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Protection of the Environment Operations (General) Regulation 2021

Approved Methods for the Sampling and Analysis of Water Pollutants in New South Wales

Notice is hereby given, under clause 3 of the Protection of the Environment Operations (General) Regulation 2021, that the attached document prepared by the NSW Environment Protection Authority replaces the previously gazetted Approved Methods for the Sampling and Analysis of Water Pollutants in New South Wales and takes effect as of the date of publication of this notice.

Dated 23 February 2022

Sonya Errington
Director Environmental Solutions (AWNFG)
NSW Environment Protection Authority

Environment Protection Authority

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

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Contents

This document 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 64 of the Protection of the Environment Operations (General) Regulation 2021 (POEO General Regulation)[1] 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 is required.

1.3. What method to use

Industry must comply with monitoring requirements and limits specified in statutory instruments. In accordance with clause 64 of the POEO General Regulation,[2] all testing to show compliance must:

- use the methodology specified in the relevant environment protection licence, notice or statutory instrument (clause 64(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 64(2)(b)).

For the purpose of clause 64(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

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[1] References to clauses of the POEO (General) Regulation are current at the time of publication. Please note that clause numberings and content may be subject to change, as regulations can be remade from time to time. References to provisions of the (POEO) General Regulation extend to the corresponding provision of the re-made regulation, consistent with section 68 of the *Interpretation Act 1987.*

[2] *idem*

    - alternative methods and methods with significant modifications that have been approved by the EPA following the procedure outlined in section 4
- record-keeping requirements.

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, following 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 that the laboratories and analysts they use:

- are accredited by the National Association of Testing Authorities (NATA), or equivalent accreditation body,[3] 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.)

The procedures used to collect, handle and preserve samples 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 except for storage temperature. (See section 2.3 for more details.)

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[3] **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.

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. The samples are to be submitted with sufficient time remaining to complete the analysis within the holding times. The information can be found in the relevant standards listed below
- chain-of-custody procedures to ensure integrity of the sample from collection to data reporting
- 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, and keeping auditable sampling records (for example, field logbooks).

Refer to the following standards for detailed guidance on 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 (such as extendable poles, buckets and nets) 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)) – the material chosen according to its interaction with the analyte of interest and the relevant standard
- sterilised sample containers must be used for microbial analysis and therefore must be opened only 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. Polytetrafluoroethylene (PTFE) should not be used for PFAS.

Refer to the standards listed in section 2.1 for detailed advice about selecting sample containers and devices.

2.3. Sample storage, preservation and holding times

Samples must be stored and preserved in accordance with the relevant standards' requirements. You must use the holding times and sample preservation procedures for various analytes that are specified in APHA (current version), AS/NZS 5667.1 and USEPA *Clean Water Act Analytical Methods* (current version). Samples for chemical analysis should be kept refrigerated at 4 ± 2°C while samples for microbial analysis should be refrigerated at 5 ± 3°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 follow 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 so that the collected samples are traceable and defensible.

3. Analysis methods

Analyses must be undertaken by a laboratory that has been accredited under ISO/IEC 17025 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
- laboratory procedures.

Table 1 lists **approved methods** – analytical methods that are published by agencies recommended by the EPA and 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.

If you use the EPA-approved methods listed in Table 1, you are responsible for ensuring that the latest published version of the method is used.

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: • methods as listed in 'Metals (acid extractable)' • APHA section 3111D* • APHA section 3111E* • APHA section 3500-Al*.
Amitrole	**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. Situation 6 in section 4.2 applies here.
Aniline	Use one of the following: • USEPA method 8131 • USEPA method 8261 • USEPA method 8270.

Analyte	Approved method
Anions Includes: • bromide (Br^-) • chloride (Cl^-) • fluoride (F^-) • nitrate (NO^{3-}) • nitrite (NO^{2-}) • phosphate (PO_4^{3-}) • sulfate (SO_4^{2-})	Use one of the following: • APHA section 4110 • APHA section 4140 • USEPA method 6500 • USEPA method 9056.
Anthracene	Use one of the following: • 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: • methods as listed in ‘Metals (acid extractable)’ • APHA section 3111B*.
Arsenic (acid extractable)	Preliminary treatment as listed in ‘Metals (acid extractable)’. Then use one of the following: • 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
Atrazine	Use one of the following: • USEPA method 8085 • USEPA method 8141 • USEPA method 8270.
Barium (acid extractable)	Preliminary treatment as listed in ‘Metals (acid extractable)’. Then also use one of the following: • 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: • methods as listed in ‘Metals (acid extractable)’ • APHA section 3111D* • APHA section 3111E*.
Biochemical oxygen demand (5-day)	Use one of the following: • APHA section 5210B (excluding clause 5e, the use of nitrification inhibitor) using APHA 4500-O for the determination of dissolved oxygen • APHA section 5210D.

Analyte	Approved method
Boron (acid extractable)	Preliminary treatment as listed in ‘Metals (acid extractable)’. Then also use one of the following: • methods as listed in ‘Metals (acid extractable)’ • APHA section 4500-B.
Bromide (Br^-)	Use one of the following: • 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: • 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: • methods as listed in ‘Metals (acid extractable)’ • APHA section 3111B* • APHA section 3111D* • APHA section 3500-Ca.
Carbonate	APHA section 2320
Carbonaceous biological oxygen demand (5-day) $CBOD_5$	APHA section 5210B – clause 5e
Chemical oxygen demand	APHA section 5220
Chlordane and isomers (cis, trans and total)	Use one of the following: • 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: • 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: • 2,4-D • 2,4,5-T • MCPA	Use one of the following: • 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.

Analyte	Approved method
Chlorinated volatile compounds	Use one of the following: • APHA section 6200 • USEPA method 8021* • USEPA method 8260* • USEPA method 8261.
Chlorine (combined residual)	Use one of the following: • APHA section 4500-Cl D • APHA section 4500-Cl F • APHA section 4500-Cl G. 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. 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. Those **not** acceptable to the EPA are kits using comparison with a colour chart to determine concentration. Normal QA procedures must be followed. These include: • analysis of blanks with every batch of samples • use of certified chlorine standards: ○ on each occasion the kit is used (if not used every day) **or** ○ weekly (if used constantly). 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. These directions are based on requirements set down in the APHA methods listed above for chlorine analysis. If the concentration of chlorine being measured is likely to be around 0.05–0.2 mg/L, you must validate the detection limit for the specific wastewater being analysed and the kit being used for the analysis.
Chlorine (free residual)	Use one of the following: • APHA section 4500-Cl D • APHA section 4500-Cl F • APHA section 4500-Cl G • APHA section 4500-Cl H. Refer to the note on the use of kits under ‘Chlorine (combined residual)’.

Analyte	Approved method
Chlorine (total residual)	Use one of the following: • 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. Refer to the note on the use of kits under ‘Chlorine (combined residual)’.
Chlorophyll a	APHA section 10200H
Chromium (acid extractable)	Preliminary treatment as listed in ‘Metals (acid extractable)’. Then also use one of the following: • methods as listed in ‘Metals (acid extractable) • APHA section 3111C*.
Chromium (hexavalent)	Use one of the following: • APHA method 3500-Cr • AS 2882 • USEPA method 218.6 • USEPA method 7196 • USEPA method 7199.
Chromium (trivalent)	Trivalent chromium is to be calculated: Cr^{3+} = Cr (acid extractable) – Cr^{6+}
Cobalt (acid extractable)	Preliminary treatment as listed in ‘Metals (acid extractable)’. Then also use one of the following: • 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)	Preliminary treatment as listed in ‘Metals (acid extractable)’. Then also use one of the following: • methods as listed in ‘Metals (acid extractable)’ • APHA section 3111B* • APHA section 3111C*.
Cyanide (free)	Preliminary recovery ASTM method D4282 Then also use one of the following: • APHA section 4500-CN^- D • APHA section 4500-CN^- E • APHA section 4500-CN^- F • ASTM D4282.

Analyte	Approved method
Cyanide (total)	Preliminary treatment, if required, using APHA section 4500-CN$^-$ B, followed by distillation using APHA section 4500-CN$^-$ C Then also use one of the following: • APHA section 4500-CN$^-$ D • APHA section 4500-CN$^-$ E • APHA section 4500-CN$^-$ F • USEPA method 335.2 • USEPA method 335.4. 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.
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: • ASTM D5073 • AS 3778.7.
Dissolved organic carbon	APHA section 5310
Dissolved organic halogen Includes: • 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: • APHA section 9230 • AS 4276.8 • AS 4276.9 • USEPA method 1106.1 • USEPA method 1600.

Analyte	Approved method
Escherichia coli	Use one of the following: • 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: • USEPA method 8015 • USEPA method 8260 • USEPA method 8261.

Extractable base/neutrals and acids. Includes: • 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	Use one of the following: • 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: • 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: • pumping capacity • pressure differences **or** • electromagnetic, ultrasonic flow meters.
Fluoride (F^-)	For the preliminary distillation step, if required, use APHA section 4500-F^- B Then also use one of the following: • 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: • APHA section 6651 • ISO 16308 • USEPA method 547.
Hardness (as calcium carbonate)	Use one of the following: • APHA section 2340 • USEPA method 130.1.
Hexachlorobenzene	Use one of the following: • methods as listed in ‘Extractable base/neutrals and acids’ • USEPA method 8081 • USEPA method 8410.
Hexachlorobutadiene	Use one of the following: • USEPA method 8021 • USEPA method 8260 • USEPA method 8261 • USEPA method 8270* • USEPA method 8410.

Analyte	Approved method
Hexachloroethane	Use one of the following: • 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: • 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: • 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: • 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: • 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: • 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: • 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) Includes: • 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) • silver (Ag) • sodium (Na) • strontium (Sr) • sulfur (S) • tin (Sn) • titanium (Ti) • thallium (Tl) • Uranium (U) • vanadium (V) • zinc (Zn) Note: For the purposes of this document, the term ‘acid extractable’ is as defined in APHA Section 3030A.	For preliminary treatment use one of the following: • APHA section 3030(E–K) • USEPA method 3005 • USEPA method 3010 • USEPA method 3015 • USEPA method 3020^. Then also use one of the following: • APHA section 3113~* • APHA section 3120* • APHA section 3125◊†* • USEPA method 200.7 • USEPA method 200.8#† • USEPA method 6010* • USEPA method 6020Δ†*. ^ Sample preparation method only for selected heavy metals (Be, Cd, Cr, Co, Pb, Mo, Tl, and V) ~ Only for analysis of Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Se, Ag and Sn ◊ Analysis for the listed analytes except for B, Ca, Fe, Mg, K, P, Na, Sn, S, and Ti # Analysis for the listed analytes except for B, Ca, Fe, Mg, K, P, Na, Sn, S, Ti, Sr, Li and U Δ Analysis for the listed analytes except for B, Li, Mo, P, S, Sn, Sr, Ti and U * Preferred methods † Used when very low concentrations (< 100µg/L) are tested

Analyte	Approved method
Metals (dissolved) Includes: • 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) • silver (Ag) • sodium (Na) • strontium (Sr) • sulfur (S) • tin (Sn) • titanium (Ti) • thallium (Tl) • uranium (U) • 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: • 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: • 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: • USEPA method 8041* • USEPA method 8270* • USEPA method 8410.
Metolachlor	Use one of the following: • USEPA method 8085 • USEPA method 8270.
Metsulfuron-methyl	**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. Situation 6 in section 4.2 applies here.
Molinate	Use one of the following: • 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: • 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: • methods as listed in 'Metals (acid extractable)' • APHA section 3111B* • APHA section 3111C*.
Nitrate (NO_3^-)	Use one of the following: • methods as listed in 'Anions' • APHA section 4120 • APHA section 4130 • APHA section 4500-NO_3^- D • APHA section 4500-NO_3^- E • APHA section 4500-NO_3^- F • APHA section 4500-NO_3^- I • USEPA method 353.2.
Nitrite (NO_2^-)	Use one of the following: • methods as listed in 'Anions' • APHA section 4120 • APHA section 4130 • APHA section 4500-NO_2^- • APHA section 4500-NO_3^- F (with cadmium colour removed) • APHA section 4500-NO_3^- I (with cadmium colour removed) • USEPA method 353.2 • USEPA method 354.1.

