A GUIDE TO THE SAMPLING AND ANALYSIS OF WATERS, WASTEWATERS, SOILS AND WASTES

Environment Protection Authority
State Government of Victoria

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FOREWORD

To effectively reduce risks of environmental damage, a regular program of monitoring industrial and other activities should be undertaken in which wastes are characterised, and potentially contaminated land is audited. This responsible approach should be taken whether or not it is a statutory requirement.

This publication significantly expands on the previous edition of *A Guide to the Sampling and Analysis of Water and Wastewater* by including soils, other non-gaseous environmental samples and wastes.

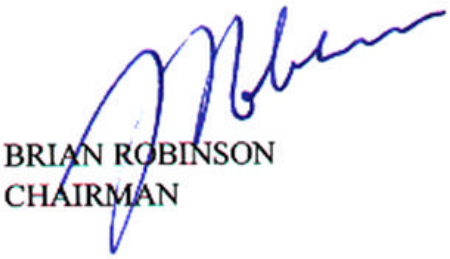
For quantified information, rigorous procedures, as outlined in this Guide, need to be followed to ensure that laboratory analysis accurately and reliably measures a pollutant or quality of the receiving environment.

Providing accurate and reliable measurements of environmental quality depends on a number of steps. Program and sampling design must have statistical rigour and ensure that representative samples are taken, with due consideration of the chemical behaviour and temporal and spatial distribution of the pollutant *in situ*. To maintain the integrity of the sample in the interval before it is analysed, most pollutants need to be preserved in some way to inhibit physical, chemical and biological transformations which can alter their concentration.

It is necessary for both the sampler and laboratory staff to work closely together, within the framework provided in this Guide. Any weak link between collection of the sample, its pre-treatment and storage, and the analysis, can jeopardise the integrity of the final result.

Laboratories need to establish a rigorous quality assurance system covering all their analytical procedures, as well as addressing field testing and sample collection.

This Guide establishes best practice procedures for collecting and analysing environmental samples. It should be used for statutory purposes under the *Environment Protection Act 1970*, and by any company or agency that wishes to obtain an accurate picture of the impact of its activities on the environment.



BRIAN ROBINSON
CHAIRMAN

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1. INTRODUCTION

Environmental samples are analysed for a range of purposes, such as to:

- determine ambient pollutant concentrations
- assess potential and known contaminated sites
- monitor effluents, trade wastes and process streams to manage performance
- identify the source and nature of accidental spills or pollution to assess their effects on the environment
- determine background levels of potential contaminants and pollutants, and
- meet statutory requirements of the *Environment Protection Act 1970* and the *Pollution of Waters by Oils and Noxious Substances Act 1986*.

The importance of obtaining representative samples, which faithfully represent a waste or element of the environment from which they are taken, cannot be underestimated. Whereas quality assurance* systems are well developed for laboratories, similar systems often do not encompass sample collection. Care needs to be taken in the field to ensure that samples are not contaminated during collection, and that the concentrations of analytical parameters of interest do not alter in the interval between collection and analysis.

Critical steps in any environmental monitoring program include, but are not limited to:

- determining the objectives of the monitoring program
- selecting chemical, physical or biological indicators which are relevant to the objectives of the monitoring program
- selecting the appropriate sampling equipment
- obtaining a representative sample or samples
- making and accurately recording site observations and measurements
- labelling, preserving, storing and transporting the sample correctly for analysis
- analysing the sample accurately and precisely for appropriate indicators
- reporting the result accurately and completely, and
- providing informed interpretation.

Good communication between the sampler and analyst is vital because they are mutually dependent on each other in order to produce a relevant and accurate output.

It is not possible to address all the issues that could arise in the field, and specialist advice may need to be called upon. Statisticians can provide useful advice on developing a sampling strategy to adequately represent a complex situation, while chemists, microbiologists or hydrogeologists may need to be consulted to advise on the behaviour of a pollutant in different elements of the environment.

This Guide aims to provide general direction on appropriate sampling, preservation, storage, and analytical and quality assurance procedures. It should be used for environmental monitoring programs, assessments, risk management, investigations and audits. The guidelines cover waters (including groundwaters), wastewaters, wastes and soils, but not biota. They must be used for analyses produced for the purposes of the *Environment Protection Act 1970* and the *Pollution of Waters by Oils and Noxious Substances Act 1986*, unless other procedures are approved by EPA.

This Guide is a companion publication to *A Guide to the Sampling and Analysis of Air Emissions* (EPA Publication 440).

* According to the International Standards Organisations (ISO), quality assurance is defined as: '...all those planned and systematic actions necessary to provide adequate confidence that a product, process or service will satisfy quality requirements.'

2. PLANNING A SAMPLING PROGRAM

Monitoring or assessment involves the collection of observations and measurements from the field for interpretation, in order to provide a reliable picture of the condition or state of a particular element of the environment.

There is no single methodology that is applicable for all monitoring and assessment needs. Therefore the design of a successful sampling strategy is dependent on firstly determining both the objectives of the program and the hypothesis to be tested. Wherever possible, an objective should be expressed as a statistically testable hypothesis.

In turn, the choice of indicators in most monitoring and assessment applications will be dictated by their capacity to reliably reflect an element of the environment to be monitored. Where characterisation or identification of pollutants is required, the choice of indicators will be dependent on the likelihood of their presence in the environment to be tested.

Any sampling program needs to be based on a good understanding of the spatial and temporal distribution of the indicator and its physico-chemical behaviour in the element of the environment being investigated. Statistical methodology should be employed to ensure that sampling locations and timing are representative of both indicator behaviour and the discharge or study area. Spatial and temporal representivity should be achieved.

Spatial representivity means that the whole study area is accurately characterised by a set of data. For elements of the environment where a pollutant's distribution is not homogeneous, a good understanding of the factors that affect this distribution will assist in developing a statistical basis for obtaining a representative picture. For example, the spatial distribution of a pollutant could be affected by spot spills onto soils. In the case of water bodies, understanding the vertical stratification in large water bodies, and the effects of mixing in flowing streams, may be important in characterising them.

Temporal representivity means that variations in time are accurately characterised by the sampling strategy selected. Examples of temporal variations include changes in industrial processes over a periodic cycle that affect effluent quality and, storm events where short term, peak concentrations of pollutants in stormwater enter natural waterways.

Composite sampling is a cost-effective means of representing study areas or flows that are heterogeneous in space or time, and is also useful as a screening tool. In composite sampling, collected samples are mixed to give an 'average' concentration. Great care needs to be taken to ensure that composites are not biased. However, if the objective of a program is to detect a 'hot spot', then composite sampling may be unsuitable because it dilutes polluted single samples, which could result in the 'hot spot' going undetected.

Some pollutants do not mix with the surrounding matrix. A good example is oil which floats on still water. If the objective is to quantify its concentration, it may prove difficult taking a representative volume of the water body. In such cases, the impact may be governed by the area covered, which needs to be estimated in the field. If, however, the objective is to characterise the nature of the oil, then skimming the oil off the water surface will suffice.

Sampling wastes stored in a drum or other storage container presents particular problems. It should not be assumed that the contents of the drum are homogeneous; the sampling strategy should take into account the nature and quantities of any distinct liquid or solid layers in the container.

In situ measurement provides a rapid and direct means of measuring certain qualities in the environment (see section 4). Where it provides relevant and reliable information, it should be used in preference to laboratory testing.

If a program objective requires pollutant loads to be calculated, accurate flow, volume or mass

measurement will be required at the sampling point.

There are also practical issues that need to be addressed in designing a sampling program. They are:

- access to the area and media being sampled;
- the availability of relevant and sufficiently sensitive analytical methods; and
- the distance from, and capacity of, the analytical laboratory.

The sampling design will need to ensure that the practicalities of on-site pre-treatment and preservation (where required) are in accordance with section 3 of this Guide.

The choice of analytical methods needs to be compatible with the sampling program design. The choice should be made in full understanding of what characteristic of, or component in, the sample needs to be measured to meet the objectives of the monitoring program.

Good design will assist in determining the limit of detection and precision required which will, in turn, determine the analytical method to be used. For example, ambient heavy metal concentrations in seawater will be in the part per billion range or lower, while determining heavy metals in polluted sludge will be many orders of magnitude higher. In some instances inexpensive screening tests may be acceptable, while in other programs a high level of accuracy will be required. Methods to be used should be chosen from those presented in section 4 of this Guide.

PROGRAM DESIGN CHECKLIST

- ❑ **The key to good program design is to first determine the objectives of the sampling program and propose hypotheses to be tested.**
- ❑ **Collect background information, including:**
- **potential pollutants, their likely sources and transport mechanisms**
- **pollutant behaviour, fate and effects in the environment**
- **the beneficial uses of the receiving environment.**
- ❑ **Equipped with the program aim and background, a statistically rigorous testing program must be developed to meet the test hypotheses.**
- ❑ **Site locations, indicators, timing, frequency and analytical methods must be determined in accordance with the program objectives and hypotheses.**

3. SAMPLE COLLECTION AND TRANSPORT

The objective of sampling is to collect and present for analysis a sample that properly represents the element of the environment, waste or waste discharge of interest.

There are physical, chemical and biological processes that can affect the sample from the time it is collected to when it is analysed. To avoid or minimise the effect of these processes, it is necessary to use the appropriate sampling equipment, select the appropriate container and apply preservation methods in order to maintain the sample's integrity. Samples must also be analysed within stipulated holding time limits.

Care is required to avoid contamination of the sample during sampling, handling and transport to the laboratory.

Health and safety precautions

Safety precautions need to be taken when sampling in the field, and when handling contaminated samples and preservative chemicals. The characteristics and features of each site and sampling point need to be assessed to ensure the safety of the sampler.

The following precautions and warnings must be observed when sampling wastewaters, other wastes or heavily polluted soils, sludges or wastes that may contain harmful chemicals or bacteriological contaminants.

