride	EC<0.3 dS/m EC> 0.3 dS/m	15B1 15B2 15B3	None Pretreatment: Soluble salts are removed using aqueous ethanol and aqueous glycerol. Adjustment: Corrected for soluble Na^{+} when NaCl is the dominant soluble salt.
Alkaline soils containing solid phase carbonates; soils dominated by colloids with permanent negative surface charges.	8.5	1M ammonium chloride with ethanol		15C1	Pretreatment: Soluble salts are removed using aqueous ethanol and aqueous glycerol.

* Based on electrical conductivity (EC) determined on a 1:5 soil/water extract.

Note: These methods are designed to provide information on the ion-exchange characteristics of soils for land surveys or soil fertility studies, where it is unlikely that highly contaminated soil is encountered. In contrast, soils heavily contaminated with soluble metals may 'saturate' the extractant's exchangeable sites and may not, without further tests, provide a true indication of the exchangeable capacity.

These methods should therefore be applied only to natural soils or background samples to provide supporting information on the potential extent of the contamination. If applied to other types of samples, the methods are qualitative and the results should be used as indicators only.

15.2 PRINCIPLE

The soil is shaken with the appropriate extractant (1:10 soil/extractant) for an hour where the exchangeable cations in the soil are replaced by ammonium ions. The extract is filtered, the soil is washed with extra extractant and the combined filtrate determined for the exchangeable cations Na^+, K^+, Ca^{2+} and Mg^{2+}.

The remaining soil is leached with a potassium-calcium solution to displace the exchangeable ammonium ions. The CEC is measured by determining the displaced ammonium ion.

Note: Although Rayment and Higginson (1992) provides two alternative methods for determining the ammonium and chloride contents of the leachate, other validated methods may be used for these analyses [2-3].

15.3 ANALYSIS

The procedure as described in Rayment and Higginson (1992) should be adhered to strictly, without any changes to the method.

15.4 METHOD PERFORMANCE

No validation data are available for this method.

15.5 REFERENCES

1. Rayment, G.E. and Higginson, F.R., 1992, Ion-exchange Properties in Australian Laboratory Handbook of Soil and Water Chemical Methods, Inkata Press, Melbourne, p145-148.

2. Standard Methods for the Examination of Water and Wastewater, 1995, Method 4500-NH3 F: Ammonia selective electrode, or 4500- NH3 G: Ammonia selective electrode using known addition, Greenberg, A.E., Clesceri, L.S. and Eaton, A.D. (eds), 19th Ed., American Public Health Association.

3. Standard Methods for the Examination of Water and Wastewater, 1995, Method 4500-Cl B: Argentometric Method, Greenberg, A.E., Clesceri, L.S. and Eaton, A.D. (eds), 19th ed., American Public Health Association.

16. WATER-SOLUBLE CHLORIDE (METHOD 401)

16.1 Scope and Application

This method measures water-soluble chloride in soil extracts (1:5 soil/water) [1].

16.2 Principle

The chloride in soil is extracted in deionised water and the chloride concentration determined by titration with silver nitrate using a chromate indicator (Mohr's titration) or other validated method.

16.3 Interferences

Water soluble colour in the soil may mask the colour change at the endpoint of the titration. If this occurs, remove the colour by adding an aluminium hydroxide suspension [2]. Alternatively, determine the chloride in the water extract by ion-selective electrode or ion-chromatography.

16.4 Reagents (for Chloride Determination by Mohr's Titration)

All reagents used should be of recognised analytical reagent grade purity.

- Saturated sodium bicarbonate solution
- Silver nitrate solution, 0.025 M
- Standard potassium chloride, 0.l00 M

16.4.1 Potassium chromate indicator:

CAUTION: Strong oxidising agent. Cr (VI) compounds are also toxic. Avoid skin contact and inhaling the chemical. Prepare this in a fumehood.

Dissolve 5 g of potassium chromate in approximately 75 mL of deionised water. Add a saturated solution of silver nitrate until a small amount of red silver chromate precipitates. Set the solution in the dark for 24 hours then filter to remove the precipitate and make the volume up to l00 mL.

16.4.2 Phenolphthalein indicator solution (not necessary if using pH electrode):

Use either the aqueous (1) or alcohol (2) solution below.

1. Dissolve 5 g phenolphthalein disodium salt in deionised water and dilute to one litre or

2. Dissolve 5 g phenolphthalein in 500 mL 95% ethanol or 2-propanol and add 500 mL water.

If necessary add 0.02 M NaOH dropwise until a faint pink colour appears in (1) or (2).

16.4.3 Methyl orange indicator solution (not necessary if using pH electrode):

Dissolve 500 mg methyl orange powder in deionised water and dilute to one litre.

16.5 PROCEDURE

1. Accurately weigh 20 g (± 0.0l g) of air-dried soil (< 2 mm) (or an amount approximately equal to 20 g of soil when dried, prepared according to Section 5.1.4), into an Erlenmeyer flask and add 100 mL deionised water. Allow the solution to stand for an hour with intermittent swirling.

2. Centrifuge or allow the solution to stand. Remove an aliquot of the extract for chloride determination by Mohr's titration or other validated method (eg. ion-chromatography or ion-selective electrode).

Chloride Determination By Mohr's Titration

3. Standardise l0.0 mL of the silver nitrate solution against the 0.l00 M standard potassium chloride solution.

4. Pipette 50 mL of the clear extract into an Erlenmeyer flask and place it on a stirring mantle. Insert a stirring bar and start the stirrer. Adjust the pH to between 4 and 8 with saturated sodium bicarbonate using a pH electrode (or that the solution is alkaline to methyl orange but acid to phenolphthalein).

5. Add l0 drops of the chromate indicator and titrate the soil extract with the standard silver nitrate solution until a permanent red or reddish-brown precipitate appears.

6. Determine a blank correction by titrating 50 mL deionised water containing one drop of saturated sodium bicarbonate solution.

16.6 CALCULATIONS

1. Standardisation of silver nitrate solution:

$$S = \frac{0.100 \times (T - B_s)}{10}$$

where: S = concentration of the standard silver nitrate solution (M)
T = volume of 0.100 M KCl titre (mL)
B_s = volume of the blank titre in the standardisation (mL)

2. Determination of the soil chloride concentration:

$$Cl = \frac{S \times (V - B_c) \times 35.45 \times 1000}{W}$$

where: Cl = water-soluble chloride concentration, air-dried basis (mg/kg)

S = concentration of the standard silver nitrate solution (M) from Calculation 1 above

V = volume of the silver nitrate titre (mL)

B_c = volume of the blank titre in the determination (mL)

W = weight of soil (g)

16.7 METHOD PERFORMANCE

No validation data are available for this method.

16.8 REFERENCES

1. Rayment, G.E. and Higginson, F.R., 1992, Soluble Chloride in Australian Laboratory Handbook of Soil and Water Chemical Methods, Inkata Press, Melbourne, p24-25.