Analyte	Approved method
Nitrogen (ammonia)	Use one of the following: • APHA section 4120 • APHA section 4130 • APHA section 4500-NH_3 • USEPA method 350.1 Note: For trade waste samples, distillation is required using APHA 4500-NH_3-C.
Nitrogen (total)	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 Where equivalent results can be demonstrated, the following direct nitrogen (total) methods can also be used: • APHA section 4120 • APHA section 4130 • ASTM D5176 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.
Nitrogen (total oxidised)	This is the sum total of oxidised forms of nitrogen, that is ‘nitrogen (nitrate)’ + ‘nitrogen (nitrite)’. For the approved methods, refer to ‘nitrate’ and ‘nitrite’.
Nonylphenol ethoxylates	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.
Oil and grease	Use one of the following: • APHA section 5520B • APHA section 5520C • APHA section 5520D • APHA section 5520F (hydrocarbons only) • USEPA method 1664*

Analyte	Approved method
Organochlorine pesticides Includes: • 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: • APHA section 6410 • APHA section 6630 • USEPA method 608.3 • USEPA method 8081* • USEPA method 8085 • USEPA method 8270*
Organophosphorus pesticides Includes: • chlorpyrifos • diazinon • dimethoate • ethion • malathion • methyl azinphos • methyl chlorpyrifos • methyl paranthion • parathion	Use one of the following: • 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: • methods as listed in ‘Extractable base/neutrals and acids’ • APHA section 6420 • APHA section 6640 • USEPA method 8041 • USEPA method 8151* • USEPA method 8321.

Analyte	Approved method
Per- and polyfluorinated alkyl substances (PFAS) Includes: • perfluorobutanesulfonic acid (PFBS) • perfluorodecanoic acid (PFDA) • perfluoroheptanoic acid (PFHpA) • perfluorohexanesulfonic acid (PFHxS) • perfluorohexanoic acid (PFHxA) • perfluorononanoic acid (PFNOA) • perfluorooctanesulfonic acid (PFOS) • perfluorooctanoic acid (PFOA) • other PFAS analytes as specified in PFAS NEMP	• Use the standard methods in accordance with the methods listed in the PFAS National Environmental Management Plan (PFAS NEMP) that are relevant to your specific monitoring requirement.
pH value	APHA section 4500-H^+
Phenol and individual phenolic compounds Includes: • 2-chlorophenol • 2,4-dichlorophenol • 2,4-dimethylphenol • Phenol • 2,3,4,6-tetrachlorophenol • 2,4,6-trichlorophenol	Use one of the following: • 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.

Analyte	Approved method
Phosphorus (total)	Use one of the following: • Preliminary treatment as listed in ‘Metals (acid extractable)’ then also methods as listed in ‘Metals (acid extractable)’ **or** • One of the following: ○ APHA section 4500-Norg with Jirka modification (Jirka et al. 1976) ○ APHA section 4500-P B (persulfate digestion) followed by one of the following: ○ 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.
Phosphorus (total dissolved)	Use one of the following: • Methods as listed in ‘Metals (dissolved)’ or • Filtration through 0.45 µm membrane filter followed by one of the following: ○ APHA section 4500-Norg with Jirka modification (Jirka et al. 1976) ○ APHA section 4500-P B (persulfate digestion) Then also use one of the following: ○ 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)	Use one of the following: • methods as listed in ‘Extractable base/neutrals and acids’ • APHA section 6431 • USEPA method 8082*.

Analyte	Approved method
Polycyclic aromatic hydrocarbons Includes: • 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	Use one of the following: • APHA section 6410 • APHA section 6440 • USEPA method 8270* • USEPA method 8310*.
Potassium (acid extractable)	Preliminary treatment as listed in ‘Metals (acid extractable)’. Then also use one of the following: • methods as listed in ‘Metals (acid extractable)’ • APHA section 3111B* • APHA section 3500-K*.
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: • methods as listed in ‘Metals (acid extractable)’ • APHA section 3114* • APHA section 3500-Se.
Semi-volatile organic hydrocarbons	Use one of the following: • APHA section 6410 • USEPA method 8270*.

Analyte	Approved method
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: • methods as listed in ‘Metals (acid extractable)’ • APHA section 3111B* • APHA section 3111C*.
Simazine	Use one of the following: • USEPA method 8085 • USEPA method 8141 • USEPA method 8270. Note: Simazine may be analysed using USEPA method 8270, provided that the extraction is performed at neutral pH as per method USEPA 8141.
Sodium (acid extractable)	Preliminary treatment as listed in ‘Metals (acid extractable)’. Then also use one of the following: • 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: • methods as listed in ‘Anions’ • APHA section 4500-SO_4^{2-} E • APHA section 4500-SO_4^{2-} 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
2,3,4,6-tetrachlorophenol	Use one of the following: • 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: • APHA section 9221 • APHA section 9222 • AS 4276.6 • AS 4276.7.
Thiobencarb	**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.

Analyte	Approved method
Tin (acid extractable)	Preliminary treatment as listed in ‘Metals (acid extractable)’. Then also use one of the following: • 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: • methods as listed in ‘Metals (acid extractable)’ • APHA section 3111D*
Total dissolved solids	Use one of the following: • APHA section 2540C • AS3550.4 For the purposes of load-based licensing, the conductivity (salt) method must be used instead of APHA 2540C and AS3550.4. See conductivity earlier in this table.
Total Kjeldahl nitrogen	Use one of the following: • 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: • APHA section 5310 • USEPA method 9060
Total petroleum hydrocarbons (TPHs) and Total recoverable hydrocarbons (TRHs) Note: According to the NEPM[4], the term TRH is equivalent to the previously used term TPH.	Use one of the following: • USEPA method 8000 • USEPA method 8015
Total phenolics	Use one of the following: • APHA section 5530 • USEPA method 420.4
Total suspended solids	Use one of the following: • APHA section 2540D • AS 3550.4 • USEPA method 160.2
Toxicity	Guidance on conducting toxicity testing is provided in Appendix 2.

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Analyte	Approved method
Tributyltin	Use one of the following: • APHA section 6710 • ISO 17353 • USEPA method 8323.
Trifluralin	Use one of the following: • USEPA method 8081 • USEPA method 8085 • USEPA method 8091 • USEPA method 8270.
Trihalomethanes and chlorinated organic solvents Includes: • Bromoform • Bromodichloromethane • Carbon tetrachloride • Chloroform • Dibromochloromethane • Tetrachloroethene • 1,1,1-Trichloroethane • 1,1,2-Trichloroethane • Trichloroethene	Use one of the following: • 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: • methods as listed in 'Metals (acid extractable)' • APHA section 3111D*.
Volatile halogenated compounds	Use one of the following: • APHA section 6200 • USEPA method 8021 • USEPA method 8260 • USEPA method 8261.

Analyte	Approved method
Volatile organic compounds (VOCs) Includes: • 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: • APHA section 6200 • USEPA method 8021* • USEPA method 8260* • USEPA method 8261.
Volume	AS 3778 covers methods for determining width, depth and velocity in open channels and waterways. The following approaches can generally be used: • 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). For pipes, the volume can be estimated from the known pump capacity multiplied by the duration of pumping. 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.
Zinc (acid extractable)	Preliminary treatment as listed in ‘Metals (acid extractable)’. Then also use one of the following: • 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

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 persons required to comply with the Approved Methods document 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. Requests for approval should be sent to info@epa.nsw.gov.au.

If you are unsure whether approval is required, contact the EPA via info@epa.nsw.gov.au.

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 licensee 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 in different situations.

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, such as an in-house method based on the approved method

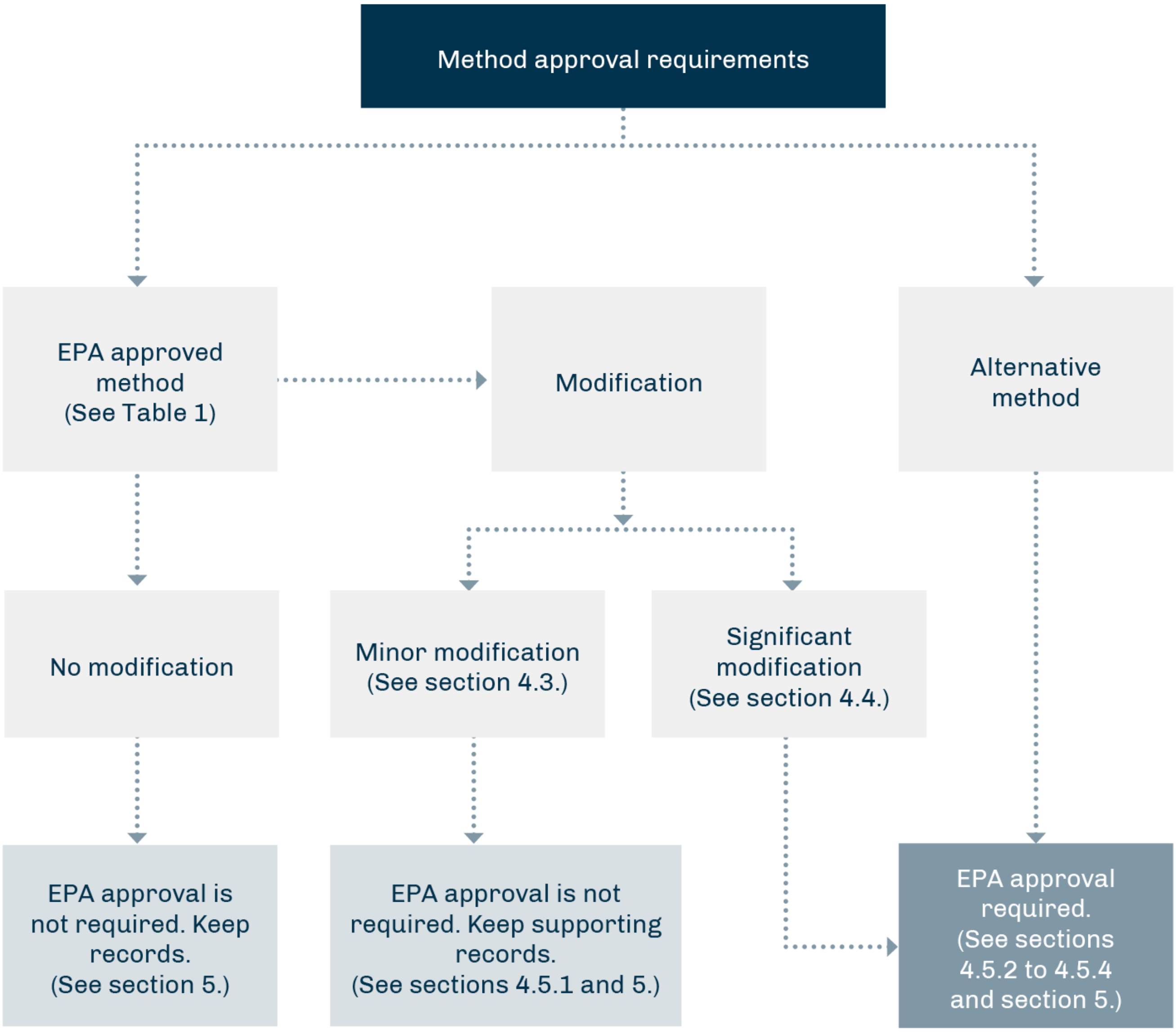
  and
- the modification is minor (see section 4.3).

