

Chapter 17: Monitoring, water treatment and drinking-water

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17.1 Introduction

Monitoring involves sample collection, delivery, storage, testing, and recording and reporting the results.

GIGO (garbage in, garbage out) is as true for water monitoring as it is for any other endeavour, perhaps more than many.

One cannot expect to obtain good data if a sample is taken incorrectly (or even inappropriately), no matter how good the laboratory procedures are. This issue is made all the more important when we recognise that many of the determinands we are looking for in water are often at very low concentrations, particularly for finished drinking-water.

Generally there is a lot of information on analytical techniques, and when a doubtful result is obtained it is a natural reaction to check the test procedure.

However, in the analysis of errors, it is not unusual to find that the reporting process is often the cause. Common causes include poor handwriting, entering results in the wrong column (ie, transcription errors), and calculation errors. Reporting procedures also require a quality assurance step. A sound approach is to get someone else to check all calculations and data entries. Whatever process is used, it should be documented.

Risk management issues related to monitoring are discussed in the MoH Public Health Risk Management Plan Guide PHRMP Ref: G2: General – Monitoring.

17.1.1 Test methods

Standard Methods (APHA, AWWA, WEF) includes most methods commonly used in water laboratories.

The USEPA regularly updates their *Analytical Methods Approved for Compliance Monitoring under the Enhanced Surface Water Treatment Rule*. See: http://www.epa.gov/safewater/methods/pdfs/methods/methods_swtrules.pdf.

The USEPA has a document titled *Chemical/Name Index to EPA Test Methods* which can be found at <http://www.epa.gov/region1/info/testmethods/pdfs/testmeth.pdf>. This gives access to details of many USEPA methods.

Going to <https://www.nemi.gov/home> and clicking on 'browse all methods' (run by USGS and USEPA) allows access to the details of many analytical procedures, although not Standard Methods (APHA, AWWA, WEF).

17.2 Sampling

Sampling is an integral part of drinking-water quality management and is discussed frequently throughout the DWSNZ and these *Guidelines*. This section discusses sampling in a fairly general manner. More detailed references to sampling appear in the specific chapters, as follows:

- Chapter 1: Appendix: Statistical issues in drinking-water standards
- Chapter 2: Management of community supplies
 - Section 2.4: Compliance
- Chapter 3: Water sources
 - Section 3.2.2: The quality of groundwater
 - Section 3.2.4: Establishing the security of an aquifer
- Chapter 4: Selection of water source and treatment
 - Section 4.4: Evaluating the sources
- Chapter 6: Bacteriological compliance (*E. coli*)
 - Section 6.2: Monitoring for *E. coli*
 - Section 6.3: Microbiological compliance
 - Section 6.4: Sampling and testing
- Chapter 8: Protozoa compliance
 - Section 8.2: Source water
 - Section 8.6: Sampling and testing for protozoa and substitute tests
- Chapter 9: Cyanobacteria compliance
 - Section 9.5: Sampling and testing
- Chapter 10: Chemical compliance
 - Section 10.4: Sampling procedures and techniques
- Chapter 12: Treatment processes, pretreatment
 - Section 12.2.3: pH Adjustment
- Chapter 18: Aesthetic considerations
 - Section 18.4: Monitoring programme design
- Chapter 19: Small, individual and tankered supplies
 - Section 19.2.4: Water quality monitoring

Section 17.5.6 of this chapter discusses chain of custody procedures.

Care must always be exercised to see to it that:

- the appropriate container is used (generally glass, or approved plastic bottles with leak-free sealing). High-density polyethylene and Teflon™ bottles are commonly used for collecting natural water samples for routine analysis. Appendix 2 of DWSNZ includes a recommendation on sample containers, and whether the sample should be collected at the treatment plant or from the distribution system
- the container is clean (ie, free of the determinand before the sampled water is deposited). Laboratories should have documented procedures for bottle washing and storage