2. Standard Methods for the Examination of Water and Wastewater, 1995, Method 4500-Cl B: Argentometric Method, Greenberg, A.E., Clesceri, L.S. and Eaton, A.D. (eds), 19th Ed., American Public Health Association.

17. BROMIDE (METHOD 402)

17.1 SCOPE AND APPLICATION

This method is applicable to the determination of water-soluble bromides in soils, sediments and other solids.

17.2 PRINCIPLE

As most bromides in soils are considerably soluble [1], they can be readily leached using water. In this method, bromide in the solid sample is extracted into water with a soil: water ratio of 1:10.

17.3 APPARATUS

- Magnetic stirrer and stirring beads
  (for processing large numbers of samples, it is more efficient to agitate the Erlenmeyer flasks on an orbital platform shaker).

17.4 PROCEDURE

A reagent blank with no soil should be included with each process of samples.

1. Accurately weigh 10.0 g (± 0.01g) of air-dried sample (< 2 mm) (or an amount approximately equal to 10 g of soil when dried, prepared according to Section 5.1.4), into a 250 mL Erlenmeyer flask.

2. Add 100 mL of deionised water.

3. Agitate for 1 hour using a magnetic stirrer or on an orbital shaker.

4. Allow the suspension to settle or centrifuge it before filtering the extract (through Whatman No.42 or similar).

5. Remove a suitable aliquot of the extract for bromide analysis. A suitable method is given in Reference 2 below.

17.5 CALCULATION

Calculate the concentration of the bromide as follows:

$$\text{Br (air-dried basis)} = \frac{(A - B) \times 100}{W}$$

where: Br = concentration of bromide in the soil, air-dried basis (mg/kg)

A = concentration of bromide in the sample extract (mg/L)

B = concentration of bromide in the blank (mg/L)

W = weight of air-dried soil sample (g)

17.6 METHOD PERFORMANCE

No validation data are available for this method.

17.7 REFERENCES

1. Adriano, D.C. and Doner, H.E., 1982, in Methods of Soil Analysis, Part 2, Page, A.L., Miller, R.H. and Keeney, D.R. (eds.), Agronomy Monograph No. 9, 2nd. Ed., American Soil Science Society, Madison WI, 449

2. Standard Methods for the Examination of Water and Wastewater, 1995, 19th Ed., Method 4500-B- B or C, Greenberg, A.E., Clesceri, L.S. and Eaton, A.D. (eds), American Public Health Association.

18. TOTAL CYANIDE (METHOD 403)

18.1 SCOPE AND APPLICATION

This method is applicable to the determination of inorganic cyanides in soils, sediments and other solids, with the exception of cyano complexes of some transition metals like cobalt, silver, gold, platinum and palladium [1,2].

18.2 PRINCIPLE

Cyanide in the soil is extracted into an alkaline solution (the high pH will enable the cyanide complexes eg. iron cyanide complexes, to be leached into solution [1]). Cyanide in the extract is then decomposed in the presence of a strong acid and magnesium chloride catalyst, during a 1-hour reflux distillation, yielding hydrogen cyanide [1,3-5].

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

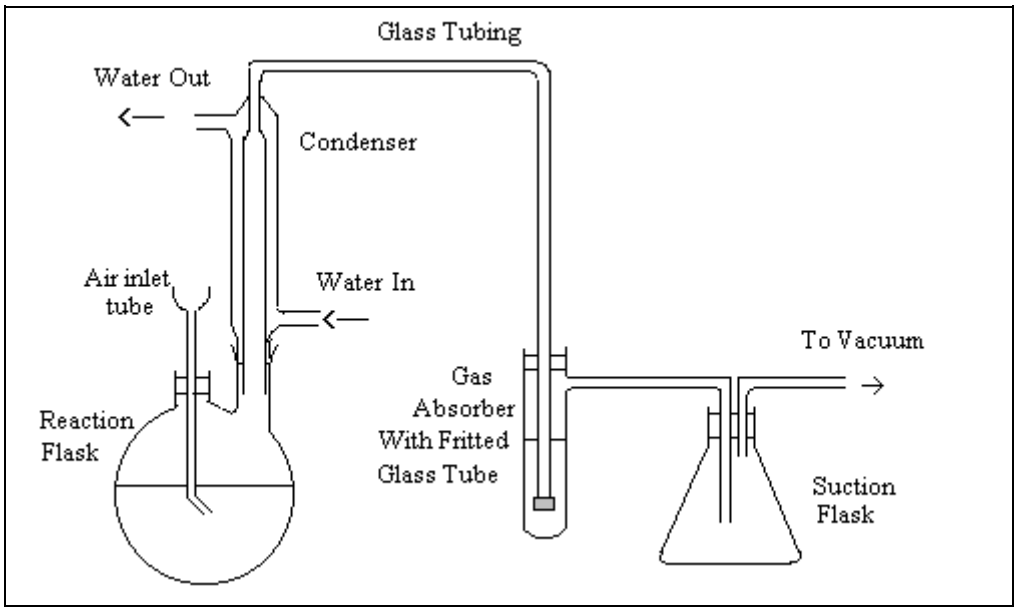
18.3 APPARATUS

- Agitation apparatus:
  Any device capable of imparting continuous contact between the soil and the extraction fluid, and which does not cause stratification of the sample and fluid. An example of such device is a tumbler which rotates continuously in an end-over-end fashion.
- Buchner funnel filtration unit of appropriate capacity
- A reflux distillation unit. A recommended set up is shown in Figure 18-I. It consists of:
  (a) A one litre round-bottom flask with provision for an inlet tube and condenser.
  (b) A gas absorber with a gas dispersion tube equipped with medium-porosity fritted outlet.
  (c) A heating mantle to fit distillation flask.

  Other distillation setups eg. microdistillation units may be used if they are based on principles similar to the one above. The laboratory has to demonstrate that such distillation units can produce results comparable to those obtained by this method or validated against a standard reference material.

Figure 18-I

A recommended cyanide distillation unit.



Note: It is necessary to decontaminate the apparatus between samples by steam distillation, filling the sample flask with about 800 mL water and sufficient NaOH solution to cover the frit in the gas absorber tube. Turn off the water to the condensers, turn on the vacuum and steam distil for 20 minutes or until the liquid level in the scrubber tube is about 80% full, then rinse the entire apparatus with deionised water.

18.4 REAGENTS

- Sodium hydroxide solution, 1 M
- Sodium hydroxide solution, 50% (w/v)
- n-hexane
- Magnesium chloride ($MgCl_2$) reagent:
- Dissolve 255 g $MgCl_2.6H_2O$ in deionised water and dilute to 500 mL.
- Sulfuric acid (50% H_2SO_4)
- Lead carbonate powder ($PbCO_3$)
- Sulfamic acid (NH_2SO_3H)

18.5 PROCEDURE

WARNING: The distillation should be set up in a properly vented fume cupboard.

A reagent blank with no soil should be included with each batch of samples.