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). You must also keep a copy of all records related to seeking and obtaining EPA approval for use of the modified method (see section 5).

Figure 1 Approval process for modifications and alternative methods



Note: EPA approval is not required in certain circumstances for alternative methods (see section 4.5.2.1); however, documentation must be provided.

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

EPA approval is required for use of an alternative method, except for certain circumstances set out in section 4.5.2.1.

Written approval from the EPA must be sought prior to use of the alternative method (see section 4.5.2). 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)

    - American Public Health Association (APHA)
    - American Society for Testing and Materials (ASTM)
    - European Committee for Standardization (CEN)
    - International Organization for Standardization (ISO)
    - United States Environmental Protection Agency (USEPA)
- supporting documentation to be retained and produced to the EPA upon request 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 to be retained and produced to the EPA upon request 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 the above requirements are met, the method proposed to be used for the testing of the analyte may proceed without the need of approval by the EPA.

If there is no recognised standard or reference test method for the analyte of interest published by the organisations listed 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).

Situation 6: There is no approved method for the listed analyte

When the analyte has no approved method listed in Table 1, EPA approval is not required when the laboratory holds current ISO/IEC 17025 accreditation for analysing the analyte of interest. Auditable records to demonstrate the method accreditation must be provided if requested by the EPA.

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 (e.g. using an interface reduction technology is one such example) that 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) to the approved method that is within the relevant water guideline value.

Acceptable reasons for modifying an approved method may include:

- to achieve lower detection limits
- to improve precision
- to reduce interferences.

Examples of minor modifications that meet points 1 to 6 above are:

- method modification where a better instrumentation/technology is used (e.g. the use of LC-MSMS instead of LC-MS and the associated changes to the sample preparation)
- the use of online distillation process followed by the colourimetric analysis based on APHA section 5530D.

Other examples of minor modifications are listed 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 this Approved Methods document 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. Applications should be sent to the EPA via info@epa.nsw.gov.au. 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).
- reference to the QC acceptance criteria used for comparison with the approved method.

The application must also include the following basic information:

- 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).

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.

4.5.2.1 Use of accredited alternative methods in certain circumstances

In certain circumstances, technology may have advanced beyond what is specified in a listed approved method for some analytes (e.g. formaldehyde, arsenite, arsenate, quaternary salts) and laboratories want to use this alternative technology. This would be considered an alternative method.

When such an alternative method is used and is accredited under ISO/IEC 17025 accreditation, EPA approval is not required. However, the EPA must be informed in writing that such a method is used and the following documents must be submitted in support of its use:

- justification for the use of the method
- the purpose and intended use of the method, including related legislative or regulatory requirements
- evidence that the alternative method is accredited, e.g. NATA certificate
- documents from the accreditation that demonstrate the performance of the alternative method including but not limited to a QC chart, evidence of equivalent reporting limit.

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. The information from the approved method (e.g. sensitivity, method detection limit, etc.) used in the method comparison can be extracted via desktop review.

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. Further guidance on method validation can be found in 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 – stating what the modification was and the reason for the modification
- a copy of EPA approval where a significantly modified or alternative method was used or the required justification (section 4.5.1) where a minor modification 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(ghl)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 *p,p’*-DDD *p,p’*-DDD (4,4)
4,4’-DDE	DDE *p,p’*-DDE *p,p’*-DDE (4,4)
4,4’-DDT	DDT *p,p’*-DDT *p,p’*-DDT (4,4)
1,2-Dichlorobenzene	*o*-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
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
Uranium (acid extractable)	Uranium
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)
Barium (acid extractable)	Barium (acid extractable) Metals (acid extractable)
Barium (dissolved)	Metals (dissolved)
Benzene	Volatile organic compounds (VOCs)
Benzo(a)pyrene Benzo(b)fluoranthene Benzo(e)pyrene Benzo(ghi)perylene Benzo(k)fluoranthene	Extractable base/neutrals and acids Polycyclic aromatic hydrocarbons
Beryllium (acid extractable)	Beryllium (acid extractable) Metals (acid extractable)
Beryllium (dissolved)	Metals (dissolved)

Analyte name	Analyte name/group in approved methods table
alpha-BHC beta-BHC gamma-BHC (lindane)	Extractable base/neutrals and acids Organochlorine pesticides
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 4,4'-DDE 4,4'-DDT	Extractable base/neutrals and acids Organochlorine pesticides
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	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)
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
Tin (acid extractable)	Metals (acid extractable) Tin (acid extractable)
Titanium (acid extractable)	Metals (acid extractable) Titanium (acid extractable)
Toluene	Volatile organic compounds (VOCs)

Analyte name	Analyte name/group in approved methods table
Total petroleum hydrocarbons Total recoverable hydrocarbons	Total petroleum 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)
Uranium (acid extractable)	Metals (acid extractable)
Uranium (dissolved)	Metals (dissolved)
Vanadium (acid extractable)	Metals (acid extractable) Vanadium (acid extractable)
Vanadium (dissolved)	Metals (dissolved)
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.

The use of animals in testing should be conducted in accordance with the NSW *Animal Research Act 1985* and related regulations, where these apply. All research involving vertebrate animals, including fish and cephalopods, requires a valid animal research authority obtained via approval from an animal ethics committee.

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 sea water, fresh water, 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).
    - Ensure the 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:

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

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 ≤20% for the traditional linear model through the origin, then the RSE acceptance limit can remain ≤20% as well. Similarly, if a method provides an RSD acceptance limit of ≤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 ≤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 ±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 detectible concentration and calibration range for all compounds. In general, a purge rate in the range 20–200mL/min and a total purge volume in the range 240–880mL 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. The QC samples must be run in every analytical batch to assess the ongoing method performance parameters. QC samples may include blanks, certified reference material, calibration verification standards and matrix spikes.

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 Australian 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

Protection of the Environment Operations (General) Regulation 2021 and Protection of the Environment Operations (Clean Air) Regulation 2021

Approved Methods for the Sampling and Analysis of Air Pollutants in New South Wales

Notice is hereby given, under clause 3 of the Protection of the Environment Operations (General) Regulation 2021 and clause 3 of the Protection of the Environment Operations (Clean Air) Regulation 2021, that the attached document prepared by the NSW Environment Protection Authority replaces the previously gazetted Approved Methods for the Sampling and Analysis of Air Pollutants in New South Wales and takes effect as of the date of publication of this notice.

Dated 23 February 2022

Sonya Errington
Director Environmental Solutions (AWNFG)
NSW Environment Protection Authority

Environment Protection Authority

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

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Contents

This document will be of interest to you if you are required, through an environment protection licence or statutory instrument, to sample and analyse air 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 air pollutants in New South Wales for comparison with limits or performance criteria listed in statutory instruments. The document covers:

- pollutant emissions from stationary sources, including stacks, exhaust pipes and vents at industrial premises
- visible emissions from motor vehicles.

This document should be referenced as:

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

1.2. Relevant legislation

This document is referred to in the:

- Protection of the Environment Operations (General) Regulation 2021
- Protection of the Environment Operations (Clean Air) Regulation 2021 (POEO Clean Air Regulation).

This 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 authorities in statutory instruments such as development consents and approvals where sampling and analysis of analytes are required.

1.3. What method to use

Industry must comply with limits specified in the POEO Clean Air Regulation and certain statutory instruments. All monitoring to show compliance must be done in one of the following three ways:

- Use the method(s) specified in the relevant Regulation or statutory instrument (such as an environment protection licence or notice).
- If no method is specified in the relevant statutory instrument, use the method(s) specified in this document.
- If a method or an analyte is not listed in this document or the statutory instrument, or a modified or alternative method is proposed, you must determine the need to seek approval from the EPA before using that method, in accordance with section 4 of this document.

This document prescribes:

- sample collection and handling requirements, specified in section 2
- approved sampling and 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.

1.4. Who is this document for?

This document is for anyone who must have air pollutants sampled or analysed for a statutory purpose in NSW, including licensees and others carrying out activities regulated by the EPA. Consultants, laboratories, testing facilities and analysts undertaking testing on the licensee's behalf must also refer to the document.

Licensees and others that carry out activities regulated by the EPA are responsible for ensuring that the laboratories and analysts they use:

- are accredited by the National Association of Testing Authorities (NATA), or equivalent accreditation body[1], under *ISO/IEC 17025: General requirements for the competence of testing and calibration laboratories* to use the approved test methods described in this document for testing and sampling the relevant analytes
- comply with the requirements in this document.

2. Sample collection and handling

Those required to comply with these Approved Methods must ensure that sampling is carried out by a person appropriately trained in collecting, handling and preserving samples in accordance with an appropriate sampling plan as described in this section.

Samples must be collected, handled and preserved according to the relevant test method. Samples must be collected at locations determined in accordance with the relevant regulation or specified in the statutory instrument. If the regulation does not provide for determination of the locations, or if no locations are specified in the instrument, samples must be collected from locations where they are representative of the total or known portion of the source emissions.

Sampling should be conducted in such a manner so as to achieve a reported measurement result above the **method detection limit** (MDL) of the relevant method. Where this is not practically achievable, a **limit of reporting** (LOR) at least 5 times (5x) below the applicable emission limit or reporting standard should be achieved.

Prior to sampling, the analytical laboratory should be contacted for an estimate of the Limit of Reporting (LOR) or Practical Quantification Limit (PQL) as mass (µg or mg) per sample. This information should be used in the sampling design in order to ensure sufficient sample volume is collected. Guidance on calculating sample volumes is provided in US Air Emission Measurement Technical Information Centre guideline document GD 038, *Description of In-Stack Detection Limit*. Further information should be sought from USEPA Method 301 and guidance published by the NSW EPA.

If the sensitivity of an approved method is not adequate for demonstrating compliance with an emission limit or standard for the relevant analyte, the EPA may consider a request for approval to use an alternative method, as per section 4 of this document.

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[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) and which provides accreditation under ISO/IEC 17025 for environmental testing.

2.1. Sampling design

All sampling must be conducted in accordance with a site-specific test plan, developed in consultation with the licensee or source owner.

The sampling plan must address the factors to be controlled to ensure a representative sample is collected. Sampling plans must be based on good environmental monitoring practices and be prepared in accordance with applicable published EPA monitoring guidance.

The following matters should be considered and accounted for when developing a sampling plan:

- factors that can affect the data quality objectives, such as location, spatial variability, timing and frequency
- a procedure for determining minimum sampling volumes and in-stack detection limits
- 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 applicable analyte holding times
- chain-of-custody procedures to ensure integrity of the sample from collection to data reporting
- adequate training of the personnel 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).