- Skin contact and inhalation of gases from the effluents and polluted samples must be avoided. Wearing disposable plastic gloves is advisable, and if necessary, wearing suitable protective clothing.
- For sewage effluents, hands should be washed with bactericidal soap after sampling such effluent.
- If accidental contact occurs, then rinse the exposed area thoroughly and seek medical advice. If regularly sampling or handling effluents containing sewage, appropriate inoculations should be obtained.
- For hazardous or heavily contaminated samples, the sample label should bear a warning to the analyst.
- Where necessary, designated sampling points, such as a suitable stable platform should be provided. Locations should be readily accessible, and where necessary, safety rails or roping points to which safety harnesses can be attached should be available. The sampler should be either accompanied by another person or make known their sampling location.
- When sampling wastes, care should be taken to avoid inhaling vapours that could be harmful. If necessary, appropriate respiratory protection should be worn by personnel trained in its use. Unless the ignition point of the contents or contaminants is known, precautions should be taken on the assumption that they are flammable.
- Cuts and skin abrasions should be covered with waterproof dressings.
- A suitable change of clothing should be worn during work.
- Eye protection should be used when there is a risk of material entering the eye.
- If dusts or aerosols are considered a problem then masks, conforming to Australian Standard AS 1715 (Standards Australia 1994), should be worn to prevent inhalation. Where possible, work upwind of the application process.

The degree of precaution taken and the type of protective equipment and clothing used should be commensurate with the level of risk. When in doubt, assume the worst case outcome will occur.

When preserving samples in the field, the following precautions should be observed:

- Familiarise yourself with the safety precautions relevant to the preservative(s) to be used.
- The preservation of samples should be performed on a stable surface such as the lid of a portable cooler or a paved surface in order to minimise the chances of spillage.
- Avoid contact with acids, solvents and other preservatives by wearing disposable plastic gloves and safety glasses and by avoiding the inhalation of vapours.
- Addition of acid preservative may release toxic gases such as hydrogen sulphide and hydrogen cyanide. This should always be done in a well-ventilated area, and with due care. After the acid has been added to the sample, time should be allowed for all evolved gas to be vented before placing the lid on the container.

Sampling devices

Sampling devices should be constructed of materials that have minimum interaction with, and do not contaminate, the sample. They should be designed in such a way as to minimise disturbance to the sample.

Sampling devices need to be cleaned appropriately, using the same approach used for sampling containers, as recommended elsewhere in this Guide. Sampling devices should be well cleaned between samples[*], particularly when heavy contamination is suspected. In some cases, it may be necessary to collect the final rinsate for analysis, in order to demonstrate that the sampling device has been sufficiently well cleaned. Wherever possible, when sampling waters and wastewaters rinse the container with some of the material to be sampled.

It is not always possible to collect a liquid sample directly into a sample container. Where access is difficult, a scoop or bucket may be used. When a bucket is used, care must be taken to ensure the contents of the bucket remain well mixed while sub-samples are withdrawn. For deep waters, wastewaters and groundwaters, a special sampling device (for example, automatic samplers, Van Dorn bottle) may be needed to collect the sample, which is then transferred into the sample container.

[*] When this involves the use of detergents or solvents, the cleaning liquid should be collected and disposed of appropriately.

Sample containers

Selecting a sample container

Containers are usually glass, polyethylene or polypropylene, and are selected based on their lack of interaction with analytical parameters. For example, glass is suitable for samples containing trace organics as leaching and adsorption are minimal. However, glass is unsuitable for sampling most trace inorganics because active sites on its surface are capable of binding inorganic ions. For some analytical parameters, fluoropolymer (PTFE) lid liners should be used.

Washing sample containers

To avoid contamination, sample containers need to be specially washed and pre-treated. Suitable containers and special instructions on washing these containers are presented in Appendix A for waters, wastewaters and groundwaters, Appendix B for soils and Appendix C for wastes. Even new containers should be washed and dried, unless specifically not recommended in this Guide.

Containers should only be washed and rinsed with high-grade reagents and solvents. These may need to be retained and submitted to the laboratory for analysis as a blank. Where reagents are added during the preservation step, a sample of the added reagents must be submitted to the laboratory for analysis as a reagent blank.

For waters, wastewaters and groundwaters, rinsing the sampling container with the sample is usually advisable. This minimises any contamination of the container that may have

occurred between washing and sampling. Do not follow this procedure when:

- the analytical parameters are associated with immiscible liquids or suspended particles that will adhere to the sides of the container and may result in higher concentrations in the sample
- sampling for bacterial or other microbiological pollutants, because it is essential that the sterility of the container is maintained before use and the removal of any de-chlorinating agent must be prevented
- containers already contain preservatives (for example solvent or acid).

In the case of waters, wastewaters and wastes, it is occasionally appropriate to overfill containers, particularly when the analytical parameter is potentially oxidisable. For requirements for specific analytical parameters see Appendices B and D.

Sampling waters

Sampling and analysis plans should be devised in accordance with the requirements of Australian Standard 5667.1-12 (Standards Australia 1998a).

Where very low ambient concentrations are expected, special precautions may need to be taken to ensure samples are not contaminated. The integrity of samples must be maintained during sampling, and sources of contamination should be avoided.

Precautions for avoiding or minimising contamination are suggested below.

- Never handle the insides of containers, lids and collection vessels.
- Where preservative is required for the sample, do not allow the device used to add the preservative to make contact with the inside of the container or sample.
- Isolate buffer solutions and preservatives that could cross-contaminate samples. For example, buffer solutions can cross-contaminate water samples being collected for phosphorus analysis.
- Sample containers and chemical preservatives may need to be specially prepared and purified to ensure no cross-contamination occurs. Specialist laboratories have clean rooms to handle the analysis of such samples.

When sampling for volatile species, care should be taken to avoid losses. The sample vial or bottle should be filled gently to reduce agitation that might drive off volatile compounds. Cool the sample immediately on ice for transportation to the analysing laboratory.

Sampling surface waters

When waters are well mixed, a sample taken 100 mm below the surface, well away from the edge, may be adequate. However, deep and stratified waters may require special devices (such as a Van Dorn sampler) and careful handling techniques if the chemical species of interest is unstable. A hand or power-driven pump with an extended inlet tube may be useful to draw water from selected depths.

When sampling shallow waters, contamination of the sample from disturbed sediment should be avoided by using an extended inlet of thin tube on the sample bottle and drawing water into the bottle by suction.

To collect a sample of the surface layer for analysis, the container should be held horizontally in the water, half submerging it. To collect a sample of the water beneath a surface layer, a syringe or other device with an extended inlet tube capable of piercing the surface layer, may be appropriate, depending on the thickness of the surface layer.

In all cases, ensure that the sampling device or method does not contaminate the sample.

Sampling groundwaters

Regular testing of groundwater quality is usually done from bores. Monitoring bores should be constructed in accordance with the guidelines of the Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ 1997).

Groundwater sampling should be undertaken in accordance with *Groundwater Sampling Guidelines* (EPA 2000).

Sampling groundwaters by pumping or bailing the sample to the surface requires special precautions to avoid contamination. All equipment that either enters a bore or carries the water from the bore to the sampling container should be cleaned before each sample is taken. Special care needs to be taken for certain analytical parameters that can be affected by the presence of dissolved gases.

Sampling a waste discharge

The most representative sample of a waste discharge is from a point where the effluent is thoroughly mixed and close to the outlet from the discharging premises. For a licensed discharge, a sampling point will normally be described in the licence, and samples must always be taken from that point.

Use of automatic samplers

Automatic samplers are used to monitor diurnal variations or to collect temporal composite samples from a water body. The probe for these samplers should be placed sufficiently far from both the surface and bottom of the water body so that the sample is not affected by the presence of the air/water or sediment/water interface.

Sampling soils

Sampling and analysis plans should be devised in accordance with the requirements of the *Australian and New Zealand Guidelines for the Assessment of Contaminated Sites* (ANZECC/NH&MRC 1992) and Australian Standard 4482.1 (Standards Australia 1997a) or Australian Standard 4482.2 (Standards Australia 1999). When sampling soils for volatile contaminants, special precautions should be taken to prevent evaporative losses.

Collection of samples should be accomplished with minimal disturbance, using a coring device. The core soil sample should either be immersed into methanol in the field; or the core should be placed into a vial that will also act as a purge vessel in the laboratory. These methods have been shown to provide generally more accurate results than placement of samples into jars (USEPA 1991).

If the soils to be sampled are suspected of being acid sulfate soils or potential acid sulfate soils, the EPA Information Bulletin *Acid Sulfate Soil and Rock* (EPA 1999) provides guidance and further references on sampling and handling.

When sampling from a test pit, samples should be taken from the lowest point first to prevent cross contamination from other sampling points.

Before sampling, vegetation and other non-soil material (including rocks and concrete) should be removed by hand. Any material removed should be weighed and its description recorded.

Sampling sediments

The best locations for sampling sediments are where fine materials accumulate. These are generally confined to areas where there is little or no flow.

Sediment samples can be collected using a number of devices including grabs, scoops, corers, shovels and buckets. When sampling for organic analysis, sampling devices should be constructed from metal. Conversely, when sampling for metals, sampling devices should be constructed from plastic.

Where there is a lack of fine sediment, more than one scoop or grab sample may be necessary to obtain a sufficient amount of material. These samples should be combined and mixed well before processing for analysis.

Sampling wastes

At all times it is important that sampling is carried out so that representative samples are obtained. Sampling wastes can be difficult if the wastes are heterogeneous, contain many different types of waste, or the contamination is not evenly distributed. In these circumstances, it can be useful to keep different types of waste separate (for example by separating the phases in a multi-phase waste), or to separate different portions that contain high levels of contaminants. General guidance on sampling can be obtained from *Pierre Gy's Sampling Theory and Sampling Practice: Heterogeneity, Sample Correctness and Statistical Process Control* (Pitard, 1989) particularly when there are large amounts of waste to be sampled.

