

# Approved methods for the sampling and analysis of water 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:

- 3 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 water.

Table 1 Overall

Issues raised by stakeholders	EPA response
<p><b>Emerging contaminants</b></p> <ul style="list-style-type: none"> <li>How will the EPA deal with emerging contaminants?</li> <li>Mentioned anti-depressant pharmaceutical compounds found in sewage influents/effluents.</li> </ul>	<p>Managing emerging contaminants is a strategic priority for the NSW EPA. As the potential list of chemicals is uncertain, the EPA will amend the approved methods or environment protection licences, or guide any licensee seeking approval of a method, when any pollutants are directly regulated and monitoring is required.</p>
<p><b>Asbestos in water</b></p> <ul style="list-style-type: none"> <li>The document should include a method for sampling and analysis of asbestos in water.</li> <li>USEPA 100.1 and 100.2 were suggested as methods for this.</li> </ul>	<p>The EPA does not routinely require monitoring of asbestos in water discharges because facilities that might have a risk of asbestos-contaminated water would not generally be permitted to discharge and must contain, treat and dispose. We note the advice on standard methods suitable for sampling and analysis of asbestos in water and we are also aware that there is currently no lab accredited to use these methods in Australia. If sampling and analysis of asbestos is required, we will amend the approved methods or environment protection licences, or guide any licensee seeking approval of a method under situation 5 in section 4.2 of the document.</p>

Table 2 Section 2: Sample collection and handling

Issues raised by stakeholders	EPA response
<p><b>AS/NZS 5667.1:1998</b></p> <ul style="list-style-type: none"> <li>There is a more up-to-date version based on ISO 5667.3 2012.</li> </ul>	<p>AS/NZ5667.1 was originally published in 1998 but was reconfirmed by Standards Australia in 2016, and is still the current, active standard used in Australia. No change made.</p>
<p><b>Passive samplers</b></p> <ul style="list-style-type: none"> <li>Passive samplers have not been included.</li> </ul> <p>Passive samplers are becoming a more robust method for time-integrated sampling. Importantly, they can lower analytical limits of detection.</p>	<p>Passive samplers are not typically used for the type of monitoring carried out for regulatory purposes. If passive sampling is the appropriate method for a particular situation, the EPA will amend the approved methods or environment protection licences, or guide any licensee seeking approval of a method under situation 5 in section 4.2 of the document.</p>
<p><b>Storing and transporting (section 2.1)</b></p> <ul style="list-style-type: none"> <li>Samples should be submitted to laboratories with sufficient time remaining to complete analysis within the holding time specified in the relevant standard e.g. samples should arrive at the lab with at least half of the holding time remaining.</li> </ul>	<p>We agree with the main comment. We've amended point 3 of section 2.1 to clarify that samples are to be submitted with sufficient time remaining to complete the analysis. However, specifying the amount of time that should remain would be unduly restrictive and is not warranted.</p>

Issues raised by stakeholders	EPA response
<p><b>PFAS containers (section 2.2)</b></p> <ul style="list-style-type: none"> <li>• Polytetrafluoroethylene (PTFE) should not be used for PFAS.</li> <li>• There is some debate as to whether glass containers are in fact <b>not</b> suitable for PFAS analysis (as the document states). Certain long chain PFAS and more neutral species are known to be 'sticky' and/or striate (sit on surfaces because they have low water solubility). Therefore, it would be appropriate to state – unless there is evidence otherwise – that HDPE is the preferred medium for PFAS collection.</li> </ul>	<p>We agree. We've amended point 8 of section 2.1 to state that PTFE should not be used for PFAS. Also, we've removed from point 8 the statement regarding the use of glass containers with lined lids.</p>
<p><b>Storage temperature (section 2.3)</b></p> <ul style="list-style-type: none"> <li>• Clarify the requirements for sample storage temperatures, as there are differing requirements listed in different standards.</li> </ul>	<p>We've reviewed this and considered current practices of laboratories, and we've now amended the storage temperature requirement for chemical analysis in water to <math>4 \pm 2^{\circ}\text{C}</math>. This change takes into account the range of storage temperatures for water and soil samples published in different standards and guidelines (i.e. APHA<sup>1</sup> (<math>\leq 6^{\circ}\text{C}</math>), NEPM<sup>2</sup> (<math>\leq 6^{\circ}\text{C}</math>), AS/NZS 5667.1<sup>3</sup> (<math>1-4^{\circ}\text{C}</math>) and ISO 5667.3<sup>4</sup> (<math>1-5^{\circ}\text{C}</math>)).</p>