2.2. Sampling containers and devices

Sampling containers and devices must meet the requirements stated in the relevant method listed in this document. Where these requirements are not specifically referenced in the test method, the following minimum requirements must be met:

- Sampling devices used to collect samples must be made of materials that do not contaminate or interact with 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 an appropriate material.

2.3. Sample storage, preservation and holding times

Sample storage and preservation procedures must ensure that the integrity of the sample is maintained and meets the requirements stated in the relevant methods listed in this document.

If the test method does not prescribe the preservation requirements and maximum holding times these items should be discussed with the analysing laboratory prior to sampling.

2.4. Sampling quality assurance and quality control procedures

The sampling quality assurance (QA) and quality control (QC) procedures must be carried out in accordance with the relevant method listed in this document and the procedures required under ISO/IEC 17025. Quality management systems implemented at a facility must include protocols 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. Sampling and analysis methods

All sampling and analysis conducted for regulatory reporting must be carried out by a facility accredited under ISO/IEC17025 to perform the method. The accreditation must be current and issued by an independent accreditation body such as the National Association of Testing Authorities (NATA), or an equivalent accreditation body.

Methods approved by the EPA for specific analytes and parameters are listed in Tables 1 to 4 and are referred to as **test methods** (TM), **continuous emissions monitoring** (CEM) methods and **other methods** (OM). In most cases, published methods in Tables 1 to 4 are referenced, with additional guidance or clarification given for some circumstances.

Where Tables 1 to 4 do not reference an existing published method for a listed parameter or analyte, a full description of the approved method is provided in appendices to this document.

Laboratories must use the latest published version of a 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 can achieve the reporting limits required to demonstrate compliance with the regulation, licence, notice or other applicable statutory instrument.

Any method approved by the EPA as a modification or alternative to a TM, CEM or OM (Tables 1 to 4) of a particular number in this document is an approved method of that same number.

Section 6 gives a full list of referenced test methods.

Appendix 7 contains a list of organisations that publish the methods listed in Tables 1 to 4.

Table 1 Methods for sampling and analysing air pollutants from stationary sources

Test method (TM) no.	Parameter measured	Method	Additional notes
TM-1	Selection of sampling positions	AS4323.1 or USEPA Method 1	-
TM-2	Velocity or volumetric flow rate or temperature or pressure of stack gases	USEPA Method 2, 2C, 2F, 2G or 2H, or ISO10780	-
TM-3	Sulfuric acid mist (H_2SO_4) or sulfur trioxide (SO_3) as SO_3 equivalent.	USEPA Method 8 or USEPA Conditional Test Method 013B	USEPA SW-846 Method 9056A is an approved alternative to the analytical procedure of USEPA Method 8. Use equations 4.1 (Appendix 1) in lieu of equation 8-1 in USEPA Method 8.
TM-4	Sulfur dioxide (SO_2)	USEPA Method 6, 6C, 8 or 320, or ISO7934, ISO7935, ISO10396 or ISO11632	USEPA SW-846 Method 9056A is an approved alternative to the analytical procedure of USEPA Methods 6 and 8. Use equation 4.1 (Appendix 1) in lieu of equation 6-2 in USEPA Method 6 and equation 8.2 in USEPA Method 8.
TM-5	Hydrogen sulfide (H_2S)	USEPA Method 11, 15 or 16	-

Test method (TM) no.	Parameter measured	Method	Additional notes
TM-7	Chlorine (Cl_2)	USEPA Method 26, 26A or 321	Method 26A must be used when water droplets are present in the gas stream, such as after a scrubber.
TM-8	Hydrogen chloride (HCl)	USEPA Method 26, 26A or 321	Method 26A must be used when water droplets are present in the gas stream, such as after a scrubber.
TM-9	Fluorine (F_2) or any compound containing fluorine, except where emitted by a primary aluminium smelter while manufacturing aluminium from alumina	USEPA 13A or 13B, or ISO15713	USEPA SW-846 Method 9056A and APHA Method 4110B are approved alternatives to the analytical procedure of USEPA Methods 13A and 13B.
TM-10	Hydrogen fluoride (HF) emitted by a primary aluminium smelter while manufacturing aluminium from alumina	USEPA Method 14 or 14A	USEPA SW-846 Method 9056A and APHA Method 4110B are approved alternatives to the analytical procedure of USEPA Methods 14 and 14A.
TM-11	Nitrogen dioxide (NO_2) or nitric oxide (NO)	USEPA Method 7, 7A, 7B, 7C, 7D, 7E or 320 ISO Method 10396	Where instrumental analysis is used, both NO and NOx must be directly measured.
TM-12	Type 1 substances: elements antimony (Sb), arsenic (As), cadmium (Cd), lead (Pb) or mercury (Hg), or any compound containing one or more of those elements)	USEPA Method 29 or 102	USEPA Method 102 may be used for mercury only in hydrogen-rich streams.
TM-13	Type 2 substances: elements beryllium (Be), chromium (Cr), cobalt (Co), manganese (Mn), nickel (Ni), selenium (Se), tin (Sn) or vanadium (V) or any compound containing one or more of those elements	USEPA Method 29	-
TM-14	Mercury (Hg) or any compound containing this element	USEPA Method 29 or 30B or USEPA Method 102	USEPA Method 30B may only be used to measure vapour-phase mercury in sources where there are low particulate concentrations. USEPA Method 102 may be used for mercury only in hydrogen-rich streams
TM-15	Solid particles (total)	AS 4323.2 or USEPA Method 5, 17 or 201A	-

Test method (TM) no.	Parameter measured	Method	Additional notes
TM-18	Dioxins or furans	USEPA Method 23	The duration of sampling must not be less than 2 hours. Reporting results must be reported as 'toxic equivalence' lower, middle and upper bound (see explanatory note below table).
TM-20	Volatile organic liquids: total mass of unrecovered organic vapours, displaced by the transfer of volatile organic liquids from vapour recovery units	Appendix 2: Test Method 20	-
TM-21	Volatile organic liquids: calculation of vapour pressure	Appendix 3	-
TM-22	Moisture content in stack gases	USEPA Method 4 USEPA Alt-008 or ASTM E337 may also be used under specific circumstances	USEPA Method 4 shall be used where isokinetic sampling is required. Where isokinetic sampling is not required, USEPA Alt-008 or ASTM E337 may be used. ASTM E337 may only be used on sources that are <50^{O}C and 1 atmosphere of pressure (±30%).
TM-23	Dry gas density or molecular weight of stack gases	USEPA Method 3	-
TM-24	Carbon dioxide (CO_2) in stack gases	USEPA Method 3A	-
TM-25	Oxygen (O_2) in stack gases	USEPA Method 3A	-
TM-31	Observation procedure for excessive air impurities: visible emissions	Appendix 4: Test Method 31	-
TM-32	Carbon monoxide (CO)	USEPA Method 10	-
TM-33	Total reduced sulfides (TRS)	USEPA Method 16, 16A,16B or 16C	USEPA SW-846 Method 9056A is an approved alternative to the analytical procedure of USEPA Method 16A. If Method 9056A is used, emission concentrations must be calculated using equation 4.1 (Appendix 1) in lieu of equation 16A-2 of Method 16A.

Test method (TM) no.	Parameter measured	Method	Additional notes
TM-34	Volatile organic compounds	USEPA Method 18, 25, 25A, 25B, 25C, 25D or 25E	For USEPA Method 18, recovery studies are necessary for demonstrating the sampling system and collection media are appropriate for the source. Recovery studies should be performed where the source comprises a complex mixture of VOC's at significant concentrations (relative to any applicable limits). All QA/QC procedures, including recovery studies, must be detailed in the test report and be accompanied by supporting evidence. If the requisite recovery studies have not been performed, then the method will not be considered to be USEPA Method 18. Instead, the method will be considered a significant modification, requiring approval, unless it can be demonstrated, to the satisfaction of the EPA, that the method otherwise meets the definition of a minor modification as per section 4.3.
TM-35	Methanol	USEPA Method 308	-
TM-37	Smoke (if determining whether standard for emission of smoke from flares has been exceeded)	USEPA Method 22	-
TM-38	Combination of air impurities from two or more sources	Appendix 5: Test Method 38	-

Note: **Lower bound** means where an individual congener is reported as a non-detect the reported concentration shall be zero. **Middle bound** means where an individual congener is reported as a non-detect the reported concentration shall be the midpoint between zero and the limit of detection. **Upper bound** means where an individual congener is reported as a non-detect the reported concentration shall be the limit of detection.

Table 2 Continuous emission monitoring (CEM) methods and procedures

Method no.	Parameter measured	Method
CEM-1	Smoke (if determining whether a specified standard of concentration of opacity has been exceeded)	USEPA Performance Specification 1 and Procedure 3
CEM-2	Sulfur dioxide (SO_2) or nitrogen dioxide (NO_2) or nitric oxide (NO)	USEPA Performance Specification 2 and Procedure 1
CEM-3	Oxygen (O_2) or carbon dioxide (CO_2) in stack gases	USEPA Performance Specification 3 and Procedure 1

Method no.	Parameter measured	Method
CEM-4	Carbon monoxide (CO)	USEPA Performance Specification 4 and Procedure 1
CEM-5	Total reduced sulfides (TRS)	USEPA Performance Specification 5 and Procedure 1
CEM-6	Velocity or volumetric flow rate of stack gases	USEPA Performance Specification 6 and Procedure 1
CEM-7	Hydrogen sulfide (H_2S)	USEPA Performance Specification 7 and Procedure 1
CEM-8	Volatile organic compounds or methanol	USEPA Performance Specification 8 and Procedure 1
CEM-9	Volatile organic compounds or methanol	USEPA Performance Specification 9 and Procedure 1
CEM-10	Volatile organic compounds or methanol	USEPA Performance Specification 15 and Procedure 1
CEM-11	Particulate matter	USEPA Performance Specification 11 and Procedure 2
CEM-12	Vapour phase mercury	USEPA Performance Specification 12A and Procedure 5
CEM-13	Gaseous hydrogen chloride	USEPA Performance Specification 18 and Procedure 6

Table 3 Other methods (OMs)

Method no.	Parameter measured	Method
OM-4	Total and hexavalent chromium emissions	California Air Resources Board Method 425 or USEPA SW-846 Test Method 0061
OM-5	‘Fine’ particulates (PM_{10}[2] and/or $PM_{2.5}$[3])	USEPA Method 201 or 201A or ISO 23210
OM-6	Polycyclic aromatic hydrocarbons (PAHs)	California Air Resources Board Method 429
OM-7	Odour sampling from point sources or odour analysis using dynamic olfactometry	AS 4323.3
OM-8	Odour sampling from diffuse sources	AS 4323.4
OM-9	‘Coarse’ particulates	Appendix 6: Other approved method 9
OM-10	Ammonia	ISO 21877
OM-11	Formaldehyde	USEPA Method 323 or USEPA Method 318 or USEPA SW-846 Test Method 0011 USEPA Compendium Method TO-5 or TO11A or NIOSH Method 2016 may be used when the source is comparable to ambient air conditions (<50°C, low moisture and low particulate concentrations).
OM-12	Isocyanates	USEPA Method 326 or USEPA Conditional Test Method 36
OM-13	Asbestos	ISO 10397

Table 4 Methods for sampling and analysing air pollutants from mobile sources

Method no.	Parameter measured	Method
TM-31	Observation procedure for excessive air impurities: visible emissions	Appendix 8: Test Method 31

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[2] PM_{10} – Particulate matter less than 10 µm in aerodynamic equivalent diameter

[3] $PM_{2.5}$ – Particulate matter less than 2.5 µm in aerodynamic equivalent diameter

4. Modifying methods, or using alternative or unlisted methods

If a modified or alternative method for sampling or analysis is proposed, you must determine the need to seek approval from the EPA.