Liquid wastes should be handled according to the methods for sampling waters described above. Waste soils should be treated according to the guidelines for soils above.

For solid wastes with particle sizes greater than soils, or non-uniform particle sizes, Australian Standard 1141.3:1996, (Standards Australia, 1996) may be relevant in some cases. Wastes containing biosolids should be handled and treated according to the procedures listed in Appendix C for the individual parameters by which the wastes are to be characterised.

Preserving samples

When biological, chemical or physical changes to the sample may occur between the time it is collected and when it is analysed, it must be either chemically or physically preserved to retard such processes.

Preservation methods vary greatly in their effectiveness and should only be employed when the sample cannot be analysed within a few hours of collection. Preservation should be carried out as soon as possible after sampling.

Recommended preservation methods for waters, wastewaters and groundwaters are given in Appendix A, for soils and sediments in Appendix B, and for wastes in Appendix C.

Freezing

Water and soil samples are best frozen in small amounts sufficient for the determination of one parameter. This procedure avoids repeated thawing and re-freezing if the total analysis is spread over a number of days. Quick freezing with dry ice is recommended.

For water, wastewater and groundwater samples provide sufficient air gap in the container to allow expansion of the liquid.

Thawed samples must be mixed and allowed to reach ambient temperature before any measurements or analysis.

Cooling

Samples that need to be cooled to between 1°C and 4°C should be placed in an insulated container or icebox containing a mixture of water and ice, and checked to ensure that some ice always remains. Alternatively, a maximum/minimum thermometer can be used in the icebox to check that the temperature remained within this range during transport to the laboratory.

Acidification

For water samples, acidification to below pH 2 is used to preserve most trace metals. This reduces precipitation and sorption losses to the container walls. A sample of the acid used, which should be of analytical grade and have low metal content, must be retained for analysis as a blank by the laboratory and correction of the analytical results for any analyte present. For groundwaters, acidification should only be applied to filtered samples.

Reagent addition

Reagents may be added to samples to chemically fix the analytical parameter. Reagents added should be of high grade, and blanks provided to the laboratory so that contamination levels can be checked.

When chemicals are added to a sample to preserve or fix an analytical parameter, it is important to separate procedures for sampling,

sample handling and analysis for each parameter, to minimise any risk of cross-contamination. For example, nitric acid used for container preparation and as a preservative for heavy metals analysis can contaminate samples to be analysed for nitrate. Similarly, copper sulfate used for preservation of phenols may contaminate samples for metals analysis.

For heavily contaminated samples, care needs to be taken when adding chemical preservatives that could release hazardous gases. For example, when adding acid to preserve a sample collected for a heavy metal analysis, care should be taken to ensure that the sample does not also contain high concentrations of cyanide which could result in release of hydrogen cyanide gas.

Solvent extraction

A solvent may, at times, be added to extract the analyte from its matrix. For analysis of organic pollutants such as hydrocarbons, PAHs and some pesticides, an initial on-site solvent extraction in the sample container may be necessary. Samples of the solvent and containers used should be submitted for analysis.

Field filtration

Filtration of water samples in the field may be required in the following circumstances.

- Where organic and inorganic contaminants adsorb onto suspended matter in water, wastewater and groundwater samples.
- Where the concentration of dissolved contaminants or the contaminants associated with suspended matter need to be determined.

Filtering should occur immediately after collection and the analysis conducted on the filtered liquid, the particles, or both.

Filtration can be undertaken under gravity or by applying vacuum or pump pressure.

Filters and filtering devices should be cleaned in a similar manner to sample containers, and care taken that contamination is not introduced in the field. Filters from the same batch as used in the field, and the filtering device should be provided to the laboratory so that blank levels can be determined. On-site (between sample) final rinses from filtration equipment should also be submitted to the laboratory as 'rinsate blanks' for analysis.

Preserving soil samples

Often soil samples are moist when collected. This moisture can accelerate microbial action, which can change the concentration of some contaminants. In these circumstances, it is recommended to store the soil at 4°C or below.

Labelling and logging

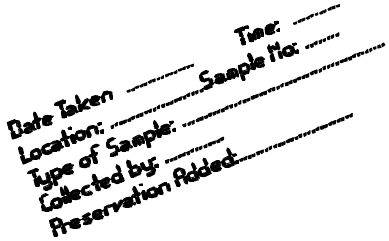
Samples should be adequately described and securely labelled at the sampling site.

The sample container must be labelled to uniquely identify the sample, and the time and location of sampling. Use a solvent based marking pen (preferably black) or similar waterproof means of marking. Any changes to a label should be initialled and dated.

The sample log must show all relevant information, including where (precise location and depth) and when (date and time of day) the sample was taken and other relevant information.

Details of preservatives added (the type, concentration before addition and quantity added) and other pre-treatment applied to the sample must be noted on the label.

An example of a label used for samples is shown below:



A submission sheet must accompany all samples when handed to the laboratory. This contains relevant information about the sample and the nature of the analyses required and is signed off by the person delivering the samples and the person receiving them.

Transporting samples

Transport of the sample to the laboratory should be done as soon as possible after sampling, and within the stipulated holding times (Appendices A, B and C).

Before and during transport, the following precautions must be taken to:

- check that container seals or caps are secured tightly to prevent leakage
- ensure sample labels remain on containers and are not damaged during transit
- store all bottles upright, and
- prevent containers from unnecessary movement during transport, and in particular ensure glass bottles are cushioned to prevent breakage.

When collecting and transporting samples, all possible sources of contamination must be avoided. A few examples are given below:

- vehicle exhausts (hydrocarbons or lead)
- airborne dusts
- ammonia solutions – including cleaning agents – must not be handled or stored in the vicinity of sampling or analytical operations
- smoking during sampling and analytical operations must be avoided –cigarette ash and smoke contain contaminants such as phosphate, nitrate, hydrocarbons, and heavy metals.

If there is concern that contamination has occurred, the sample and container should be discarded, and a fresh sample collected.

Approved samplers

Sampling requires special expertise and must be undertaken by trained people.

Whenever sampling or field analysis is undertaken, it must done within the framework of a well-documented quality system. This applies whether the analysing laboratory is also responsible for the sampling, whether a company monitoring its own wastes or wastewaters does it, or another organisation is contracted to conduct the sampling.

Preferably, sampling should be undertaken by people operating within a laboratory system accredited by the National Association of Testing Authorities (NATA) for sampling. Otherwise, people taking samples must meet the following requirements.

- Samplers must have undertaken face-to-face training by an appropriate body with experience in sampling, and be able to demonstrate that they have the knowledge and ability to safely take, preserve, store and transport samples within the requirements of this Guide. This would include programmed refresher training, with records to be kept on the nature and frequency of training provided.
- The laboratory conducting the analysis is to provide appropriately prepared sample containers and preservatives, for the analytes of interest.
- Sufficient records of the sampling are to be prepared and maintained by the samplers so that the results obtained by the laboratory can be related back to the date, time and location of sampling.

Evidence showing that the above requirements have been satisfied shall be documented.

SAMPLE HANDLING AND PREPARATION CHECKLIST

- ❑ **Ensure that there is good communication between sampling staff and the laboratory on precautions to be taken in the field.**
- ❑ **Observe all safety precautions during sampling, in particular taking care to avoid contact with contaminated samples.**
- ❑ **Ensure that the selection of sample containers, the container pre-treatment procedures (such as washing), the sample preservation procedures and the sample holding times stipulated in this Guide are followed.**
- ❑ **Ensure that, where reagents are added to the sample or the sample is filtered, blanks are collected and delivered to the laboratory for analysis of blanks.**
- ❑ **Take precautions to ensure samples are not contaminated by reagents, polluted samples or environmental sources in the field or during transport, and that samples are secured during transport to avoid damage.**
- ❑ **Complete the sample identification and description on a label attached to the sample and on the submission sheet, including any treatment of the sample undertaken in the field.**

4. ANALYTICAL METHODS AND QUALITY ASSURANCE PROCEDURES

Approved laboratories

Laboratories performing analyses should be accredited by NATA for all the tests conducted. In addition, the laboratory should be experienced and proficient at testing the types of samples, at the concentration ranges required, for the particular program.

Where testing is being undertaken for statutory purposes under the *Environment Protection Act 1970* or the *Pollution or Waters by Oils and Noxious Substances Act 1986*, NATA accreditation of the laboratory is a requirement, unless permission is given by EPA to use a non-accredited laboratory.

Approved analytical methods

Only analytical methods chosen from the approved references listed for each environmental matrix in this chapter should be used. Minor changes can be made to these methods, provided that the changes are of little consequence.

For all methods used, the laboratory needs to demonstrate that it can accurately analyse for the relevant analytes, in the types of environmental samples, and in the concentration range normally encountered. This can be done by either:

- proficiency tests, or
- checking against standard reference materials.

It is also necessary to determine the precision (both reproducibility and repeatability), selectivity, limits of detection, linearity and applicable range of concentrations when using the method.

Procedures that should be followed for method validation are available in *Requirements for the Format and Content of Test Methods and Recommended Procedures for the Validation of Chemical Test Methods* [NATA Technical Note No. 17] (NATA 1997).

For statutory testing, methods not based on any of the methods in the approved references can only be used with prior approval of EPA. Validation of the proposed procedure must be demonstrated before approval can be granted.

It is important that the analyst verifies the suitability of the procedure used for the particular sample type under investigation, before commencing the analysis.

Limits of detection and reporting

It is important that the limits of detection and reporting are reliably established before sampling and analysis are undertaken. A method for estimating the limit of detection and the limit of reporting (also known as the 'limit of quantitation') is provided in NATA Technical Note No. 17 (NATA 1997).

