

Environment Protection Authority

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



© 2022 State of NSW and the NSW Environment Protection Authority

With the exception of photographs, the State of NSW and the NSW Environment Protection Authority (EPA) are pleased to allow this material to be reproduced in whole or in part for educational and non-commercial use, provided the meaning is unchanged and its source, publisher and authorship are acknowledged. Specific permission is required for the reproduction of photographs.

The EPA has compiled this document in good faith, exercising all due care and attention. No representation is made about the accuracy, completeness or suitability of the information in this publication for any particular purpose. The EPA shall not be liable for any damage which may occur to any person or organisation taking action or not on the basis of this publication. Readers should seek appropriate advice when applying the information to their specific needs.

All content in this publication is owned by the EPA and is protected by Crown Copyright, unless credited otherwise. It is licensed under the Creative Commons Attribution 4.0 [International](#) (CC BY 4.0), subject to the exemptions contained in the licence. The legal code for the licence is available at [Creative Commons](#).

The EPA asserts the right to be attributed as author of the original material in the following manner: © State of New South Wales and the NSW Environment Protection Authority 2022.

Cover: EPA officers inspecting air quality at Newcastle. Photo: Nick May

Published by:

NSW Environment Protection Authority

4 Parramatta Square

12 Darcy Street, Parramatta NSW 2150

Locked Bag 5022, Parramatta NSW 2124

Phone: +61 2 9995 5000 (switchboard)

Phone: 131 555 (NSW only – environment information and publications requests)

Fax: +61 2 9995 5999

TTY users: phone 133 677, then ask
for 131 555

Speak and listen users:

phone 1300 555 727, then ask for 131 555

Email: info@epa.nsw.gov.au

Website: www.epa.nsw.gov.au

Report pollution and environmental incidents

Environment Line: 131 555 (NSW only) or info@epa.nsw.gov.au

See also www.epa.nsw.gov.au

ISBN 978 1 922447 37 1

EPA 2022P3487

January 2022

Contents

1. Introduction	1
1.1. Purpose of this document	1
1.2. Relevant legislation	1
1.3. What method to use	1
1.4. Who is this document for?	2
2. Sample collection and handling	2
2.1. Sampling design	3
2.2. Sampling containers and devices	3
2.3. Sample storage, preservation and holding times	3
2.4. Sampling quality assurance and quality control procedures	3
3. Sampling and analysis methods	4
4. Modifying methods, or using alternative or unlisted methods	10
4.1. Terminology	10
4.2. Approval requirements	10
4.3. Minor modifications	12
4.4. Significant modifications and alternative methods	13
4.5. Documentation and validation requirements	13
5. Reporting requirements	15
5.1. Record-keeping	15
5.2. Air emission sampling report inclusions	15
5.3. Analytical report	16
5.4. General reporting requirements	16
6. Referenced test methods	17
Appendix 1: Stationary-source monitoring and reporting – definitions and generic procedures	23
Appendix 2: Test Method 20 (TM-20) – determination of total mass of unrecovered organic vapours from vapour recovery units	29
Appendix 3: Test Method 21 (TM-21) – volatile organic liquids: calculation of vapour pressure	30
Appendix 4: Test Method 31 (TM-31) – observation procedure for excessive air impurities: visible emissions from mobile sources	32
Appendix 5: Test Method 38 (TM-38) – combination of air impurities from two or more sources	33
Appendix 6: Other approved method 9 (OM-9) – ‘coarse’ particulates	34
Appendix 7: Test method sources	35

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 body¹, 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.

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 ₂ SO 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 ₂ S)	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 NO _x 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°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 ₂ S)	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

² PM₁₀ – 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.