**Table 3 Section 3: Sampling and analysis methods**

Issues raised by stakeholders	EPA response
<p><b>Latest published version of the method</b></p> <ul style="list-style-type: none"> <li>• The process for validating and seeking NATA accreditation for new, updated methods can take 6–12 months, and this time frame needs to be taken into account.</li> </ul>	<p>The document currently requires the latest published version of the approved method to be used as soon as practical after publication, taking into account any transitional period associated with the updated method. We acknowledge that time frames to update methods and seek accreditation can vary, and consider this requirement is sufficiently flexible and not unduly constraining. No change made.</p>

<sup>1</sup> *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association (APHA), current version)

<sup>2</sup> National Environment Protection (Assessment of Site Contamination) Measure 1999, Volume 4, Schedule B3

<sup>3</sup> Australian/New Zealand Standard (AS/NZS) 5667.1:1998 *Water quality: sampling part 1 – guidance on the design of sampling programs, sampling techniques and the preservation and handling of samples*

<sup>4</sup> ISO 5667.3

Issues raised by stakeholders	EPA response
<p><b>Aluminium</b></p> <ul style="list-style-type: none"> <li>One of the methods listed for Aluminium, APHA 3500-AI, is an old method that is probably obsolete, and is relatively inaccurate compared to the 'gold standard' method of ICP-MS (APHA 3125, USEPA 6020 and 200.8).</li> </ul>	<p>The methods APHA 3125, USEPA 6020 and 200.8 are already listed in the Table 1 of the Approved Methods under 'Metals (acid extractable)' for the preliminary treatment required for aluminium. APHA 3500-AI is included because it is still a current standard method listed in the <i>Standard Methods for the Examination of Water and Wastewater</i> by APHA. No change made.</p>
<p><b>Amitrole</b></p> <ul style="list-style-type: none"> <li>There is a viable method for sampling and analysing amitrole using in-house methodology via LC-MSMS.</li> </ul>	<p>Amitrole is listed in Table 1 of the Approved Methods, but there is no standard method available. We've reviewed this situation and determined that, where there is no standard method listed, the use of in-house methodology is acceptable if the laboratory holds current ISO/IEC 17025 accreditation for analysing amitrole in the relevant matrix. A new situation (situation 6) has been added to section 4.2 to give guidance for where there is no standard method listed. EPA approval will not be required in this circumstance. This situation also applies to metsulfuron-methyl.</p>
<p><b>Arsenic III (arsenite) and arsenic V (arsenate)</b></p> <ul style="list-style-type: none"> <li>While the listed method for these analytes (USEPA 1632) may still be used in some labs, the use of LC coupled to ICP-MS is a far superior method and is used by many labs that are accredited to use this technique.</li> </ul>	<p>While USEPA 1632 is very old, it is still the current standard method for these analytes. We acknowledge that technology has rapidly advanced and labs are using new technology where the underlying chemistry of the analysis differs from the standard method. We consider this to be a special case, one in which we should be informed and certain documents provided. We have amended section 4.5.2 (by adding a new section 4.5.2.1) so that these type of applications will not need approval, only a statement setting out</p> <ul style="list-style-type: none"> <li>why this method is being used</li> <li>the purpose and intended use</li> </ul> <p>and accreditation documents that show the performance of the alternative method.</p>
<p><b>Biochemical oxygen demand (5-day)</b></p> <ul style="list-style-type: none"> <li>APHA 5210D should also be included because it is a commonly used standard method for this analyte.</li> </ul>	<p>We agree that APHA 5210D is a suitable method for this analyte and have included it in the table.</p>
<p><b>Chromium (trivalent)</b></p> <ul style="list-style-type: none"> <li>The <b>Cr (acid extractable)</b> term in the equation should be <b>Cr (filterable)</b> as the test is carried out on the filtered liquid phase only (particulate excluded as this can bias the results).</li> </ul>	<p>For measuring environmental pollution, we typically require monitoring of the total Cr (trivalent), not dissolved Cr (trivalent). No change is needed.</p>
<p><b>Formaldehyde</b></p> <ul style="list-style-type: none"> <li>More modern instruments, such as LC-MSMS, are being used rather than the HPLC-UV-Vis used in the listed standard method, USEPA 8315. LC-MSMS should not be excluded as a viable method where a laboratory is accredited to use it.</li> </ul>	<p>This is a similar situation to that discussed above for arsenic III: the standard method is old, and there are newer techniques in use where the underlying chemistry of the analysis differs from that of the standard method. EPA approval is not required however the EPA should be informed and certain documents must be provided as outlined in Section 4.5.2.1..</p>

