

Environment Protection Authority

Approved methods for the sampling and analysis of water pollutants in NSW

Draft for consultation



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Cover: an EPA officer using water-testing equipment near an industrial site. Photo: John Spencer/EPA.

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This document is intended to update the *Approved Methods for the Sampling and Analysis of Water Pollutants in New South Wales* (DEC 2004). It will be of interest to you if you are required, through an environment protection licence or statutory instrument, to sample and analyse water pollutants, or you are a laboratory or consultant that carries out this work for persons regulated by the EPA.

1. Introduction

1.1. Purpose of this document

This document prescribes the methodology that must be used when sampling and analysing water pollutants in NSW for statutory purposes. The document includes methods to test for:

- the presence or concentration of matter in water
- the volume, depth and flow of water or wastewater.

This document should be referenced as:

Approved Methods for the Sampling and Analysis of Water Pollutants in NSW.

1.2. Relevant legislation

This document is referred to in clause 60 of the Protection of the Environment Operations (General) Regulation 2009 (POEO General Regulation) and the *Load Calculation Protocol* (DECC, 2009).

The document may be referred to in conditions attached to statutory instruments (such as licences or notices) issued by the NSW Environment Protection Authority (EPA) under environment protection legislation, as defined in the *Protection of the Environment Operations Act 1997*.

This document may also be referred to by other regulatory authorities in planning documents and development consents and approvals where sampling and analysis of analytes are required.

1.3. What method to use

Industry must comply with monitoring requirements and limits specified in statutory instruments. In accordance with clause 60 of the POEO General Regulation, all testing to show compliance must:

- use the methodology specified in the relevant environment protection licence, notice or statutory instrument (clause 60(2)(a))
- or
- if no methodology is specified in the relevant environment protection licence, notice or statutory instrument, use the methodology prescribed in this document (clause 60(2)(b)).

For the purpose of clause 60(2)(b) of the POEO General Regulation, this document prescribes:

- sample collection and handling requirements, specified in section 2
- approved analysis methods:
 - methods listed in section 3
 - methods with minor modifications that do not require EPA approval as described in section 4
 - alternative methods and methods with significant modifications that have been approved by the EPA following the procedure outlined in section 4
- record-keeping requirements.

Variations to methods are permitted under clause 60(3) only if it can be established that the variation does not affect the results of the test. If a method or an analyte is not listed in this document, or a modified or alternative method is proposed, you must determine if you need to seek approval from the EPA before using that method, in accordance with the process set out in section 4 of this document.

1.4. Who is this document for?

This document is for anyone who must have water pollutants sampled or analysed for a statutory purpose in NSW, including licensees and other persons regulated by the EPA. It must also be referred to by consultants, laboratories, testing facilities and analysts they hire.

Licensees and other persons regulated by the EPA are responsible for ensuring the laboratories and analysts they use:

- are accredited by the National Association of Testing Authorities (NATA), or equivalent accreditation body¹ under *ISO/IEC 17025: General requirements for the competence of testing and calibration laboratories* to use the approved analysis methods described in this document for testing the relevant analytes in the relevant matrix
- comply with the requirements in this document.

2. Sample collection and handling

Those required to comply with this document must ensure that sampling is carried out by a person trained in collecting, handling and preserving samples and who has designed an appropriate sampling plan in accordance with this section.

A sampling plan backed by a robust quality-management system is required for the collection of data to ensure that it is representative of the condition being investigated and is accurate, reliable and complete (see sections 2.1–2.4 below for more details).

Sample collection, handling and preservation procedures must be consistent with the collection, handling and preservation principles in the following standards:

- *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association (APHA), current version)
- Australian/New Zealand Standard (AS/NZS) 5667.1:1998 *Water quality: sampling part 1 – guidance on the design of sampling programs, sampling techniques and the preservation and handling of samples*
- *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (Australian and New Zealand Governments (ANZG), current version).

If there is any inconsistency between the information in this document and the latest versions of the standard methods listed above, then the requirements set out in AS/NZS 5667.1 prevail.

2.1. Sampling design

The sampling plan should take into account:

- factors that can affect the data quality objectives, such as location, spatial variability, timing and frequency
- correct sampling procedures for the target analytes, including adequate quality control/quality assurance (QC/QA)
- adequate procedures for storing and transporting the samples quickly to the laboratory within the analyte holding times specified in the relevant standards listed below
- chain-of-custody procedures to ensure integrity of the sample from collection to data reporting

¹ **Equivalent accreditation body:** for the purpose of this document, this means an independent national body that is a member of the International Laboratory Accreditation Cooperation (ILAC) that provides accreditation under ISO/IEC 17025 for environmental testing.

- adequate training of the personnel who will be involved in conducting the sampling
- the making and keeping of appropriate documentation, such as documenting sampling equipment, detailing procedural steps for sample collection methods, and keeping auditable sampling records (for example field logbooks).

These following standards should be referred to for details on sampling guidance for specific sampling situations:

- AS/NZS 5667.4 *Water quality: sampling guidance on sampling from lakes, natural and man-made*
- AS/NZS 5667.5 *Water quality: sampling guidance on sampling of drinking water and water used for food and beverage processing*
- AS/NZS 5667.6 *Water quality: sampling guidance on sampling of rivers and streams*
- AS/NZS 5667.9 *Water quality: sampling guidance on sampling from marine waters*
- AS/NZS 5667.10 *Water quality: sampling guidance on sampling of waste waters*
- AS/NZS 5667.11 *Water quality: sampling guidance on sampling of groundwaters*

2.2. Sampling containers and devices

Sampling containers and devices must comply with the following key requirements:

- sampling devices (for example extendable poles, buckets and nets) used to collect samples must be made of materials that do not contaminate, interact with or disturb the sample
- sampling devices must be cleaned between samples to avoid potential cross-contamination
- sample containers must be clean; free of contaminants; and made of glass, polyethylene, polypropylene or a fluoropolymer (such as polytetrafluoroethylene (PTFE)) – chosen according to the material interaction with the analyte of interest and the relevant standard
- sterilised sample containers must be used for microbial analysis and therefore must only be opened immediately prior to sample collection. Sample containers for microbial analysis are generally pre-packed with a dechlorinating agent (such as sodium thiosulfate) and a complexing agent (such as ethylenediaminetetraacetic acid (EDTA)) for samples with high metal content. Consequently, the bottle must not be rinsed with the sample prior to collection.

The following considerations should be taken into account when selecting sample containers:

- Plastic containers (except PTFE) are not suitable for samples containing organic compounds because contaminants (such as phthalate esters) may leach into samples.
- Glass containers should be used for organic analytes (such as volatile organics, semi-volatile organics, pesticides, polychlorinated biphenyls (PCBs), and oil and grease).
- Some analytes (such as some pesticides and polynuclear aromatic compounds) are light-sensitive and should be collected in amber-coloured glass containers to minimise degradation.
- Polypropylene or high-density polyethylene (HDPE) containers should be used for PFAS samples. Glass containers with lined lids are not suitable for PFAS analysis.'

Refer to the standards listed in section 2 for detailed advice about selecting sampling containers and devices.

2.3. Sample storage, preservation and holding times

Samples must be stored and preserved in accordance with AS/NZS 5667.1. The holding times and sample preservation procedures for various analytes specified in APHA (current version), AS/NZS 5667.1 and USEPA *Clean Water Act Analytical Methods* (current version) must be followed. For example, samples for chemical analysis should be kept refrigerated between 1°C and 4°C

(AS/NZS 5667.1) while samples for microbial analysis should be refrigerated at $5 \pm 3^{\circ}\text{C}$ (AS 2031-2012 *Water quality: sampling for microbiological analysis*).

Following the relevant standards, noted above, will help satisfy the quality requirements for sampling. It also minimises the possibility of samples deteriorating or being contaminated or compromised, which could lead to significant changes in the analytes prior to analysis. In some cases, the use of *in situ* tests and test kits may be appropriate for some analytes with extremely short holding times (such as pH and chlorine).

The EPA recommends that, prior to sampling, preservation requirements and maximum holding times are discussed with the analysing laboratory.

2.4. Sampling quality assurance and quality control procedures

The sampling quality assurance (QA) and quality control (QC) procedures must be in accordance with the principles in APHA (current version), AS/NZS 5667 and ANZG (current version). Quality-management systems implemented at a facility must include protocols described in the sampling plan to enable collection of quality samples adequate for the required analytical measurement. The QA programs must ensure proper training of personnel for sample collection and implementation of good practice for collection of traceable and defensible samples.

3. Analysis methods

Analyses must be undertaken by a laboratory that has been accredited under ISO/IEC17025 to perform those analyses. The accreditation must be current and issued by NATA or equivalent accreditation body. Analyses should conform to the guidance in Part 1000 of APHA (current version), covering quality assurance, data quality, expression of results, method development and evaluation, and laboratory procedures.

The methods listed in Table 1 are approved methods. The approved methods refer to those analytical methods published by agencies recommended by the EPA and which are approved by the EPA for specific analytes.

Laboratories must use the latest published version of the approved method as soon as practical after publication, taking into account any transitional period associated with the updated method.

Unless stated otherwise by the relevant environment protection licence, notice or statutory instrument, any of the approved methods listed for that analyte may be used, provided that the method used can achieve the reporting limits required to demonstrate compliance with the particular licence, notice or statutory instrument. Standard methods with modifications may be accepted with or without EPA approval, depending on the significance of the modifications: see Figure 1 and section 4 for guidance about this.

Appendix 5 lists organisations that publish the methods listed in Table 1.

3.1. How to find an analyte in Table 1

The analytes are listed as follows:

- Analytes are listed in alphabetical order.
- If the individual analyte falls into a group of analytes, the analyte will be listed in the relevant group(s). For example, dieldrin is listed in 'extractable base/neutrals and acids' and 'organochlorine pesticides'.
- If the approved methods listed for an analyte group do not cover all approved methods available for a particular analyte, the analyte is listed again as an individual analyte.

If an analyte listed on the licence is not listed in Table 1, refer to Table A1 in Appendix 1, which gives alternative names for analytes. Table A2 in Appendix 1 lists individual analytes and the group(s) they fall into.

It is responsibility of those using the EPA-approved methods listed in Table 1 to ensure that the approved method used by the laboratory is the latest published version of the method.