The limit of detection is defined as the lowest concentration of analytical parameter in a sample that can be detected, but not necessarily quantitated. The limit of reporting is defined as the lowest concentration of an analytical parameter that can be determined with acceptable precision and accuracy. In practice, the limit of reporting is frequently taken to be ten times the limit of detection (NATA, 1997). However, some laboratories may use limits of reporting that are five times the limit of detection (APHA 1995).

The selected methods should have appropriate detection limits for the objectives of the program. This is particularly relevant when testing ambient waters, as dissolved species are invariably at much lower concentrations than wastewaters. For instance the detection limit for lead using flame atomic absorption spectroscopy is 50 µg/L, whereas using graphite furnace atomic absorption spectroscopy it is 1 µg/L,

more suitable for pristine waters. Detection limits may also be affected by interferences.

Waters, wastewaters and groundwaters

For waters, wastewaters and groundwaters methods selected from the standard references listed below* should be used.

1. American Public Health Association 1995, *Standard Methods for the Examination of Water and Wastewater*.
2. US Environmental Protection Agency 1979, *Methods for Chemical Analysis of Water and Wastes*.
3. American Society for Testing and Materials 1992, *Water and Environmental Technology*.
4. US Environment Protection Agency 1978, *Microbiological Methods for Monitoring the Environment, Water and Wastes.*
5. Department of the Environment 1994, *The Bacteriological Examination of Drinking Water Supplies*, Report on Public Health and Medical Subjects, No. 71, Method for the Examination of Waters and Associated Material.
6. Relevant Australian Standards.

Trace analysis

For analysis at very low contractions (at µg/L and below) special precautions need to be taken.

Publications such as USEPA Method 1669 (USEPA 1995) should be referred to for the specifics of sampling at trace levels. For all trace level work, sample container cleanliness must be established before sampling is undertaken. Treating a statistically significant number of containers from any batch by the relevant extraction method and analysing the extract for the analytical parameters of interest should do this.

For guidance on the installation and use of clean rooms and clean workstations see Australian Standards 1386.1–7 (Standards Australia 1989).

Trace level analysis methods for seawaters can be obtained from either *Methods of Seawater Analysis* (Grasshoff 1983), *A Manual of Chemical and Biological Methods for Seawater Analysis* (Parsons 1989*)* or *A Practical Handbook of Seawater Analysis* (Strickland 1974).

During sampling of seawaters, extreme care should be taken to avoid contamination of the sample by the sampling equipment or boat. The publications listed should be consulted for guidance on choice of equipment and procedures.

In situ measurements

While most of the methods cited above relate to laboratory analyses, they also include field or *in situ* measurements for selected environmental indicators.

In situ measurement provides a rapid means to assess certain aspects of water quality. It has the advantage of overcoming the possibility of contamination or change in sample composition between collection and analysis.

Common *in situ* measurements include pH, temperature, turbidity, dissolved oxygen and conductivity. Some ions, such as fluoride and sulphide can also be determined using ion selective electrodes, although their determination can be subject to matrix interferences.

Ensure field instruments are robust and reliable, and that they are capable of measuring to the appropriate level of accuracy. They must be calibrated with fresh solutions before use. pH and dissolved oxygen meters need to be calibrated before every use. This can be performed either in the laboratory or in the field. The manufacturer's instructions are the best guide for the use of any particular meter; however, meters must be calibrated according to the NATA publications *General Requirements for Registration: Supplementary Requirements:*

* The latest editions of these references at the time of publishing this *Guide* are referenced. Where they are superseded, the most recent edition should be used.

Chemical Testing (NATA 1993) and Technical Note No. 19 (NATA 1994).

The meter must be calibrated over an appropriate range for the samples analysed. If the meter is to be used over a period of several hours, periodic readings of a reference solution must be made to ensure the calibration is stable. If excessive drift is observed, readings taken over the period of drift must be discarded.

While field meters are designed to take a certain level of harsh treatment (such as knocks, vibration, extreme temperature changes), good maintenance and calibration regimes ensure that they produce reliable and accurate data.

Secondary parameters such as temperature salinity, altitude and air pressure may affect certain field measurements. For instance, dissolved oxygen readings are affected by all of the above parameters. If the field meter does not automatically measure and compensate for the secondary parameter, then this parameter must be measured, using the appropriate equipment, and a manual compensation performed. The manufacturer's instructions should be consulted for correction factors.

Many factors may cause interference when taking field measurements. These interferences cannot be compensated for; in particular, oily films and high levels of suspended solids may cause problems. If the measurements are being taken in unusual situations, the manufacturer's instructions should be consulted to check whether interference could occur.

Where *in situ* measurements are incorporated into a process or effluent stream to provide continuous monitoring, adequate levels of data validation through frequent calibration checks are required. The manufacturer's instructions for the meter concerned should be consulted for the appropriate calibration method. Any calibration regime must be based on a sound knowledge of the process and the nature of the effluent stream. Guidance may be obtained from *Process Instruments and Controls Handbook* (Considine 1985).

Radioactivity measurements

Some of the references cited above include methods for the measurement of radioactivity. Other suitable methods for the measurement of gross radioactivity can be found in the international standards ISO 9696:1992 (ISO 1992a) and ISO 9697:1992 (ISO 1992b).

Soils and sediments

For the analysis of soils, *Guidelines for the Laboratory Analysis of Contaminated Soils* (ANZECC 1996) or *Test Methods for Evaluating Solid Wastes: Chemical/ Physical Methods* (USEPA 1997) should be followed. The procedures for quality control, described in the latter document, should also be followed.

For measuring radioactivity in soils, use the methods included in *Eastern Environmental Radiation Facility Radiation Procedures Manual* (Lieberman 1984).

For the analysis of acid sulfate soils or potential acid sulfate soils, EPA Information Bulletin *Acid Sulfate Soil and Rock* (EPA 1999) should be consulted.

Depending on the objectives of the program, it may be necessary to remove interstitial water from the sample by filtration. This may need to be done in the field if the contaminant equilibrium between the solid and liquid phases is dynamic.

As the nature of the soil or sediment can have a significant effect on the behaviour and environmental availability of contaminants, it is often desirable to characterise the soil type, including other relevant information such as pH, ion exchange capacity, clay content, moisture content and permeability

Determination of contaminants in soils and sediments may entail measurement of the total concentration. Alternatively, a bio-available or leachable fraction may be determined. Therefore, the digestion step is of paramount importance in determining the fraction of total contaminants present.

Often it is necessary to determine the permeability or hydraulic conductivity of a soil.

The test methods to be used will vary depending on the range of permeability values likely to be encountered and the purpose for which the measurements are being made. Test methods will, generally be applicable to either laboratory tests or field tests, but not both.

Relevant Codes of Practice, published as part of the EPA Best Practice Environmental Management Series*, contain details of tests to be used to determine soil permeability. For example, the requirements for testing soil percolation rates for septic tank installations are given in *Code of Practice-Septic Tanks* (EPA 1996).

In the absence of a relevant Code of Practice, ASTM Standard D5126–90 (ASTM, 1998) contains references to a number of field tests for soil permeability, and their applicable range of permeability values.

There are also American Society for Testing and Materials (ASTM) Standards (ASTM 1990) and Australian Standards (Standards Australia 1998b) which describe laboratory methods for testing soil permeability. There is some uncertainty about the applicability to field conditions of the results obtained from tests according to these methods. As such, these methods should be treated with some caution if field permeability is to be assessed.

In situ measurements

As for waters, a range of *in situ* measurements may be appropriate for characterising soils, for example, field soil gas measurements using a photo-ionisation analyser. Consult the section on *in situ* measurements above as similar requirements regarding use and calibration apply to waters and to soil samples.

* This series of publications is updated from time to time, and only the latest editions should be used.

Wastes

Procedures to determine total concentrations of a range of contaminants in wastes are listed in *Test Methods for Evaluating Solid Wastes. Chemical/ Physical Methods* (USEPA 1997).

There are a number of other characteristics of wastes that affect their environmental impact, and may need to be measured. They are leachability (the tendency for contaminants to be leached by rain or groundwater), flammability or ignitability, corrosivity and the amount of contained free liquids. Some of the suitable test methods are listed below.

Leachability and leachates

Leachable organics (volatile and semi-volatile), metals and anions (except cyanide) may be determined using the Toxicity Characteristic Leaching Procedure (TCLP), which is method 1311 in Test Methods for Evaluating Solid Wastes. Chemical/ Physical Methods (USEPA, 1997).

Alternatively, Australian Standard 4439.2 (Standards Australia 1997b) can be used for volatile organics, and Australian Standard 4439.3 (Standards Australia 1997c) can be used for semi-volatile organics, metals and anions.

The methods in the Australian Standards are different from the USEPA method in that a wider range of leaching reagents is allowed. All methods are designed to simulate leaching conditions in the environment to determine available pollutants. The choice of leach reagent should be based on the environmental conditions to which the wastes are, or will be, exposed .

Leachable cyanide may be determined by Method 1312, the Synthetic Precipitation Leaching Procedure (USEPA 1997) or by leaching with distilled or de-ionised water only, using the methods in Australian Standard 4439.2 (Standards Australia1997b).

Leachates collected from the environment should be analysed using the methods listed for waters and wastewaters.

Flammability and ignitability

Flammability of liquid wastes may be assessed by determining whether a flash occurs on application of a flame to sample vapours. A suitable procedure is described in ASTM Method D327–96 (ASTM 1992). 'Ignitability' is a characteristic of a waste that once ignited, burns. This characteristic can be measured using Method 1030 in *Test Methods for Evaluating Solid Wastes: Chemical/Physical Methods* (USEPA, 1997).