Issues raised by stakeholders	EPA response
<p><b>Glyphosate</b></p> <ul style="list-style-type: none"> <li>A similar comment to the one made for formaldehyde was made for glyphosate.</li> <li>ISO 16308 is an additional standard method.</li> </ul>	<p>We agree with the additional standard and have added it to the table. The use of LC-MSMS instead of LC-MS is considered a minor modification because the underlying chemistry is the same as for the standard method. We've amended section 4.3 to clarify this.</p>
<p><b>Iron (acid extractable)</b></p> <ul style="list-style-type: none"> <li>Ferrous iron (<math>\text{Fe}^{2+}</math>) determination is missing from the table.</li> </ul>	<p>Ferrous iron is not an analyte that is typically of interest for environment protection purposes. If <math>\text{Fe}^{2+}</math> is required to be sampled and analysed, the EPA will amend the approved methods or environment protection licences, or guide any licensee seeking approval of a method under situation 5 in section 4.2 of the document.</p>
<p><b>Methane</b></p> <ul style="list-style-type: none"> <li>USEPA draft SOP RSK175 should be included as a method for dissolved methane analysis. This is an accredited (ISO 17025) method using GC-FID.</li> </ul>	<p>USEPA draft SOP RSK175 is not an official USEPA-approved method. The document has not yet been peer reviewed. No change.</p>
<p><b>Metsulfuron-methyl</b></p> <ul style="list-style-type: none"> <li>There is a viable method for sampling and analysing metsulfuron-methyl using in-house methodology via LC-MSMS.</li> </ul>	<p>As for amitrole above. A new situation (situation 6) has been added to the document for analytes where there is no standard method listed. The use of in-house methodology is acceptable if the laboratory holds current ISO/IEC 17025 accreditation for analysing amitrole in the relevant matrix.</p>
<p><b>Nitrite (<math>\text{NO}_2^-</math>) and nitrate (<math>\text{NO}_3^-</math>)</b></p> <ul style="list-style-type: none"> <li>The table should include the colourimetric method using <math>\text{V(III)Cl}_3</math> as the reductant.</li> </ul>	<p>The use of <math>\text{V(III)Cl}_3</math> as the reductant does not change the reduction process from nitrate to nitrite (i.e. the underlying chemistry still the same). Thus, the use of <math>\text{V(III)Cl}_3</math> is considered to be a minor modification and does not require approval. We've amended section 4.3 to clarify this.</p>
<p><b>Total nitrogen</b></p> <ul style="list-style-type: none"> <li>The method using combustion chemiluminescence determination is appropriate here.</li> </ul>	<p>We agree that the ISO 17025-accredited ASTM D5176- <i>Determination of total nitrogen by pyrolysis and chemiluminescence determination</i> is a suitable standard method for total nitrogen. We've added it to the list of standard methods for this analyte.</p>