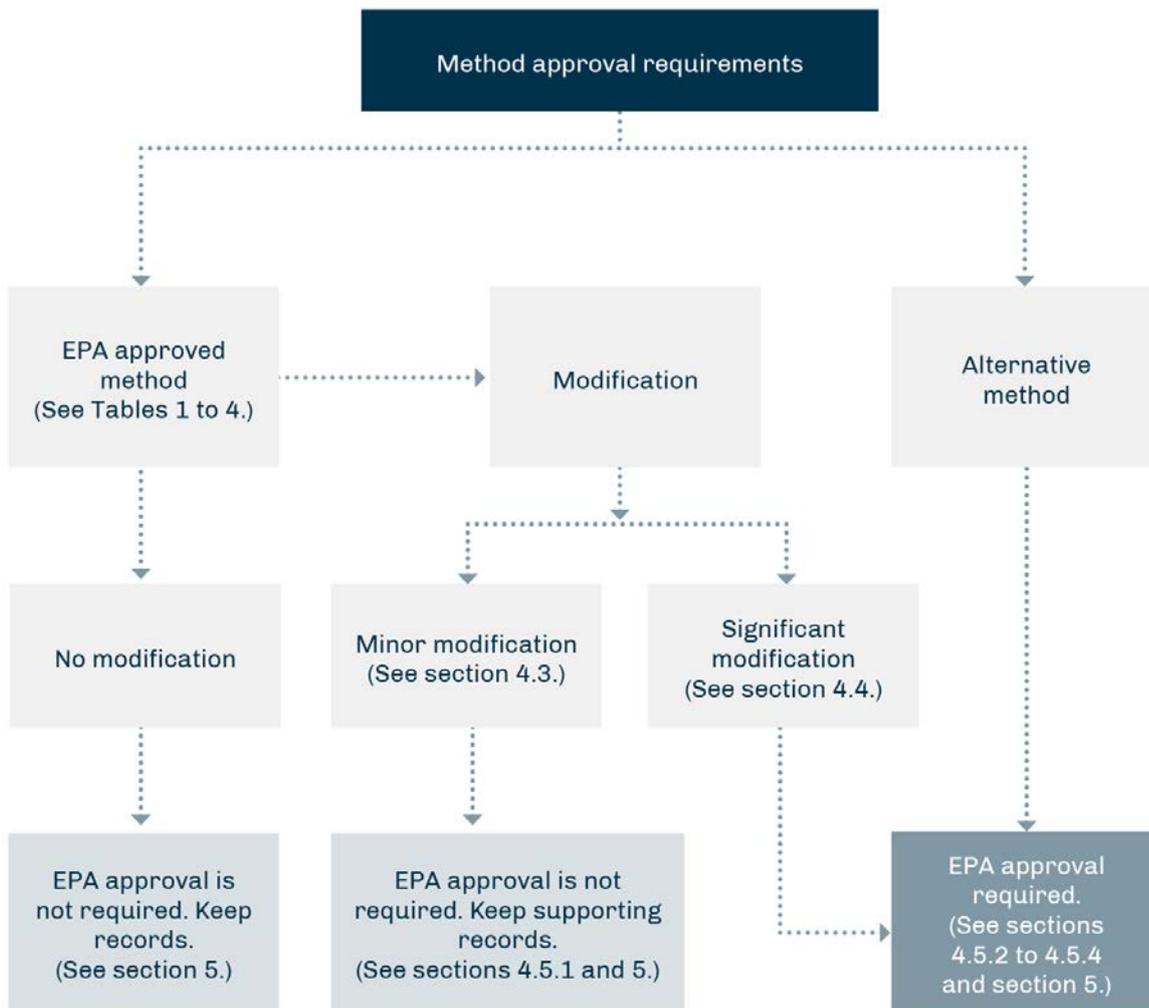
Equivalent performance

‘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 PFAS⁴) 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

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 PM₁₀ emissions (exhaust gas recycle procedure).*

US Environmental Protection Agency, Code of Federal Regulations, Title 40, Part 51, Appendix M, **Method 201A**: *Determination of PM₁₀ 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 SO₂ 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 O₂ and CO₂ 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 H₂S 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 (m³)

In this document a cubic metre (m³) refers to the volume of dry gas that occupies 1m³ 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):

$$V_b = V_a \times (100 - MC) \div 100 \quad \text{Equation 1.1}$$

MC = Moisture Content

Standard temperature

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

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

Standard pressure

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

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

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):

$$C_a = M_a \div V_d \quad \text{Equation 1.4}$$

Oxygen

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

$$C_b = C_a \times \frac{(21 - \text{reference oxygen concentration as volume \%})}{(21 - \text{measured oxygen concentration as volume \%})} \quad \text{Equation 1.5}$$

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:

$$C_c = C_a \times \frac{12}{\text{measured carbon dioxide concentration as volume \%}} \quad \text{Equation 1.6}$$

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:

$$\text{Equivalent NO}_2 = \text{calculated NO}_2 + (\text{measured NO} \times 46 \div 30) \quad \text{Equation 1.7}$$

where:

calculated NO_2 = measured NO_x – 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:

$$P \times V = n \times R \times T \quad \text{Equation 2.1}$$

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:

$$V = \frac{m RT}{P MW} \quad \text{Equation 2.2}$$

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):

$$ppm = \frac{V_p}{V_a} 10^6 \quad \text{Equation 2.3}$$

Conversion from volume-to mass-based units of concentration

Substituting Equation 2.2 into Equation 2.3 yields:

$$ppm = \frac{m}{V_a} \frac{R \times T}{P \times MW} 10^6 \quad \text{Equation 2.4}$$

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.