18.5.1 Extraction

1. Accurately weigh 25 g (± 0.01 g) of field-moist soil into a wide-mouthed bottle.

2. Add 500 mL of deionised water to the flask.

3. Add 5 mL 50% NaOH solution.

4. If a heavy grease is present, add 50 mL n-hexane.

5. Cap the bottle and shake it to mix. Check that the pH is greater than 10. If it is below 12, add 50% NaOH in 5 mL increments until it is at least 12. Recap the bottle, shake and repeat the pH check until the pH no longer drops below 12. Record the total volume of 50% NaOH added.

6. Place the bottle in an agitation apparatus with enough foam insulation to cushion the bottle. Agitate the mixture for 16 hours. Either allow the solids to settle, centrifuge a suitable volume of extract for the subsequent distillation or filter a suitable volume of extract through a Buchner funnel.

18.5.2 Distillation

1. Transfer an appropriate aliquot of extract into a 1-litre distillation flask. If there is more than one liquid phase, ensure that only the aqueous phase is removed for distillation.

   Note: The volume of extract to be distilled depends on several factors eg. detection limit of the cyanide determination, the expected cyanide concentration and the cyanide concentration of interest.

2. Transfer 10 mL of 1 M NaOH solution to the gas absorber and dilute if necessary, with deionised water to obtain an adequate liquid depth for the absorption.

3. Add 0.1 g powdered lead carbonate to the 1 M NaOH absorber solution (to eliminate sulfide interference in the analysis).

4. Connect the distillation flask, condenser, gas absorber and turn on the suction. Adjust the suction such that approximately 1 air bubble/sec enters the reaction flask.

   Maintain airflow throughout the distillation.

5. Add 2 g sulfamic acid through the air inlet tube and wash down with deionised water (this procedure eliminates nitrite and nitrate interference during the distillation).

6. Slowly add 50 mL 50% H_2SO_4 through the air inlet tube. Rinse with deionised water and let air mix the flask contents for 3 min.

7. Pour 20 mL $MgCl_2$ reagent into the air inlet tube and rinse with deionised water.

8. Heat with rapid boiling, taking care to prevent the solution in the reaction flask backing up into the air inlet tube.

9. Reflux for at least 1 hour.

10. Discontinue heating but maintain airflow and allow to cool for at least 15 min.

11. After cooling, disconnect the gas absorber and quantitatively transfer the contents into a 100 mL volumetric flask. Rinse the distillation train between the condenser and gas absorber with deionised water and add to the volumetric flask. Make up to the mark with deionised water.

    Note: Do not expose the distillate to light but store under refrigeration if the analysis cannot be performed immediately.

18.5.3 Cyanide Determination

1. Remove a suitable aliquot of the distillate for cyanide analysis, either titrimetrically, colorimetrically or potentiometrically (using cyanide selective electrode) [1,3-5].

    Note: 1. The cyanide selective electrode is subject to significant interferences (in some matrix effects and temperature)[6]. It should therefore be used with the appropriate temperature controls eg. constant temperature bath or temperature compensator, and in conjunction with an inert reference electrode. To avoid interference due to matrix effects, the standard addition method is preferred over the direct calibration method.

    Note: 2. Autoanalysers may be used for the determinative step if they can be demonstrated to produce results comparable to the above method or validated against a standard reference material.

18.6 CALCULATION

Calculate the concentration of the cyanide as follows:

$$CN\ (\text{air-dried basis}) = \frac{(A - B) \times V_{ex} \times 100}{V_{dis} \times W}$$

where:

CN = concentration of cyanide in the soil, dry weight basis (mg/kg)

A = concentration of cyanide in the 100 mL volumetric flask (mg/L)

B = concentration of cyanide in the blank distillate (mg/L)

V_{ex} = total volume of deionised water and 50% sodium hydroxide used in the extraction (mL)

V_{dis} = volume of extract distilled (mL)

W = weight of air-dried soil sample (g)

18.7 METHOD PERFORMANCE

In a single laboratory study, recoveries of 60 - 90 % are reported for solids with a coefficient of variation less than 13 [2].

18.8 REFERENCES

1. Standard Methods for the Examination of Water and Wastewater, 1995, 19th Ed., Method 4500-CN: D, E or F, Greenberg, A.E., Clesceri, L.S. and Eaton, A.D. (eds), American Public Health Association.

2. Method 9013 (Appendix to Method 9010): Cyanide Extraction Procedure for Solids and Oils, Revision 0, Test Methods for Evaluating Solid Waste, USEPA Publication SW-846, Third edition, 1992.

3. Method 9010B: Total and Amenable Cyanide, Revision 2, Test Methods for Evaluating Solid Waste, USEPA Publication SW-846, Third edition, Final Update, 1996.

4. Method 9012A: Total and Amenable Cyanide (Colorimetric, Automated UV), Revision 1, Test Methods for Evaluating Solid Waste, USEPA Publication SW-846, Third edition, Final Update, 1996.

5. ASTM, 1994, Annual Book of ASTM Standards, Water and Environmental Technology, Vol. 11.02, Method D4374, American Society for Testing and Materials.

6. R.S. Schulz, 1995, Chemistry Centre, East Perth, Western Australia, personal communication.

19. FLUORIDE (METHOD 404)

19.1 Scope and Application

This method is applicable to the determination of total fluoride in plants, soils, sediments and other solids. [1,2]

19.2 Principle

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

19.3 Apparatus

- Muffle furnace
- Nickel crucibles (130 mL capacity)

19.4 Reagents

- Sodium hydroxide solution, 17 M
- Hydrochloric acid, concentrated

19.5 Procedure

IMPORTANT: To avoid fluoride losses, do not use glassware to hold sample extracts for long periods. As far as possible, plasticware should be used.

A reagent blank with no soil should be included with each process batch of samples.

1. Accurately weigh 0.5 g (± 0.02 g) of air-dried soil (<0.15 mm) (or an amount approximately equal to 0.5 g of soil when dried, prepared according to Section 5.1.4), into a nickel crucible.

2. If air-dried, moisten the sample slightly with a few drops of deionised water. Add 6.0 mL of 17 M NaOH. Gently tap the crucible to uniformly disperse the sample in the NaOH solution.

3. Place the crucible in an oven set at 150°C for 1 hour to drive off the water.

4. Transfer the crucible to a muffle furnace set at 300°C and gradually raise the temperature to 600°C. Allow the sample 30 minutes to fuse at this temperature.

5. Carefully remove the crucible from the furnace and allow it to cool.

6. Add 60 mL deionised water to the sample. If necessary, heat the sample slightly (on a hot plate) to facilitate dissolution of the NaOH fusion cake. Cool the solution.

7. Transfer the solution to a plastic beaker, combining the rinses (three 5 mL portions) from the crucible.

8. Using a pH meter and magnetic stirrer, adjust the pH to 8.0 to 8.5 using conc. HCl (approximately 8 mL).

   Note: Care must be taken during the pH adjustment. Avoid neutral or acidic conditions during this step to prevent loss of fluoride as HF and etching of the electrode.

9. When the sample has cooled, filter and transfer the solution to a 100 mL volumetric flask. Make up to the mark with deionised water.