- there is no contamination of the sample by its inappropriate handling. Those collecting water samples should not make contact with samples. Smoking (of cigarettes, etc) is known to contaminate samples by elevating concentrations of ammonia, for example. People sampling for microbiological tests need to be trained in aseptic technique
- a sufficient volume is taken; different determinands (and analytical methods) can require very different volumes, eg, 100 mL for an *E. coli* test, and 100–400 L for a protozoan (oo)cyst assay of drinking-water
- the sample has been collected from the correct place, and if collected for compliance testing, includes the site identification code as listed in the *Register of Drinking-water Suppliers and Supplies in New Zealand*
- the sample container is unambiguously labelled, and in a fashion such that the label is still readable at the end of the laboratory procedures
- the sample is transported to the laboratory in reasonable time (especially for microbiological assays). Analytical laboratories should be consulted in advance about what is a reasonable period between sample collection and arrival at the laboratory, and about preservation measures (eg, storing samples in the dark and on ice) is usually acceptable for a wide range of determinands; other may have to be stabilised on site
- samples are stored in the laboratory in a suitable manner while the tests are being conducted
- samples are stored, for the time agreed with the client, after the results have been reported, so that any apparent discrepancies can be checked.

The safety and wellbeing of the sampling staff needs to be protected (eg, sampling environmental waters in high flow conditions, sampling water mains under pressure, sampling from pits, tunnels, valve chambers, boats, etc).

Given the broad sweep of issues that such considerations invoke, a list cannot be provided here of the all the issues and procedures. Details should appear in the water suppliers' WSPs or sampling manual, and/or laboratory documentation, or other appropriate manual(s). This should cover routine sampling and for responses to transgressions. Fortunately, there are three ready sources of information that should be used.

First, always contact in advance the laboratory that is to perform the analysis, so that correct and clean sample containers are used, in the correct manner. This contact should also elicit any special care that needs to be taken in performing the sampling (eg, protozoal assays may require that the sample be filtered in the field). At the same time, there should be a discussion with the laboratory about the detection limit that is desired for the analysis. This issue deserves careful attention if the usual detection limit is close to the MAV. In such cases it is much better to analyse the compounds with a method that has a lower limit of detection, reducing the number of measurements if budgets are limited.

Second, detailed advice can be obtained from texts and standards. Pre-eminent amongst these is *Standard Methods for the Examination of Water and Wastewater* (APHA, AWWA, WEF). The UK Water Research Centre has also published detailed guidance on many issues for water quality analysis (Hunt and Wilson 1986). BS 8550 (2010) is a standard for those involved in testing water and making it safe for use; it

provides an audit protocol to monitor conformity with declared, or assumed, practices in all areas of water quality sampling.

Third, the Drinking Water Inspectorate (DWI 2016) produced a manual for chemical and microbiological sampling.

Water suppliers will generally not always have ready access to the first two documents, but water laboratories will; yet another reason to consult with the laboratory before sampling.

Closer to home is the AS/NZS 5667 (1998), Water Quality – Sampling. Relevant publications comprise:

- Part 1: Guidance on the design of sampling programs, sampling techniques and the preservation and handling of samples
- Part 4: Guidance on sampling from lakes, natural and man-made
- Part 5: Guidance on sampling drinking water and water used for food and beverage processing
- Part 6: Guidance on sampling rivers and streams
- Part 7: Guidance on sampling of water and steam in boiler plants
- Part 8: Guidance on sampling wet deposition
- Part 11: Guidance on sampling of groundwaters.

Another matter to be considered in sampling is the location and time of sampling. These matters are addressed in Chapter 4: Selection of Water Source and Treatment, section 4.4, and Chapter 16: The Distribution System, section 16.2. And many are specified in the relevant compliance conditions in the DWSNZ.

Sections 4.3.8.1 and 4.4.4 of the DWSNZ refer to the need to collect samples for *E. coli* analysis on different days of the week. Water supplies are delivered seven days a week so suppliers need to know that the water quality is equally satisfactory on all seven; two conditions could make it not so:

- a) the treatment process or its monitoring is different during weekends/public holidays due to a lower staffing level
- b) the quality of the raw water varies due to some cyclic activity in the catchment.

Some examples of cyclic activities include:

- stock sale/auction day
- milking operations that lead to pulsed discharges of dairy shed wastes
- truck cleaning on (say) Friday afternoons or Saturday mornings
- factories that operate five days per week
- factories that perform different functions on one or more days
- vegetable growers that pick/wash produce in time for weekend or Monday markets
- holiday homes, motels and camping grounds that attract weekend visitors
- school holidays and weeks with statutory holidays
- Wednesday or Saturday horse race or sports meetings

- seasonal spraying, topdressing, ploughing activities, burn-offs
- irrigation or 'muck spreading'
- ski fields with high weekend patronage, etc.