Generally, EPA approval will not be required for minor modifications that produce results that meet or exceed QC acceptance criteria of the approved method. However, you must keep supporting records.

Where approval is required, you must obtain this in writing from the EPA before the alternative or modified method is used. Requests for approval should be sent to info@epa.nsw.gov.au.

Any method approved by the EPA as a modification or alternative to a TM, CEM or OM (Tables 1 to 4) of a particular number in this document is an approved method of that same number.

Contact the EPA (via info@epa.nsw.gov.au) if there is any uncertainty about using modified or alternative test methods.

4.1. Terminology

Approved method

A method listed in Tables 1–4 of a particular number is an approved method of that same number.

Minor modification

A modification to a method listed in Tables 1–4 is considered minor if it satisfies the conditions of section 4.3 of this document.

Significant modification

A modification to a method listed in Tables 1–4 is significant if it satisfies the conditions of section 4.4 of this document.

Alternative method

An alternative method is a method used in place of an approved method listed in Tables 1–4.

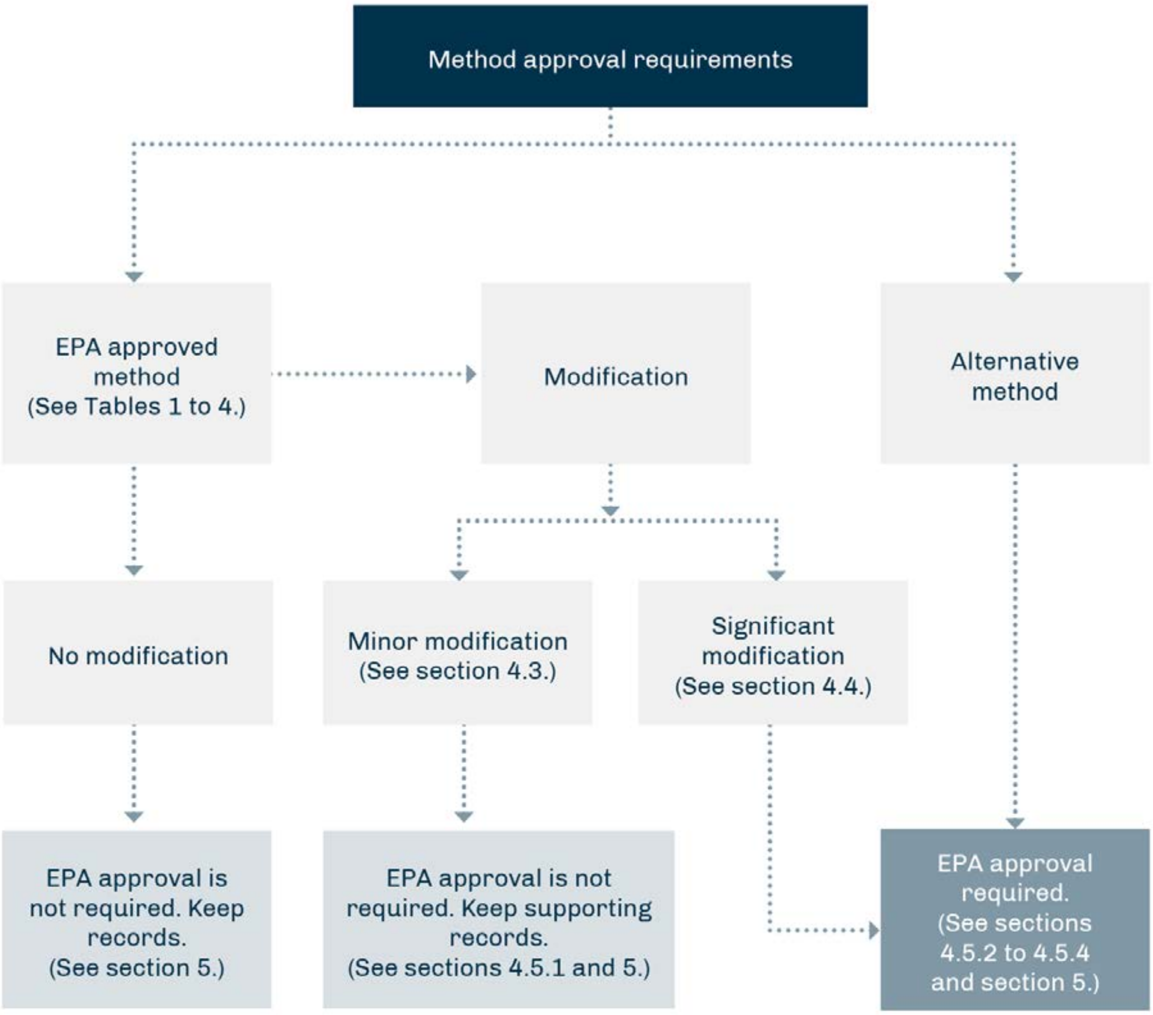
Equivalent performance

'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. The approval requirements for modifications and alternative methods are shown in Figure 1. Where approval is required, this may be sought by the licensee or a laboratory working on behalf of the licensee.

Figure 1 **Approval process for modifications and alternative methods**



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

Where there is an approved method listed in Tables 1–4, EPA approval is not required for use of the approved 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 the laboratory analysis of the analyte of interest and the modified method produces an equivalent performance to the approved method. Note that this does not apply to modifications to sampling or other elements of the method, and
- 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).

You must seek written approval from the EPA prior to use (see section 4.5.2).

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

EPA approval is required for use of an alternative method.

You must seek written approval from the EPA prior to use (see section 4.5.2).

Situation 5: The analyte is not listed in this document

If an analyte is not listed in Tables 1–4 (e.g. such as PFAS[4]) 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 or equivalent
  - Australian Standard (AS)
  - International Organization for Standardization (ISO)
  - United States Environmental Protection Agency (USEPA)
  - American Public Health Association (APHA)
  - California Environmental Protection Agency Air Resources Board (CARB)
  - American Society for Testing and Materials (ASTM)
- supporting documentation to be retained and produced to the EPA upon request 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 to be retained and produced to the EPA upon request 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 where the method will be used routinely.

If the above requirements are met, the method proposed to be used for the testing of the analyte may proceed without approval by the EPA.

If there is no recognised standard or reference test method available for the analyte of interest, and testing is required under a condition of licence or statutory notice issued by the EPA, then you need to obtain EPA approval of the proposed testing method. The EPA will not approve the use of the method 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 considered one that does not adversely affect or bias the results of the test. Typically, a minor modification should maintain or improve the level of accuracy afforded by the use of the approved method.

To qualify as a minor modification, the modification must:

- retain the underlying sample collection principles of the approved method
- retain the underlying chemistry and determinative technique of the approved method
- not introduce (or increase the potential for) significant additional interferences
- use proven technology generally accepted by the scientific community as equivalent to or better than the approved method (e.g. using an interface reduction technology)
- account for site- and/or emission-source-specific operational characteristics, physical constraints or safety concerns

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[4] PFAS – Per- and polyfluoroalkyl substances

- achieve the applicable performance criteria of the approved method, where specified
- achieve a comparable limit of reporting (LOR) to the approved method
- not compromise the ability to determine compliance with an applicable emission limit.

Acceptable reasons for modifying an approved method may include:

- to achieve lower detection limits
- to improve precision
- to reduce interferences.

4.4. Significant modifications and alternative methods

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 a significantly modified or alternative method.

A proposal for a significant modification may be site-specific or method-specific.

Examples of significant modifications and alternative methods include, but are not limited to, use of:

- an unvalidated analytical process
- an alternative measurement principle
- 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 sampling and analysis holds all documentation required under ISO/IEC 17025 (or equivalent) for demonstrating the performance of the modified or alternative method, including:

- a procedure or method write-up or an addendum
- evidence of method validation
- essential QC requirements.

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

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

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 EPA approval obtained prior to use of the method. Applications should be sent to EPA's Environment Line at info@epa.nsw.gov.au. 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
- comparability data for the performance of the significant modification (or alternative method) as compared to 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 by the applicant in a 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 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 significantly modified or alternative method.

4.5.3. Method comparison table

When a significantly modified or alternative method is proposed, the applicant must compare their 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. The information from the approved method (e.g. sensitivity, method detection limit, etc.) used in the method comparison can be extracted via desktop review.

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 modified 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 method. The extent of validation required will depend on the status of the method under consideration and its intended application.

The method validation should be sufficient to demonstrate that the method is suitable for its intended purpose. Method validation should meet the requirements outlined in ISO 17025. Further guidance on method validation can be found in 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. An alternative validation method may be used only upon written approval from the EPA.

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

5. Reporting requirements

5.1. Record-keeping

The following records must be kept for a period of four years for any sampling and analysis required by a statutory instrument and must be retained and provided to the EPA, if and when requested or required:

- air emission sampling report (see section 5.2)
- analytical report (see section 5.3)
- a statement about the representativeness of the plant conditions at the time of sampling. Representativeness of conditions at the time of sampling should be demonstrated through the inclusion of process and operational data. General statements, such as 'normal operation', are not considered sufficient for this purpose
- details of any factors, conditions or interferences that may have affected the monitoring results
- details of any modifications made to the approved method (see section 4)
- a statement
  - confirming whether a modified (including minor) or alternative method was used, and
  - stating what the modification was and the reason for it
- a copy of EPA approval, where a significantly modified or alternative method was used or the required justification (s4.5.1) where a minor modification was used
- details of assurance criteria (validation and verification) used to evaluate sampling results and reporting systems.

Appendix I includes definitions and generic procedures that apply to stationary-source monitoring and reporting.

5.2. Air emission sampling report inclusions

At a minimum, sampling reports must include the following information, unless the statutory instrument states otherwise:

- all analytical reports (see section 5.3)
- name and address of reporting organisation or individual
- date of issue of the report
- date, time and place of measurements
- description of the emission source being tested

- description of any installed pollution control equipment
- details of the plant operating status during the sampling
- a statement about the representativeness of the collected samples
- reference to the sampling plan and test methods used
- location of sampling plane, with respect to the nearest upstream and downstream flow disturbances (images, sketches or technical drawings should be provided)
- number of sampling points
- period of sampling (start and end times)
- average stack-gas velocity in metres per second
- average stack-gas temperature in kelvin
- stack-gas molecular weight or density in kilograms per cubic metre
- water content of stack gas, expressed as a percentage by volume
- stack-gas volumetric flow rate on a dry basis under standard conditions, in cubic metres per second
- concentration of contaminant on a dry basis under standard conditions, in milligrams per cubic metre
- mass emission rate of contaminant on a dry basis under standard conditions, in grams per second
- details confirming that all quality assurance requirements, in regard to sample collection, storage, transport and preservation complied with the methods requirement where applicable
- a copy of chain-of-custody forms where applicable
- estimation of measurement uncertainty in accordance with ISO 17025 and ISO/IEC Guide 98-3:2008 *Uncertainty of Measurement: Part 3 – Guide to the expression of uncertainty in measurement*
- all additional relevant information required under section 7.8 of ISO 17025.