10. Pipette a suitable aliquot of the extract for fluoride analysis using a validated method. A recommended method is the ion-selective electrode technique with standard addition.

19.6 CALCULATION

Calculate the concentration of the fluoride as follows:

$$F \text{ (air-dried basis)} = \frac{(A-B) \times 100}{W}$$

where:
- F = concentration of fluoride in the soil, air-dried basis (mg/kg)
- A = concentration of fluoride in the sample melt (mg/L)
- B = concentration of fluoride in the blank melt(mg/L)
- W = weight of air-dried soil sample (g)

19.7 METHOD PERFORMANCE

No validation data are available for this method.

19.8 REFERENCES

1. McQuaker, N.R. and Gurney, M., 1977, Anal. Chem. 49, 53.

2. Adriano, D.C. and Doner, H.E., 1982, Methods of Soil Analysis, Part 2: Chemical and Microbiological Properties-Agronomy Monograph No. 9, 2nd. Ed., Soil Sci. Soc. Amer., Madison WI, p466-468.

20. TOTAL SULFUR

20.1 Scope and Application

This method [1,2] is applicable to the determination of total sulfur in soil, sediment, plants and other solids.

20.2 Principle

Sulfur present in the sample is oxidised to the sulfate form by fusion. The sample is ignited with sodium bicarbonate and silver oxide at 550°C for 3 hours and the melt is dissolved in acetic acid. The resultant solution is analysed for total sulfur as sulfate (SO_4^{2-}).

Note: Other decomposition methods for total sulfur analysis eg. high temperature furnace combustion method, may be used but has to be demonstrated to be at least as rigorous as this method or validated against a standard reference material.

20.3 Apparatus

- Crucibles (approx. 30 mL capacity) of platinum or nickel.
- Muffle furnace
- Sand bath

20.4 Reagents

All reagents should be of recognised analytical reagent grade.

- Sodium bicarbonate ($NaHCO_3$)
- Silver oxide (Ag_2O)
- Acetic acid, 1 M

20.5 Procedure

A reagent blank with no soil should be included with each process batch of samples.

1. Accurately weigh 0.5 g (± 0.01 g) of air-dried soil (< 0.15 mm) (or an amount approximately equal to 0.5 g of soil when dried, prepared according to Section 5.1.4), into a 30 mL crucible.

2. Add 0.5 g of sodium bicarbonate and 0.02 g of silver oxide. Mix the solids thoroughly.

3. Cover this mixture by placing a layer of 0.5 g of sodium bicarbonate on top of it.

4. Place the crucible in a cold muffle furnace and heat to 550°C for 3 hours. Remove the crucible and allow it to cool.

5. Transfer the ignition residue into an Erlenmeyer flask, wash the crucible with a small portion of deionised water and add the washings to the same flask (do not use more than a total of 60 mL deionised water).

6. Dissolve the ignition residue by adding 15 mL of 1 M acetic acid and heating the flask to near boiling on a sand bath or other suitable heating appliance set at 200°C (about 30 min. heating time).

7. After the flask has cooled, transfer the contents and the washing into a 100 mL volumetric flask. Make up the volume.

8. Pipette a suitable aliquot of the sample extract for sulfate-sulfur analysis using a validated method. There may be potential interference from the acetate ions if the sulfate-sulfur is to be determined by ion-chromatography [3].

20.6 CALCULATION

Calculate the concentration of the sulfur as follows:

$$S = \frac{(A - B) \times 100}{W}$$

where:
- S = concentration of sulfate-sulfur in the soil, air-dried basis (mg/kg)
- A = concentration of sulfate-sulfur in the sample (mg/L)
- B = concentration of sulfate-sulfur in the blank (mg/L)
- W = weight of soil sample extracted (g)

20.7 METHOD PERFORMANCE

No validation data are available for this method.

20.8 REFERENCES

1. Tabatabai, M.A., Basta, N.T. and Pirela, H.J., 1988, Comm. Soil Sci. Plant Anal. 19, 1701.

2. Tabatabai, M.A., 1982, in Methods of Soil Analysis, Part 2, Page, A.L., Miller, R.H. and Keeney, D.R. (eds.), Agronomy Monograph No. 9, 2nd. Ed., American Soil Science Society, Madison WI, 513.

3. Standard Methods for the Examination of Water and Wastewater, 1995, 19th Ed., Method 4110: Determination of anions by ion-chromatography, Greenberg, A.E., Clesceri, L.S. and Eaton, A.D. (eds), American Public Health Association.

21. SULFATE (METHOD 406)

21.1 Scope and Application

This method is applicable to the determination of soluble and adsorbed inorganic sulfate in soils, sediments and other solids [1-5].

21.2 Principle

The soil sample is shaken in a calcium phosphate solution (500 mg phosphorus/L). The phosphate ion displaces the adsorbed sulfate while calcium ions depress the extraction of soil organic matter thus eliminating interference from extractable organic sulfur.

21.3 Apparatus

- Laboratory shaker

21.4 Reagents

- Extractant (calcium phosphate - 500 mg phosphorus/L):
  Dissolve 2.02 g of calcium phosphate monohydrate ($Ca(H_2PO_4)_2.H_2O$) in deionised water and dilute to 1 L.

21.5 Procedure

A reagent blank with no soil should be included with each process batch of samples.

1. Accurately weigh 5 g (± 0.01 g) of homogenised field-moist soil (<2 mm) (or an amount approximately equal to 5 g of soil when dried, prepared according to Section 5.1.4), into an Erlenmeyer flask.

2. Pipette 50 mL of extractant and shake the contents of the flask on a laboratory shaker for 30 min. (the speed of shaking should be such that there is sufficient agitation for contact between the extractant and the soil surfaces).

3. Either centrifuge or allow the suspension to settle, then filter the sample (eg. through Whatman No.42 filter paper).

4. Remove a suitable aliquot of the soil extract for sulfate analysis by a validated method. There may be potential interference from phosphate ions if the sulfate is to be determined by ion-chromatography [6]. Report the sulfate content corrected for moisture in the soil.

21.6 CALCULATION

Calculate the concentration of the sulfate as follows:

$$S_m = \frac{(A - B) \times 50}{W}$$

$$S_d = \frac{100 \times S_m}{(100 - M)}$$

where:
- S_m = concentration of sulfate in the soil, field-moist basis (mg/kg)
- A = concentration of sulfate in the sample melt (mg/L)
- B = concentration of sulfate in the blank (mg/L)
- W = weight of soil sample (g)
- S_d = concentration of sulfate in the soil, air-dried basis (mg/kg)
- M = moisture content (%)

21.7 METHOD PERFORMANCE

No validation data are available for this method.

21.8 REFERENCES

1. Tabatabai, M.A., 1982, in Methods of Soil Analysis, Part 2, Page, A.L., Miller, R.H. and Keeney, D.R. (eds.), Agronomy Monograph No. 9, 2nd. Ed., American Soil Science Society, Madison WI, 521.