Table 1 EPA-approved methods for the analysis of water pollutants

* Preferred methods

† Used when very low concentrations (< 100µg/L) are tested

Analyte	Approved method
Alkalinity (bicarbonate)	APHA section 2320
Alkalinity (total)	APHA section 2320
Aluminium (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111D* • APHA section 3111E* • APHA section 3500-Al*.
<i>Amitrole</i>	There are no standard methods for this analyte. If you need to monitor for this analyte, seek advice from the EPA before commencing sampling or analysis.
Aniline	Use one of the following: <ul style="list-style-type: none"> • USEPA method 8131 • USEPA method 8261 • USEPA method 8270.
Anions Includes: <ul style="list-style-type: none"> • bromide (Br⁻) • chloride (Cl⁻) • fluoride (F⁻) • nitrate (NO³⁻) • nitrite (NO²⁻) • phosphate (PO₄³⁻) • sulfate (SO₄²⁻) 	Use one of the following: <ul style="list-style-type: none"> • APHA section 4110 • APHA section 4140 • USEPA method 6500 • USEPA method 9056.
Anthracene	Use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Polycyclic aromatic hydrocarbons' • USEPA method 8410.
Antimony (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111B*.

Analyte	Approved method
Arsenic (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3114 • APHA section 3500-As.
Arsenic III (arsenite)	USEPA method 1632
Arsenic V (arsenate)	USEPA method 1632
Barium (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111D*.
Beryllium (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111D* • APHA section 3111E*.
Biochemical oxygen demand (5 day)	APHA section 5210B
Boron (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 4500-B.
Bromide (Br ⁻)	Use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Anions' • APHA section 4500-Br.
Cadmium (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111B* • APHA section 3111C*.
Calcium (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111B* • APHA section 3111D* • APHA section 3500-Ca.
Carbonate	APHA section 2320
Chemical oxygen demand	APHA section 5220

Analyte	Approved method
Chlordane and isomers (cis, trans and total)	Use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Extractable base/neutrals and acids' • APHA section 6630 • USEPA method 8081* • USEPA method 8085.
Chloride (Cl ⁻)	Use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Anions' • APHA section 4500-Cl⁻ B • APHA section 4500-Cl⁻ D • APHA section 4500-Cl⁻ E.
Chlorinated phenoxy acids herbicides Includes: <ul style="list-style-type: none"> • 2,4-D • pentachlorophenol • 2,4,5-T • MCPA 	Use one of the following: <ul style="list-style-type: none"> • APHA section 6640 • USEPA method 8151* • USEPA method 8321. Note: When using method 8321, samples should be hydrolysed to the ester form to simplify analysis.
Chlorinated volatile compounds	Use one of the following: <ul style="list-style-type: none"> • APHA section 6200 • USEPA method 8021* • USEPA method 8260* • USEPA method 8261.

Analyte	Approved method
Chlorine (combined residual)	<p>Use one of the following:</p> <ul style="list-style-type: none"> • APHA section 4500-Cl D • APHA section 4500-Cl F • APHA section 4500-Cl G. <p>Note: Loss of free chlorine due to reaction with organic material and/or reducing agents and/or by volatilisation from water samples can make it difficult to analyse for chlorine (total residual), chlorine (free residual) or chlorine (combined residual). As a result, the most appropriate analytical technique to demonstrate compliance with a limit requirement is likely to be analysis on site using a kit.</p> <p>The only kits acceptable to the EPA are those using a portable spectrophotometer or colorimeter to measure the colour development indicating the concentration of chlorine present.</p> <p>Those not acceptable to the EPA are kits using comparison with a colour chart to determine concentration.</p> <p>Normal QA procedures must be followed. These include:</p> <ul style="list-style-type: none"> • analysis of blanks with every batch of samples • use of certified chlorine standards: <ul style="list-style-type: none"> ○ on each occasion the kit is used (if not used every day) <p>or</p> <ul style="list-style-type: none"> ○ weekly (if used constantly). <p>Samples need to be taken immediately before analysis and in bottles (e.g. BOD bottles) that can be filled completely. The bottles must be wrapped in foil.</p> <p>These directions are based on requirements set down in the APHA methods listed above for chlorine analysis.</p> <p>If the concentration of chlorine being measured is likely to be around 0.05–0.2mg/L, you must validate the detection limit for the specific wastewater being analysed and the kit being used for the analysis.</p>
Chlorine (free residual)	<p>Use one of the following:</p> <ul style="list-style-type: none"> • APHA section 4500-Cl D • APHA section 4500-Cl F • APHA section 4500-Cl G • APHA section 4500-Cl H. <p>Refer to the note on the use of kits under 'Chlorine (combined residual)'.</p>
Chlorine (total residual)	<p>Use one of the following:</p> <ul style="list-style-type: none"> • APHA section 4500-Cl B • APHA section 4500-Cl C • APHA section 4500-Cl D • APHA section 4500-Cl E • APHA section 4500-Cl F • APHA section 4500-Cl G • APHA section 4500-Cl I. <p>Refer to the note on the use of kits under 'Chlorine (combined residual)'.</p>
Chlorophyll a	APHA section 10200H

Analyte	Approved method
Chromium (acid extractable)	<p>Preliminary treatment as listed in 'Metals (acid extractable)'</p> <p>Then also use one of the following:</p> <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable) • APHA section 3111C*.
Chromium (hexavalent)	<p>Use one of the following:</p> <ul style="list-style-type: none"> • APHA method 3500-Cr • AS 2882 • USEPA method 218.6 • USEPA method 7196 • USEPA method 7199.
Chromium (trivalent)	<p>Trivalent chromium is to be calculated:</p> $\text{Cr}^{3+} = \text{Cr (acid extractable)} - \text{Cr}^{6+}$
Cobalt (acid extractable)	<p>Preliminary treatment as listed in 'Metals (acid extractable)'</p> <p>Then also use one of the following:</p> <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111B* • APHA section 3111C*.
Colour (true)	APHA section 2120
Conductivity	APHA section 2510
Copper (acid extractable)	<p>Preliminary treatment as listed in 'Metals (acid extractable)'</p> <p>Then also use one of the following:</p> <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111B* • APHA section 3111C*.
Cyanide (free)	<p>Preliminary recovery ASTM method D4282</p> <p>Then also use one of the following:</p> <ul style="list-style-type: none"> • APHA section 4500-CN⁻ D • APHA section 4500-CN⁻ E • APHA section 4500-CN⁻ F • ASTM D4282.
Cyanide (total)	<p>Preliminary treatment, if required, using APHA section 4500-CN⁻ B;</p> <p>followed by distillation using APHA section 4500-CN⁻ C</p> <p>Then also use one of the following:</p> <ul style="list-style-type: none"> • APHA section 4500-CN⁻ D • APHA section 4500-CN⁻ E • APHA section 4500-CN⁻ F • USEPA method 335.2 • USEPA method 335.4. <p>Note: If the discharge is a slurry (that is, it contains a high fraction of solids), contact the EPA for further advice on the appropriate method.</p>

Analyte	Approved method
Cyanide (weak acid dissociable)	Preliminary treatment, if required, using APHA section 4500-CN ⁻ B. Then also use APHA section 4500-CN ⁻ I. Note: If the discharge is a slurry (that is, it contains a high fraction of solids), contact the EPA for further advice on the appropriate method.
Depth	Use one of the following: <ul style="list-style-type: none"> • ASTM D5073 • AS 3778.7.
Dissolved organic carbon	APHA section 5310
Dissolved organic halogen Includes: <ul style="list-style-type: none"> • tetrachloroethene • trichloroethene • trihalomethanes • other halogenated alkanes and alkenes • chlorinated and brominated pesticides • polychlorinated biphenyls • hexachlorobenzene • 2,4-dichlorophenol 	APHA section 5320 Note: This is a general screening method to determine overall total dissolved organic halogen. If quantification of individually listed compounds is required then they must be tested by their specific approved methods, where included in this table.
Dissolved oxygen	APHA section 4500-O
Diuron	USEPA method 8321
Enterococci	Use one of the following: <ul style="list-style-type: none"> • APHA section 9230 • AS 4276.8 • AS 4276.9 • USEPA method 1106.1 • USEPA method 1600.
Escherichia coli	Use one of the following: <ul style="list-style-type: none"> • APHA section 9221F • APHA section 9221G • APHA section 9222 • AS 4276 (several volumes) • USEPA method 1103.1 • USEPA method 1603 • USEPA method 1604.
Ethanol	Use one of the following: <ul style="list-style-type: none"> • USEPA method 8015 • USEPA method 8260 • USEPA method 8261.

Extractable base/neutrals and acids. Includes:	Use one of the following:
<ul style="list-style-type: none"> • acenaphthene • acenaphthylene • aldrin • alpha-BHC • anthracene • benzidine • benzo(a)anthracene • benzo(a)pyrene • benzo(b)fluoranthene • benzo(ghi)perylene • benzo(k)fluoranthene • beta-BHC • chlordane • 2-chlorophenol • chrysene • 4,4'-DDD • 4,4'-DDE • 4,4'-DDT • dibenzo(a,h)anthracene • 1,2-dichlorobenzene • 1,3-dichlorobenzene • 1,4-dichlorobenzene • 3,3'-dichlorobenzidine • 2,4-dichlorophenol • dieldrin • 2,4-dimethylphenol • endosulfan I • endosulfan II • endosulfan sulfate • fluoranthene • gamma-BHC (lindane) • heptachlor • heptachlor epoxide • hexachlorobenzene • indeno(1,2,3-cd)pyrene • naphthalene • nitrobenzene • pentachlorophenol • phenol • polychlorinated biphenyls (PCB-1016, PCB-1221, PCB-1232, PCB-1242, PCB-1248, PCB-1254, PCB-1260) • pyrene • 2,4,6-trichlorophenol • 2,3,4,6-tetrachlorophenol 	<ul style="list-style-type: none"> • APHA section 6410 • USEPA method 625.1 • USEPA method 8270*.