The extent and duration of these effects will vary depending on whether the source is surface water or groundwater, and on the size, flow time and mixing conditions of the source, and the type of waste treatment (if any) employed by the above.

Standard Methods (APHA 2005) no longer has a procedure for protozoal assays. The DWSNZ (section 5.2.2.2) requires the use of a modified USEPA method (method 1623, a method that enumerates both *Cryptosporidium* oocysts and *Giardia* cysts). Sampling requirements for this method must be checked with the laboratory. Use accredited laboratories for compliance monitoring.

Sampling techniques are specialised, depending on the determinand and the site. It is recommended that sampling instructions be written up in a procedure manual or equivalent. See Sinton (1986) and Sundaram et al (2009) for discussion on groundwater sampling. Bottle washing, preservation, and storage requirements of collected samples should be included. Sample sites need an unambiguous descriptor so there is no confusion when different personnel are involved.

Training courses are available, such as: NZQA unit standards: 17891 Demonstrate knowledge of quality sampling techniques and programme design for a water treatment site (Level 4) (5 credits) and 29999 Undertake sampling and site testing procedures for drinking water treatment (Level 4) (6 credits). Contact Ministry of Health, Water NZ for further information, or <https://opusetc.co.nz/water-treatment-training>.

Automatic sampling can present a labour saving option, especially if samples are needed overnight or for a long period. Battery operated models are on the market, and samplers may be available for hire. Flow-proportional samplers are more common when sampling wastewaters. Matters that require consideration include:

- ensuring that the sample suction point is appropriate
- that the sampler can lift the water from the suction point to the bottles
- sample lines are not too long or too wide, ie, not allowing substances like algae, aluminium, iron, manganese and turbidity to settle out or adhere to the pipe surface
- the velocity through the sample tubing should exceed 0.6 m/s, for the same reason
- whether a composite sample or discrete samples are required or are more appropriate
- what sample volumes are required
- the frequency and duration of sampling
- whether the determinand(s) are stable during the collection and delivery period
- whether the samples should be stored refrigerated
- whether the sample bottles should contain a preservative.

17.3 Monitoring for process control

Control of all the processes used in water treatment is an important part of ensuring good water quality. Good control allows a process to be optimised. As a result, excessive dosing can be avoided, any carry-over of chemicals may be reduced, chemical costs are minimised, and problems become easier to solve.

Therefore good process control monitoring is needed to keep the process operating correctly or optimally. These process control tests contrast with the regulatory tests that produce data to demonstrate compliance, eg, with the Drinking-water Standards for New Zealand (DWSNZ). Regulatory testing is discussed in section 17.4.

For a particular plant, the type and amount of process control that should be used is determined by a balance of the requirements of the DWSNZ, raw water quality, the manufacturer's recommendations, the water supplier's policy, operator capability, complexity of the system, sensitivity of the process to optimisation, potential labour savings, and cost.

Good documentation of monitoring records can provide helpful information for when unusual raw water conditions recur.

17.3.1 Planning a monitoring programme

The monitoring undertaken at a water treatment plant will be a mix of manual and automatic monitoring. Automatic (online) monitoring is becoming increasingly common and results can be used to modify/control the process. Automatic monitoring minimises labour requirements and allows large amounts of data to be collected so trends can be examined and occasional changes in performance can be picked up and the process improved. Automatic monitoring can be expensive so is not always practical. In these cases either regular samples are collected and analysed in a laboratory, or the determinand is measured manually on-site using an instrument.

An excellent way to arrive at an appropriate level of process monitoring and control is by the compilation of a Water Safety Plan (WSP – formerly known as a Public Health Risk Management Plan, PHRMP). This process is described briefly in Chapters 1 and 2. Whether or not a WSP is undertaken, these risk management principles should be used when deciding how each determinand is to be measured and how often.

Table 17.1 shows examples of where process monitoring is commonly installed online or undertaken manually at a water treatment plant. In some cases monitoring is specifically required by the DWSNZ.