Corrosivity

'Corrosivity' is defined as the ability of a substance to attack human skin or plant and equipment. Often this is due to extreme acidity or alkalinity, and waste pH is normally tested. Liquid waste pH may be measured directly using a calibrated pH meter. The prescribed test for soils and solid wastes is Method 103 in *Guidelines for the Laboratory Analysis of Contaminated Soils* (ANZECC 1996). To measure corrosivity of a waste towards steel use Method 1110, 'Corrosivity Toward Steel' from *Test Methods for Evaluating Solid Wastes: Chemical/Physical Methods* (USEPA 1997).

Free liquid determination

To determine free liquid use Method 9095A: 'Paint Filter Liquids Test' in *Test Methods for Evaluating Solid Wastes. Chemical/Physical Methods* (USEPA 1997).

Volatile contaminants in soils and wastes

For determination of volatile contaminants in soils and wastes, special precautions must be taken to avoid losses during sampling, transport, storage and analysis.

As samples for volatile analysis cannot be taken from thoroughly homogenised bulk samples, small samples should not necessarily be regarded as representative of the whole material. Therefore, a sufficient number of samples should be taken to confidently obtain an accurate measure of average concentrations.

Samples taken for analysis of volatile components should be separate from those taken for other analytical parameters. This will allow for volatile analysis to be repeated, if necessary, on samples that have not been homogenised or otherwise inappropriately treated.

Volatile components should be determined using the 'purge and trap', procedure. Methods involving measurement of headspace concentrations may be less rigorous, and should only be used for screening soil samples. Use the methods outlined in *Test Methods for Evaluating Solid Wastes: Chemical/Physical Methods* (USEPA 1997) for both these procedures.

Qualitative analysis

Sometimes, it is necessary to identify components in a sample or confirm their presence prior to conducting a quantitative analysis. In such cases, a qualitative test may be used. Texts such as *Spot Tests In Organic Analysis* (Feigl and Anger 1966), *Spot Tests in Inorganic Analysis* (Feigl and Anger 1972) and *Vogel's Qualitative Inorganic Analysis* (Vogel 1996) are useful references.

Commercially available qualitative and semi-quantitative test kits may also be used. But, in either instance, the analyst must be familiar with the limitations of the method used, particularly possible interferences and what factors are likely to contribute to false positive or false negative results. Whenever qualitative tests are used, quality control should be incorporated, including a blank, at least one standard or reference material, and a spike of standard into a sample.

For solid materials that have a limited solubility, x-ray diffraction analysis (XRD) may provide useful information on the identity of compounds present in the sample. However, XRD does suffer from some limitations. Only crystalline substances will give an XRD response. Components representing less that 5% of the sample cannot be identified with any reliability. *Elements of X-ray Diffraction* (Cullity 1978) and *X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials*

(Klug and Alexander 1974) are useful references.

Toxicity screening testing

If contaminated samples require screening tests to give an indication of their likely toxicity, the Microtox® is the recommended technique. The use of this technique is described in EPA Scientific series publication SRS 89/012 (Hinwood 1990). Other toxicity screening tests may be used if approval is obtained from EPA.

Quality assurance

A laboratory quality assurance system is a requirement of NATA accreditation, and laboratories should seek to constantly assess their competence by participating, whenever possible, in inter-laboratory proficiency programs. Additional details on quality assurance and quality control are presented in Appendix D.

Analysts receiving samples need to assure themselves that they were collected in appropriate containers and they have been preserved in a manner recommended in this Guide. A statement should be included in the report on whether there have been any departures from the requirements outlined in this Guide.

TEST METHODS CHECKLIST

- ❑ **Select the appropriate method of analysis from those approved in this Guide.**
- ❑ **For field measurements, ensure that meters are calibrated beforehand.**
- ❑ **Ensure that an adequate Quality Assurance regime is in place in the laboratory and field procedures.**
- ❑ **Report analytical data on NATA-endorsed reports, where appropriate.**
- ❑ **Analysts should include a statement in their report that samples have been collected in a manner recommended in this Guide.**

5. REPORTING AND REVIEW OF RESULTS

Analytical reports

The final product of sampling and analysis, the analytical report, must have sufficient information for the end user to make a critical evaluation of its contents. The analytical report format should comply with the NATA requirements.

The following information is usually reported with the analytical result for each parameter determined. This information is either provided by the person taking the sample or by the laboratory and should include:

- identification of the sample (include sample description, location, sample number and unique laboratory number)
- date and time of sampling
- field observations and *in situ* measurements
- field pre-treatment details, if any sample preservation procedure
- reference to analytical method used.
- date of determination
- accurate description of the parameter
- results, in the appropriate units
- notations of any deviation from the sampling or analytical procedures recommended in this Guide.

Analysts should define the quality measured and ensure reporting meets the formats required in the standard method.

The limit of detection for each analyte should be quoted with quantitative test results. Concentrations below the limit of reporting should be quoted as a 'less than' (<) figure.

Results are normally reported as mg/L or µg/L for concentrations in solutions, mg/kg or µg/kg for concentrations in solids and organisms/100 mL for concentrations of bacterial organisms in liquids. For radioactivity measurements, the units are Bq/L for concentrations in solutions and Bq/g for concentrations in solids.

It is preferable to report results that are not corrected for spike recovery unless a test method specifically requires analytical results to be reported after correcting for recovery (NATA 1997). A statement of the spike recovery achieved provides the maximum information on the quality of the test result to the recipient of the report.

Reviewing data

All analytical results should be reviewed on receipt by the person or organisation requesting the analysis, and action taken if abnormal or unexpected levels are detected. When reviewing data:

- compare results with those expected and query unusual results
- as a general rule duplicates should agree within 10% and spike recovery values should be between 80–120%. (If quality control results fall outside of this range, query the laboratory)
- identify problems, and
- take appropriate action to address the problems identified.

If monitoring is being undertaken as a discharge licence condition, then whenever the licence emission limits are exceeded, the breach should be reported immediately to EPA, in accordance with the licence conditions. The reasons leading to the breach and action taken to ensure future licence compliance should be included in this report.

REPORTING CHECKLIST

- ❑ **Analytical reports should include all relevant information**
- ❑ **Analytical reports should include a statement that samples have been collected in accordance with procedures recommended by this Guide.**
- ❑ **Detection of abnormal or unexpected concentrations or polluted samples should be reported quickly so that action can be taken to address the problem.**

6. REFERENCES

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APPENDIX A: CONTAINERS, PRESERVATION AND HOLDING PERIODS FOR WATERS, GROUNDWATERS AND WASTEWATERS

Sample containers and their preparation

Selection and preparation of containers, sample pre-treatment, preservation and holding periods must comply with this Appendix, which is based, in part, on AS/NZS 5667.1:1998*. The third column lists typical volumes for a single determination, and should only be used as a guide. To determine very low concentrations that may be present in uncontaminated samples, larger volumes may be required. Typical volumes are dependent on the analytical method used, and the analyst should be consulted prior to sampling on his or her requirements. Unless otherwise stated, the requirements listed are those for quantitative determination. The analyst should always be consulted for advice on the actual sample volumes required when a choice of preservation methods exists in the Table.

Container types, preservation and maximum sample holding times

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Acidity and alkalinity	Polyethylene or borosilicate glass	500	Fill bottle to exclude air. Immediately store between 1°C and 4°C.	24 hours	Samples should preferably be analysed in the field, particularly if they contain high levels of dissolved gases.
Aluminium	Acid washed glass or acid washed polyethylene	500	Acidify with nitric acid to pH 1 to 2.	28 days	

* *EPA is grateful to Standards Australia for the permission to reproduce information presented in AS/NZS 5667.1:1998 on which this Table is, in part, based.*

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Ammonia	Polyethylene or glass	500	Store between 1°C and 4°C. Filter sample on site (0.45 µm cellulose acetate membrane filter) and store between 1°C and 4°C. Filter sample on site (0.45 µm cellulose acetate membrane filter) and freeze sample immediately upon collection.	6 hours 24 hours 28 days	When samples containing low levels of ammonia are encountered, special care should be taken to avoid contamination. Pressure filtering is preferred.
Antimony	Acid washed polyethylene or acid washed glass	500	Acidify with nitric or hydrochloric acid to pH 1 to 2.	28 days	Hydrochloric acid should be used for acidification if the hydride generation technique is used for analysis. Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Arsenic	Acid washed polyethylene	500	Acidify with nitric or hydrochloric acid to pH 1 to 2.	28 days	Hydrochloric acid should be used for acidification if the hydride generation technique is used for analysis. Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Barium	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	
Beryllium	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Biochemical oxygen demand (BOD) and Carbonaceous Biological Oxygen Demand (CBOD)	Plastic or glass	1000	Fill bottle to exclude air. Store between 1°C and 4°C in the dark.	24 hours	Do not pre-rinse container with sample. Glass containers should be used for samples with low BOD (<5 mg/L). Nitrification inhibition is not to be implemented when performing the BOD test unless carbonaceous biological oxygen demand (CBOD) is required.
Boron	Polyethylene	100	Fill bottle to exclude air.	28 days	
Bromate	Polyethylene or glass	100	Store between 1°C and 4°C.	7 days	
Bromide	Polyethylene or glass	500	Store between 1°C and 4°C in the dark.	28 days	
Bromine (residual)	Polyethylene or glass	500	Store between 1°C and 4°C in the dark.	24 hours	Samples should be kept out of direct sunlight.
Cadmium	Acid washed polyethylene	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Calcium	Polyethylene	500	Fill bottle to exclude air. Fill container completely to exclude air, acidify with nitric acid to pH 1 to 2 and store between 1°C and 4°C.	7 days 28 days	Samples of water of pH > 8 or high total carbonate, taken solely for the determination of calcium, magnesium or hardness should be acidified with nitric acid. Acidification permits the determination of calcium and the other metals in the sample.
Carbamates	Solvent washed amber glass	1000	Store between 1°C and 4°C.	28 days	Extract the sample in the container as part of the sample extraction procedure. If the sample is chlorinated, for each 1000 mL of sample, add 80 mg of sodium thiosulfate to the container prior to collection.