5.3. Analytical report

All analytical reports must meet the reporting requirements and include all requisite information required under section 7.8 of ISO 17025.

5.4. General reporting requirements

If an air impurity cannot be detected, results must be reported as less than the method’s limit of reporting (LOR), not as zero.

All volumes and concentrations must be reported using the following reference conditions in descending order:

1. Use the reference conditions specified in the environment protection licence, notice or statutory instrument, as applicable to the testing requirement.
2. If reference conditions are not specified in the environment protection licence, notice or statutory instrument, the reference conditions specified in the POEO Clean Air Regulation should be used.
3. If reference conditions are not specified in the POEO Clean Air Regulation, then results should be reported at a temperature of 0°C, dry and at an absolute pressure of 101.3 kPa.

6. Referenced test methods

American Public Health Association (APHA)

American Public Health Association, **Method 4110 B**: *Ion chromatography with chemical suppression of eluent conductivity*, Standard methods for the examination of water and wastewater, 23rd edition.

American Society for Testing and Materials (ASTM)

American Society for Testing and Materials, *D323 Standard test method for vapor pressure of petroleum products (Reid Method).*

California Environmental Protection Agency Air Resources Board (CARB)

California Environmental Protection Agency Air Resources Board, **Method 425**: *Determination of total chromium emissions from stationary sources*, Sacramento, CA.

California Environmental Protection Agency Air Resources Board, **Method 429**: *Polycyclic aromatic hydrocarbon (PAH) emissions from stationary sources*, Sacramento, CA.

Environment Protection Authority (EPA)

NSW Environment Protection Authority 2007, *Approved Methods for the Sampling and Analysis of Air Pollutants in New South Wales*, Department of Energy and Conservation NSW, Sydney.

National Institute for Occupational Safety and Health (NIOSH)

National Institute for Occupational Safety and Health Manual of Analytical Methods (NMAM), **Method 2016:** *Formaldehyde.*

International Organization of Standardization (ISO)

International Organization of Standardization, **ISO Method 7934**: *Stationary source emissions – Determination of mass concentration of sulphur dioxide – Hydrogen peroxide/barium perchlorate/Thorin method*.

International Organization of Standardization, **ISO Method 7935***: Stationary source emissions – Determination of the mass concentration of sulphur dioxide – Performance characteristics of automated measuring methods*.

International Organization of Standardization, **ISO Method 10396**: *Stationary source emissions – Sampling for the automated determination of gas concentrations*.

International Organization of Standardization, **ISO Method 10397**, *Stationary source emissions – determination of asbestos plant emissions – Method by fibre count measurement*.

International Organization of Standardization, **ISO Method 10780:** *Stationary source emissions – Measurement of velocity and volume flowrate of gas streams in ducts.*

International Organization of Standardization, **ISO Method 11632**: *Stationary source emissions – Determination of mass concentration of sulphur dioxide – Ion chromatography method.*

International Organization of Standardization, **ISO Method 15713**: *Stationary source emissions – Sampling and determination of gaseous fluoride content.*

International Organization of Standardization, **ISO Method 17025**: *General requirements for the competence of testing and calibration laboratories.*

International Organization of Standardization, **ISO Method 21877**: *Stationary source emissions – Determination of the mass concentration of ammonia – Manual method.*

International Organization of Standardization, ISO/IEC Guide 98-3, *Uncertainty of measurement: Part 3: Guide to the expression of uncertainty in measurement.*

National Association of Testing Authorities (NATA)

National Association of Testing Authorities 2018, *General Accreditation Guidance: Validation and verification of quantitative and qualitative test methods.*

Standards Association of Australia (AS)

Standards Association of Australia 1995, **AS 4323.1–2021**: *Stationary source emission method 1 – Selection of sampling positions.*

Standards Association of Australia 1995, **AS 4323.2–1995**: *Stationary source emissions: Method 2: Determination of total particulate matter – Isokinetic manual sampling – Gravimetric method.*

Standards Association of Australia 2001, **AS 4323.3–2001**: *Stationary source emissions: Method 3: Determination of odour concentration by dynamic olfactometry.*

Standards Association of Australia 2001, **AS 4323.4–2009**: *Stationary source emissions: Area source sampling – Flux chamber technique.*

United States Environmental Protection Agency (USEPA)

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 1**: *Sample and velocity traverses for stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 2**: *Determination of stack gas velocity and volumetric flow rate (type S pitot tube).*

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 2C**: *Determination of stack gas velocity and volumetric flow rate from small stacks or ducts (standard pitot tube)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 2F**: *Determination of stack gas velocity and volumetric flow rate with three-dimensional probes*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 2G**: *Determination of stack gas velocity and volumetric flow rate with two-dimensional probes*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 2H**: *Determination of stack gas velocity taking into account velocity decay rate near the stack wall*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 3**: *Gas analysis for the determination of dry molecular weight*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 3A**: *Determination of oxygen and carbon dioxide concentrations in emissions from stationary sources (instrumental analyzer procedure)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 4**: *Determination of moisture content in stack gases*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 5**: *Determination of particulate emissions from stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 6**: *Determination of sulfur dioxide emissions from stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 6C**: *Determination of sulfur dioxide emissions from stationary sources (instrumental analyzer procedure)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 7**: *Determination of nitrogen oxide emissions from stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 7A**: *Determination of nitrogen oxide emissions from stationary sources (ion chromatographic method)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 7B**: *Determination of nitrogen oxide emissions from stationary sources (ultraviolet spectrophotometry)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 7C**: *Determination of nitrogen oxide emissions from stationary sources (alkaline-permanganate/colorimetric method)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 7D**: *Determination of nitrogen oxide emissions from stationary sources (alkaline-permanganate/ion chromatographic method)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 7E**: *Determination of nitrogen oxide emissions from stationary sources (instrumental analyzer procedure)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 8**: *Determination of sulfuric acid mist and sulfur dioxide emissions from stationary sources.*

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 10**: *Determination of carbon monoxide emissions from stationary sources (Instrumental Analyzer Procedure)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 11**: *Determination of hydrogen sulfide content of fuel gas streams in petroleum refineries*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 13A**: *Determination of total fluoride emissions from stationary sources (SPADNS zirconium lake method)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 13B**: *Determination of total fluoride emissions from stationary sources (specific ion electrode method)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 14**: *Determination of fluoride emissions from roof monitors for primary aluminum plants*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 14A**: *Determination of total fluoride emissions from selected sources at primary aluminum production facilities*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 15**: *Determination of hydrogen sulfide, carbonyl sulfide and carbon disulfide emissions from stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 16**: *Semicontinuous determination of sulfur emissions from stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 16A**: *Determination of total reduced sulfur emissions from stationary sources (impinger technique)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 16B**: *Determination of total reduced sulfur emissions from stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 16C**: *Determination of total reduced sulfur emissions from stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 17**: determination of particulate matter emissions from stationary sources.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 18**: *Measurement of gaseous organic compound emissions by gas chromatography*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 22**: *Visual determination of fugitive emissions from material sources and smoke emissions from flares*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 23**: *Determination of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 25**: *Determination of total gaseous non-methane organic emissions as carbon*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 25A**: *Determination of total gaseous organic concentrations using a flame ionization analyser*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 25B**: *Determination of total gaseous organic concentrations using a nondispersive infrared analyser*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 25C**: *Determination of non-methane organic compounds (NMOC) in MSW landfill gases.*

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 25D**: *Determination of the volatile organic concentration of waste samples*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 25E**: *Determination of vapor phase organic concentration in waste samples*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 26**: *Determination of hydrogen chloride emissions from stationary sources – isokinetic method*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 26A**: *Determination of hydrogen halide and halogen emissions from stationary sources – isokinetic method*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix A, **Method 29**: *Determination of metal emissions from stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 61, Appendix B, **Method 102**: *Determination of particulate and gaseous mercury emissions from chlor-alkali plants (hydrogen streams)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 51, Appendix M, **Method 201**: *Determination of PM_{10} emissions (exhaust gas recycle procedure)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 51, Appendix M, **Method 201A**: *Determination of PM_{10} emissions (constant sampling rate procedure)*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 63, Appendix A, **Method 301**: *Field validation of pollutant measurement methods from various waste media.*

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 63, Appendix A, **Method 308**: *Procedure for determination of methanol emissions from stationary sources.*

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 63, Appendix A, **Method 318**: *Extractive FTIR method for the measurement of emissions from the mineral wool and wool fibreglass industries*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 63, Appendix A, **Method 320**: *Measurement of vapor phase organic and inorganic emissions by extractive Fourier transform infrared*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 63, Appendix A, **Method 321**: Measurement of gaseous hydrogen chloride emissions at Portland cement kilns by Fourier transform Infrared (FTIR) spectroscopy.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 63, Appendix A**,** **Method 323**: *Measurement of formaldehyde emissions from natural gas-fired stationary sources – Acetyl acetone derivitization method*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 63, Appendix A, **Method 326**: *Determination of isocyanates in stationary source emissions*.

US Environmental Protection Agency, Technical Support Division (1992), **Guideline Document 038**, *Description of in-stack detection limit*.

US Environmental Protection Agency, Emission Measurement Center **Approved Alternative Method Alt-008,** *Alternative Moisture Measurement Method Midget Impingers*

US Environmental Protection Agency, Emission Measurement Center **Approved Alternative Method Alt-133**, *Alternative analytical approach for Methods 6, 8, 15A, and 16A CFR Part 60*

US Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," EPA Publication **SW-846 Test Method 9056A**: *Determination of inorganic anions by ion chromatography*.

US Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA Publication **SW-846 Test Method 0011**: *Sampling for selected aldehyde and ketone emissions from stationary sources*.

US Environmental Protection Agency, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA Publication **SW-846 Test Method 0061**: *Determination of hexavalent chromium emissions from stationary sources, Test methods for evaluating solid waste*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix B, **Performance Specification 1**: *Specifications and test procedures for opacity continuous emission monitoring systems in stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix B, **Performance Specification 2**: *Specifications and test procedures for* SO_2 *and* NO_x *continuous emission monitoring systems in stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix B, **Performance Specification 3**: *Specifications and test procedures for* O_2 *and* CO_2 *continuous emission monitoring systems in stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix B, **Performance Specification 4**: *Specifications and test procedures for CO continuous emission monitoring systems in stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix B, **Performance Specification 5**: *Specifications and test procedures for TRS continuous emission monitoring systems in stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix B, **Performance Specification 6**: *Specifications and test procedures for flow rate continuous emission monitoring systems in stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix B, **Performance Specification 7**: *Specifications and test procedures for H_2S continuous emission monitoring systems in stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix B, **Performance Specification 8**: *Specifications and test procedures for VOC continuous emission monitoring systems in stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix B, **Performance Specification 9**: *Specifications and test procedures for gas chromatographic continuous emission monitoring systems in stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix B, **Performance Specification 11**: *Specification and test procedures for particulate matter continuous emission monitoring systems at stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix B, **Performance Specification 12A**: *Specifications and test procedures for total vapor phase mercury continuous emission monitoring systems in stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix B, **Performance Specification 15**: *Performance specification for extractive FTIR continuous emission monitoring systems in stationary sources*.