The ability to measure different contaminants is steadily improving with the development and refinement of new instruments.

Particularly in larger plants, important variables may be measured online by two identical instruments so that the values may be compared (dual validation). An alarm is raised if the measured value varies between the two instruments by more than a set

amount. In some systems, values are measured by three identical instruments (triple validation). In these systems, if one value varies from the other two by more than a set amount, it is assumed that this value is in error and the process continues to operate using the two agreeing values.

Often it is sufficient to install a second, cheaper type of instrument to give an alarm at very high or low levels. A common example is the installation of a level switch at high-high level (above normal high level) to activate an alarm if an ultrasonic level meter fails.

A great deal of data can be generated by monitoring systems. Where applicable, it is important that the data is stored in a manner that allows demonstration of compliance as required in section 3.2 of the DWSNZ. This should be taken into account when purchasing monitoring equipment. Some advice appeared in Colton (2015).

The monitoring of aspects of equipment condition is also recommended as part of the careful management of water treatment plant assets. This information can usually be obtained from the manufacturer. The AWWA Manual (M2, 3rd edition, 2001) covers instrumentation and control.

Table 17.1: Process control monitoring by treatment stage in a conventional process

Determinand	Stage of treatment				
	Raw water	Coagulation	Clarification	Filtration	Disinfection and water to supply*
Turbidity	R	O	R	S	S
Temperature	O		O		O or S
pH	O	R	O		S
Dissolved oxygen	O				
Colour (or UV ₂₅₄)	O				R or S
Organic carbon	O		O		O
Conductivity	O				O
Aluminium			O	R	
Alkalinity	O	O	O		R
Chemical dose		R			R
Sludge level/density			O		
Flow rate	R	R	R	R	R
Head loss/run time				R	
Disinfectant C.t					S
Disinfectant residual					S
Fluoride					S
Water level/volume	R				R
Pressure					R

* Monitoring requirements depend on disinfection process used.

Notes: See turbidity row if using particle counting. S refers to DWSNZ for specific minimum requirements. R means recommended. O means optional.

Some of the more common instruments used in water treatment plants are listed in Table 17.2.

Table 17.2: Instruments and examples of their application

Variable	Examples of application
Equipment status (on/off)	Confirmation of correct starting/stopping of equipment
Position switch	Confirmation of correct valve opening/closing
Temperature (process or equipment)	Temperature compensated filter back wash flow rate Monitoring for disinfection efficiency, c.t value
Voltage or current draw	Confirmation of condition of pumps and other motorised equipment
Pressure/head loss	Indication of a blockage in a component of the plant Differential pressure across a filter indicating head loss development Pressure in distribution system
Flow rate	Recycle return rate Control of processes such as flow proportional dosing of chemicals Drinking-water production rate Accurate flow splitting (eg, to settling tanks or filters) Control of rate of change of flow to flow sensitive processes
Level	Warning of overflow Indication of filter head loss development Indication of storage volume (and time for c.t value) Control of pump wells
pH	Control of pH adjusting chemicals Monitoring for effect on coagulation Monitoring for effect on disinfection Monitoring for effect on water aggressiveness
Alkalinity	Monitoring for effect on coagulation Monitoring for effect on water aggressiveness
Conductivity	Can indicate raw water changes not detected by other instruments
Streaming current	Control of coagulant dose
Sludge level/density	Operation of sedimentation tanks
Disinfectant residual concentration	Control/confirmation of disinfectant dose and residual
UV intensity	Control/confirmation of UV disinfectant dose
Fluoride	Control/confirmation of fluoride dose, final concentration
Aluminium	Control of coagulation; individual filter performance
Dissolved oxygen	Monitoring condition of raw water (eg, aeration of groundwater) Can affect oxidation state of metals in raw water
Turbidity/particle count	May be used as indicator of coagulant requirement Quality of recycle water Measuring performance of coagulation/sedimentation/filtration Disinfection efficacy Indicates contaminant (eg, protozoa) breakthrough from filters
Colour/organic carbon/UV ₂₅₄	May be used as indicator of coagulant requirement/performance May be used to indicate DBP potential in treated water Transmittance/absorbance needed for UV disinfection
Hour run meter	Various, eg, pumps, UV lamps, filter run
Direct integrity test	Membrane filtration status/compliance
Weight	For example monitoring the rate of consumption of chlorine

17.3.2 Installation

Where a water treatment plant is fitted with continuous monitoring, instruments should always be installed in a way that they:

- measure samples that are representative of the full flow of water past a given point
- measure samples taken from the optimum point in the process, eg, raw water should be measured before any chemicals or recycle flows are added
- are accessible for maintenance and standardisation.