Analyte	Approved method
Filterable reactive phosphate (as phosphorus)	APHA section 4500-P B Then also use one of the following: <ul style="list-style-type: none"> • APHA section 4110 • APHA section 4120 • APHA section 4130 • APHA section 4500-P E • APHA section 4500-P F • APHA section 4500-P G • USEPA method 365.2 • USEPA method 365.3.
Flow	AS 3778 (several volumes) Note: This standard covers methods for use in open channels and waterways. To determine flow in pipes, you must use: <ul style="list-style-type: none"> • pumping capacity • pressure differences or <ul style="list-style-type: none"> • electromagnetic, ultrasonic flow meters. <p>Note: As part of consultation, EPA is seeking feedback on what devices are being used to measure flow in pipes.</p>
Fluoride (F ⁻)	For the preliminary distillation step, if required, use APHA section 4500-F ⁻ B Then also use one of the following: <ul style="list-style-type: none"> • the methods as listed in 'Anions' • APHA section 4500-F⁻ C • APHA section 4500-F⁻ D • APHA section 4500-F⁻ E.
Formaldehyde	USEPA method 8315
Glyphosate	Use one of the following: <ul style="list-style-type: none"> • APHA section 6651 • USEPA method 547.
Hardness (as calcium carbonate)	Use one of the following: <ul style="list-style-type: none"> • APHA section 2340 • USEPA method 130.1.
Hexachlorobenzene	Use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Extractable base/neutrals and acids' • USEPA method 8081 • USEPA method 8410.
Hexachlorobutadiene	Use one of the following: <ul style="list-style-type: none"> • USEPA method 8021 • USEPA method 8260 • USEPA method 8261 • USEPA method 8270* • USEPA method 8410.

Analyte	Approved method
Hexachloroethane	Use one of the following: <ul style="list-style-type: none"> USEPA method 8260 USEPA method 8270 USEPA method 8410.
Hydrogen sulfide (un-ionised)	APHA section 4500-S ²⁻ H Note: Use dissolved sulfide value in the calculations.
Iron (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> methods as listed in 'Metals (acid extractable)' APHA section 3111B* APHA section 3111C*.
Lead (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> methods as listed in 'Metals (acid extractable)' APHA section 3111B* APHA section 3111C*.
Lithium (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> methods as listed in 'Metals (acid extractable)' APHA section 3111B*.
Magnesium (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> methods as listed in 'Metals (acid extractable)' APHA section 3111B*.
Manganese (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> methods as listed in 'Metals (acid extractable)' APHA section 3111B* APHA section 3111C*.
Mercury (dissolved)	Preliminary treatment APHA section 3030B Then also treat according to Mercury (total).
Mercury (total)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> methods as listed in 'Metals (acid extractable)' APHA section 3112 USEPA method 245.1 USEPA method 245.7 USEPA method 1631.

Analyte	Approved method
Metals (acid extractable)	For preliminary treatment use one of the following:
Includes:	<ul style="list-style-type: none"> • APHA section 3030(E-K) • USEPA method 3005 • USEPA method 3010 • USEPA method 3015 • USEPA method 3020[^].
<ul style="list-style-type: none"> • aluminium (Al) • antimony (Sb) • arsenic (As) • barium (Ba) • beryllium (Be) • boron (B) • calcium (Ca) • cadmium (Cd) • chromium (Cr) • cobalt (Co) • copper (Cu) • iron (Fe) • lead (Pb) • lithium (Li) • magnesium (Mg) • manganese (Mn) • molybdenum (Mo) • nickel (Ni) • phosphorus (P) • potassium (K) • selenium (Se) • silica (SiO₂) • silver (Ag) • sodium (Na) • strontium (Sr) • sulfur (S) • tin (Sn) • titanium (Ti) • thallium (Tl) • vanadium (V) • zinc (Zn) 	<p>Then also use one of the following:</p> <ul style="list-style-type: none"> • APHA section 3113~* • APHA section 3120* • APHA section 3125[^]†* • USEPA method 200.7 • USEPA method 200.8[#]† • USEPA method 6010* • USEPA method 6020[^]†*. <p>[^] Sample preparation method only for selected heavy metals (Be, Cd, Cr, Co, Pb, Mo, Tl, and V)</p> <p>~ Only for analysis of Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Ag and Sn</p> <p>◇ Analysis for the listed analytes except for B, Ca, Fe, Mg, K, P, Na, SiO₂, Sn, S, and Ti</p> <p>[#] Analysis for the listed analytes except for B, Ca, Fe, Mg, K, P, Na, SiO₂, Sn, S, Ti, Sr and Li</p> <p>^Δ Analysis for the listed analytes except for B, Li, Mo, P, S, Sn, Sr, SiO₂ and Ti</p>
Note: For the purposes of this document, the term 'acid extractable' is as defined in APHA Section 3030A.	

Analyte	Approved method
Metals (dissolved) Includes: <ul style="list-style-type: none"> aluminium (Al) antimony (Sb) arsenic (As) barium (Ba) beryllium (Be) boron (B) cadmium (Cd) calcium (Ca) chromium (Cr) cobalt (Co) copper (Cu) iron (Fe) lead (Pb) lithium (Li) magnesium (Mg) manganese (Mn) molybdenum (Mo) nickel (Ni) phosphorus (P) potassium (K) selenium (Se) silica (SiO₂) silver (Ag) sodium (Na) strontium (Sr) sulfur (S) tin (Sn) titanium (Ti) thallium (Tl) vanadium (V) zinc (Zn) 	Preliminary treatment APHA section 3030B then also treat according to 'Metals (acid extractable)'.
Methane	APHA section 6211
Methomyl	Use one of the following: <ul style="list-style-type: none"> APHA section 6610 USEPA method 8318 USEPA method 8321.
Methylene blue active substances (MBAS)	APHA section 5540
Methyl ethyl ketone (MEK)	Use one of the following: <ul style="list-style-type: none"> USEPA method 8015 USEPA method 8260 USEPA method 8261.

Analyte	Approved method
Methylphenols Includes: 2-methylphenol 3-methylphenol 4-methylphenol	Use one of the following: <ul style="list-style-type: none"> • USEPA method 8041* • USEPA method 8270* • USEPA method 8410.
Metolachlor	Use one of the following: <ul style="list-style-type: none"> • USEPA method 8085 • USEPA method 8270.
<i>Metsulfuron-methyl</i>	There are no standard methods for this analyte. If you need to monitor for this analyte, seek advice from the EPA before commencing sampling or analysis.
Molinate	Use one of the following: <ul style="list-style-type: none"> • USEPA (1993) method 634 • USEPA method 8085 • USEPA method 8141 • USEPA method 8270* • USEPA method 8321.
Molybdenum (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111D*.
Nickel (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111B* • APHA section 3111C*.
Nitrate (NO ₃ ⁻)	Use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Anions' • APHA section 4120 • APHA section 4130 • APHA section 4500-NO₃⁻ D • APHA section 4500-NO₃⁻ E • APHA section 4500-NO₃⁻ F • APHA section 4500-NO₃⁻ I • USEPA method 353.2.
Nitrite (NO ₂ ⁻)	Use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Anions' • APHA section 4120 • APHA section 4130 • APHA section 4500-NO₂⁻ • APHA section 4500-NO₃⁻ F (with cadmium colour removed) • APHA section 4500-NO₃⁻ I (with cadmium colour removed) • USEPA method 353.2 • USEPA method 354.1.

Analyte	Approved method
Nitrogen (ammonia)	<p>Use one of the following:</p> <ul style="list-style-type: none"> • APHA section 4120 • APHA section 4130 • APHA section 4500-NH₃ • USEPA method 350.1 <p>Note: For trade waste samples, distillation is required using APHA 4500-NH₃-C.</p>
Nitrogen (total)	<p>Nitrogen (total) can be determined through calculation, using nitrogen (total) = total Kjeldahl nitrogen + nitrogen (total oxidised) or measured directly using APHA section 4500-N C</p> <p>Where equivalent results can be demonstrated, the following direct Nitrogen (total) methods can also be used:</p> <ul style="list-style-type: none"> • APHA section 4120 • APHA section 4130 <p>Note: The direct persulfate digestion method (4500-N C) for analysis of nitrogen (total) may not be suitable where there are high levels of particulates in the sample.</p>
Nitrogen (total oxidised)	<p>This is the sum total of oxidised forms of nitrogen, that is 'nitrogen (nitrate)' + 'nitrogen (nitrite)'.</p> <p>For the approved methods, refer to 'Nitrate' and 'Nitrite'.</p>
Nonylphenol ethoxylates	<p>There are no standard methods for this analyte. If you need to monitor for this analyte, seek advice from the EPA before commencing sampling or analysis.</p>
Oil and grease	<p>Use one of the following:</p> <ul style="list-style-type: none"> • APHA section 5520B • APHA section 5520C • APHA section 5520D • APHA section 5520F (hydrocarbons only) • USEPA method 1664*

Analyte	Approved method
Organochlorine pesticides Includes: <ul style="list-style-type: none"> • aldrin • alpha-BHC • beta-BHC • gamma-BHC (lindane) • cis-chlordane • trans-chlordane • 4,4'-DDD • 4,4'-DDE • 4,4'-DDT • dieldrin • endosulfan i • endosulfan ii • endosulfan sulfate • endrin • heptachlor • heptachlor epoxide • methoxychlor 	Use one of the following: <ul style="list-style-type: none"> • APHA section 6410 • APHA section 6630 • USEPA method 608.3 • USEPA method 8081* • USEPA method 8085 • USEPA method 8270*
Organophosphorus pesticides Includes: <ul style="list-style-type: none"> • atrazine • chlorpyrifos • diazinon • dimethoate • ethion • malathion • methyl azinphos • methyl chlorpyrifos • methyl parathion • parathion 	Use one of the following: <ul style="list-style-type: none"> • USEPA method 8085 • USEPA method 8141 • USEPA method 8270 Note: Chlorpyrifos and diazinon may be analysed using USEPA method 8270, provided that the extraction is performed at neutral pH as per method USEPA 8141.
Oxidation–reduction potential	APHA section 2580
Pentachlorophenol	Use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Chlorinated phenoxy acids herbicides' • methods as listed in 'Extractable base/neutrals and acids' • APHA section 6420 • USEPA method 8041.