Issues raised by stakeholders	EPA response
<p><b>PFAS</b></p> <ul style="list-style-type: none"> <li>• Not all PFAS compounds are listed in the table.</li> <li>• USEPA method 537.1 replaces USEPA method 537.</li> <li>• No laboratories in Australia are accredited to use the methods listed (USEPA 533 and 537). USEPA is lagging behind in the analyte list and the SPE phase. (WAX is used by &gt;99% of labs, as opposed to DVB.)</li> <li>• Most Australian labs have signed up to follow the US Department of Defence (DoD)/Department of Energy (DOE) QSM 5.3 Table B-15 for all water matrices.</li> </ul>	<p>We've reviewed the analytes and methods listed in light of Australia's <i>PFAS National Environmental Management Plan Version 2 (NEMP)</i><sup>5</sup>. The Approved Methods should reflect the national approach for PFAS analysis.</p> <p>USEPA methods 537 and 537.1 are listed in section 19 of the PFAS NEMP, along with other standard methods. There are laboratories in Australia that have developed in-house methods based on USEPA 537 or USEPA 537.1 and which are accredited by NATA. An in-house method that is based on a USEPA-approved method, and which holds ISO/IEC 17025 accreditation, will fall under 'minor modification' and hence not require EPA approval (situation 2, section 4.2).</p> <p>The suggested DOD/DOE methods cover the quality parameters for PFAS analysis rather than being a standard method, so it's not appropriate to include them.</p> <p>Overall, we've amended the entry for PFAS so that it:</p> <ul style="list-style-type: none"> <li>• includes other PFAS analytes as specified in the PFAS NEMP</li> <li>• requires the use of the standard methods listed in the PFAS NEMP.</li> </ul>
<p><b>PAHs</b></p> <ul style="list-style-type: none"> <li>• Remove USEPA method 8100 (GC-FID) because its sensitivity and selectivity are inferior to that of other (default) methods such as 8270 GC-MS.</li> </ul>	<p>We've reviewed this and agree. We've removed USEPA method 8100.</p>
<p><b>Quaternary salts</b></p> <ul style="list-style-type: none"> <li>• A similar issue to the issue raised for formaldehyde and arsenic is raised here. The standard method listed, in this case USEPA 549.2, uses HPCL with a UV-Vis detector, but LC-MSMS is a more commonly used method that provides more selectivity and specificity.</li> </ul>	<p>This situation is the same as that for formaldehyde and arsenic III: the current standard method is old, and labs are using better, newer technology where the underlying chemistry of the analysis is different to that of the standard method. This is a special case. EPA approval is not required however the EPA should be informed and certain documents must be provided as outlined in Section 4.5.2.1.</p>
<p><b>Total dissolved solids</b></p> <ul style="list-style-type: none"> <li>• Include an equation for estimating total dissolved solids from electrical conductivity.</li> </ul>	<p>The Approved Methods is focused on the actual sampling and analysis of analytes and so it's not appropriate to include estimation techniques. No change.</p>

<sup>5</sup> *PFAS National Environmental Management Plan Version 2.0*, Heads of EPA Australia and New Zealand 2020

