

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

We consulted stakeholders on a draft of this document (Approved Methods) from 19 April to 31 May 2021.

Stakeholders included:

- EPA licensed entities
- laboratories
- consultants
- technical and professional bodies
- government agencies.

We invited stakeholders to make submissions or respond to a survey. We received:

- 4 written submissions
- 4 survey responses.

The tables below summarise the key issues raised and the EPA's responses.

We took this stakeholder feedback into account when finalising the Approved Methods for air.

Table 1 Overall

Issues raised by stakeholders	EPA response
<p>Ambient air methods</p> <ul style="list-style-type: none"> Where do ambient air monitoring methods sit now? 	<p>The indexed list of ambient air methods and associated guidance will be on the EPA website, not in the Approved Methods.</p> <p>The indexed list of method numbers (AMs) is consistent with the 2007 version of the air Approved Methods.</p> <p>The list of reference methods has been updated to reflect the latest available version of published methods.</p> <p>Where a condition of an environment protection licence specifies an ambient air monitoring method, you are required to use this method.</p>
<p>Optical particle counters</p> <ul style="list-style-type: none"> More clarity is needed on when new technology, such as optical particle counters, may be used. 	<p>Test methods usually set or describe analytical criteria or acceptability criteria – including performance standards – for the measurement technology.</p> <p>Optical particle counters (as opposed to opacity monitors) are commonly used for monitoring in ambient air and are not typically used for point source emission testing for regulatory purposes.</p>

Table 2 Section 2: Sample collection and handling

Issues raised by stakeholders	EPA response
<p>PFAS</p> <ul style="list-style-type: none"> Section lacked methods for the determination of PFAS. USEPA OTM-45 could be used as the standard method. 	<p>PFAS testing of point-source air emissions is not routinely required in NSW at present. The Approved Methods document details the methods for sampling and analysis of major/common air pollutants from stationary sources. It does not cover every possible air pollutant, only the common/major air pollutants emitted from stationary sources.</p> <p>Sometimes a test may be needed for a less-common air pollutant. The EPA would assess such cases individually. Situation 5 in section 4.2 gives guidance on selecting appropriate methods where an analyte is not listed.</p> <p>We are aware of the introduction of USEPA OTM-45 but have not yet chosen to include it in the Approved Methods. OTM-45 is designated as an ‘other test method’ (OTM). OTM’s have not yet been subject to the federal rulemaking process by the US EPA and are subject to change based on the review of additional validation studies or public comment. OTM-45 was published only in January 2021 and so very little data is available on the performance and suitability of the test method. NSW may consider the inclusion of OTM-45, or other suitable methods, as validation and performance data becomes available.</p> <p>Where PFAS monitoring is required, we will continue to assess it on a case-by-case basis.</p>

Issues raised by stakeholders	EPA response
<p>Asbestos</p> <ul style="list-style-type: none"> Asbestos as an airborne analyte is missing. Methods such as NIOSH 7400, ASTM 7201 and ISO10312 could be used to test for airborne asbestos. 	<p>We support the inclusion of asbestos in the Approved Methods and have included sampling method ISO 10397, <i>Stationary source emissions – determination of asbestos plant emissions – Method by fibre count measurement</i> as OM-13. ISO 10397 is specific to point source emissions, while the suggested methods are for ambient air monitoring.</p>
<p>Method detection limit</p> <ul style="list-style-type: none"> Minor amendments to the text suggested to describe method detection limits and how to calculate sample volumes. 	<p>We have amended the text in section 2 of the Approved Methods to address the comment.</p>