Analyte	Approved method
Per- and polyfluorinated alkyl substances Includes: <ul style="list-style-type: none"> perfluorobutanesulfonic acid (PFBS) perfluorodecanoic acid (PFDA) perfluoroheptanoic acid (PFHpA) perfluorohexanesulfonic acid (PFHxS) perfluorohexanoic acid (PFHxA) perfluorononanoic acid (PFNOA) perfluorooctanesulfonic acid (PFOS) perfluorooctanoic acid (PFOA) 	Use one of the following: <ul style="list-style-type: none"> USEPA method 533 USEPA method 537 USEPA method 537.1.
pH value	APHA section 4500-H ⁺
Phenol and individual phenolic compounds Includes: <ul style="list-style-type: none"> 2-chlorophenol 2,4-dichlorophenol 2,4-dimethylphenol Phenol 2,3,4,6-tetrachlorophenol 2,4,6-trichlorophenol 	Use one of the following: <ul style="list-style-type: none"> APHA section 6410 APHA section 6420 USEPA method 8041* USEPA method 8270*. For individual phenolic compounds refer to their individual listings or look under 'Extractable base/neutrals and acids' in this table.
Phosphorus (total)	Use one of the following: <ul style="list-style-type: none"> Preliminary treatment as listed in 'Metals (acid extractable)' then also methods as listed in 'Metals (acid extractable) or <ul style="list-style-type: none"> One of the following: <ul style="list-style-type: none"> APHA section 4500-Norg with Jirka modification (Jirka et al 1976) APHA section 4500-P B (persulfate digestion) Followed by one of the following: <ul style="list-style-type: none"> APHA section 4500-P E APHA section 4500-P F APHA section 4500-P H USEPA method 365.2 USEPA method 365.3 USEPA method 6010. Note: The direct persulfate digestion method (4500-P B) for analysis of phosphorus (total) may not be suitable where there are high levels of particulates in the samples.

Analyte	Approved method
Phosphorus (total dissolved)	<p>Use one of the following:</p> <ul style="list-style-type: none"> • Methods as listed in 'Metals (dissolved)' or • Filtration through 0.45µm membrane filter followed by one of the following: <ul style="list-style-type: none"> ○ APHA section 4500-Norg with Jirka modification (Jirka et al 1976) ○ APHA section 4500-P B (persulfate digestion) <p>Then also use one of the following:</p> <ul style="list-style-type: none"> ○ APHA section 4500-P E ○ APHA section 4500-P F ○ APHA section 4500-P H ○ USEPA method 365.2 ○ USEPA method 365.3.
Polychlorinated biphenyls (PCBs)	<p>Use one of the following:</p> <ul style="list-style-type: none"> • methods as listed in 'Extractable base/neutrals and acids' • APHA section 6431 • USEPA method 8082*.
<p>Polycyclic aromatic hydrocarbons</p> <p>Includes:</p> <ul style="list-style-type: none"> • acenaphthene • acenaphthylene • anthracene • benzo(a)anthracene • benzo(a)pyrene • benzo(b)fluoranthene • benzo(e)pyrene • benzo(ghi)perylene • benzo(k)fluoranthene • coronene • chrysene • dibenzo(a,h)anthracene • fluoranthene • indeno(1,2,3-cd)pyrene • naphthalene • phenanthrene • pyrene 	<p>Use one of the following:</p> <ul style="list-style-type: none"> • APHA section 6410 • APHA section 6440 • USEPA method 8100* • USEPA method 8270* • USEPA method 8310*.
Potassium (acid extractable)	<p>Preliminary treatment as listed in 'Metals (acid extractable)'</p> <p>Then also use one of the following:</p> <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111B* • APHA section 3500-K*.

Analyte	Approved method
Quaternary salts Includes: diquat paraquat	USEPA method 549.2
Salinity	APHA section 2520
Selenium (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3114* • APHA section 3500-Se.
Semi-volatile organic hydrocarbons	Use one of the following: <ul style="list-style-type: none"> • APHA section 6410 • USEPA method 8270*.
Silver (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' or acid digestion by the method of Yang et al. (2002) Then also use one of the following <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111B* • APHA section 3111C*.
Simazine	Use one of the following: <ul style="list-style-type: none"> • USEPA method 8085 • USEPA method 8141 • USEPA method 8270. <p>Note: Simazine may be analysed using USEPA method 8270, provided that the extraction is performed at neutral pH as per method USEPA 8141.</p>
Sodium (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111B* • APHA section 3500-Na.
Standing water level	Refer to the section on 'Depth'.
Sulfate (SO ₄ ²⁻)	Use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Anions' • APHA section 4500-SO₄²⁻ E • APHA section 4500-SO₄²⁻ F • USEPA method 375.4 • USEPA method 375.2.
Sulfide (dissolved)	APHA section 4500-S ²⁻ Note: If sample contains suspended solids, then use 4500-S ²⁻ B followed by 4500-S ²⁻ D. If sample contains no suspended solids, then use 4500-S ²⁻ D.
Sulfide (total)	APHA section 4500-S ²⁻
Temperature	APHA section 2550

Analyte	Approved method
2,3,4,6-tetrachlorophenol	Use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Extractable base/neutrals and acids' • methods as listed in 'Phenol and individual phenolic compounds' • USEPA method 8085.
Thermotolerant coliforms (also known as faecal coliforms)	Use one of the following: <ul style="list-style-type: none"> • APHA section 9221 • APHA section 9222 • AS 4276.6 • AS 4276.7.
<i>Thiobencarb</i>	<i>There are no standard methods for this analyte. If you need to monitor for this analyte, seek advice from your licensing officer before commencing sampling or analysis.</i>
Tin (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111B • APHA section 3111D
Titanium (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111D*
Total dissolved solids	APHA section 2540C
Total Kjeldahl nitrogen	Use one of the following: <ul style="list-style-type: none"> • APHA section 4120 • APHA section 4130 • APHA section 4500-Norg • APHA section 4500-Norg with Jirka modification (Jirka et al, 1976) • USEPA method 351.2
Total organic carbon (in water)	Use one of the following: <ul style="list-style-type: none"> • APHA section 5310 • USEPA method 9060
Total petroleum hydrocarbons (TPHs) and Total recoverable hydrocarbons (TRHs)	Use one of the following: <ul style="list-style-type: none"> • USEPA method 8000 • USEPA method 8015
Total phenolics	Use one of the following: <ul style="list-style-type: none"> • APHA section 5530 • USEPA method 420.4
Total suspended solids	Use one of the following: <ul style="list-style-type: none"> • APHA section 2540D • AS 3550.4 • USEPA method 160.2
Toxicity	Guidance on conducting toxicity testing is provided in Appendix 2.

Analyte	Approved method
Tributyltin	Use one of the following: <ul style="list-style-type: none"> • APHA section 6710 • USEPA method 8323.
Trifluralin	Use one of the following: <ul style="list-style-type: none"> • USEPA method 8081 • USEPA method 8085 • USEPA method 8091 • USEPA method 8270.
Trihalomethanes and chlorinated organic solvents Includes: <ul style="list-style-type: none"> • Bromoform • Bromodichloromethane • Carbon tetrachloride • Chloroform • Dibromochloromethane • Tetrachloroethene • 1,1,1-Trichloroethane • 1,1,2-Trichloroethane • Trichloroethene 	Use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Volatile organic compounds (VOCs)' • APHA section 6232.
Turbidity	APHA section 2130
Vanadium (acid extractable)	Preliminary treatment as listed in 'Metals (acid extractable)' Then also use one of the following: <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111D*.
Volatile halogenated compounds	Use one of the following: <ul style="list-style-type: none"> • APHA section 6200 • USEPA method 8021 • USEPA method 8260 • USEPA method 8261.

Analyte	Approved method
Volatile organic compounds (VOCs) Includes: <ul style="list-style-type: none"> benzene bromoform bromodichloromethane carbon tetrachloride chlorobenzene chloroform dibromochloromethane 1,2-dichlorobenzene 1,3-dichlorobenzene 1,4-dichlorobenzene 1,1-dichloroethane 1,2-dichloroethane 1,1-dichloroethene ethyl benzene naphthalene styrene tetrachloroethene toluene 1,1,1-trichloroethane 1,1,2-trichloroethane trichloroethene vinyl chloride xylene (includes: m-xylene, o-xylene, p-xylene) 	Use one of the following: <ul style="list-style-type: none"> APHA section 6200 USEPA method 8021* USEPA method 8260* USEPA method 8261.
Volume	<p>AS 3778 covers methods for determining width, depth and velocity in open channels and waterways.</p> <p>The following approaches can generally be used:</p> <ul style="list-style-type: none"> for standing waterbody: volume = width x length x depth for flowing waterbody: volume = cross-sectional area x flow (velocity) (where cross-sectional area = width x depth). <p>For pipes, the volume can be estimated from the known pump capacity multiplied by the duration of pumping.</p> <p>In all calculations, measuring instruments must be calibrated and the units of measurements must be the same. Averages of several measurements should be used when calculating values.</p> <p>Note: The EPA notes that this standard does not directly measure volume and, as part of consultation, is seeking feedback from stakeholders on what other standards could be used.</p>

Analyte	Approved method
Zinc (acid extractable)	<p>Preliminary treatment as listed in 'Metals (acid extractable)'</p> <p>Then also use one of the following:</p> <ul style="list-style-type: none"> • methods as listed in 'Metals (acid extractable)' • APHA section 3111B* • APHA section 3111C* • APHA section 3130B*.

* Preferred methods

† Used when very low concentrations (< 100µg/L) are tested

4. Modifying methods, or using alternative or unlisted methods

Clause 60(3) of the POEO General Regulation allows for procedural details of the test methodology to be varied where it can be established that the variation does not affect the results of the test. This section outlines the process for establishing the acceptability of the variation.

If no method is specified for an analyte, an analyte is not listed, or your laboratory uses a modified or alternative method for sampling or analysis of an analyte, you must determine the need to seek approval from the EPA for any alternative or modified method you are proposing to use.

For minor modifications to an approved method

Generally, EPA approval will not be required for minor modifications that produce results that meet or exceed QC acceptance criteria for the approved method, where an approved method is listed for the analyte in this method. However, both those required to comply with the Approved Methods and those conducting the test must keep supporting records.

For all other variations

You must obtain written EPA approval before using any significantly modified or alternative method, as outlined in this section.

Contact the EPA if you are unsure whether approval is required.

4.1. Terminology

Approved method

An Approved Method is an approved sampling or analysis method in the *Approved Methods for Sampling and Analysis of Water Pollutants in NSW* (this document). These are the recognised standard methods given in Table 1.

Minor modification

A modification to a method listed in Table 1 is considered minor if it satisfies the conditions set out in section 4.3 of this document.

Significant modification

A 'signification modification' is described in section 4.4 of this document.

Alternative method

An alternative method is a method used in place of an approved method listed in this document.