2. Beaton, J.D. and Burns, G.R., 1968, Determination of Sulfur in Soils and Plant Material, The Sulfur Institute, London SW1, England, Technical Bulletin No:14.

3. Tabatabai, M.A. and Dick, W.A., 1979, Soil Sci. Soc. Amer. J. 43, 899.

4. Fox, R.L., Olson, R.A. and Rhoades, H.F., 1964, Soil Sci. Soc. Amer. Proc. 28, 243.

5. David, M.B., Mitchell, M.J. and Nakas, J.P., 1982, Soil Sci. Amer. J. 46, 847.

6. Standard Methods for the Examination of Water and Wastewater, 1995, 19th Ed., Method 4110: Determination of anions by ion-chromatography, Greenberg, A.E., Clesceri, L.S. and Eaton, A.D. (eds), American Public Health Association.

22. SULFIDE (METHOD 407)

Source: USEPA SW-846 Method 9030A [1]

22.1 SCOPE AND APPLICATION

This method is suitable for soil samples containing 0.2 to 50 mg/kg of sulfide. It measures the "total" sulfide which is usually defined as the acid-soluble sulfide. For soils in which significant metal sulfides may be present, total sulfide is defined as both the acid-soluble and acid-insoluble fractions, and both procedures must be employed.

22.2 PRINCIPLE

For acid-soluble sulfides, separation of the sulfide from the sample is accomplished by the addition of sulfuric acid to the heated sample. The hydrogen sulfide (H_2S) formed is distilled under acidic conditions and carried by a nitrogen stream into a zinc acetate gas scrubbing bottles where it is precipitated as ZnS.

For acid-insoluble sulfide samples (eg. containing metal sulfides such as CuS and SnS_2), separation of sulfide from the sample matrix is accomplished by suspending the sample in concentrated hydrochloric acid by vigorous agitation. Stannous chloride is added to prevent oxidation of sulfide. The prepared sample is distilled under acidic conditions at 100°C under a stream of nitrogen. Hydrogen sulfide is collected in gas scrubbing bottles containing Zn(II) and a strong acetate buffer. The sulfide is finally collected as a ZnS precipitate.

Sulfide in the ZnS precipitated from either of the above methods is oxidised to sulfur with a known excess of iodine, and the unreacted iodine determined by titration.

22.3 ANALYSIS

The procedure as described in USEPA SW-846 Method 9030A should be adhered to strictly, without any changes to the method.

22.4 METHOD PERFORMANCE

Refer USEPA Method 9030B.

22.5 REFERENCE

1. Test Methods for Evaluating Solid Waste, 1986, Method 9030B, USEPA Publication SW-846, Third edition, Final Update, 1996.

23. VOLATILE ORGANICS (METHOD 501)

This section lists the methods for three classes of volatile compounds. These classes are:

23.1 Volatile Alkanes and Monocyclic Aromatic Hydrocarbons (MAH);

23.2 Volatile Halogenated Hydrocarbons;

23.3 Miscellaneous Volatile Organics

23.1 VOLATILE ALKANES AND MONOCYCLIC AROMATIC HYDROCARBONS (MAH) - 501.1

Source: USEPA SW-846

This method is applicable to most volatile compounds which have boiling points less than 200°C and are insoluble or slightly soluble in water but not limited to the analysis of the following:

Alkanes (C_6-C_{10})
Benzene
Ethyl benzene
Styrene (vinyl benzene, ethenyl benzene)
Toluene
Xylenes
Trimethylbenzenes

23.1.1 Preliminary Screening

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

Note: Method 5021 (Headspace) may not be as rigorous or reliable as purge-and-trap analysis. It will be suitable, however, as a "screening" analysis as described in Section 3.9 and 5.3 above.

23.1.2 Sample Extraction

5035

Low concentration: (individual compounds approximately 0.5 to 200µg/kg)

- Purge and trap technique

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

- Methanol extraction followed by
- Purge and trap technique (Method 5035 or 5030B)

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

23.1.3 Sample Clean-up

Not applicable

23.1.4 Sample Analysis

	8015 B	GC/FID
	8021A or B	GC/PID
(P)	**8260B**	GC/MS (capillary column technique)

Note: Flame ionisation may be substituted for MS or PI detection, for screening and quantitative 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.

23.2 VOLATILE HALOGENATED HYDROCARBONS - 501.2

Source: USEPA SW-846

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

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

23.2.1 Sample Extraction

5035

Low concentration: (individual compounds approximately 1 to 200µg /kg)

- Purge and trap technique.

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

- Methanol extraction followed by
- Purge and trap technique.

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

23.2.2 Sample Clean-up

Not applicable

23.2.3 Sample Analysis

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

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

23.3 MISCELLANEOUS VOLATILE ORGANICS - 501.3

Source: USEPA SW-846

The following volatile compounds which do not fall into the aromatic or chlorinated categories detailed in the sections above, may be analysed using the stated methods. The list below does not preclude the analysis of other volatile organics by these methods.

These methods would 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 (eg. as in petrol)
2-Butanone (MEK)*	Malononitrile
t-Butylalchohol	Methacrylonitrile
Carbon disulfide**	Methyl methacrylate
Chloral hydrate	4-Methyl-2-pentanone (MIBK)*
bis-(2-Chloroethyl) sulfide	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

* Listed in Method 8015A or B GC/FID

** Poor sensitivity by GC/FID

23.3.1 Sample Extraction

5035

Low concentration: (individual compounds approximately 1 to 200µg /kg):

- Purge and trap technique.

High concentration: (individual compounds >1 mg/kg):

- Methanol extraction followed by
- Purge and trap technique.

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

23.3.2 Sample Clean-up

Not applicable.

23.3.3 Sample Analysis

	8015 B	GC/FID.
(P)	**8260**	GC/MS for volatile organics (capillary column technique)

24. POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) (METHOD 502)

This section lists two extraction methods for polycyclic aromatic hydrocarbons . These are:

24.1 Polycyclic Aromatic Hydrocarbons (PAHS) By Solvent Extraction

24.2 Polycyclic Aromatic Hydrocarbons (PAHS) By Supercritical Fluid Extraction (SFE)

24.1 POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) BY SOLVENT EXTRACTION - 502.1

Source: USEPA SW-846

This method is applicable but not limited to the analysis of the following polycyclic aromatic hydrocarbons.

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

Note: Proper separation of compounds with similar superscripts is not possible using packed columns and sometimes difficult using shorter capillary columns. Use of either a capillary column GC method or HPLC method is recommended if the pooled result for unresolved compounds is insufficient.

24.1.1 Sample Extraction

3540 C Soxhlet extraction using:

Acetone/Hexane (1:1); or

Dichloromethane/Acetone (1:1).

3550 B Sonication extraction using:

(a) For low concentration (individual compounds <20 mg/kg):

- Dichloromethane; or

- Dichloromethane/Acetone (1:1); or
- Hexane/Acetone (1:1); or
- Methyl tertiary-butyl ether; or
- Methyl tertiary-butyl ether/Methanol (2:1).