Table 3 Section 3: Sampling and analysis methods

Issues raised by stakeholders	EPA response
<p>TM-2 Velocity or volumetric flow rate</p> <ul style="list-style-type: none"> ISO 10780 is an approved test method for velocity/flowrate. 	<p>We have added ISO 10780 as an additional approved method for TM-2 in Table 1 of the Approved Methods.</p>
<p>TM-4 Sulfur dioxide</p> <ul style="list-style-type: none"> USEPA 8 could be included as an approved method to measure sulfur dioxide. USEPA 8 is essentially the isokinetic version of USEPA 6 but uses larger impingers and sample volumes. As a result, USEPA 8 is more sensitive to SO₂ (1.2 mg/m³) than USEPA 6 (3.4 mg/m³) (as noted in USEPA 8 section 1.1). In addition, the use of USEPA 8 for SO₂ measurement allows for simultaneous measurement of SO₃/H₂SO₄ mist within the same sample train, which in turn allows for better comparison of results and reduced on-site testing labour. 	<p>We have reviewed USEPA Method 8 and consider it is suitable for the measurement of SO₂. The method also allows for the simultaneous measurement of SO₂, SO₃ and H₂SO₄. We have added USEPA Method 8 to Table 1 of the Approved Methods as an additional method for TM-4.</p>
<p>TM-9 Fluorine</p> <ul style="list-style-type: none"> USEPA 26A could be included as an approved method for measuring hydrogen fluoride when used in conjunction with analysis of particulate fluoride according to the listed approved method, USEPA 13B. The combined result would be reported as total fluoride. 	<p>USEPA Method 26A is specifically for hydrogen fluoride (HF). The POEO (Clean Air) Regulation 2010 requires testing (in NSW) for total fluoride, as HF equivalent. USEPA 26A is reasonable for certain applications but it is not appropriate for all situations. Furthermore, USEPA 26A and USEPA 13B have different requirements for filter specifications that would also need to be considered on a case-by-case basis.</p> <p>Section 4 of Approved Methods allows licensees to seek approval for the use of modified methods. Use this pathway if you propose to combine USEPA Method 26A with USEPA 13B.</p>

Issues raised by stakeholders

EPA response

TM-15 Solid particles (total)

- AS4323.2 specifies velocity/flow rate measurement (in conjunction with solid particle monitoring) to be measured according to ISO 10780. However, ISO 10780 is not listed as an approved method for velocity/flow rate under TM-2. USEPA 2 could be an acceptable replacement for ISO 10780 when measuring velocity/flow rate in conjunction with solid particles in compliance with AS4323.2.
- USEPA 201A should be included as an approved method for the measurement of solid particles as per USEPA 201A section 1.6, under the following conditions as specified in the method:
 - isokinetics maintained at 90–110% and
 - number of sampling traverse points chosen as per USEPA 5 instead of the recommended maximum of 12 as noted in USEPA 201A.
- USEPA 17 should also be included as an approved method for the measurement of solid particles.

USEPA 17 is in principle very similar to AS4323.2 and uses essentially the same sampling equipment. One point of difference is that the minimum sampling time per traverse point for AS4323.2 is 5 minutes while for USEPA 17 it is 2 minutes. We understand that the POEO (Clean Air) Regulation (Schedule 5, Part 2) specifies a minimum total test duration (averaging period) of 1 hour, so the '2 minute per point' specification could not be used for smaller diameter stacks; however, for larger diameter stacks the use of USEPA 17 could enable shorter test periods and would bring test durations into line with USEPA 5 ('out of stack filter' particulates) testing, as well as other USEPA isokinetic methods approved by the NSW EPA.

TM-18 Dioxins and furans

- The listed approved method, USEPA Method 23, specifically recommends the use of a high-resolution mass spectrometry (capable of routine operation at a resolution of 1:10000 with a stability of ± 5 ppm) for the measurement of dioxin and furans. But there is only one laboratory in Australia that can offer this service. GC-MSMS should be an option for the determination of dioxin and furans as long as it is validated with the associated (NATA) accreditation.

We have added ISO 10780 for velocity measurement as an additional approved method for TM-2 in Table 1 of the Approved Methods.

USEPA 201A is predominantly used for the determination of particles $<10 \mu\text{m}$; however, the method allows for the determination of total particulates under strict conditions. USEPA 201A extensively references USEPA methods 5 and 17. Our preferred methods for quantifying total filterable particulate are AS4323.2 or USEPA Method 5 or 17, because they are the most direct and provide better precision and accuracy.

Collecting particle size data provides valuable information regarding the percentage of each size fraction in the total particulate emissions. Simultaneous measurement of total and size-fractionated particulates provides the most reliable measure of this distribution. We consider it is appropriate to use USEPA 201A for this purpose, providing the measurement criteria of Method 5 or 17 are satisfied. We have added USEPA 201A as an approved method under TM-15 in Table 1 of the Approved Methods.