Equivalent performance

'Equivalent performance' means that the modified method produces results that meet the QC acceptance criteria of the approved method.

4.2. Approval requirements

This section outlines the situations where EPA approval is and is not required.

Where EPA approval is required, this may be sought on behalf of the laboratory or sought directly by the laboratory.

When seeking EPA approval, you must:

- specify which laboratory will be conducting the test
- submit supporting documentation from the laboratory confirming that:
 - the QC criteria for the AM are met by the modification
 - the test results will not be affected by the modification or by the use of the alternative method.

If the laboratory seeks approval directly from the EPA, you must ensure that:

- the laboratory has indicated where a modified or alternative method has been used for an analyte
- the laboratory has kept records in relation to EPA approval of the use of that method.

The approval requirements are outlined in Figure 1 (below).

The following scenarios clarify the method approval requirements, depending on the circumstances:

Situation 1: There is an approved method and it has not been modified

Where there is an approved method listed in Table 1, EPA approval is not required for use of the method.

Situation 2: There is an approved method and it has been modified (minor modification)

EPA approval is not required where:

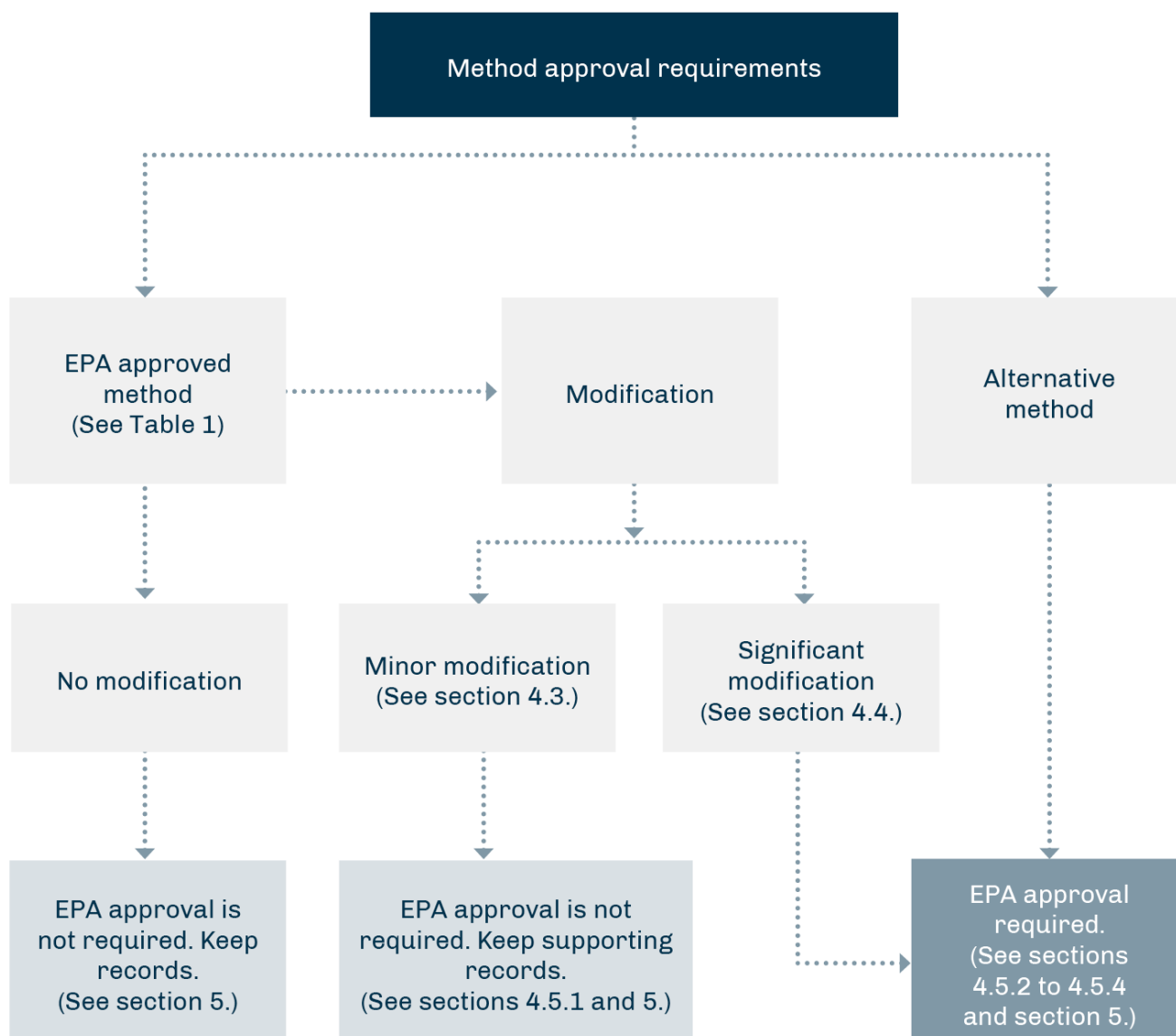
- the laboratory holds current ISO/IEC 17025 accreditation for analysing the analyte of interest and the modified method produces an equivalent performance to the approved method
- the modification is minor (see section 4.3).

Auditable records must be kept as outlined in section 4.5.1 and evidence of minor modification must be provided if requested by the EPA.

Situation 3: There is an approved method and it has been modified (significant modification)

EPA approval is required where the modification is significant (see section 4.4). Written approval from the EPA must be sought prior to use of the modification (see section 4.5.2) and a copy of all records in relation to seeking and obtaining EPA approval for use of the modified method must be kept (see section 5).

Figure 1 Approval process for modifications and alternative methods



Situation 4: There is an approved method, but an alternative method is proposed

EPA approval is required for use of an alternative method.

Written approval from the EPA must be sought prior to use of the alternative method (see section 4.5.2) and a copy of all records in relation to seeking and obtaining approval for use of the alternative method must be kept either by the person who was granted approval or, if the laboratory was granted approval, by the laboratory (see section 5).

Situation 5: The analyte is not listed in this document

If an analyte is not listed in this document, the EPA requires **all** of the following:

- use of a method which is based on a recognised standard or reference test method published by one of the following organisations:
 - Australian Standard (AS)
 - International Organization for Standardization (ISO)
 - United States Environmental Protection Agency (USEPA)

- supporting documentation demonstrating that the method to be used is fit for purpose and capable of achieving the reporting limits required to demonstrate compliance with the requirement by or under the licence, notice or environment protection legislation
- supporting documentation demonstrating that the analytical laboratory is competent in the analysis technique for the method to be used and, where practicable, is accredited under ISO/IEC 17025 for performing the analysis. Accreditation under ISO/IEC 17025 is required if the method will be used routinely.

If there is no recognised standard or reference test method for the analyte of interest published by the organisations listed in paragraph 1 immediately above, EPA approval is required for testing conducted under a condition of an environment protection licence or EPA-issued statutory notice. The EPA will not approve the use of a method for the analyte unless it is satisfied that the proposed method is fit for purpose and has been appropriately validated (see sections 4.5.2 to 4.5.4).

4.3. Minor modifications

A minor modification to an approved method is one that satisfies all the following conditions:

1. retains the underlying chemistry and determinative technique of the approved method
2. does not introduce (or increase potential for) significant additional interferences
3. uses proven technology and is generally accepted by the scientific community as equivalent to, or better than, the approved method
4. accounts for site- and/or emission-source-specific operational characteristics, physical constraints or safety concerns
5. achieves the applicable performance criteria of the unmodified approved method, where specified in the standards
6. achieves a comparable limit of reporting (LoR), being an increase in the limit of LoR by not more than 10% compared with the approved method.
7. Acceptable reasons for modifying an approved method may include:
 - to achieve lower detection limits
 - to improve precision
 - to reduce interferences.
8. Examples of minor modifications that meet points 1 to 6 above are included in Appendix 3.

4.4. Significant modifications

A significant modification to an approved method is either:

- a modification to be used by a laboratory that has not been accredited under ISO/IEC 17025 to carry out the testing using the modified technique

or

- a modification that does not fall under the definition of a minor modification.

EPA approval is required, prior to use of the method, where a significant modification to an approved method is proposed.

Examples of significant modifications to an approved method include, but are not limited to, use of:

- a peer-reviewed analytical process
- non-standard sampling equipment
- a method developed in-house that is not covered under the laboratory's scope of accreditation.

4.5. Documentation and validation requirements

4.5.1. Use of modified methods where EPA approval is not required

Those required to comply with these Approved Methods must ensure that the laboratory performing the testing and analysis prepares and holds all documentation required under ISO/IEC 17025 (or equivalent) for demonstrating the performance of the modified method, including:

- a procedure or method write-up or an addendum
- evidence of method validation
- essential QC requirements (see Appendix 4).

Unless the EPA requests them, specific modification details do not need to be provided to the EPA. The EPA can request relevant laboratory documentation and records, as listed in section 5.

4.5.2. Application for method approval (significant modification and alternative methods)

EPA approval for the use of a significantly modified or alternative method will only be considered if the EPA is satisfied that:

- the application for approval provides adequate details of the proposed method
- the proposed method has been appropriately validated (see sections 4.5.3 and 4.5.4).

An application for approval to use a significantly modified or alternative method must be made in writing to the EPA and obtained prior to use of the method. The application must include:

- adequate justification for the use of the method
- the purpose and intended use of the method, including related legislative or regulatory requirements
- a detailed description of the proposed method
- data that compares the performance of the significant modification (or alternative method) with that of the existing approved method
- a table that gives a side-by-side comparison of the proposed modified method (or alternative method) and the approved method, as outlined in section 4.5.3
- method-validation studies confirming the general applicability of the method for analysis of the analyte or parameter including supporting data (as outlined in section 4.5.4 below).

The following basic information must be provided in the written application:

- the name and address of the applicant
- the application submission date
- the environment protection licence number of the applicant where applicable
- the number and title of the proposed method
- the citation (i.e. number) of the EPA approved method (where an approved method has been modified)
- reference to the QC acceptance criteria used for comparison with the approved method.

If the EPA approves the application for use of a significantly modified or alternative method, the approval remains in force for the period stipulated in the approval, or until such time as the approval is revoked in writing by the EPA.

If the method is to be used for more than 12 months, the analysing laboratory should work towards attaining accreditation from NATA (or equivalent) for the modified method.