Many instruments have samples piped to them. In this case the installation should:

- not introduce excessive lag time or where this will affect process control or alarms (this can occur through the use of long sampling lines or excessively large air traps)
- not allow adsorption or precipitation in the sample line (a continuous flow greater than 0.6 m/s through the sample line should prevent this)
- allow for the safe disposal of analyser waste, particularly where buffers and other chemicals are added and where wastewater is returned for treatment
- not be sited where there may be electrical interference, in direct sunlight, or where there is excessive vibration
- allow the flow to analysers to be regulated and checked. Other uses on the sample line should be restricted so there are no variations of flow. Normally the drain from the analyser should be visible so that the continuity of flow can be observed easily.

The location of an instrument or sampling tap on a pipe can also be important. For example, a sample collected from the crown of the pipe can contain entrained air that will lead to false high results for determinands such as turbidity. Samples taken from near the bottom of a tank might include uncharacteristic amounts of grit or silt.

Most instruments have their own specific installation requirements. An inexperienced instrument installer might be caught out by common issues such as:

- flow to a turbidimeter should not be pumped as this will break up particles and may change the turbidity. Air bubbles need to be excluded as they can cause false high turbidity readings. A bubble trap is often used to control air bubbles
- light shining on sample lines or cell/sensor housings can result in algal growth which can affect readings such as turbidity
- conventional magnetic flowmeters are well known for being very sensitive to turbulent flow. For this reason they are always installed in a straight section of pipe. Variable conductivity in the water (such as from hydrated lime that has not been dispersed fully) can also severely disrupt accuracy
- the extremely low conductivity found in some waters can cause erroneous pH readings. Many manufacturers supply electrodes designed specifically for low conductivity waters.

As is the case with any equipment, the installation should always be in accordance with the manufacturer's recommendations.

17.3.3 Standardisation

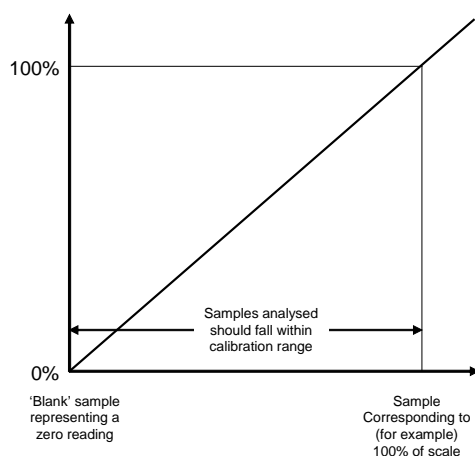
Values measured by instruments often drift away from the true value as a sensor accumulates dirt or is affected by use in some other way. As a result it is important to check the value regularly. This is essential in the case of variables that are monitored for compliance.

Standardisation is usually achieved by comparing the instrument reading against standards. Standards are solutions (usually), of a known (traceable) concentration.

Most instruments must be checked regularly against a zero reference. Generally this is achieved by running a sample through the unit that is known to be at the zero level (eg, distilled water) then re-setting the zero reading. Some instruments also require an electrical zero check.

Then the feed is changed to a sample with a known concentration, ideally at the high end of the measuring range to set the span. The high end should be just above the maximum readings expected. For most instruments used at a water treatment plant this two-point calibration would be adequate, provided the standard curve is known to be a straight line. The standardisation procedure for each instrument should be documented in the WSP or other appropriate manual. When deciding how, and how often, to standardise, guidance should be sought from the manufacturer's instructions and, when relevant, from the DWSNZ. If the instrument standardisation shows that frequent readjustment is needed, checks (and/or servicing) will be needed more frequently.