USEPA 17 is very similar to AS4323.2, and so we did not originally consider including it in the draft Approved Methods document. However, USEPA 17 is considered applicable for the determination of solid particles and has a comparable performance with AS4323.2. We further recognise that many of the listed approved methods refer to USEPA 17. To ensure fluency between the methods and remove unnecessary limitations, we have included USEPA 17 as an approved method under TM-15 in Table 1 of the Approved Methods.

The US EPA is currently considering revisions to Method 23. The primary aim of the proposed revisions is to change the method from a prescriptive method to a performance-based method, which will allow users to have flexibility in implementing the method.

It is expected these proposed revisions, if adopted, should address the issues raised.

If you wish to use a modified version of USEPA Method 23, seek approval from the EPA (as allowed under the Approved Methods).

Issues raised by stakeholders

EPA response

TM-22 Moisture

- USEPA Alt-008 should be included as an approved method for the measurement of moisture content. The USEPA Emission Measurement Center states within USEPA Alt-008 that:

The EMTIC recommends that this method may be applied in compliance tests for which stack gas moisture measurements are necessary to correct pollutant concentration or flow rate data to appropriate moisture conditions (e.g., both pollutant and flow data on dry or wet basis).

- Chemical engineering calculations, such as the use of psychrometric formulas and tables, should be included to determine moisture content by measurement of wet- and dry-bulb temperature for stack gases below 60°C. This would be especially useful and likely more accurate than USEPA 4 or Alt-008 for emission sources comprising ambient air which typically have moisture levels <3% v/v.

The USEPA considers Alt-008 to be an approved alternative method to USEPA Method 4. Although the method is considered broadly acceptable for source sampling, the EPA does not consider it appropriate for all sources, situations or test conditions: for example, it is not considered appropriate where a high degree of accuracy is required, or for determining moisture over long test periods or in gas streams with high particulate concentrations. For these reasons, the EPA prefers USEPA Method 4 for moisture determination when isokinetic sampling is being undertaken. Alt-008 may be used in place of USEPA method 4 where isokinetic sampling is not being undertaken, providing Alt-008 is fit-for-purpose for the given application. We have amended Table 1 in the Approved Methods to conditionally include USEPA Alt-008.

The EPA recognise that wet-bulb/dry-bulb methods, coupled with psychrometric tables, are used extensively for relative humidity testing in ambient air environments. However, these methods are considered approximation methods and should only be used where:

- the conditions of the sampled source preclude the use of reference test methods
or
- where a high degree of measurement accuracy is not required.

In such circumstances, we consider the use of wet- or dry-bulb methods reasonable.

We have included method ASTM E337 for use – in specific circumstances – under TM-22 in Table 1 of the Approved Methods.

Issues raised by stakeholders

EPA response

TM-34 Volatile organic compounds (VOCs)

- There is an issue in relation to the recovery studies referred to in section 8.4.1 to 8.4.3 of USEPA method 18.
- Need to clarify the requirement to complete the recovery studies in accordance with the method, because of:
 - issues relating to access and availability of standards for field spiking
 - cost implications.

Recovery studies are an important QA/QC step and serve to validate that the sampling approach (media) is appropriate and that the sampling and analysis was performed well, ensuring the accuracy of collected emissions data.

The need to undertake recovery studies should be evaluated on a case-by-case basis. When determining the need, consider the complexity of the VOC profile, the expected concentration of each VOC and the emission limit/ standard of concentration for the plant.

If testing is being performed on an emission source comprised of a complex mixture of VOC's at significant concentrations (relative to any applicable limits), the EPA expects that an appropriate level of QA/QC is applied, including field spiking of a representative number of VOC compounds. Failing to undertake the field spike would be considered a major modification.

More discretion may be applied for low-risk sources, such as high-efficiency coal combustion boilers. At such sources, a minor method modification would likely apply if field spike recoveries are not done.

The Approved Methods for air document provides guidance on the use of modified methods: consider this when undertaking VOC sampling. Modifications to a method should be validated and may require EPA approval and or NATA accreditation, as outlined in the Approved Methods for air.

Where USEPA method 18 is used, the emission test report needs to include sufficient detail regarding the QA/QC procedures performed, including any recovery studies. If there have been no recovery studies, the report should justify why.