4.5.3. Method comparison table

When a significantly modified or alternative method is proposed, the applicant must compare the proposed method with the corresponding approved method and document the comparison in a two-column table. The table must include the number, title and description of each method. The applicant must highlight any differences between the proposed method and the approved method including any differences in the sensitivity, reliability and robustness of the results.

If the proposed method is an automation of a previously approved manual method, the comparison table must include:

- any differences in kinetics and interferences
- a comparison of the final ratios of the concentrations of the reactants in the proposed method and in the approved method.

4.5.4. Validation study report

Method validation is required for any non-standard method, in-house method or significantly modified approved method. The extent of validation required will depend on the status of the method under consideration and its intended application.

The method validation must be sufficient to demonstrate that the method is suitable for its intended purpose. Method validation should meet the requirements outlined in ISO/IEC 17025 and be undertaken in accordance with NATA's *General Accreditation Guidance: Validation and verification of quantitative and qualitative test methods* (January 2018).

Full method validation must be performed in accordance with the procedures set out in USEPA Method 301 or APHA section 1040, unless it can be demonstrated that the proposed method is an appropriately validated standard method.

Contact the EPA if you are unsure about any validation requirements.

5. Record-keeping

The following records must be kept for a period of four years for any sampling and analysis required by or under environment protection legislation, including by a notice or environment protection licence issued under that legislation, and must be provided to the EPA, if and when requested or required:

- site identification, including a map showing sampling locations with GPS coordinates (if applicable)
- number of samples collected and analysed
- sampling methods used, including pattern; depth; locations; sampling containers, devices and procedures; and, whenever possible, photographs of the sample locations and sample(s)
- list of field quality-control samples (if applicable)
- chain-of-custody forms
- analytical reports, including the QA/QC data
- a statement regarding whether a modified method (including a minor modification) or alternative method was used
- a copy of EPA approval where a significantly modified or alternative method was used

- any reports associated with the request for approval.

Any person required to comply with this document must ensure that laboratories include the following information in their analytical reports:

- analytical method number and title, including laboratory accreditation for analytical methods used
- date and time of sample collection
- date and time of analysis
- list of the analyte(s) measured
- method reporting limit, interferences and method limitation (if applicable)
- description of surrogates and spikes used as well as percent recoveries of surrogates and spikes (if applicable).

Where reporting is required under environment protection legislation or a statutory instrument, the analytes and units of measure reported on must be in the same format as they are in the environment protection legislation or statutory instrument. This means that unit conversions may need to be made in cases where laboratories have provided data in units that differ from the reporting requirements in the statutory instrument. When reporting is required, the laboratory should be consulted to ensure accurate conversions.

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Appendix 1: Alternative names for analytes

Table A1 lists the names of the approved methods analytes and the possible synonymous alternative names. Alternative names may appear in regulations and load-calculation protocols, and on licences and notices. Table A2 lists the analyte names and their corresponding names or categories in the approved methods table (Table 1).

Table A1 Names of analytes, as listed in the approved methods table (Table 1), and their common alternative names

Analyte name in approved methods table	Alternative analyte name(s)
Alkalinity (bicarbonate)	Bicarbonate
Alkalinity (total)	Alkalinity (as calcium carbonate)
Aluminium (acid extractable)	Aluminium Total aluminium
Antimony (acid extractable)	Antimony Total antimony
Arsenic (acid extractable)	Arsenic Total arsenic
Barium (acid extractable)	Barium Total barium
Benzo(ghi)perylene	Benzo(ghi)perylene Benzo(g,h,l)perylene (Note: incorrect names)
Beryllium (acid extractable)	Beryllium Total beryllium
alpha-BHC	a-BHC
beta-BHC	b-BHC
gamma-BHC	Lindane g -BHC (lindane)
Biochemical oxygen demand (5 day)	Biochemical oxygen demand BOD BOD5 BOD (for the purpose of determining the 3DGM)
Boron (acid extractable)	Boron Boron (total)
Cadmium (acid extractable)	Cadmium Total cadmium
Calcium (acid extractable)	Calcium
Chemical oxygen demand	COD
Chlorine (combined residual)	Chloramines
Chlorine (free residual)	Chlorine FRC Free residual chlorine
Chlorine (total residual)	TRC Total residual chlorine

Analyte name in approved methods table	Alternative analyte name(s)
Chromium (acid extractable)	Chromium (total) Total chromium
Chromium (hexavalent)	Chromium (VI) compounds Hexavalent chromium
Chromium (trivalent)	Chromium (III) compounds Trivalent chromium
Cobalt (acid extractable)	Cobalt Total cobalt
Conductivity	Salt (load calculation protocol only)
Copper (acid extractable)	Copper Total copper
Cyanide (free)	Free cyanide
Cyanide (total)	Total cyanide
Cyanide (weak acid dissociable)	WAD cyanide
2,4-D	2,4-Dichlorophenoxyacetic acid
4,4'-DDD	DDD <i>p,p'</i> -DDD <i>p,p'</i> -DDD (4,4)
4,4'-DDE	DDE <i>p,p'</i> -DDE <i>p,p'</i> -DDE (4,4)
4,4'-DDT	DDT <i>p,p'</i> -DDT <i>p,p'</i> -DDT (4,4)
1,2-Dichlorobenzene	<i>o</i> -Dichlorobenzene
3,3'-Dichlorobenzidine	Dichlorobenzidine
Dissolved organic carbon	DOC
Dissolved organic halogen	AOX absorbable organic halogens DOX
Dissolved oxygen	DO
Filterable reactive phosphate (as phosphorus)	Phosphorus (dissolved reactive)
Hexachlorobenzene	Hexachlorobenzene (HCB)
Iron (acid extractable)	Iron Total iron
Iron (dissolved)	Filterable iron
Lead (acid extractable)	Lead Total lead
Lead (dissolved)	Soluble lead
Lithium (acid extractable)	Lithium
Magnesium (acid extractable)	Magnesium
Manganese (acid extractable)	Manganese Total manganese

Analyte name in approved methods table	Alternative analyte name(s)
Manganese (dissolved)	Filterable manganese
MCPA	2-methyl-4-chlorophenoxyacetic acid
Mercury (total)	Mercury Mercury (inorganic)
Methyl azinphos	Azinphos-methyl Azinophos-methyl Guthion
Methylene blue active substances (MBAS)	Anionic surfactants
Methyl ethyl ketone (MEK)	2-Butanone Butanone
2-Methylphenol	o-cresol ortho-cresol
3-Methylphenol	m-cresol meta-cresol
4-Methylphenol	p-cresol para-cresol
Molybdenum (acid extractable)	Molybdenum
Nickel (acid extractable)	Nickel
Nitrate (NO ₃ ⁻)	Nitrogen (nitrate)
Nitrite (NO ₂ ⁻)	Nitrogen (nitrite)
Nitrogen (ammonia)	Nitrogen as ammonia Ammonia Ammonia nitrogen NH ₃ -N
Nitrogen (total)	Nitrogen TN Total nitrogen
Nitrogen (total oxidised)	Nitrate + nitrite (oxidised nitrogen)
Oil and grease	O&G
Organophosphorus pesticides	Organophosphate pesticides
Oxidation-reduction potential	Redox potential
Pentachlorophenol	PCP
Phosphorus (dissolved reactive)	Orthophosphate Reactive phosphorus Soluble phosphorus
Phosphorus (total)	TP, Total phosphorus Total phosphorus – unfiltered
Phosphorus (total dissolved)	Total phosphorus – filtered
Polychlorinated biphenyls	PCBs
Polycyclic aromatic hydrocarbons	Polynuclear aromatic hydrocarbons Total PAHs
Salinity	Salt (load calculation protocol only)

Analyte name in approved methods table	Alternative analyte name(s)
Selenium (acid extractable)	Selenium
Silica (acid extractable)	Silicate (SiO ₂)
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
Thermotolerant coliforms	FC fc Faecal coliforms
Total dissolved solids	TDS
Total Kjeldahl nitrogen	TKN TKN-N
Total organic carbon	TOC
Total suspended solids	TSS
Tributyltin	TBT
Vanadium (acid extractable)	Vanadium
Zinc (acid extractable)	Zinc Total zinc

Table A2 Names of analytes and their groups in the approved methods table (Table 1)

Analyte name	Analyte name/group in approved methods table
Aldrin	Extractable base/neutrals and acids
Aluminium (acid extractable)	Aluminium (acid extractable) Metals (acid extractable)
Aluminium (dissolved)	Metals (dissolved)
Antimony (acid extractable)	Antimony (acid extractable) Metals (acid extractable)
Antimony (dissolved)	Metals (dissolved)
Anthracene	Anthracene Polycyclic aromatic hydrocarbons
Arsenic (acid extractable)	Metals (acid extractable)
Arsenic (dissolved)	Metals (dissolved)
Atrazine	Organophosphorus pesticides
Barium (acid extractable)	Barium (acid extractable) Metals (acid extractable)
Barium (dissolved)	Metals (dissolved)
Benzene	Volatile organic compounds (VOCs)
Benzo(a)pyrene	Extractable base/neutrals and acids
Benzo(b)fluoranthene	Polycyclic aromatic hydrocarbons
Benzo(e)pyrene	
Benzo(ghi)perylene	
Benzo(k)fluoranthene	
Beryllium (acid extractable)	Beryllium (acid extractable) Metals (acid extractable)
Beryllium (dissolved)	Metals (dissolved)

Analyte name	Analyte name/group in approved methods table
alpha-BHC	Extractable base/neutrals and acids Organochlorine pesticides
beta-BHC	
gamma-BHC (lindane)	
Boron (acid extractable)	Boron (acid extractable) Metals (acid extractable)
Boron (dissolved)	Metals (dissolved)
Bromide (Br ⁻)	Anions Bromide (Br ⁻)
Bromoform	Trihalomethanes and chlorinated organic solvents Volatile organic compounds (VOCs)
Bromodichloromethane	Trihalomethanes and chlorinated organic solvents Volatile organic compounds (VOCs)
Cadmium (acid extractable)	Cadmium (acid extractable) Metals (acid extractable)
Cadmium (dissolved)	Metals (dissolved)
Calcium (acid extractable)	Calcium (acid extractable) Metals (acid extractable)
Calcium (dissolved)	Metals (dissolved)
Carbon tetrachloride	Trihalomethanes and chlorinated organic solvents Volatile organic compounds (VOCs)
Chlordane and isomers (cis, trans and total)	Chlordane and isomers (cis, trans and total) Extractable base/neutrals and acids Organochlorine pesticides
Chloride	Anions Chloride (Cl ⁻)
Chloroform	Trihalomethanes and chlorinated organic solvents Volatile organic compounds (VOCs)
Chlorpyrifos	Organophosphorus pesticides
Chromium (acid extractable)	Chromium (acid extractable) Metals (acid extractable)
Chromium (dissolved)	Metals (dissolved)
Cobalt (acid extractable)	Cobalt (acid extractable) Metals (acid extractable)
Cobalt (dissolved)	Metals (dissolved)
Copper (acid extractable)	Copper (acid extractable) Metals (acid extractable)
Copper (dissolved)	Metals (dissolved)
1,2-Dichloroethane	Volatile organic compounds (VOCs)
2,4-D	Chlorinated phenoxy acids herbicides
4,4'-DDD	Extractable base/neutrals and acids Organochlorine pesticides
4,4'-DDE	
4,4'-DDT	
Diazinon	Organophosphorus pesticides