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Carbon dioxide	Polyethylene or glass	500	Fill container completely to exclude air. Store between 1°C and 4°C.	24 hours	Determination preferably carried out in the field.
Carbon, total organic (TOC)	Amber glass with PTFE cap liner	100	Acidify with sulphuric acid to pH 1 to 2, store between 1°C and 4°C in the dark.	7 days	
Chemical oxygen demand (COD)	Glass or polyethylene	100	Fill container completely to exclude air. Acidify with sulphuric acid to pH 1 to 2 and store between 1°C and 4°C in the dark. Freeze (only if polyethylene containers are used).	7 days 28 days	Glass containers are preferable for samples with low COD (<5 mg/L).
Chloramine	Polyethylene or glass	500	Keep sample out of direct sunlight.	Begin analysis within five minutes of sample collection.	Analysis should be carried out in the field.
Chlorate	Polyethylene or glass	500	Store between 1°C and 4°C.	7 days	
Chloride	Polyethylene or glass	100	None required.	28 days	
Chlorine (residual)	Polyethylene or glass	500	Keep sample out of direct sunlight.	Begin analysis within five minutes of sample collection.	Analysis should be carried out in the field.

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Chlorine dioxide	Polyethylene or glass	500	Keep sample out of direct sunlight.	Begin analysis within five minutes of sample collection.	Analysis should be carried out in the field.
Chlorite	Polyethylene or glass	500	Store between 1°C and 4°C.	24 hours	
Chlorophyll	Polyethylene or amber glass	Filter on site	Filter and snap freeze filter paper in the dark. Store in the dark between 1°C and 4°C.	28 days 24 hours	Samples should be filtered at the time of collection. The volume filtered will depend largely on the amount of particulate matter present and expected chlorophyll concentrations. Filters must not be touched with fingers and all sample handling apparatus must be kept free of acids, as this causes degradation of chlorophylls to phaeophytins. Filter and process promptly upon reception at the laboratory and ensure minimum exposure to light. Use polyethylene containers only when snap freezing sample filters.
Chromium (total)	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Chromium (VI)	Acid washed polyethylene or acid washed glass	500	Store between 1°C and 4°C.	24 hours	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater. Sample containers should be thoroughly rinsed after acid washing to ensure there is no residual nitric acid present.

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Cobalt	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Coliforms (total)	Polyethylene or glass, sterile and containing pre-sterilised sodium thiosulfate solution sufficient to give 100 mg/L in preserved sample	500	Store between 1°C and 4°C.	6 hours	Do not rinse container before taking sample. Leave approximately 2 cm head space. In exceptional circumstances, such as sampling in a remote location, a holding period of up to 24 hours is acceptable.
Colour	Polyethylene or glass	500	Store between 1°C and 4°C and in the dark.	48 hours	
Conductivity	Polyethylene or glass	100	Fill container completely to exclude air. None required. Fill container completely to exclude air. Store between 1°C and 4°C.	24 hours 28 days	Preferably on site or *in situ.* The meter must be calibrated prior to use.
Copper	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Cyanide	Polyethylene or glass	500	If no interfering compounds are present, then add sodium hydroxide solution to pH ≥ 12. Store between 1°C and 4°C in the dark.	24 hours	If hydrogen sulphide is present it can be removed by adding cadmium nitrate after adjusting the pH of the sample to pH ≥ 12. If oxidising agents are present, add ascorbic acid. Excess ascorbic acid has been added when a starch iodide paper fails to turn blue on contact with the sample.

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
E. coli	Plastic or glass, sterile and containing pre-sterilised sodium thiosulfate solution sufficient to give 100 mg/L in preserved sample	500	Store between 1°C and 4°C.	6 hours	Do not rinse container before taking sample. Leave approximately 2 cm head space. In exceptional circumstances, such as sampling in a remote location, a holding period of up to 24 hours is acceptable.
Fluoride	Polyethylene	500	None required.	28 days	
Hardness	Polyethylene	200	Fill bottle to exclude air. Immediately store between 1°C and 4°C or acidify with nitric acid to pH 1 to 2.	7 days	Water samples of high pH (pH > 8) or high total carbonate taken solely for the determination of hardness, calcium or magnesium should be acidified with nitric acid.
Herbicides (acidic)	Glass with PTFE cap liner	1000	Acidify with hydrochloric acid to pH 1 to 2 and store between 1°C and 4°C. Do not completely fill container.	14 days	If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.
Herbicides (non-acidic)	Amber glass with PTFE cap liner	1000	Store between 1°C and 4°C.	7 days	If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.
Herbicides (glyphosate)	Polypropylene	1000	Store between 1°C and 4°C in the dark.	14 days	If residual chlorine is present, add 80 mg of sodium thiosulfate per litre of sample.
Hydrazine	Glass	500	Acidify with 100 mL of concentrated hydrochloric acid for every litre of sample and store in the dark.	24 hours	

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Hydrocarbons,	Solvent rinsed glass with PTFE faced liner	500	Solvent extract on site with the appropriate solvent where practical.	Analyse as soon as possible but within 7 days	If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample. Store in an area free of solvent fumes.. For purge and trap analysis collect samples in duplicate in 40 mL vials with PFTE faced septum Store in an area free of solvent fumes.
		80	Fill container to completely exclude air and store between 1°C and 4°C.	Analyse as soon as possible but within 24 hours	
		80	Fill container to completely exclude air and acidify to pH 1 to 2 with hydrochloric acid and store between 1°C and 4°C.	Analyse as soon as possible but within 7 days	. .
Hydrocarbons (qualitative identification)	Solvent washed glass with PTFE cap liner	500	Do not completely fill container. Acidify with sulphuric or hydrochloric acid to pH 1-2. Store between 1°C and 4°C.	7 days	Do not pre-rinse container with sample. This procedure may also be suitable for unreactive hydrocarbon derivatives.
Hydrocarbons (halogenated)	Solvent rinsed glass with PTFE cap liner	250	Fill container to completely exclude air and acidify to pH 1 to 2 with hydrochloric acid and store between 1°C and 4°C.	Analyse as soon as possible but within 7 days	If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample. For purge and trap analysis collect samples in duplicate in 40 mL vials with PFTE faced septum Store in an area free of solvent fumes.
Iodide	Polyethylene or glass	500	Store between 1°C and 4°C.	28 days	
Iodine	Glass	500	Store between 1°C and 4°C in the dark.	24 hours	

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Iron (II)	Acid washed polyethylene or acid washed glass	500	Fill container completely to exclude air. Acidify with hydrochloric acid to pH 1 to 2.	24 hours	Do not use nitric acid to wash sample containers.
Iron (total)	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	
Lead	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Lignins and tannins	Glass	250	Store between 1°C and 4°C.	7 days	
Lithium	Polyethylene	500	None required.	28 days	If samples for lithium are also to be determined for other metals they can be acidified without effecting the analysis.
Magnesium	Polyethylene	500	Fill bottle to exclude air. Fill bottle to exclude air. Acidify with nitric acid to pH 1 to 2 and store between 1°C and 4°C.	7 days 28 days	Water samples of high pH (pH > 8) or high total carbonate taken solely for the determination of magnesium, calcium or hardness should be acidified with nitric acid.
Manganese	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater
Mercury	Acid washed borosilicate glass	500	Immediately acidify the unfiltered sample to pH <2 with nitric acid and add potassium dichromate to give 0.05% m/V final concentration.	28 days	For contaminated waters more oxidant may be required. Reference should be made to the analyst for further instruction. Acid washed fluoropolymer or borosilicate containers with a fluoropolymer lined lid should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Molybdenum	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater
Monocyclic aromatic hydrocarbons (MAHs)	Solvent rinsed glass with PTFE faced liner	500	Fill container to completely exclude air. Acidify to pH 1 to 2 with hydrochloric acid and store between 1°C and 4°C.	Analyse as soon as possible but within 7 days	If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample. Store in an area free of solvent fumes. For purge and trap analysis collect samples in duplicate in 40 mL vials with PFTE faced septum. If the sample is chlorinated, for each 40 mL of sample add 3 mg of sodium thiosulfate. Store in an area free of solvent fumes.
Nickel	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Nitrate	Polyethylene or glass	500	Store between 1°C and 4°C. Filter on site (0.45 µm cellulose acetate membrane filter) and freeze sample immediately upon collection.	24 hours 28 days	
Nitrite	Polyethylene or glass	200	None required. Freeze sample immediately upon collection.	Analyse in the field 48 hours	
Nitrogen (all forms)					See individual entries under Ammonia, Nitrogen (Kjeldahl), Nitrate and Nitrite.
Nitrogen (Kjeldahl)	Polyethylene or glass	500	Store between 1°C and 4°C. Freeze sample immediately upon collection.	24 hours 28 days	The sample may be acidified with sulphuric acid to pH <2 if required for other analyses.

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Nitrogen (total)	Polyethylene or glass	500	Store between 1°C and 4°C. Freeze sample immediately upon collection.	24 hours 28 days	
Odour	Polyethylene or glass	500	Store between 1°C and 4°C.	6 hours	
Organic carbon (total)					See Carbon, total organic (TOC)
Oxygen, dissolved (DO)	Polyethylene or glass	300	None required.	On site or *in situ*	Excessive turbulence should be avoided to minimise oxygen entrainment. The meter must be calibrated on the day of use and preferably checked after measurements.
Pesticides (carbamates)					See entry under Carbamates
Pesticides (nitrogen-containing, organo-chlorine and organo-phosphate)	Solvent washed glass with PTFE cap liner	1000 to 3000	Do not completely fill container. Store between 1°C and 4°C.	7 days	Solvent extract on-site with the appropriate solvent where practical. Extract the sample in the container as part of the sample extraction procedure. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.
pH	Polyethylene or borosilicate glass	100	None.	Determine *in situ*	The meter must be calibrated on the day of use and preferably checked after measurements.
Phenolic compounds	Solvent washed glass (amber) with PTFE cap liner	1000	Store between 1°C and 4°C in the dark. Do not completely fill sample container.	24 hours	Do not pre-rinse container with sample. Oxidising agents such as chlorine may be neutralised by the addition of excess sodium arsenite or iron (II) sulfate prior to acidification. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample. Sulphur dioxide or hydrogen sulphide may be removed by briefly aerating the acidified sample.