Figure 17.1: Typical standard curve applicable to most test parameters



Between standardisations, the meter reading should be checked (verified) by an alternative method such as testing a control sample, or comparing the reading against a standardised hand-held meter. If this check is outside acceptable limits, the instrument should be restandardised. Acceptable limits need to be defined, eg, by the instrument manufacturer, and the procedure should be documented in the WSP. The control sample check is generally performed at least weekly depending upon the environment, operating conditions and manufacturer's instructions, but generally no less frequently than monthly.

A permanent record, eg, a standardisation book, of checks (standards and control samples) is needed. Information should show the concentrations checked, the concentration the instrument read for these, the time and date, the person doing the work, and a comments column for entering actions such as adjustments made to the instrument, or whether it was repaired or parts replaced. If the instrument needs to be adjusted, it should be restandardised to show that it was adjusted correctly.

Details relating to the preparation of standards need to be recorded as well, eg, when standardising ferrous ammonium sulphate for chlorine titrations using DPD. Section 10.5 of the *Guidelines* discusses measurement of pH.

Standards should be stored carefully, and be dated, either the date prepared or date received, and they should also show the expiry date. When standardising with a new standard for the first time, compare it against the readings of the old standards. This will show whether the old standard has been deteriorating at a faster rate than expected, or may show that the new standard is incorrect – it happens! When there is doubt, the process control instrument can be checked against a laboratory instrument.

Appendix A2.4 of the DWSNZ specifies the requirements for standardising turbidimeters used for compliance testing. It also discusses verification of the turbidimeter, which is equivalent to using a control sample as discussed above. Further information appears in section 8.6.2.1 of the *Guidelines*.

Generally, standards are prepared (or purchased) with a known uncertainty (see section 17.5.5), and the instrument reading is taken at face value. For example, if a 0.40 mg/L FAC standard with an uncertainty of measurement of 0.03 mg/L used to calibrate an online chlorine analyser reads 0.38 or 0.42 mg/L, the instrument is operating acceptably. If it reads 0.36 or 0.44 mg/L it would need to be restandardised. See Chapter 8: Protozoa Compliance, section 8.6.2.1 for further discussion relating to calibration of turbidimeters.

Although the previous paragraph stated that 'the instrument reading is taken at face value', the DWSNZ state (in Appendix A1.2.3) that 'equipment used to demonstrate compliance must be suitable for the purpose'. The DWSNZ could not be more precise than that because of the large number of possible determinands and the large number of techniques available for measuring them. For example, an online chlorine analyser with an uncertainty of measurement of 10 percent at the 0.2 mg/L level would be suitable for compliance monitoring. A turbidimeter with an uncertainty of measurement of 10 percent at the 0.50 NTU level would also be suitable for most purposes. But that same turbidimeter may have an uncertainty of measurement of 50 percent at the 0.10 NTU level, and this would not be suitable for use at such low turbidities.

Instrument condition assessment

The condition of the instrument and any supply tubing should be checked as part of standardisation procedure. Transparent supply tubing will need replacing if there are growths or deposits developing that could affect results. The flow rate of the sample and any other requirements (eg, buffer supply) should be confirmed as part of the check. The sample flow rate may vary depending on the head available at the sampling point so check the flow at high and low water levels.

Chemical cleaning will be needed if a sensor has been coated by chemical deposits. For example, alum floc, lime, iron and manganese in water can cause chemical build-up that is often removed with a mild acid (check instrument operating manual first). In the case of raw water monitoring, there may be an accumulation of sediment in the unit that needs cleaning, particularly when raw water turbidity is high.