Analyte name	Analyte name/group in approved methods table
Dibromochloromethane	Trihalomethanes and chlorinated organic solvents Volatile organic compounds (VOCs)
Dieldrin	Extractable base/neutrals and acids Organochlorine pesticides
Diquat	Quaternary salts
Endosulfan I	Extractable base/neutrals and acids Organochlorine pesticides
Endrin	Organochlorine pesticides
Ethyl benzene	Volatile organic compounds (VOCs)
Fluoranthene	Extractable base/neutrals and acids Polycyclic aromatic hydrocarbons
Fluoride	Fluoride (F-) Anions
Heptachlor Heptachlor epoxide	Extractable base/neutrals and acids Organochlorine pesticides
Hexachlorobenzene	Extractable base/neutrals and acids Hexachlorobenzene
Iron (acid extractable)	Iron (acid extractable) Metals (acid extractable)
Iron (dissolved)	Metals (dissolved)
Lead (acid extractable)	Lead (acid extractable) Metals (acid extractable)
Lead (dissolved)	Metals (dissolved)
Lithium (acid extractable)	Lithium (acid extractable) Metals (acid extractable)
Lithium (dissolved)	Metals (dissolved)
Magnesium (acid extractable)	Magnesium (acid extractable) Metals (acid extractable)
Magnesium (dissolved)	Metals (dissolved)
Malathion	Organophosphorus pesticides
Manganese (acid extractable)	Manganese (acid extractable) Metals (acid extractable)
Manganese (dissolved)	Metals (dissolved)
MCPA	Chlorinated phenoxy acids herbicides
Mercury (total)	Mercury (total) Metals (acid extractable)
Mercury (dissolved)	Mercury (dissolved) Metals (dissolved)
Methoxychlor	Organochlorine pesticides
Molybdenum (acid extractable)	Metals (acid extractable) Molybdenum (acid extractable)
Molybdenum (dissolved)	Metals (dissolved)

Analyte name	Analyte name/group in approved methods table
Naphthalene	Extractable base/neutrals and acids Polycyclic aromatic hydrocarbons Volatile organic compounds (VOCs)
Nickel (acid extractable)	Metals (acid extractable) Nickel (acid extractable)
Nickel (dissolved)	Metals (dissolved)
Nitrate	Anions Nitrate (NO ₃ ⁻)
Nitrite	Anions Nitrite (NO ₂ ⁻)
Paraquat	Quaternary salts
Pentachlorophenol	Chlorinated phenoxy acids herbicides Extractable base/neutrals and acids Pentachlorophenol
Phenanthrene	Polycyclic aromatic hydrocarbons
Phenol	Extractable base/neutrals and acids Phenol and individual phenolic compounds
Polychlorinated biphenyls	Extractable base/neutrals and acids Polychlorinated biphenyls (PCBs)
Potassium (dissolved)	Metals (acid extractable) Potassium (acid extractable)
Potassium (acid extractable)	Metals (dissolved)
Pyrene	Extractable base/neutrals and acids Polycyclic aromatic hydrocarbons
Selenium (acid extractable)	Metals (acid extractable) Selenium (acid extractable)
Selenium (dissolved)	Metals (dissolved)
Silica (acid extractable)	Metals (acid extractable)
Silica (dissolved)	Metals (dissolved)
Silver (acid extractable)	Metals (acid extractable) Silver (acid extractable)
Silver (dissolved)	Metals (dissolved)
Sodium (acid extractable)	Metals (acid extractable) Sodium (acid extractable)
2,4,5-T	Chlorinated phenoxy acids herbicides
Tetrachloroethene	Dissolved organic halogen Trihalomethanes and chlorinated organic solvents Volatile organic compounds (VOCs)
2,3,4,6-tetrachlorophenol	Extractable base/neutrals and acids Phenol and individual phenolic compounds 2,3,4,6-tetrachlorophenol
Thermotolerant coliforms (also known as faecal coliforms)	Thermotolerant coliforms

Analyte name	Analyte name/group in approved methods table
Tin (acid extractable)	Metals (acid extractable) Tin (acid extractable)
Titanium (acid extractable)	Metals (acid extractable) Titanium (acid extractable)
Toluene	Volatile organic compounds (VOCs)
Total petroleum hydrocarbons	Total petroleum hydrocarbons
Total recoverable hydrocarbons	Total recoverable hydrocarbons
1,1,1-Trichloroethane	Trihalomethanes and chlorinated organic solvents Volatile organic compounds (VOCs)
1,1,2-Trichloroethane	Trihalomethanes and chlorinated organic solvents Volatile organic compounds (VOCs)
Trichloroethene	Dissolved organic halogen Trihalomethanes and chlorinated organic solvents Volatile organic compounds (VOCs)
Vanadium (acid extractable)	Metals (acid extractable) Vanadium (acid extractable)
Volatile organic compounds (VOCs)	Volatile organic compounds (VOCs)
Xylenes	Volatile organic compounds (VOCs)
Zinc (acid extractable)	Metals (acid extractable) Zinc (acid extractable)

Appendix 2: Toxicity testing

Toxicity tests are procedures in which test organisms are exposed to a series of increasing concentrations of a test material to determine, or measure, the response of an organism to the integrated effects of the material's physico-chemical characteristics. It is recognised as an integral component in determining potential changes in, or effects on, the environmental quality and values of a system.

Toxicity tests are used where chemical analysis may not be sufficient to give information on the environmental effects of the chemicals present in a test material. Chemicals can interact with each other and the action of the chemicals could be affected by the complex matrix of the environmental system. Overall, the important parameter determining the potential toxic effects on organisms is the bioavailable concentration of toxicant(s) present.

Toxicity test methods must be based on published standard methods or guides to methods where appropriate, e.g. those produced by organisations such as the USEPA, OECD, ISO and ASTM.

The toxicity test method must be suitable for the purpose outlined above and meet the following criteria (based on Rand et al 1995, Batley et al 2018, Warne et al 2018):

- The test should be widely accepted by the scientific community i.e. published in a peer-reviewed journal or scientific report or published by the organisations listed above.
- The test should be sensitive, economical, easy to conduct, and as realistic as possible in design to detect and measure the effects.
- Test procedures should have a sound statistical basis and should be repeatable (that is, generate similar results in different laboratories).
- The data should include effects of a range of environmentally-relevant concentrations within realistic exposure duration (acute or chronic), and be quantifiable through statistical analysis, graphical method or another accepted method of evaluation.
- The test should have some field predictive capability for similar organisms.
- Data generated from the test should be useful for risk assessment.

Sensitive and environmentally-relevant species should be used. A range of single-species (at different trophic levels) tests is typically carried out to allow for better prediction of effects at higher levels of organisation.

The objectives of the toxicity assessment should be defined and QC practices should be established to ensure that data generated will address the objectives. Following is a general guide for requirements for conducting toxicity tests:

- There is a ready, or reliable and traceable, source of test organisms when needed. Organisms can be laboratory-cultured (such as cladocerans and rainbowfish), collected from a known source (such as sea urchins and amphipods) or pre-purchased and stored appropriately in the laboratory (such as Microtox and earthworms).
- There is a reliable supply of culture water or test diluent (such as seawater, freshwater, clean sediment and clean soil).
- There is adequate space and there are well-planned holding, culturing, lighting, testing and glassware washing facilities (such as equipment for temperature control and for measuring water quality parameters).
- The conduct of the test is according to the following requirements for a valid test (ASTM 1997).
 - Test concentrations are preferably geometrically increasing and covering no-toxic effects at the lowest concentration and effects as high as possible at the highest concentration (test treatments).
 - Test acceptability criteria must be stated. These usually include criteria for controls and solvent controls (if relevant) and a reference toxicant, all of which are tested concurrently with the test solutions. If solvent is used it should generally be at a concentration of <0.1 mL/L in aquatic tests and it should be at a constant concentration across the test treatments. The effects in controls should be less than a pre-determined level (usually 10–20% in aquatic tests).

- Loading of animals in test containers is appropriate for the test species and requirements of the animals.
- Animals are randomly assigned into test containers.
- Length and method (that is static, renewal and flow) of exposure as well as considerations of feeding are appropriate for the objectives of the toxicity assessment.
- Quality parameters of test treatments are measured (i.e. pH, EC, temperature and DO) and parameters may need to remain within specified limits (such as 70% saturation for fish tests).
- A specialised statistical package should be used to calculate the required parameters of toxicity (such as EC/ICxx and NOEC/LOEC).
- A reference toxicant test should be conducted concurrently with the sample tests to assess the laboratory conditions, relative sensitivity of the population of test organisms, and precision and reliability of data produced. Acceptability of the test data should be determined by criteria such as laboratory-based data produced over a specific number of recent tests done or recommended by the source of the test species. Repeatability in results obtained for a reference toxicant test should be demonstrated.

The EPA must be contacted about any proposed ecotoxicology methodology prior to testing.

Appendix 3: Examples of allowable minor modifications

Examples of allowable minor modifications (obtained from 40 CFR 136.6: *Method modifications and analytical requirements*) include, but are not limited to, the following.