Issues raised by stakeholders	EPA response
<p><b>Total petroleum hydrocarbons (TPH)</b></p> <ul style="list-style-type: none"> <li>TPH is old terminology and is misleading. TRH-Silica, used in the NEPM, is representative of the petrogenic (less polar) fraction of TRH.</li> </ul>	<p>According to the NEPM<sup>6</sup>, the term TRH is equivalent to the previously used term TPH. When silica gel is used for clean-up prior to sample analysis, the result is then reported as 'TPH-silica' or 'TRH-silica'. Thus, the use of the 'TPH/TRH' terminology used in the table is not misleading as it refers to the analysis without silica-gel clean-up. We've added a note to clarify that TPH and TRH are equivalent terms.</p>
<p><b>Total phenolics</b></p> <ul style="list-style-type: none"> <li>There are innovative new approaches such as on-line distillation followed by a colourimetric finish. (The listed APHA 5530D method describes the colourimetric finish.)</li> </ul>	<p>The distillation process is an additional step during sample preparation. Since the distillation process is followed by APHA 5530D, this is considered a minor modification of the method. We've amended section 4.3 to clarify that this is a minor modification.</p>
<p><b>Tributyltin</b></p> <ul style="list-style-type: none"> <li>ISO 17353 is a viable option and commonly used/validated approach.</li> </ul>	<p>We agree, and have included ISO 17353 as a suitable standard method for this analyte.</p>
<p><b>Uranium</b></p> <ul style="list-style-type: none"> <li>Methods for uranium should be included because requirements for sampling and monitoring of uranium are in environment protection licences.</li> </ul>	<p>We agree, and have added uranium to the document in Table 1 under 'Metals (acid extractable)' and in Tables A1 and A2.</p>

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

Issues raised by stakeholders	EPA response
<p><b>Situation 5 – methods where analyte not listed</b></p> <ul style="list-style-type: none"> <li>The document should include methods from other key organisations such as <ul style="list-style-type: none"> <li>American Public Health Association (APHA)</li> <li>American Society for Testing and Materials (ASTM)</li> <li>country specific bodies.</li> </ul> </li> </ul>	<p>We agree. We've added APHA, ASTM and the European Committee for Standardization (CEN) to the list of organisations that publish methods for situation 5 in section 4.2.</p>

<sup>6</sup> National Environment Protection (Assessment of Site Contamination) Measure 1999, Volume 2, Schedule B1

### Use of modified methods for multiple clients

- The approval to use a modified method should be applied to the laboratory so that it has approval to use the method for any client.

The current process allows a laboratory to seek approval directly from the EPA. If we approve the application, the approval remains in force for the period stipulated in the approval, or until such time as we revoke the approval in writing. If the method is to be used for more than 12 months, the analysing laboratory should work towards attaining accreditation from NATA (or equivalent) for the modified method.

### Minor modifications – section 4.3

- Would certain changes in process – for example
  - using an interface reduction technology
  - using LC-MSMS instead LC-MS
  - using on-line distillation processes followed by colourimetric analysis based on APHA 5530D
- require EPA approval?

We consider these types of changes to be minor, because they do not change the underlying chemistry and determinative technique of the approved method. As such, they would not require EPA approval. We've amended section 4.3 to clarify that these type of changes would constitute a minor modification.

### Limit of reporting (LoR) – section 4.3

- The 10% tolerance specified for LoR for a minor modification (point 6 of section 4.2) maybe optimistic.
- Approved methods generally do not have a defined LoR as this is developed through validation.

We agree. We've amended this point to clarify that a minor modification is one that:

- achieves a comparable LoR to the approved method and
- is within the relevant water guideline value.

### Approval group – section 4.5.2

- Which consultation group at the EPA would be responsible for approving any method modification approval requests? This group's contact details should be in the document.
- Give an example process and timeline for method approval.

Send any requests for method modifications to the EPA's Environment Line, by email to [info@epa.nsw.gov.au](mailto:info@epa.nsw.gov.au). We'll include information on how to seek a method modification in implementation material on the EPA website.

Table 5 Section 5: Record keeping

Issues raised by stakeholders	EPA response
<b>Record keeping</b> <ul style="list-style-type: none"><li>• The required record keeping should be covered by the facility's NATA accreditation.</li></ul>	The record keeping requirements in section 5 align with NATA's record keeping requirements. We've sought to align our requirements with good laboratory practice wherever possible.