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 60, Appendix B, **Performance Specification 18**: Performance specification and test procedures for gaseous hydrogen chloride (HCl) continuous emission monitoring systems at stationary sources.

US Environmental Protection Agency, **Conditional Test Method 013B**: *Determination of sulfuric acid and sulfur dioxide emissions from combination boilers, recovery furnaces, and thermal oxidizers – Isokinetic method*.

US Environmental Protection Agency, **Conditional Test Method 036:** *Method for measurement of isocyanate compounds in stack emissions*

US Environmental Protection Agency, **Compendium Method TO-5:** *Determination of Aldehydes and Ketones in Ambient Air Using High Performance Liquid Chromatography (HPLC).*

US Environmental Protection Agency, **Compendium Method TO-11A:** *Determination of Formaldehyde in Ambient Air Using Adsorbent Cartridge Followed by High Performance Liquid Chromatography (HPLC).*

Appendix 1: Stationary-source monitoring and reporting – definitions and generic procedures

Cubic metre (m^3)

In this document a cubic metre (m^3) refers to the volume of dry gas that occupies $1 m^3$ at a temperature of 0°C (273 K) and at an absolute pressure equivalent to 1 atmosphere (101.3 kPa).

Measuring concentrations and volumes in gases

When reporting concentrations of pollutants in gases for comparison with emission standards or with limits in regulations, licences, approvals, statutory notices, guidelines, codes of practice, environmental management plans or other statutory instruments, you must use the conversions given below in Appendix 1.

However, where any of these conversions are part of the test method used to determine the concentration, they do not need to be repeated for reporting.

The test method for a pollutant gives the volume of gas sampled at the test conditions (such as moisture, temperature, pressure, oxygen and carbon dioxide) at the sample point, V_a.

Adjustment to reference conditions

Dry basis

Calculate the volume of dry gas at sample-point conditions (V_b):

$V_b = V_a \times (100 - MC) \div 100$ Equation 1.1

MC = Moisture Content

Standard temperature

Calculate the volume of dry gas at standard temperature (273 K) (V_c):

$V_c = V_b \times 273 \div (273 + \text{gas meter temperature in °C})$ Equation 1.2

Standard pressure

Calculate the volume of dry gas at standard pressure (101.3 kPa) (V_d):

$V_d = V_c \times (\text{gas meter pressure in kPa}) \div 101.3$ Equation 1.3

Determine concentration as dry basis, standard temperature and standard pressure

Divide the measured mass of pollutant (M_a) by V_d to determine the concentration (C_a):

$C_a = M_a \div V_d$ Equation 1.4

Oxygen

For adjustment to an oxygen reference, the adjusted concentration of a pollutant, C_b, is determined by:

$C_b = C_a \times$ (21 - **reference** oxygen concentration as volume %) ÷ (21 - **measured** oxygen concentration as volume %) Equation 1.5

where:

C_a = the measured concentration of the pollutant, reported at the standard reference conditions

Carbon dioxide

For adjustment to a carbon dioxide reference, the adjusted concentration of a pollutant, C_c, is determined by:

$C_c = C_a \times 12 \div$ measured carbon dioxide concentration as volume % Equation 1.6

where:

C_a = the measured concentration of the pollutant, reported at the standard reference conditions

Nitrogen dioxide

Oxides of nitrogen (NO_x) from combustion of fossil fuels consist predominantly of nitric oxide (NO) and nitrogen dioxide (NO_2). Oxides of nitrogen concentrations are converted to equivalent NO_2 as follows:

Equivalent NO_2 = calculated NO_2 + (measured NO $\times$ 46 ÷ 30) Equation 1.7

where:

calculated NO_2 = measured NOx – measured NO

46 = molecular weight of NO_2

30 = molecular weight of NO

Both NO and NO_x must be measured directly.

Conversion from volume- to mass-based units of concentration

Ideal gas law

The physical state of gaseous air pollutants at environmental concentrations may be described by the ideal gas law, as follows:

$P \times V = n \times R \times T$ Equation 2.1

where:

P = absolute pressure of gas (atm)

V = volume of gas (L)

n = number of moles of gas (mol), calculated from the mass of a pollutant (m) divided by its molecular weight (MW)

R = universal gas constant (L.atm/mol.K)

T = absolute temperature (K)

Substituting number of moles (n) for mass of pollutant (m) divided by molecular weight (MW) into Equation 2.1 and rearranging terms yields:

$$V = \frac{\mathrm{m\,R\,T}}{\mathrm{P\,MW}}$$

Equation 2.2

Calculating volume as parts per million

Parts per million (ppm) refers to the volume of pollutant (V_p) per million volumes of air (V_a):

$$ppm = \frac{Vp}{V_a} 10^6$$

Equation 2.3

Conversion from volume-to mass-based units of concentration

Substituting Equation 2.2 into Equation 2.3 yields:

$$ppm = \frac{m}{V_a} \frac{R \times T}{P \times MW} \; 10^6$$

Equation 2.4

Using the appropriate values for the variables in Equation 2.4, a conversion from volume to mass-based units of concentration for carbon monoxide may be derived as shown below.

T = 298.1°C

P = 1 atm

MW = 28 g/mol

R = 0.08205 L atm/mol K

$$ppm = \frac{m(mg) \times 10^{-3}(g/mg)}{V_a(m^3) \times 10^3(L/m^3)} \times \frac{0.08205(L.atm/mol.K) \times 298.15(K)}{1(atm) \times 28(g/mol)} \; 10^6$$

Equation 2.5

1 ppm = 1.15 mg/m^3

1 mg/m^3 = 0.873 ppm

Conversions at 273 K and 1 atmosphere

C (mg/m^3) = C (ppm) ×(MW/22.4) Equation 2.6

C (ppm) = C (mg/m^3) × (22.4/MW) Equation 2.7

where:

C = concentration

MW = molecular weight (g/mol)

22.4 = the volume of 1 mole of air (in L) at 1 atmosphere and 273 K

Volatile organic compounds

Calculation of VOC as n-propane equivalent on a mass basis

VOC as n-propane equivalent is the sum of the concentrations of each individual VOC species as measured by a GC or a similar method, and corrected to VOC as n-propane equivalent.

If speciated gaseous non-methane organics (SGNMOs) have been measured using TM-34, use the following procedure to convert the concentration of each individual VOC species to VOC as n-propane equivalent:

$$C_{VOC} = \sum_{i=1}^{N} \left(\frac{C_i}{MW_i} \right) \times \; 44$$

Equation 3.1

where:

C_{VOC} = the calculated concentration of VOC as n-propane equivalent in mg/m^3 (dry, 273 K, 101.3 kPa)

C_i = the measured concentration of each individual VOC species in mg/m^3 (dry, 273 K, 101.3 kPa)

MW_i = the molecular weight of each individual VOC species in g/mol

44 = the molecular weight of n-propane in g/mol

Calculation of TOC equivalent on a mass basis

Total organic carbon (TOC) equivalent is the sum of the concentrations of each individual VOC species as measured by a GC or a similar method, and corrected to TOC equivalent.

If speciated gaseous non-methane organics (SGNMOs) have been measured using TM-34, use the following procedure to convert the concentration of each individual VOC species to TOC equivalent:

$$C_{TOC} = \sum_{i=1}^{N} \left(\frac{C_i K_i}{MW_i} \right) \times 12 \qquad \text{Equation 3.2}$$

where:

C_{TOC} = the calculated concentration of TOC in mg/m^3 (dry, 273 K, 101.3 kPa)

C_i = the measured concentration of each individual VOC species in mg/m^3 (dry, 273 K, 101.3 kPa)

MW_i = the molecular weight of each individual VOC species in g/mol

K_i = the carbon correction factor (number of carbon atoms in the molecule) for each species

Conversion of total VOC as n-propane equivalent to TOC equivalent on a volume basis

TOC equivalent is a measure of the amount of gaseous or vapour-phase organic carbon, as measured by an FID or similar method, and expressed as TOC equivalent.

If total gaseous non-methane organics (TGNMOs) have been measured using TM-34, use the following procedure to convert VOC as n-propane equivalent (or other calibrating gas) to total organic carbon (TOC) equivalent and vice versa:

$$C_{TOC} = K \times C_{VOC} \qquad \text{Equation 3.3}$$

where:

C_{TOC} = the calculated concentration of TOC as carbon equivalent in ppmv

C_{VOC} = the measured concentration of VOC as n-propane equivalent (or other calibrating gas) in ppmv

K = the carbon equivalent correction factor. (This is the number of carbon atoms in the molecule and has a value of 3 if n-propane is used as the calibrating gas. An appropriate carbon-equivalent correction factor should be selected if a calibrating gas other than n-propane is used.)

Conversion of TOC equivalent on a volume basis to TOC equivalent on a mass basis

$$C_{TOC}(mg/m^3) = C_{TOC}(ppm) \times \frac{12}{22.4}$$ Equation 3.4

where:

C_{TOC} = the concentration of TOC as total organic carbon equivalent

12 = the molecular weight of carbon (g/mol)

22.4 = the volume of 1 mole of air (in L) at 1 atmosphere and 273 K

Sulfur species

Equations required for calculating concentrations of analytes

The following equations were originally published by the USEPA in *Alternative Test Method 133 (Alt-133), Approval of alternative analytical approach for Methods 6, 8, 15A and 16A of 40 CFR Part 60.*

The equation to calculate sulfur dioxide (SO_2) and total reduced sulfur (TRS) as SO_2 (to use in place of Equation 6.2 in USEPA Method 6, Equation 8.2 in USEPA Method 8 and Equation 16A.2 in USEPA Method 16A) is:

$$C_{SO_2}\ or\ C_{TRS} = \frac{0.339}{V_{std}}(0.653)(C_S V_S - C_B V_B)$$ Equation 4.1

where:

C_{SO2} = measured concentrations of SO_2 in ppmv at 273 K, 1 atm.

C_{TRS} = measured concentration of TRS as SO_2, in ppm at 273 K, 1 atm.

0.339 = conversion constant, mg/m^3 to ppmv SO_2

0.653 = gravimetric factor, SO_2/SO_4^{2-}

C_S = measured concentration of SO_4^{2-} per sample (mg/L)

C_B = measured concentration of SO_4^{2-} per blank (mg/L)

V_S = volume of sample collected (L)

V_B = volume of blank sample (L)

V_{std} = dry gas volume as measured by the dry gas meter, corrected to standard conditions

The equation to calculate sulfuric acid mist (H_2SO_4), in place of Equation 8.1 in USEPA Method 8, is:

$$C_{H_2SO_4} = \frac{0.228}{V_{std}}(1.021)(C_S V_S - C_B V_B)$$ Equation 4.2

C_{H2SO4} = measured concentrations of H_2SO_4 (including SO_3) in ppmv at 273 K, 1 atm.

0.228 = conversion constant, mg/m^3 to ppmv H_2SO_4

1.021 = gravimetric factor, H_2SO_4/SO_4^{2-}

C_S = measured concentration of SO_4^{2-} per sample (mg/L)

C_B = measured concentration of SO_4^{2-} per blank (mg/L)

V_S = volume of sample collected (L)

V_B = volume of blank sample (L)

V_{std} = dry gas volume as measured by the dry gas meter, corrected to standard conditions

Appendix 2: Test Method 20 (TM-20) – determination of total mass of unrecovered organic vapours from vapour recovery units

Sampling

Sampling must be performed in accordance with TM-34.