Issues raised by stakeholders

EPA response

OM-5 Fine particulates (PM₁₀ and PM_{2.5})

- A suggestion relates to measuring the distribution of particle sizes (including PM₁₀ and PM_{2.5}) on filters used to collect total solid particles.

On some occasions, USEPA 201A is not appropriate for the emission source e.g.:

- where water droplets are present in the emission source
or
- where the emission source gas is above a specified temperature, say 300°C.

In these instances, laser diffraction analysis could be used instead. ISO13320:2020 was suggested.

We have considered this suggestion and determined that it is not appropriate to include laser diffraction analysis, for the following reasons:

- Particle sizing sampling methods, such as Method 201A, determine particle size based upon the aerodynamic properties of the particulate, not just the physical size. Particle sizing is controlled by the cyclone design, the aerodynamic particle size and based on a reference particle density of 1 gram per cubic centimetre.
- Particle size data collected via laser diffraction, would not be directly comparable with the data collected using a method based on the aerodynamic properties, including USEPA 201A, for the reasons provided in point 1 above.
- Particle sizing via laser diffraction (or similar techniques) typically requires the use of specific filter media such as cellulose or Teflon. These filters are not suitable for use in typical in-stack applications. Cellulose does not have the required temperature stability characteristics and is reactive with stack gas components. Teflon® does not have required the temperature stability characteristics.

OM-11 Formaldehyde

- Include USEPA TO-5 *Method for the Determination of Aldehydes and Ketones in Ambient Air using High Performance Liquid Chromatography (HPLC)* for the measurement of formaldehyde under specific circumstances.

USEPA TO-5 is the non-isokinetic equivalent of USEPA SW846-0011 but uses smaller impingers and sample sizes.

- The stakeholder proposes the use of USEPA TO-5 where:
 - there is no appreciable dust in the emission source
or
 - the emission source is venting indoor air to atmosphere.
- The stakeholder also suggests that if USEPA TO-5 is being used under the above conditions, and there is also no free moisture in the emission source gas, then DNPH adsorption tubes could be an allowable substitution for DNPH impinger solution.

We have considered this issue and determined that it is appropriate to include options for sampling formaldehyde in air streams that are comparable to ambient air conditions, such as ventilation exhaust systems. USEPA TO-5 specifies the use of DNPH solution. Where DNPH-coated silica tubes or cartridges are proposed, a method that specifically allows for their use should be employed. We have therefore included in Table 3 of the Approved Methods the following additional methods for the sampling and analysis of formaldehyde:

- USEPA (Compendium Method) TO-5
- NIOSH Method 2016
- USEPA Compendium Method TO-11A

These three methods are designed for use in ambient air environments and are not directly applicable to point-source sampling. As such, these methods may only be used where the source is predominantly composed of ambient air, and where dust, moisture and temperature are low. We have added a note to Table 3 of the Approved Methods document to clarify this.

Issues raised by stakeholders	EPA response
<p>OM-12 Isocyanates</p> <ul style="list-style-type: none"> The approved method listed for isocyanates is USEPA method 326, which is an isokinetic test method. Include a non-isokinetic method, VIC EPA Method 4210, for the determination of isocyanates (2,4 TDI, 2,6 TDI and MDI). Vic EPA Method 4210 comprises sampling emission source gas into ethanol (midjet impingers) with subsequent analysis by HPLC. The stakeholder notes that isocyanate monitoring is often required at foam manufacturing facilities where emission sources are mostly dust-free and a non-isokinetic option is desirable. The option of non-isokinetic testing opens up the possibility for conducting multiple tests simultaneously, which is often requested by licensees (e.g. for scrubber efficiency testing) because isokinetic equipment requires more testing staff and is more labour-intensive. 	<p>Method 4210 is no longer supported by VIC EPA and it is not listed in VIC EPA's <i>Guide to sampling and analysis of air emissions and air quality publication 440.1</i>. Copies of the method are no longer readily available.</p> <p>Isocyanates in air are challenging to sample and analyse because of their complexity and chemical properties. Isocyanates can exist in air as vapor, or as aerosols having a wide range of particle sizes. Isokinetic sampling is therefore recommended. USEPA conditional test method 36 has been included to provide greater sampling flexibility. However, this is an isokinetic sampling method.</p> <p>Some sources sampled in NSW are predominantly composed of cool, moisture-free air. Under such conditions, aerosols and particles are less likely to be present in significant concentrations. Non-isokinetic methods may be appropriate for sampling such sources if the methods are fit for the specific sampling application. Various non-isokinetic methods for monitoring workplace air quality have been developed and published by institutions including ASTM, OSHA and NIOSH: these could be adapted for stack-source sampling. See section 4 of the Approved Methods for air for guidance on the use of alternative or modified methods.</p>