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

(b) For high concentration (individual compounds >20 mg/kg):

- Dichloromethane

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

3545 Accelerated Solvent Extraction using Dichloromethane/Acetone (1:1).

24.1.2 Sample Clean-up

3630C Silica gel column clean-up.

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

24.1.3 Extract Analysis

8100 GC/FID* (packed or capillary column)

Note: Proper separation of compounds with similar superscripts is not possible using packed columns and sometimes difficult using shorter capillary columns. Use of either a capillary column GC method or HPLC method is recommended if the pooled result for unresolved compounds is insufficient.

(P) 8270C 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 3630B or C will normally be necessary. Protocols for verification of analyte identities should be developed when Method 8100 or 8310 is used.

24.2 POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) BY SUPERCRITICAL FLUID EXTRACTION (SFE) - 502.2

Source: USEPA SW-846

An SFE method for polynuclear aromatic hydrocarbons has recently been proposed for addition to USEPA SW-846. The method is:

3561	Supercritical Fluid Extraction of Polynuclear Aromatic Hydrocarbons

24.2.1 Sample Extraction

The extraction is a three-step process using:

1. Supercritical CO_2
2. Supercritical CO_2 plus water and methanol modifiers
3. Supercritical CO_2 (to purge system of modifiers)

Collection of SFE extract:

Either;

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

or

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

24.2.2 Sample Clean-up

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

24.2.3 Extract Analysis

	8121	GC/ECD (capillary column method)
(P)	**8270C**	GC/MS (capillary column)
	8310	HPLC/UV and/or F

25. CHLORINATED HYDROCARBONS (METHOD 503)

Source: USEPA SW-846

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

Benzal chloride	Benzotrichloride
Benzyl chloride	2-Chloronaphthalene
Dichlorobenzene	Trichlorobenzene
Tetrachlorobenzene	Pentachlorobenzene
Hexachlorobenzene	Hexachlorobutadiene
Hexachlorcyclopentadiene	Hexachloroethene

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

25.1 SAMPLE EXTRACTION

3540C Soxhlet extraction using:

- Acetone/Hexane (1:1); or
- Dichloromethane/Acetone (1:1).

3550B Sonication Extraction using:

(a) For low concentration (individual compounds <20 mg/kg):

- Dichloromethane; or
- Dichloromethane/Acetone (1:1); or
- Hexane/Acetone (1:1); or
- Methyl tertiary-butyl ether; or
- Methyl tertiary-butyl ether/Methanol (2:1).

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

(b) For high concentration (individual compounds >20 mg/kg):

- Dichloromethane; or
- Hexane

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

25.2 SAMPLE CLEAN-UP

3620B Florisil column clean-up; or

3640A Gel permeation column clean-up; and

3660B Sulfur clean-up if necessary

25.3

25.4 EXTRACT ANALYSIS

8121 GC/ECD (capillary column method)

(P) 8270C GC/MS (capillary column)

26. ORGANOCHLORINE INSECTICIDES (OCS) AND POLYCHLORINATED BIPHENYLS (PCBS) (METHOD 504)

Source: USEPA SW-846

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

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

26.1 SAMPLE EXTRACTION

3540C Soxhlet extraction using:

- Acetone/Hexane (1:1); or
- Dichloromethane/Acetone (1:1).

3550B Sonication Extraction using:

(a) For low concentration (individual compounds <20 mg/kg):

- Dichloromethane; or
- Dichloromethane/Acetone (1:1); or
- Hexane/Acetone (1:1); or
- Methyl tertiary-butyl ether; or
- Methyl tertiary-butyl ether/Methanol (2:1).

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

(b) For high concentration (individual compounds >20 mg/kg):

- Dichloromethane; or
- Hexane

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

26.2 EXTRACT CLEAN-UP

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

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

   3640A Gel permeation column clean-up.

2. If only PCBs are to be determined:

   3665A Sulfuric acid/permanganate clean-up followed by:

   3620B Florisil column clean-up; or

   3630C Silica gel fractionation

3. If both PCBs and pesticides are to be measured:

   3630C Silica gel fractionation

4. If only pesticides are to be determined:

   3620B 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 3660A: Sulfur clean-up, which utilises reaction with reactive copper or mercury.

26.3 EXTRACT ANALYSIS

8080A GC/ECD or GC/ELCD

8081A GC/ECD (capillary column)

8082 GC/ECD or GC/ELCD (capillary column)

(P) 8270C GC/MS (capillary column)

27. ORGANOPHOSPHORUS PESTICIDES (METHOD 505)

Source: USEPA: SW846

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

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

27.1 SAMPLE EXTRACTION

3540C Soxhlet extraction using:

- Acetone/Hexane (1:1); or
- Dichloromethane/Acetone (1:1).

3550B Sonication Extraction using:

(a) For low concentration (individual compounds <20 mg/kg):

- Dichloromethane; or
- Dichloromethane/Acetone (1:1); or
- Hexane/Acetone (1:1); or
- Methyl tertiary-butyl ether; or
- Methyl tertiary-butyl ether/Methanol (2:1).

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

(b) For high concentration (individual compounds >20 mg/kg):

- Dichloromethane; or
- Hexane

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

27.2 SAMPLE CLEAN-UP (NOT USUALLY NECESSARY)

3620B Florisil column clean-up (the analyst needs to verify the use of this step for the OP of interest as low recoveries have been reported for certain organophosphorus pesticides, particularly carbophenothion 1).

3660B Sulfur clean-up.

27.3 SAMPLE ANALYSIS

8141A GC/FPD or GC/NPD (capillary column)

8270C GC/MS (capillary column)

27.4 REFERENCE

1. FDA Pesticide Analytical Manual, 1977, Volume I: Methods which detect multiple residue, Food and Drug Administration, Washington, D.C., NTISUB/C/118, Section 252.

28. PETROLEUM HYDROCARBONS (PHCS) (METHOD 506)

Sources: USEPA [1,2]

In Australian laboratories, methods for analysis of PHCs in soils have never been standardised, but have been mostly based upon methods for 'Oil and Grease' and 'Total Petroleum Hydrocarbons (TPH)' in water, involving solvent extraction of a soil/sodium sulfate mixture with Freon-113 (1,1,2-Trichlorotrifluoroethane), followed by infrared spectroscopic or gas chromatographic detection of the extracted hydrocarbons.

Although variations of the above method have been well accepted, it is now likely that Freon-113 will shortly become unavailable. As a signatory to the Montreal Protocol, Australia is bound to cease production and use of a range of ozone depleting substances (ODS) by deadlines specified in that agreement. Exemptions have been granted to allow use of freons and other halogenated solvents for laboratory and analytical uses until the end of 1997, but extension beyond this date is not likely, and supplies are already limited. Consequently, these guidelines do not recommend a method requiring freon extraction. Dichloromethane is likely to remain available for some years however and this solvent, either alone or mixed with acetone, is already in common usage for hydrocarbon extraction in Australia and the USA.