Calculation of mass of unrecovered organic vapours

The mass of unrecovered organic vapours emitted for each litre of volatile organic liquid is:

$$(318 \times C \times A \times M \times P \times V) \div (L \times T) \text{ milligrams} \qquad \text{Equation 5.1}$$

where:

C = the average concentration of hydrocarbons expressed as equivalent propane in ppm over the test period

A = the cross-sectional area of the exhaust duct at the plane where the measurements are made in m^2

M = the total time for volatile organic liquid to pass into the tank or out of the industrial plant in minutes

P = the atmospheric pressure in kPa

V = the average exhaust gas velocity in metres per second

L = the volume of volatile organic liquid passing into the tank or out of the industrial plant in litres

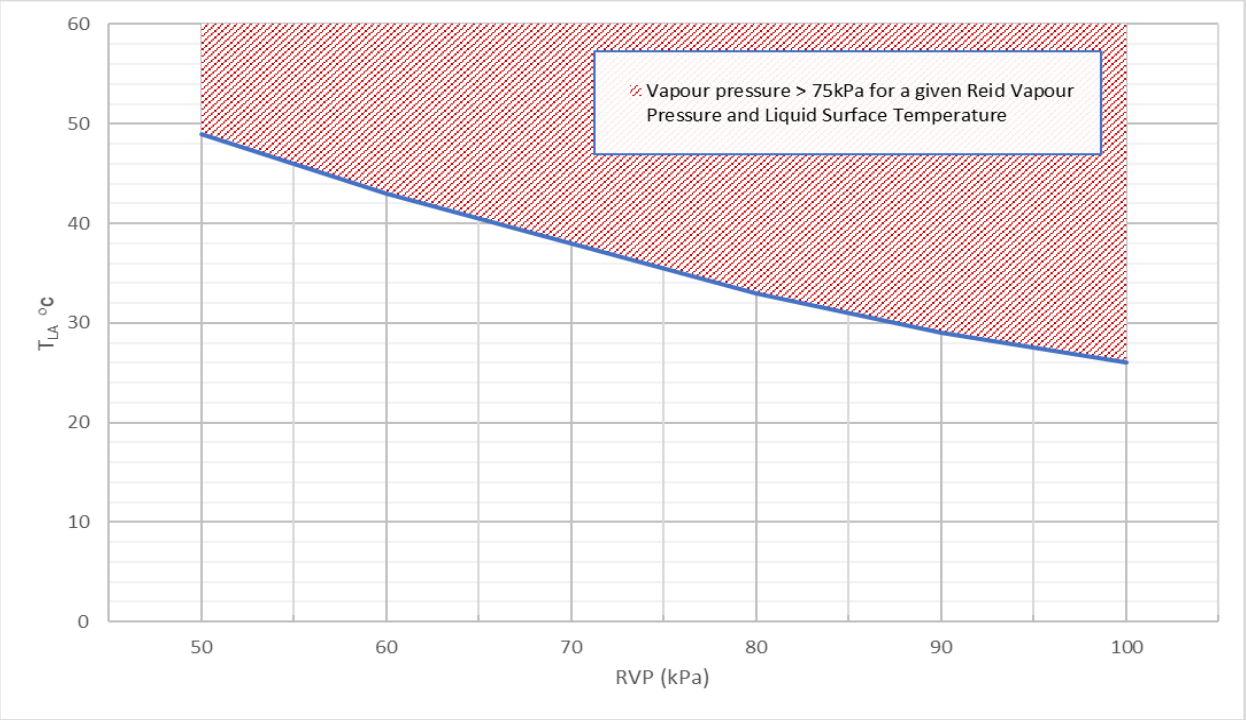
T = the average exhaust gas temperature in kelvin (273 + temperature in °C)

318 = a conversion factor

Appendix 3: Test Method 21 (TM-21) – volatile organic liquids: calculation of vapour pressure

A volatile organic liquid for which a Reid vapour pressure (RVP)[5] can be ascertained (typically gasoline products) is said to have a vapour pressure above 75 kPa if the surface liquid temperature, T_{LA}, corresponding to the RVP of the liquid, is above the line in Figure 2.

Figure 2 75 kPa vapour pressure relative to RVP and LST



T_{LA}, the surface liquid temperature in degrees Celsius, is calculated in one of two ways:

1. from ambient air temperature (T_{AA}),

$$T_{LA} = T_{AA} + 0.435\alpha I \qquad \text{Equation 6.1}$$

or

2. from measured bulk storage temperature,

$$T_{LA} = T_B + 0.0934\alpha I \qquad \text{Equation 6.2}$$

where:

- T_{AA} is the maximum average daily temperature over the past five years, in degrees Celsius. Average daily ambient temperature is the average of the maximum and minimum daily temperatures and can be determined from the Bureau of Meteorology website, using climate

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[5] RVP as determined by ASTM D323 *Standard test method for vapor pressure of petroleum products (Reid Method)* or equivalent.

data from the nearest meteorology station. If T_{AA} is unknown, the default value of 33°C should be used.

- T_B is the measured bulk storage temperature in degrees Celsius. This is measured in the tank, or in a tank of similar dimensions and finish at the same location.
- I is the maximum daily insolation (daily solar exposure) over the last five years in MJ/m^2. This can be determined from the Bureau of Meteorology website, using climate data from the nearest meteorology station. If I is unknown, the default value of 36 MJ/m^2 should be used.
- α is the surface absorptance (dimensionless) and is dependent on the surface finish of the tank. Values of α for different surface finishes are given below in Table 5.

Table 5 Values of α for different tank surfaces

Surface finish/colour of the tank	α
Light or metallic finish, e.g. metal, white	0.2
Medium colour finish, e.g. grey	0.6
Dark finish, e.g. red, green, black	0.9

To determine whether the vapour pressure is above or below 75 kPa:

1. Ascertain the surface finish of the tank (light/medium/dark), and hence determine the surface absorptance, α, from the table above.
2. Calculate T_{LA} from equation 1 (if using ambient temperature) or equation 2 (if using bulk liquid temperature).
3. Determine the RVP in kPa of the liquid being stored. This is a property of the petroleum product, and should be provided by the supplier.
4. Locate the point on the graph that corresponds to the RVP and T_{LA} of the liquid in the tank. If the point is above the line, the vapour pressure of the liquid is above 75 kPa. If it is below the line, the vapour pressure is below 75 kPa.

Other volatile organic liquids

For pure volatile liquids, the total vapour pressure can be calculated using Antoine's Equation –

$$P = 100 \text{ x } 10^{\left(\mathrm{A} - \frac{\mathrm{B}}{\mathrm{T_{LA}} + \mathrm{C}}\right)} \qquad \text{Equation 6.3}$$

– where P is the vapour pressure in kPa, T_{LA} is the surface liquid temperature (in °C), defined and calculated above, and the constants A, B and C are properties of the liquid. Note that C should be in the same units as T_{LA}.

Table 6 Constants for use in Antoine's Equation

Liquid	A	B	C
Ethanol	5.37229	1670.4	232.809
Methanol	5.20409	1581.3	239.500
Hexane	4.00266	1171.5	224.216
Acetone	4.42448	1312.3	240.555

For example, the vapour pressure of ethanol is 18.7 kPa if the liquid temperature is 41°C.

The vapour pressure of mixtures of organic liquids that are not petroleum products (and hence do not have a Reid vapour pressure) should be obtained from the supplier.

Appendix 4: Test Method 31 (TM-31) – observation procedure for excessive air impurities: visible emissions from mobile sources

When an observer is determining whether a vehicle is being used in breach of the clause limiting visible emissions, the following principles apply:

- The observer must be satisfied that the vehicle generating the visible emissions is correctly identified.
- The observer must be satisfied that the emissions are visible not just because of heat or the condensation of water vapour.
- The emissions must be continuously visible for more than 10 seconds.

The following details of the observation must be recorded:

- length of time in seconds that the visible emissions were observed
- registration number of the motor vehicle under observation
- type of motor vehicle under observation
- colour and darkness, in the opinion of the observer, of the air impurities emitted
- location, date and approximate time of day that the observation was made.

In the case of observation of digital imagery

When an observer of digital imagery is determining whether a vehicle is being used in breach of the clause limiting visible emissions, the following principles apply:

- The observer must be satisfied that the vehicle generating the visible emissions is correctly identified.
- The observer must be satisfied that the visible emissions are visible not just because of heat or the condensation of water vapour.
- The emissions must be continuously visible on any digital video imagery for more than 10 seconds.

The following details of the observation must be recorded:

- length of time in seconds that the visible emissions were observed
- registration number of the motor vehicle depicted in the digital imagery
- type of motor vehicle depicted in the digital imagery
- colour and darkness, in the opinion of the observer, of the air impurities which, by reference to the digital imagery, were emitted
- location, date and approximate time of day that the digital imagery was created.

Appendix 5: Test Method 38 (TM-38) – combination of air impurities from two or more sources

A combined source is a discharge point that combines discharge streams from two or more emission units, prior to discharge to the atmosphere. ‘Emission unit’ is defined in the POEO Clean Air Regulation as an item of plant that forms part of, or is attached to, some larger plant, being an item of plant that emits, treats or processes air impurities or controls the discharge of air impurities into the atmosphere.

The procedure for calculating the standard of concentration for a combined source is detailed in the following equation.

$$C_T = \frac{C_1 \cdot q_1 + C_2 \cdot q_2 + \cdots + C_N \cdot q_N}{q_1 + q_2 + \cdots + q_N} \qquad \text{Equation 7.1}$$

where:

C_T = the alternative standard of concentration for the combined source

C_i = the standard of concentration that are applicable to emission unit i

q_i = the volumetric flow rate of emission unit i

Appendix 6: Other approved method 9 (OM-9) – ‘coarse’ particulates

To determine ‘coarse’ particulates:

1. determine solid particles (total) using TM-15
2. simultaneously determine ‘fine’ particulates (PM_{10}) using OM-5
3. subtract the result of OM-5 (‘fine’ particulates (PM_{10})) from the result of TM-15 (solid particles (total)) to determine ‘coarse’ particulates.

Sampling and analysis for solid particles (total) and ‘fine’ particulates (PM_{10}) must be carried out simultaneously using TM-15 and OM-5 respectively, to ensure process variations do not affect the results.

Appendix 7: Test method sources

Australian Standard

Australian Standards can be bought from:

Standards Australia: www.standards.org.au/access-standards/buy-standards

SAI Global: https://infostore.saiglobal.com/en-au/

American Public Health Association

Standard Methods for the Examination of Water and Wastewater (20th edition) can be bought from the Australian 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/Standard/index.html

United States Environmental Protection Agency

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

Website: www.epa.gov/emc/emc-promulgated-test-methods

SW-846 series: www.epa.gov/hw-sw846/sw-846-compendium

Compendium of Methods for the Determination of Toxic Organic (TO) Compounds in Ambient Air Series (Ambient Monitoring Technology Information Center): www3.epa.gov/ttnamti1/airtox.html

California Environmental Protection Agency: Air Resources Board

Test methods are available from the Air Resources Board.

Website: www.arb.ca.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: www.iso.org/home.html

National Institute for Occupational Safety and Health

National Institute for Occupational Safety and Health methods are published in the NIOSH Manual of Analytical Methods (NMAM).

Website: www.cdc.gov/niosh/nmam/