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
			Acidify to pH 1 to 2 with orthophosphoric acid, hydrochloric acid or sulphuric acid. Store between 1°C and 4°C and store in dark.	21 days	
Phosphate (ortho or dissolved)	Polyethylene or glass	50 to 300	Filter on site (0.45 µm cellulose acetate membrane filter). Store between 1°C and 4°C. Filter on site (0.45 µm cellulose acetate membrane filter) and freeze upon collection.	24 hours 28 days	

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Phosphate (total)	Polyethylene or glass	300	Store between 1°C and 4°C. Freeze immediately upon collection. Acidify with sulphuric or hydrochloric acid to pH 1 to 2 and store between 1°C and 4°C in the dark.	24 hours 28 days 28 days	The use of the acid preservation method should not be used for the persulfate oxidation method of analysis.
Polychlorinated biphenyls (PCBs)	Solvent washed glass with PTFE cap liner	1000 to 3000	Store between 1°C and 4°C in the dark. Do not completely fill sample container.	7 days	Do not pre-rinse container with sample. Extract on-site, where practical, in the container as part of the sample extraction procedure. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.
Polycyclic aromatic hydrocarbons (PAHs)	Solvent washed glass with PTFE cap liner	1000	Store between 1°C and 4°C in the dark. Do not completely fill sample container.	7 days	Do not pre-rinse container with sample. Extract on-site, where practical, in the container as part of the sample extraction procedure. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.
Potassium	Polyethylene	500	None required. Acidify with nitric acid to pH 1 to 2.	28 days 28 days	Acidification permits the determination other metals in the sample.
Radioactivity (specific forms)					See Table 2 in AS/NZS 5667.1:1998.
Radioactivity, α and β activity (gross)	Polyethylene or glass	1000	Acidify with nitric acid to pH 1 to 2. Fill container to exclude air.	28 days	

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Selenium	Acid washed polyethylene or acid washed glass	500	Acidify with nitric or hydrochloric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Silica (reactive)	Polyethylene	200	Store between 1°C and 4°C. Filter in the field (0.45 µm cellulose acetate membrane filter) and store between 1°C and 4°C.	24 hours 28 days	 Turbid river samples should be filtered in the field (0.45 µm cellulose acetate membrane filter).
Silver	Acid washed polyethylene (wrapped in foil) or acid washed amber glass	100	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater.
Sodium	Polyethylene	500	None required. Acidify with nitric acid to pH 1 to 2.	28 days 28 days	 Acidification permits the determination of other metals in the sample.
Solids (dissolved)	Polyethylene or glass	500	Store between 1°C and 4°C. Fill container to exclude air.	24 hours	Also known as ‘filtrable residues’ and ‘total dissolved solids’ or TDS.
Solids (suspended)	Polyethylene or glass	500	Store between 1°C and 4°C.	24 hours	Also known as ‘non-filtrable residues’ and ‘suspended solids’ or SS.
Solids (total)	Polyethylene or glass	500	Store between 1°C and 4°C.	24 hours	
Sulfate	Polyethylene or glass	200	Store between 1°C and 4°C.	7 days	
Sulphide (dissolved)	Polyethylene	50 by pipette	Add 10 mL copper-DMP reagent.	12 hours	
Sulphide (total)	Polyethylene or glass	500	None required. Completely fill bottle without aeration.	Determine on site	

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
			Fix samples immediately on site by adding 2 mL of 10% (m/v) zinc acetate solution per 500 mL of sample. Store between 1°C and 4°C.	7 days	
Sulfite	Polyethylene	1000	Fix in the field by addition of 10 mL of 2.5% EDTA solution per 1 L.	7 days	
Surfactants (anionic)	Glass rinsed with methanol	500	Acidify with sulphuric acid to pH 1 to 2, fill container to exclude air and store between 1°C and 4°C. Add 40% formaldehyde solution to give 1% (v/v) final concentration and store between 1°C and 4°C.	48 hours 96 hours	Glassware should not previously have been washed with detergent.
Surfactants (cationic)	Glass rinsed with methanol	500	Fill container to exclude air and store between 1°C and 4°C.	48 hours	Glassware should not previously have been washed with cationic detergent.
Surfactants (non-ionic)	Glass rinsed with methanol	500	Fill container to exclude air. Add 40% formaldehyde solution to give 1% (v/v) final concentration and store between 1°C and 4°C.	28 days	Glassware should not previously have been washed with detergent.
Temperature	None required		Not applicable.	Determine *in situ*	

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Tin	Acid washed polyethylene or acid washed glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater
TOC					See entry for Carbon, total organic
Total dissolved solids (TDS)					See entry for Solids (dissolved)
Total solids					See entry for Solids (total)
Total suspended solids (TSS)					See entry for Solids (suspended)
Toxicity (by Microtox®)	As for the suspected toxicant	200	Store between 1°C and 4°C.	As for the suspected toxicant	
Trihalomethanes	Solvent washed glass vial with PTFE faced septum	100	Fill container to exclude air.	14 days	If residual chlorine is present, for each 40 mL of sample add 3 mg of sodium thiosulfate.
Turbidity	Polyethylene	100	None required. Store between 1°C and 4°C in the dark.	On site 24 hours	
Uranium	Acid washed polyethylene or glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater
Vanadium	Acid washed polyethylene or glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater

Analytical parameter	Container	Typical volume (mL)	Preservation procedure	Maximum holding period	Comments
Zinc	Acid washed polyethylene or glass	500	Acidify with nitric acid to pH 1 to 2.	28 days	Acid washed polyethylene, polycarbonate or fluoropolymer containers should be used for determinations at very low concentrations, such as encountered in uncontaminated streams and seawater

APPENDIX B: CONTAINERS, PRESERVATION AND HOLDING PERIODS FOR SOILS AND SEDIMENTS

Sample containers and their preparation

The requirements are taken from Table 3.1 of ANZECC *Guidelines for the Laboratory Analysis of Contaminated Soils* (1996)*. Unless otherwise specified, samples should be stored refrigerated between 1°C and 4°C.

The analyst should always be consulted for advice on the actual sample sizes required.

Container types, preservation and maximum sample holding times

Analytical parameter	**Container**	**Preservation procedure**	**Maximum holding period**	**Comments**
Acid sulfate soils	Plastic bag	Exclude as much air as is possible from the bag and seal. Freeze the sample in the field using dry ice or a portable freezer.	24 hours for submission to the laboratory 14 days for analysis	Drying of the sample at 80°C – 85°C must commence as soon as possible after reception at the laboratory. If the presence of monosulphides is suspected, the sample must be freeze-dried.
Asbestos	Glass or LDPE	Store between 1°C and 4°C.	48 hours	Polypropylene containers are unsuitable.
Bromide (water soluble)	Polyethylene or glass	None.	7 days	Air dry
Carbon, organic	Glass	Store between 1°C and 4°C in the dark.	7 days	Air dry
Cation exchange capacity and exchangeable cations	Acid washed polyethylene	None.	6 months	Air dry
Chloride (water soluble)	Polyethylene or glass	If field moist, store between 1°C and 4°C.	7 days	Field moist or air dry

Analytical parameter	**Container**	**Preservation procedure**	**Maximum holding period**	**Comments**
Cyanide	Polyethylene or glass	Store between 1°C and 4°C in the dark.	7 days	Field moist
Electrical conductivity	Polyethylene or glass	None.	7 days	Air dry
Fluoride	Polyethylene	If moist, store between 1°C and 4°C.	7 days	Field moist or air dry
Leachable metals and semi-volatile organics	As for the analytical parameter of interest (see below)	As for the analytical parameter of interest.	No preservatives to be added prior to leaching. Metals 6 months Anions 7 days Hydrocarbons (including Total Petroleum Hydrocarbons and PAHs) 14 days Pesticides, organochlorine 14 days Pesticides, other 14 days Phenolics 14 days Polychlorinated biphenyls 28 days Other 14 days	As for the analytical parameter of interest (see below).
Leachable volatile organics	As for the analytical parameter of interest	Store between 1°C and 4°C in the dark.	7 days	
Mercury	Acid washed polyethylene	Store between 1°C and 4°C in the dark.	28 days	Field moist
Metals (except mercury)	Acid washed polyethylene	If moist, store between 1°C and 4°C.	6 months	Field moist or air dry
Moisture content	Polyethylene or glass (As for the analytical parameter of interest)	Store between 1°C and 4°C.	7 days, and on the same day as sample extraction for other analytical parameters.	Field moist
Net acid generating potential				See entry for acid sulfate soils

Analytical parameter	**Container**	**Preservation procedure**	**Maximum holding period**	**Comments**
Organics, semi-volatile	Solvent rinsed glass	Store between 1°C and 4°C in the dark.	14 days	Field moist
Organics, volatile	Solvent rinsed glass	Store between 1°C and 4°C in the dark.	14 days	Field moist
pH	Polyethylene or glass	None.	7 days	Air dry
Sulfate	Polyethylene or glass	If moist, store between 1°C and 4°C.	7 days	Field moist or air dry
Sulphide	Polyethylene or glass	Add sufficient 1 molar zinc acetate to fully cover soil surface and allow minimal headspace. Store between 1°C and 4°C.	7 days	Field moist
Sulphur – total	Polyethylene or glass	If moist, store between 1°C and 4°C.	7 days	Field moist or air dry

APPENDIX C: CONTAINERS, PRESERVATION AND HOLDING PERIODS FOR CONCENTRATED LIQUID WASTES, SLUDGES AND SOLID WASTES, OTHER THAN SOILS AND SEDIMENTS

Where the sample is being collected to determine a specific component, the following containers and sample handling procedures should be followed. Other procedures apply when the sample is being collected for a general identification (See the second Table, at the end of this Appendix).