The following recommended procedure is an interim method only. No validation data are currently available for the entire method, although all components of the method are in common use. It will most likely be replaced as national standard methods become available.

Two methods for determining petroleum hydrocarbons are given below:

28.1 Petroleum Hydrocarbons (PHCS) By Solvent Extraction

28.2 Aliphatic Petroleum Hydrocarbons By Supercritical Fluid Extraction (SFE)

28.1 PETROLEUM HYDROCARBONS (PHCS) BY SOLVENT EXTRACTION - 506.1

28.1.1 Scope of Test

This solvent extraction method for soil PHCs is considered reliable for semi-volatile hydrocarbons, including semivolatile fuel oils (eg. kerosene, diesel), mineral oils, paraffins and coal tar.

This method may be used as a screening procedure only (see Section 3.9) for volatile PHCs (C_6-C_9), and only where adequate attention is given to keeping samples cool

and sample transfer, mixing and extraction is performed rapidly so that adequate recoveries for matrix spikes may be demonstrated. The method is unsuitable for volatile PHCs if solvent exchange and cleanup are required.

The 16 USEPA priority PAHs should be extracted and determined with PHCs. Analysts should verify that they are quantitatively recovered from the matrix by the method used.

28.1.2 Sample Pretreatment

Store samples chilled (1-4°C) prior to analysis and rapidly but thoroughly homogenised in the original container prior to sub-sampling for analysis. Analysis portions should be intimately mixed with sufficient sodium sulfate to create a dry, free-flowing mixture

28.1.3 Sample Extraction

Use one of the following three alternative methods:

3540B or C Soxhlet extraction using:

- Dichloromethane/Acetone (1:1).

3550B Sonication Extraction using:

- Dichloromethane/Acetone (1:1)

Sequential bath sonication and agitation

This procedure may be employed only after demonstration by the user that extraction is as rigorous, for the matrix in question, as method A or B.

To a 125 mL Erlenmeyer flask or bottle add 50 g anhydrous sodium sulfate, stopper and place in a refrigerator for approx. 30 minutes. After the cooling period, weigh the flask and contents and record the weight.

Rapidly homogenised the cool sample with a clean metal spatula and transfer 10±1g to the flask, stopper and reweigh accurately (± 0.1 g). With vigorous shaking, rapidly mix the soil and sodium sulfate to obtain a free flowing, apparently dry mixture. More sodium sulfate may be needed for very wet samples. If so, add a similar extra amount to the reagent blank determination.

Place 50 mL of Dichloromethane/Acetone (1:1) in the flask and securely stopper. Shake the flask briefly by hand and place in a sonic bath for 15 minutes. A sonic bath power of at least 300W is required, and not more than six samples to be placed in the bath at one time. Maintain a cool bath temperature (ie. not more than about 40°C) by addition of ice as required. Maintain the liquid level in the bath at approximately the same the sample extract solvent levels.

Remove from the bath and shake vigorously using a wrist action flask shaker or orbital laboratory shaker for 30 minutes. Allow to stand for sufficient time to produce a clear supernatant layer. If solids are slow to settle, centrifuge prior to analysis or cleanup.

28.1.4 Extract Clean-up (optional)

Clean-up will be necessary if the extract contains interfering quantities of non-petroleum compounds as evidenced by GC/FID profile uncharacteristic of PHCs or by GC/MS analysis. Clean-up may only be achieved after solvent exchange to hexane.

Transfer a measured portion (10 mL or more) of the sample extract into a Kuderna Danish evaporator and evaporate on a steam bath until the solvent level just reaches the top of the KD flasks narrow spotting tube adaptor. Immediately add 15 mL hexane and again evaporate until the liquid level begins to enter the narrow adaptor. *Do not allow the extract to evaporate to dryness.*

Allow the flask to cool and dilute the extract to known volume consistent with desired minimum detectable hydrocarbon concentration. Treat with silica gel as described in USEPA Method 1664 with silica activity adjusted by water addition to retain PAHs.

28.1.5 Extract Analysis Options

Use one of the following three alternative methods:

8270B GC/MS (capillary column)

GC/FID Due to the non-specific response of this detector, identities of unusual mixtures and predominant individual compounds should be confirmed by GC/MS.

It is possible to determine both the more volatile (eg. C_7 to C_{14}) and less volatile components (eg. heavy oils) in a single GC injection if injector configuration and temperature are optimised. However, best resolution and sensitivity will normally require sample extracts to be injected twice, using split injection mode for more volatile components and splitless or on-column injection for heavier compounds. Typical GC conditions for petroleum hydrocarbons are given in Table 28-A below.

Table 28-A

Typical GC conditions for petroleum hydrocarbons

ANALYTES	C_6-C_9 alkanes and MAHs*	Semivolatile compounds C_{10}-C_{36}, PAHs
INJECTOR TYPE	Split-splitless in split mode. Temperature 250 to 270°C.	Split-splitless in splitless mode (temperature 250 to 270°C) OR on-column.
COLUMN TYPE	Bonded phase capillary 25-50 m length, phase thickness 0.5-2*m (longer columns and thicker phases required for volatiles).	Bonded phase capillary, 12-30 m length, phase thickness 0.1-0.5 *m.
COLUMN STATIONARY PHASE	Methylsilicone or 5% phenylmethyl silicone or silphenylene, eg. SGE BP-1, BP-5, BPX-5 (or special purpose solvent analysis phase)	Methylsilicone or 5% phenylmethyl silicone or silphenylene, eg. SGE BP-1, BP-5, BPX-5
TYPICAL GC OVEN PROGRAM	Initial temperature: 35-50°C for 4 min Ramp rate: 5 to 15°C Final temperature: 100-200°C (depending on phase) for sufficient time to elute xylenes.	Initial temperature: 40-50 °C for 4 min. Ramp rate: 5 to 15 °C Final temperature: 300°C for sufficient time to elute C_{36} to C_{38} alkanes
CALIBRATION COMPOUNDS	A four-point calibration (three positive levels plus solvent zero), using mixtures in extraction solvent of: n-nonane (C_9) for C_6-C_9 alkanes* MAHs (benzene, toluene , ethylbenzene xylenes and styrene)*	A three-point calibration, using mixtures in hexane or extraction solvent of: n-nonane (C_9) for the C_7-C_9 range;* tetradecane (C_{14}) for the C_{10}-C_{14} range; n-hexacosane (C_{26}) for C_{15}-C_{28} range; n-dotriacontane (C_{32}) for C_{29}-C_{36} range.

* This method is regarded as a screening test only for the C_6 to C_9 range. Should solvent exchange and cleanup be required, the method would be unsuitable for this range.

Note: Quantitative assessment of higher boiling oils and greases may be unreliable by GC methods due to injector discrimination and difficulty in quantifying those products which do not elute as discrete peaks. The analyst should take steps to optimise the GC system to overcome these potential problems. The use of an on-column injection system is recommended.