Table 4 Section 4: Modifying methods or using alternative or unlisted methods

Issues raised by stakeholders	EPA response
<p>Situation 5 – methods where analyte not listed</p> <ul style="list-style-type: none"> The list of allowable organisations that publish recognised standards should include the: <ul style="list-style-type: none"> American Public Health Association (APHA) California Environmental Protection Agency Air Resources Board (CARB) American Society for Testing and Materials (ASTM). 	<p>We have added APHA, CARB and ASTM to the list of organisations that publish methods for situation 5 in section 4.2.</p>

Table 5 Section 5: Record-keeping

Issues raised by stakeholders	EPA response
<p>Limit of detection</p> <ul style="list-style-type: none"> Section 5.4 states that if an air impurity cannot be detected, results must be reported as less than the method's limits of detection (LOD), not as zero. A stakeholder notes that LOD is rarely used, and that limit of reporting and PQL are the standard detection limits. 	<p>We have changed the terminology in section 2 of the Approved Methods document to include limit of reporting (LOR) and practical quantification limit (PQL).</p>

Table 6 Ambient air monitoring guidance in NSW – guidance note

Issues raised by stakeholders	EPA response
<ul style="list-style-type: none"> Previously approved monitoring methods for ambient air monitoring should be recognised. The move to ISO accreditation may be onerous. 	<p>Ambient air monitoring is undertaken for various reasons, including compliance or management purposes. Methods should be selected according to individual site considerations and must be appropriate for the intended purpose of the monitoring, as outlined in the <i>Ambient air monitoring guidance in NSW</i> document.</p> <p>Where ambient air monitoring is specified in an environment protection licence (EPL), the monitoring method that must be used is typically specified.</p> <p>The EPA's <u>implementation and transitional arrangements</u> clarify that if</p> <ul style="list-style-type: none"> ambient air monitoring is required under an EPL <p>and</p> <ul style="list-style-type: none"> a specific method is listed in the EPL <p>then this method must continue to be used. A licensee may seek approval to use an alternative method by applying to vary the licence.</p> <p>Ambient air monitoring methods, previously listed in the Approved Methods as AM codified methods, remain valid. They can now be found on the EPA website, via the webpage on <u>Approved Methods for air</u>.</p> <p>Where a specific method is already approved via an existing EPL condition or PRP or similar, there is no requirement to seek another approval.</p> <p>Where monitoring is undertaken for management purposes, the licensee should select monitoring options that are fit for purpose and suitably time-resolved to ensure the data collected can be used in an effective and responsive manner. When choosing a monitoring method, consider the broader air-quality management strategy for the site.</p> <p>Accreditation</p> <p>The EPA's recommended use of accredited testing facilities remains consistent with section 3 of the current (2007) Approved Methods for air. However, we allow for some flexibility in this requirement in the ambient air monitoring guidance as indicated by using the term 'should' rather than 'shall'.</p> <p>We expect that, where monitoring is undertaken for demonstrating compliance with a statutory instrument, an appropriate level of quality control and quality assurance will be applied to ensure the integrity and accuracy of the data. Using an accredited service provider will give greater confidence in the data.</p> <p>The licensee is responsible for ensuring that sampling and analysis for statutory purposes is done using the methods prescribed in their environment protection licence (where the methods have been prescribed). When deciding whether to use an accredited facility, consider what the data is being used for, how complex the monitoring method is, and how competent the equipment owners/operators are at managing and maintaining the monitoring systems.</p>

References

Streicher RP, Reh CM, Key-Schwartz RJ, Schlecht PC, Cassinelli ME, O'Connor PF (2000). *Determination of airborne isocyanate exposure: considerations in method selection*.

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