Additional details on sampling for soils and sediments can be obtained from USEPA Publication: *Test Methods for Evaluating Solid Waste: Volume 1A Laboratory Manual Physical/Chemical Methods*, USEPA Publication No SW-846, Third Edition, Final Update III (1997)), or its latest update.

Aqueous trade wastes should be handled in accordance with the requirements set out in Appendix A.

Analytical parameter	Container	Preservation procedure	Maximum holding period
Antimony	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C. For liquid samples, acidify to pH<2 with nitric acid.	6 months 6 months
Arsenic	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C.	6 months
		For liquid samples, acidify to pH<2 with nitric acid.	6 months
Asbestos	Glass or LDPE	Store between 1°C and 4°C.	6 months
Barium	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C. For liquid samples, acidify to pH<2 with nitric acid.	6 months 6 months
Cadmium	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C. For liquid samples, acidify to pH<2 with nitric acid.	6 months 6 months

Analytical parameter	Container	Preservation procedure	Maximum holding period
Carbon, total organic (TOC)	Polyethylene or glass (glass is preferable)	For liquid samples, acidify to pH < 2 using sulphuric acid or hydrochloric acid. Store between 1°C and 4°C in the dark.	28 days
Chloride	Polyethylene or glass	None.	28 days
Chromium (total)	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C. For liquid samples, acidify to pH<2 with nitric acid.	6 months 6 months
Chromium (VI)	Polyethylene or glass	For solid samples, store between 1°C and 4°C. For liquid samples, store between 1°C and 4°C.	28 days until extraction and 4 days after extraction. 24 hours
Copper	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C. For liquid samples, acidify to pH<2 with nitric acid.	6 months 6 months
Cyanide	Polyethylene or glass	For solid samples, store between 1°C and 4°C in the dark. For liquid samples, if oxidising agents are present add an excess of 0.6 g ascorbic acid per litre (excess ascorbic acid has been added when a starch iodide paper fails to turn blue on contact with the sample) and adjust pH>12 with 50% sodium hydroxide. Store between 1°C and 4°C in the dark.	7 days 14 days
Dioxins and furans	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction

Analytical parameter	Container	Preservation procedure	Maximum holding period
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.	30 days until extraction and 45 days after extraction
Hydrocarbons (halogenated)	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.	7 days until extraction and 40 days after extraction
Lead	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C.	6 months
		For liquid samples, acidify to pH<2 with nitric acid.	6 months
Mercury	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C.	28 days
		For liquid samples, acidify to pH<2 with nitric acid.	28 days
Metals (except mercury and chromium (VI))	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C.	6 months
		For liquid samples, acidify to pH<2 with nitric acid.	6 months
Nitrate	Polyethylene or glass	For liquid samples, store between 1°C and 4°C.	48 hours
Polychlorinated biphenyls (PCBs)	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C.	7 days until extraction and 40 days after extraction
Pesticides and herbicides (organochlorine)	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction

Analytical parameter	Container	Preservation procedure	Maximum holding period
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C.	7 days until extraction and 40 days after extraction
Pesticides and herbicides (organophosphate)	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, adjust the samples to pH 5-8 using sodium hydroxide or sulphuric acid.	7 days until extraction and 40 days after extraction
pH	Polyethylene or glass	None.	For solid samples 7 days
	Polyethylene or glass	None.	For liquid samples 6 hours
Phenols	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction.
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.	7 days until extraction and 40 days after extraction
Phthalate esters	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C.	7 days until extraction and 40 days after extraction
Polycyclic aromatic hydrocarbons (PAHs)	Solvent washed glass with PTFE-lined cap	For solid samples, store between 1°C and 4°C.	14 days until extraction and 40 days after extraction.
	Solvent washed amber glass with PTFE-lined cap	For liquid samples, store between 1°C and 4°C. If residual chlorine is present, add 80 mg sodium thiosulfate per 1000mL of sample.	7 days until extraction and 40 days after extraction
Residues, volatile	Polyethylene or glass	Store between 1°C and 4°C.	7 days

Analytical parameter	Container	Preservation procedure	Maximum holding period
Selenium	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C.	6 months
		For liquid samples, acidify to pH<2 with nitric acid.	6 months
Sulfate	Polyethylene or glass	For solid samples, store between 1°C and 4°C.	6 months
		For liquid samples, store between 1°C and 4°C.	28 days
Sulphide	Polyethylene or glass	For solid samples, fill the surface of the solid with 1 M zinc acetate until moistened. Store between 1°C and 4°C and store headspace free.	6 months
		For liquid samples, add 4 drops 1 M zinc acetate per 100 mL, adjust pH to >9 using 6 M sodium hydroxide. Fill bottle completely and stopper with minimum aeration. Store between 1°C and 4°C.	7 days
Zinc	Acid washed polyethylene or acid washed glass	For solid samples, store between 1°C and 4°C.	6 months
		For liquid samples, acidify to pH<2 with nitric acid.	6 months

Where the sample is being collected for a general identification, then the following procedures should be followed.

Analytical parameter	Container	Preservation procedure	Maximum holding period
Concentrated wastes	Glass with a fluoropolymer cap	Store at 1°C and 4°C.	14 days
Aqueous samples	Glass with a fluoropolymer cap	Store at 1°C and 4°C and adjust pH <2 with hydrochloric acid.	7 days

Analytical parameter	**Container**	**Preservation procedure**	**Maximum holding period**
Solids and sludges	Glass with a fluoropolymer cap	Store at 1°C and 4°C.	7 days

APPENDIX D: QUALITY ASSURANCE SYSTEMS

Quality assurance procedures are mandatory for NATA accreditation. The recommended methods (see Chapter 4) contain detailed guidance on appropriate QA/QC systems, and these should be followed.

The terms 'quality assurance' (QA) and 'quality control' (QC) are often confused. In terms of laboratory analysis activities, they are defined below.

Quality assurance

Quality assurance (QA) is all of the actions, procedures, checks and decisions undertaken to ensure the accuracy and reliability of analysis results. For example: routine procedures ensure proper sample control, data transfer, instrument calibration; proper decisions are required to select and properly train staff, select equipment and analytical methods; and day-to-day judgments result from regular scrutiny and maintenance of the laboratory system.

Any of the following publications could be used in developing a QA program:

1. Australian and New Zealand Environment and Conservation Council, *Guidelines for the Laboratory Analysis of Contaminated Soils*, Chapter 2 (ANZECC 1996).
2. American Public Health Association, *Standard Methods for the Examination of Water and Wastewater*, Method 1020 (APHA 1995).
3 US Environment Protection Agency, *Test Methods for Evaluating Solid Waste*, SW-846, Chapter 2 (USEPA 1997).
4 National Association of Testing Authorities, *Guide to Development of a Quality System For a Laboratory* (NATA 1995a).

Quality control

Quality control (QC) is those parts of QA which serve to monitor and measure the effectiveness of other QA procedures compared with previously decided objectives. These may include measurement of the quality of reagents, cleanliness of apparatus, accuracy and precision of methods and instrumentation, and reliability as implemented daily in the laboratory.

For more information, readers are referred to documentation available from NATA. In particular, Technical Note No. 23 (NATA, 1995b).

QC procedures

Analysts should implement the following QC steps with each analytical batch, or with each twenty samples, whichever is the smaller.

Analysis blank – determination of the contribution to the analytical signal by reagents, glassware, etc. The contribution measured should be subtracted from the gross analytical signal for each analysis, before calculation of each sample's measured concentration.

Replicate Analysis – repeated analysis of at least one sample from the batch.

Laboratory Control Samples – comprise a control matrix (for example deionised or tap water) or a replicate portion of a sample under analysis, fortified with components representative of the analytical parameter class. Recovery check portions should be fortified at concentrations that are easily quantified, but within the range of concentrations expected for real samples.

Surrogate Spikes – known additions to each sample, blank and matrix spike or reference sample of compounds that are similar to the analytical parameters of interest in terms of:

- extraction,
- recovery through clean-up procedures,

and

- response to chromatographic or other determination,

but which:

- are not expected to be found in real samples,
- will not interfere with quantification of any analytical parameter of interest,

and

- may be separately and independently quantified.

Surrogate spikes are added to the analysis portion before extraction. The purpose of surrogates is to provide a means of checking that no gross errors leading to significant analytical parameter losses have occurred at any stage of the procedure.

In the case of organic analyses, the surrogate spike compounds may be deuterated, alkylated or halogenated analogues, or structural isomers of compounds under analysis. They should be added for each analysis by chromatographic analysis.

Internal Standards – are added to samples after all extraction, clean-up and concentration steps. The addition is a constant amount of one or more compounds with similar qualities to surrogate compounds.

The purpose of internal standards is to check the consistency of the analytical step (for example, injection volumes, instrument sensitivity and retention times for chromatographic systems) and provide a reference against which results may be adjusted in case of variation.

Use of internal standards is required for chromatographic analysis of organics.

Reference Materials – are homogeneous materials that have been rigorously characterised by several different procedures. They may be prepared in-house or obtained from commercial suppliers. Reference materials should be certified and traceable to a recognised authority. A reference material of comparable matrix should be analysed with each batch of samples.

QC records

Records of the results of QC procedures should be maintained to establish method reliability, confidence intervals for analysis results, and trends in precision and accuracy. NATA accreditation means that analytical methods and QA systems are regularly reviewed. However, no QA system is perfect. As the user of the service, any organisation having analyses performed is entitled to question the analytical service regarding methods and QA procedures.