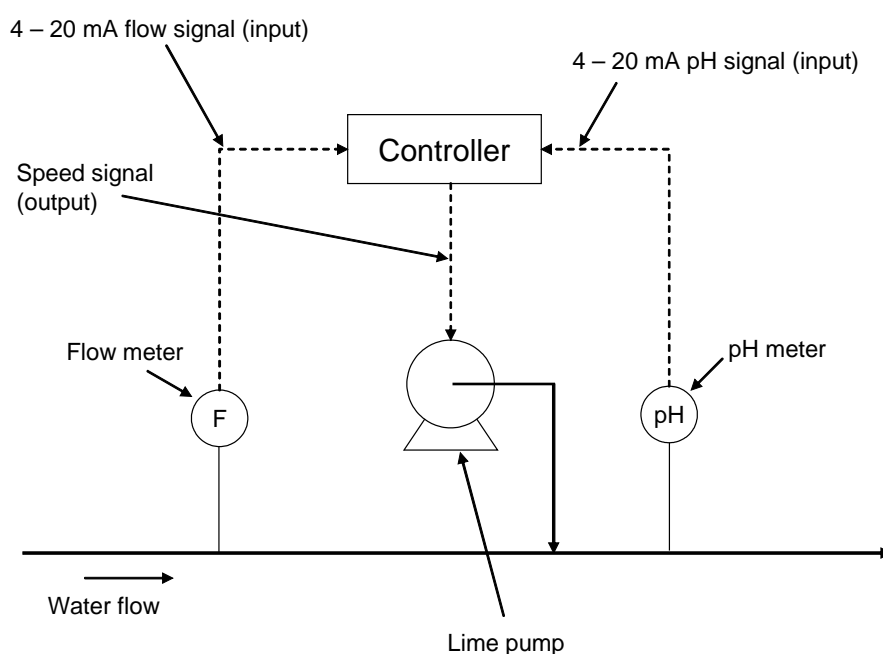
17.3.4 Process control

The value of a measured variable may be used as an input to a controller (usually a Programmable Logic Controller or PLC).

Controllers for automatic operation are usually designed to:

- control critical tasks (eg, the use of flow and target alum dose to control alum dosing pump speed and/or stroke)
- minimise tedious repetitive tasks (eg, at a certain time or head loss, operate valves and pumps to carry out a filter backwash)
- provide a tool for process supervision (eg, measure/record pH, turbidity, free available chlorine, etc).

Figure 17.2: Closed loop control – a flow paced lime pump with pH correction



Many PLCs are programmed to control a number of processes. However, in some situations an instrument or sensor may have a built-in controller, or it may be connected to a single controller that is dedicated to the process. The number of inputs and outputs is fewer than for a centralised controller, and they can be located in the field close to the process.

When a sensor measures a variable, the measured value must be transmitted to the controller in some way. Similarly the controller output signal must be transmitted to the actuator (a controlled device such as a valve actuator or variable frequency drive). These signals may be transmitted over a very short distance or over thousands of metres.

Process control may be either feed-forward, where information from the process is measured before the process is acted on to correct the controlled variable (ie, predictive), or feedback control, in which information from the process is used to correct the controlled variable after the process has been acted on.

A feedback controller needs only measure the process variable, determine if it has deviated too far from the setpoint, apply the necessary corrective action, wait to see if the error goes away, and repeat as necessary. This closed-loop control procedure will eventually have the desired effect provided the controller parameters match the process reaction time.

On the other hand, a controller that tries to eliminate errors too quickly can end up over-correcting to the point that the process variable overshoots the setpoint, causing an error in the opposite direction. Process oscillations can go on forever as the process variable will always be too high or too low; this is referred to as hunting. Worse still, the oscillations can sometimes grow in magnitude until tanks start overflowing or equipment fails.

Control can be made more or less aggressive by adjusting the proportional (P), integral (I), and derivative (D) gains; this is referred to as 3-term control.

Electrical signals

The most common transmission system is an electrical 4–20 mA signal. A screened twisted pair (STP) of copper wires is used to form a DC current loop. A 4–20 mA transmission system can be used for analogue signals. Alternatively, fibre optic cable that transmits a light signal is being used increasingly, although usually more expensive. For a water treatment process there may be a need for thousands of twisted pair cables. The use of modern fieldbus devices can minimise cable requirements.

Pneumatic signals

Pneumatic control is still common and is often preferred on membrane systems due to the number of valves and low cost. Many water suppliers remain standardised on pneumatic control. Pneumatic transmission may be used over shorter distances than for electrical transmission. The controlled variable is measured and converted to air pressure at the sensor. A transmitter sends the air pressure through a single tube to a receiver in the controller where the pressure is converted into a movement of bellows

or a diaphragm. Pneumatic control creates lags with long distances as the air pressure is transmitted through a tube. Typical pressure control ranges are 20–100 kPa.