$$T = 298.1^\circ\text{C}$$

$$P = 1 \text{ atm}$$

$$MW = 28 \text{ g/mol}$$

$$R = 0.08205 \text{ L atm/mol K}$$

$$ppm = \frac{m(mg) \times 10^{-3}(g/mg)}{V_a(m^3) \times 10^3(L/m^3)} \times \frac{0.08205(L.atm/mol.K) \times 298.15(K)}{1(atm) \times 28(g/mol)} 10^6 \quad \text{Equation 2.5}$$

$$1 \text{ ppm} = 1.15 \text{ mg/m}^3$$

$$1 \text{ mg/m}^3 = 0.873 \text{ ppm}$$

Conversions at 273 K and 1 atmosphere

$$C \text{ (mg/m}^3\text{)} = C \text{ (ppm)} \times (MW/22.4) \quad \text{Equation 2.6}$$

$$C \text{ (ppm)} = C \text{ (mg/m}^3\text{)} \times (22.4/MW) \quad \text{Equation 2.7}$$

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:

$$C_{VOC} = \sum_{i=1}^N \left(\frac{C_i}{MW_i} \right) \times 44 \quad \text{Equation 3.1}$$

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:

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

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:

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

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

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

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 (SO₂) and total reduced sulfur (TRS) as SO₂ (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:

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

where:

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

C_{TRS} = measured concentration of TRS as SO₂, in ppm at 273 K, 1 atm.

0.339 = conversion constant, mg/m³ to ppmv SO₂

0.653 = gravimetric factor, SO₂/SO₄²⁻

C_S = measured concentration of SO₄²⁻ per sample (mg/L)

C_B = measured concentration of SO₄²⁻ 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 (H₂SO₄), in place of Equation 8.1 in USEPA Method 8, is:

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

$C_{H_2SO_4}$ = measured concentrations of H₂SO₄ (including SO₃) in ppmv at 273 K, 1 atm.

0.228 = conversion constant, mg/m³ to ppmv H₂SO₄

1.021 = gravimetric factor, H₂SO₄/SO₄²⁻

C_S = measured concentration of SO₄²⁻ 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:

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

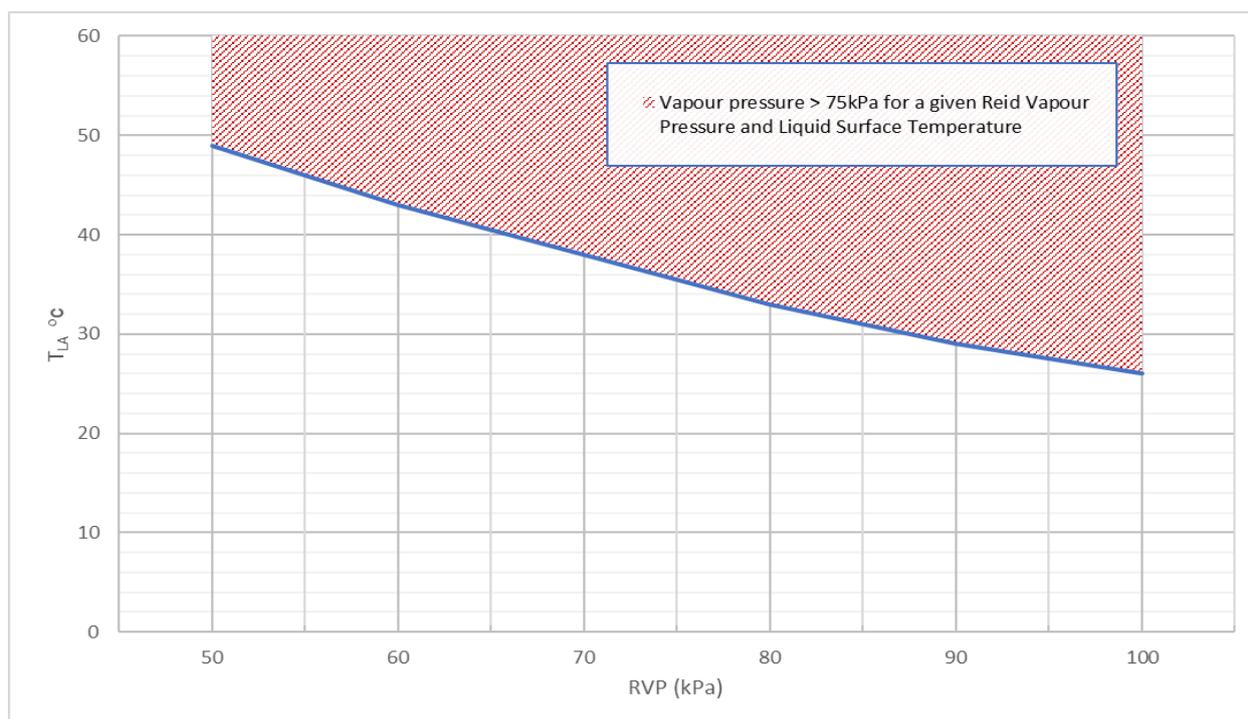
where:

- 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 m²
- 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}),

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

or

2. from measured bulk storage temperature,

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

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

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/m². 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/m² 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 –

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

– 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.

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

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/