1. Addition of new analyte(s) of interest.
2. Changes between manual method, flow analyser and discrete instrumentation.
3. Changes in chromatographic columns or temperature programs.
4. Changes between automated and manual sample preparation (e.g. digestions, distillations and extractions). In-line sample preparation is an acceptable form of automated sample preparation for the AMs.
5. Use of interference reduction technologies (e.g. collision cells or reaction cells) when using inductively coupled plasma mass spectrometry (ICP-MS), provided the method performance specifications relevant to ICP-MS measurements are met. In general, ICP-MS is a sensitive and selective detector for metal analysis. However, isobaric interference can cause problems for quantitative determination, as well as identification based on the isotope pattern. Interference reduction technologies are designed to reduce the effect of spectroscopic interferences that may bias results for the element of interest.
6. Changes in pH adjustment reagents. Changes in compounds used to adjust pH are acceptable provided they do not produce interference (e.g. using a different acid to adjust pH in colorimetric methods).
7. Changes in buffer reagents provided they do not produce interferences.
8. Changes in the order of reagent addition provided they do not alter the chemistry or produce an interference. For example, it is allowable to use the same reagents but to add them in a different order or to prepare them in combined or separate solutions (so they can be added separately) if reagent stability or method performance is equivalent or improved post modification.
9. Changes in calibration range provided the modified range covers any relevant regulatory limit and meets the method performance specifications for calibration.
10. Changes in calibration model.
 - a. Linear calibration models do not adequately fit calibration data with one or two inflection points. For example, vendor-supplied data acquisition and processing software on some instruments may provide quadratic fitting functions to handle such situations. If the calibration data for a particular analytical method routinely display quadratic character, the use of quadratic fitting functions may be acceptable. In such cases, the minimum number of calibrators for second order fits should be six, and in no case should concentrations be extrapolated for instrument responses that exceed the most concentrated calibrator. Examples of methods with nonlinear calibration functions include chloride by APHA 4500-Cl- E and hardness by US EPA Method 130.1.
 - b. The calibration quality may be evaluated using the relative standard error (RSE), as an alternative to using the average response factor. The acceptance criterion for the RSE is the same as the acceptance criterion for relative standard deviation (RSD). RSE is calculated as:

$$\%RSE = 100 \times \sqrt{\frac{\sum_{i=1}^n \left[\frac{x'_i - x_i}{x_i} \right]^2}{(n - p)}}$$

where:

x'_i = calculated concentration at level i

x_i = actual concentration of calibration level i

n = number of calibration points

p = number of terms in the fitting equation (average = 1, linear = 2, quadratic = 3).

- c. Using the RSE as a metric has the added advantage of allowing the same numerical standard to be applied to the calibration model, regardless of the form of the model. If the method includes a numerical criterion for the RSD, then the same numerical value is used for the RSE. Thus, if a method states that the RSD should be $\leq 20\%$ for the traditional linear model through the origin, then the RSE acceptance limit can remain $\leq 20\%$ as well. Similarly, if a method provides an RSD acceptance limit of $\leq 15\%$, then that same figure can be used as the acceptance limit for the RSE. Some older methods do not include any criterion for the calibration curve. For the methods without any criterion, if RSE is used the value should be $\leq 20\%$. Note that the use of the RSE is included as an alternative to the use of the correlation coefficient as a measure of the suitability of a calibration curve. It is not necessary to evaluate both the RSE and the correlation coefficient.
11. Changes in equipment (e.g. equipment from a vendor being different from the one specified in the method).
12. Use of micro or midi distillation apparatus in place of macro distillation apparatus.
13. Use of pre-packaged reagents.
14. Use of digital titrators and methods where the underlying chemistry used for the determination is similar to that used in the AM.
15. Use of selected ion monitoring (SIM) mode for analytes that cannot be effectively analysed in full-scan mode and reach the required sensitivity. False positives are more of a concern when using SIM analysis. So, at a minimum, one quantitation and two qualifying ions must be monitored for each analyte (unless fewer than three ions with intensity greater than 15% of the base peak are available). The ratio of each of the two qualifying ions to the quantitation ion must be evaluated and should agree with the ratio observed in an authentic standard within $\pm 20\%$. Analyst judgement must be applied to the evaluation of ion ratios because the ratios can be affected by co-eluting compounds present in the sample matrix. The signal-to-noise ratio of the least sensitive ion should be at least 3:1. Retention time in the sample should match within 0.05 minute of an authentic standard analysed under identical conditions. Matrix interferences can cause minor shifts in retention time and may be evident as shifts in the retention times of the internal standards. The total scan time should be such that a minimum of eight scans are obtained per chromatographic peak.
16. Changes in purge-and-trap sample volumes or operating conditions. Some examples are:
 - a. Changes in purge time and purge-gas flow rate. A change in purge time and purge-gas flow rate is allowed provided sufficient total purge volume is used to achieve the required minimum detectable concentration and calibration range for all compounds. In general, a purge rate in the range 20–200 mL/min and a total purge volume in the range 240–880 mL are recommended.
 - b. Use of nitrogen or helium as a purge gas provided the required sensitivities for all compounds are met.
 - c. Sampling temperature during the purge state. Gentle heating (e.g. 40°C) of the sample during purging increases purging efficiency of hydrophilic compounds and may improve sample-to-sample repeatability because all samples are purged under precisely the same conditions.
 - d. Trapping sorbent. Any trap design is acceptable provided the data acquired meet all quality control (QC) criteria.
 - e. Changes to the desorb time. A desorb time of 4 minutes is recommended. A shorter desorb time may be used provided all QC specifications in the method are met. Shortening the desorb time (e.g. from 4 minutes to 1 minute) may not affect compound recoveries. It can shorten the overall cycle time and significantly reduce the amount of water introduced to the analytical system thus improving the precision of analysis, especially for water-soluble analytes.
 - f. Use of water management techniques. Water is always collected on the trap along with the analytes and is a significant interference for analytical systems (gas chromatography and gas chromatography mass spectrometry). Modern water management techniques (e.g. dry purge or condensation points) can remove moisture from the sample stream and improve analytical performance.
17. If the characteristics of a wastewater matrix prevent efficient recovery of organic pollutants and prevent the method from meeting QC requirements, the analyst may attempt to resolve the issue by adding salts to the sample. This is provided such salts do not react with, or introduce the target pollutant into, the sample (as evidenced by the analysis of method blanks, laboratory control samples

and spiked samples that also contain such salts). Samples having residual chlorine or other halogen must be dechlorinated prior to the addition of such salts.

18. If the characteristics of a wastewater matrix result in poor sample dispersion or reagent deposition on equipment and prevent the analyst from meeting QC requirements, the analyst may attempt to resolve the issue by adding an inert surfactant that does not affect the chemistry of the method, such as Brij-35 or sodium dodecyl sulfate. This is provided that such surfactant does not react with, or introduce the target pollutant into, the sample and that all QC requirements are met. Samples having residual chlorine or other halogen must be dechlorinated prior to the addition of such surfactant.
19. Use of gas diffusion (using pH change to convert the analyte to gaseous form and/or heat to separate an analyte contained in steam from the sample matrix) across a hydrophobic semi-permeable membrane to separate the analyte of interest from the sample matrix in place of manual or automated distillation in methods for analysis (e.g. ammonia, total cyanide, total Kjeldahl nitrogen and total phenols). These procedures do not replace the digestion procedures specified in the AMs and must be used in conjunction with those procedures.
20. Changes in equipment operating parameters (e.g. the monitoring wavelength of a colorimeter or the reaction time and temperature as needed to achieve the chemical reactions defined in the unmodified AM. For example, molybdenum blue phosphate methods have two absorbance maxima: one at about 660nm and another at about 880nm. The former is about 2.5 times less sensitive than the latter. Wavelength choice provides a cost-effective, dilution-free means to increase sensitivity of molybdenum blue phosphate methods).
21. Interchange of oxidants (e.g. the use of titanium oxide in UV-assisted automated digestion of TOC and total phosphorus, provided complete oxidation can be demonstrated).
22. Use of an axially viewed torch with US EPA Method 200.7.

Appendix 4: Essential QC requirements

Laboratories must use suitable quality assurance/quality control (QA/QC) procedures when conducting analyses for any approved method. The performance of modified methods must meet the relevant QC acceptance criteria of the approved method.

Generally, the QA/QC procedures are included in the approved method or in part of the methods compendium for an approved method from a consensus organisation. For example, the American Public Health Association (APHA) Standard Methods contains QA/QC procedures in section 1020.

If the approved method contains QC tests and acceptance criteria, the modified method must use them. The method modification must not be used if the modified method performance does not meet the QC acceptance criteria of the approved method being modified.

If the approved method does not contain QC tests and acceptance criteria, the analyst must implement QC tests published in the 'equivalent' EPA method (i.e. any other method listed in Table 1 for the analyte of interest) or a method published by APHA, the American Water Works Association, the United States Environmental Protection Agency (USEPA), ASTM International, Standards Australia and the International Organization for Standardization (ISO).

Where a method lacks QA/QC procedures, the laboratory must use the appropriate QA/QC procedures listed below (in the following order):

1. the QA/QC published in the 'equivalent' EPA method (i.e. any other method listed in Table 1 for the analyte of interest) for that parameter that has such QA/QC procedures
2. the procedures in the appropriate QA/QC section(s) of an approved method from a consensus organisation compendium.

The modified method must use the appropriate QC procedures (as listed above) and meet the minimum QC acceptable criteria in accordance with the following conditions:

- The analyst may only rely on QC acceptance criteria in a method if the method includes matrix QC tests and acceptable criteria as well as both initial (start-up) QC tests and acceptance criteria.
- In addition, the analyst must perform ongoing QC tests. This includes performance assessment of the modified method on the sample matrix (e.g. analysis of a matrix spike/matrix spike duplicate pair for every twenty samples), analysis of an ongoing precision and recovery sample (e.g. laboratory fortified blank or blank spike), and a blank with each batch of twenty or fewer samples.

Appendix 5: Test method sources

Australian Standard

Test methods can be purchased from Standards Australia.

Website: www.standards.com.au

American Public Health Association

Standard Methods for the Examination of Water and Wastewater (current version) can be purchased from the American Water Association.

Website: www.awa.asn.au

American Society for Testing and Materials

Test methods are available from Standards Australia (see above) or from American Society for Testing and Materials International.

Website: www.astm.org/index.html

United States Environmental Protection Agency

Test methods are available from the United States Environmental Protection Agency (USEPA).

Website (for online ordering): www.epa.gov

International Organization for Standardization

International Organization for Standardization (ISO) catalogue information is available from Standards Australia, as detailed above, or at the ISO website.

Website: <https://www.iso.org/home.html>