28.1.6 References

1. USEPA SW-846

2. USEPA Method 1664: N-Hexane Extractable Material (HEM) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM) by Extraction and Gravimetry (Oil and Grease and Total Petroleum Hydrocarbons)", USEPA Office of Water, Publication EPA-821-B-94-004, October 1994 (26 pages).

28.2 Aliphatic Petroleum Hydrocarbons By Supercritical Fluid Extraction (SFE) - 506.2

Source: USEPA SW-846

A method for SFE of hydrocarbons has recently been proposed for addition to USEPA SW-846. The method is:

3560 Supercritical Fluid Extraction of Total Recoverable Petroleum Hydrocarbons

Method 3560 is known to be unsuitable for high molecular weight PAHs, but may be appropriate for sites where aromatic hydrocarbons are not of significance. Alternatively, it may be possible to show that the method for PAHs, USEPA SW-846 Method 3561 (see Method 502.2), is also capable of adequately recovering aliphatics. It is the responsibility of the analyst to verify the efficiency of whichever method is chosen.

USEPA SW-846 Method 3561 is not recommended as an appropriate method for volatiles. See Method 501 for the analysis of volatile organics.

28.2.1 Sample Extraction

3560 Supercritical Fluid Extraction

28.2.1.1 Collection solvent choices:

Perchlorethylene (PCE) for subsequent analysis by infrared spectroscopy or another solvent (e.g DCM) for GC analysis. Solvent system chosen must be shown to give satisfactory, reproducible recovery of analytes spiked into the particular matrix (soil type) under test.

28.2.1.2 Extract cleanup -

Infrared determination - silica gel as per method 8440

GC/FID - none recommended

28.2.1.3 Extract analysis

8440 Infrared determination

8015 GC/FID or use GC conditions as described in Method 506.1

Due to the non-specific response of this detector, identities of unusual mixtures and predominant individual compounds should be confirmed by GC/MS.

29. PHENOLS (METHOD 507)

Source: USEPA SW846

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

29.1 SAMPLE EXTRACTION

3540C Soxhlet extraction using:

- Acetone/Hexane (1:1); or
- Dichloromethane/Acetone (1:1), plus
- exchange solvent (2-propanol).

3550B Sonication Extraction using:

(a) For low concentration (individual compounds <20 mg/kg):

- Dichloromethane; or
- Dichloromethane/Acetone (1:1); or
- Hexane/Acetone (1:1); or
- Methyl tertiary-butyl ether; or
- Methyl tertiary-butyl ether/Methanol (2:1), and
- exchange solvent (2-propanol).

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

(b) For high concentration (individual compounds >20 mg/kg):

- Dichloromethane

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

29.2 EXTRACT CLEAN-UP

3630C Silica gel column clean up (for samples derivatised for GC/ECD determination)

3640A Gel permeation clean-up

3650B Acid/base partition extraction (it is recommended that all extracts undergo this cleanup)

8040A Pentafluorobenzyl bromide derivatisation (for GC/ECD analysis)

8041A Phenols by GC/Capillary column technique

29.3 EXTRACT ANALYSIS

8040A GC/FID

GC/ECD (after derivatisation, if interferences prohibit proper analysis by GC/FID)

(P) 8270C GC/MS (capillary column)

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

30. HERBICIDES (METHOD 508)

Source: USEPA SW-846

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

2,4-D	Dichlorprop
2,4-DB	Dinoseb
2,4,5-T	MCPA
2,4,5-TP (Silvex)	MCPP
Dalapon	4-Nitrophenol
Dicamba	Pentachlorophenol

The following additional compounds may be determined:

Acifluoren	3,5-Dichlorobenzoic acid
Bentazon	5-Hydroxydicamba
Chloramben	Picloram
DCPA diacid	

30.1 SAMPLE EXTRACTION

(P) 8151A The soil is extracted and derivatised as above or may be derivatised with 2,3,4,5,6-pentafluorobenzyl bromide.

30.2 SAMPLE CLEAN-UP

See method 8151A for the procedure.

30.3 EXTRACT ANALYSIS

8151A	GC/ECD
	GC/MS

31. PHTHALATE ESTERS (METHOD 509)

Source: USEPA; SW-846

This method is applicable but not limited to the 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

31.1 SAMPLE EXTRACTION

3540C Soxhlet extraction using:

- Acetone/Hexane (1:1); or
- Dichloromethane/Acetone (1:1).

3550B Sonication Extraction using:

(a) For low concentration (individual compounds <20 mg/kg):

- Dichloromethane; or
- Dichloromethane/Acetone (1:1); or
- Hexane/Acetone (1:1); or
- Methyl tertiary-butyl ether; or
- Methyl tertiary-butyl ether/Methanol (2:1).

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

(b) For high concentration (individual compounds >20 mg/kg):

- Dichloromethane; or
- Hexane

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

31.2 EXTRACT CLEAN-UP

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

3620B Florisil column clean-up

3640A Gel-permeation clean-up

31.3 EXTRACT ANALYSIS

8060 GC/FID or GC/ECD (packed column)

8061 or 8061A GC/ECD (capillary column)

8270C GC/MS (capillary column)

APPENDIX 1
AUSTRALIAN STANDARDS FOR THE LABORATORY ANALYSIS OF CONTAMINATED SOIL

AS 4439.2 – 1997 wastes, sediments and contaminated soils Part 2: Preparation of leachates – Zero headspace procedure.

AS 4439.3 - 1997 wastes, sediments and contaminated soils Part 2: Preparation of leachates – Bottle leaching procedure.

APPENDIX 2
ANALYSIS OF WATERS, WASTEWATERS AND GROUNDWATERS

For waters, wastewaters and groundwaters use procedures selected from the standard texts listed below*.

1. American Public Health *Association Standard Methods for the Examination of Water and Wastewater* (APHA, 1995).

2. US Environmental Protection Agency *Methods for Chemical Analysis of Water and Wastes* (USEPA, 1979).

3. American Society for Testing and *Materials Water and Environmental Technology* (ASTM, 1992).

4. Relevant Australian Standards (catalogue of publications available from Standards Australia, 19-25 Raglan Street, South Melbourne, 3205).

5. US Environmental Protection Agency, *Microbiological Methods for Monitoring the Environment Water and Wastes* (USEPA, 1978).

6. Department of the Environment *The Bacteriological Examination of Drinking Water Supplies*, Report on Public Health and Medical Subjects, No. 71. Method for the Examination of Waters and Associated Material (Department of the Environment, 1994).

7. Test Methods for Evaluating Solid Waste, USEPA Publication SW-846, Third Edition, Final Update, 1996.

Minor changes can be made to these methods, provided validation demonstrates they do not adversely affect the quality of results. Test methods not based on any of the above references, but intended for use for statutory purposes can only be used with prior approval of the relevant jurisdictional regulatory agency.

It is important that the analyst verifies the suitability of the procedure used for the particular sample type under investigation. Details of procedures for method validation are available in NATA Technical Note 17 (NATA, 1997).

* The latest editions at the time of publishing this Guide are reference. Where they are superseded, the most recent edition should be used.