**Table 6 Appendix 1: Alternative names for analytes**

Issues raised by stakeholders	EPA response
<p><b>Dissolved versus filterable – Table A1</b></p> <ul style="list-style-type: none"> <li>There are inconsistencies in the use of the terms ‘dissolved’ and ‘filterable’ – for example, filterable reactive phosphate and iron (dissolved).</li> <li>These terms should be standardised as ‘filterable’ and defined by filtration through a 0.45 µm filter (USEPA).</li> </ul>	<p>We consider that it is common usage and understanding that dissolved metals are operationally defined as those which pass through a 0.45 µm filter (USEPA). No change is needed.</p>
<p><b>Silica (acid extractable) – Table A1</b></p> <ul style="list-style-type: none"> <li>‘Digesting silica’ is misleading as many forms are insoluble. It should be listed as filterable reactive silica (colourimetric method APHA 4500-SiO<sub>2</sub>) or filtered silica (from Si using ICP-AES)</li> </ul>	<p>We acknowledge the complexity surrounding analysis methods for silica and note that silica is not routinely regulated as an environmental pollutant of concern. For these reasons, we’ve decided to remove both ‘silica (acid extractable)’ and ‘silica (dissolved)’ from Table 1. Should monitoring of silica be required, laboratories should use their discretion as to the most appropriate method to use and follow the requirements specified in situation 5 of section 4.2.</p>
<p><b>Atrazine – Table A2</b></p> <ul style="list-style-type: none"> <li>Atrazine is not an organophosphorus pesticide (OPP) because it does not contain phosphorus. It is a triazine.</li> </ul>	<p>We agree, but note that the same methods still apply. We’ve removed this analyte from the OPP grouping and included it as a separate entry in Table 1, with the same methods applying.</p>
<p><b>Pentachlorophenol</b></p> <ul style="list-style-type: none"> <li>This compound is not a phenoxy acid, just a phenol.</li> </ul>	<p>We agree, and have removed pentachlorophenol from the chlorinated phenoxy acid herbicide grouping.</p>

**Table 7 Appendix 3: Examples of minor modifications**

Issues raised by stakeholders	EPA response
<p><b>Point 12 – micro or midi distillation</b></p> <ul style="list-style-type: none"> <li>Diffusion methods should be included for matrix separation (cyanide species). Distillation methods can be prone to false positives (e.g. in the presence of SCN-species) and diffusion as a techniques in segmented flow analysis is much less prone to such effects.</li> </ul>	<p>The examples listed in Appendix 3 are based on 40 CFR 136.6<sup>7</sup> and are not exhaustive. Modification(s) can be considered minor if they satisfy the conditions in section 4.3. If not, such a change would fall under alternative methods addressed under situation 5 of section 4.2. No change.</p>
<p><b>Point 16 – purge-and-trap sample volumes</b></p> <ul style="list-style-type: none"> <li>Headspace analysis for VOCs should be included as a viable analysis technique e.g. ISO 20595:2018.</li> </ul>	<p>No change required. See response above for point 12.</p>

<sup>7</sup> USEPA, Code of Federal Regulations, Title 40, *Section 136.6 – Method modifications and analytical requirements, Washington DC.*

Table 8 Appendix 4: Essential QC requirements

Issues raised by stakeholders	EPA response
<p><b>Ongoing QC tests – 2nd dot point</b></p> <ul style="list-style-type: none"><li>Matrix spike duplicates are no longer used in Australia – that is, labs do not use this as a QC check.</li></ul>	<p>We've reviewed this section and updated the text to require QC samples to be run in every analytical batch to assess the ongoing method performance parameters. Such QC samples may include:</p> <ul style="list-style-type: none"><li>blanks</li><li>certified reference material</li><li>calibration verification standards</li><li>matrix spikes.</li></ul>

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