Hydraulic control

Alternatively, some systems may still use hydraulic control, either water or oil, to transmit the signals. This form of control still exists on many older plants. An application of hydraulic control in water systems is the diaphragm valve that has smaller control valves connected to it to allow pressure and flow control functions to operate on the main valve.

Hydraulic control systems require that water used in the hydraulic system be clean, to prevent clogging of the pilot valves and the control lines. Hydraulic control lines must be protected where there is a danger of freezing.

Digital data links

There has been increasing emphasis to remove the need for thousands of twisted pair cables to transmit signals that were previously transmitted as a 4–20 mA current. To do this an analogue signal must be converted to a digital signal via a microprocessor in a transmitter. A term that describes the digital replacement for the 4–20 mA DC communication system is the digital fieldbus.

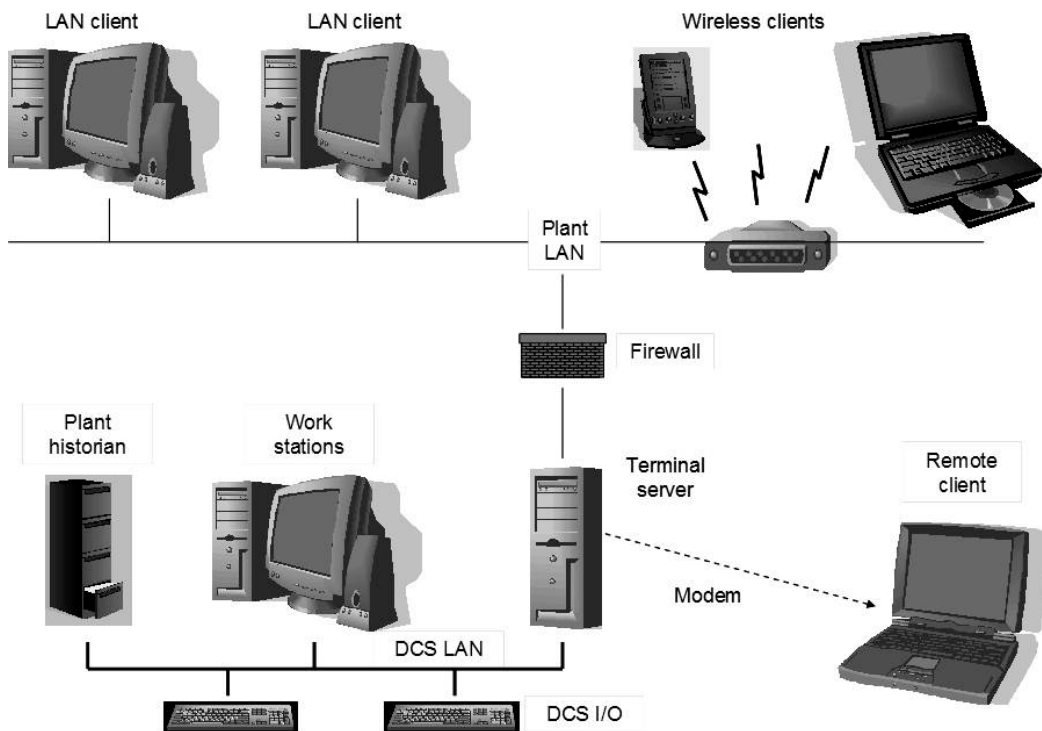
Distributed control

Distributed control systems (DCS) were first introduced in the 1970s as an efficient system for large installations where there were many field based sensors, actuators and controllers. A DCS allows for the feedback controllers to be located closer to the sensors and actuators, instead of in a centralised control room. The communication between the controllers and the operator interface screen(s) is provided via a digital fieldbus, or data highway, or Local Area Network (LAN) typically using Ethernet that connects the controllers, displays and computers. An advantage of this system is that if the communication link is lost, the individual controllers can remain functional.

Typical processes controlled are chemical addition and filtration. The processes are controlled by monitoring the status of pumps, tanks levels and turbidity.

Like SCADA systems, the data collected from plant and equipment on site can be massaged and displayed as useful information on screens in control rooms and specific plant areas. The information can be logged within plant historian databases to support operations, maintenance and planning activities.

Figure 17.3: An example of a distributed control arrangement



SCADA

It is increasingly common for the values recorded by online instruments to be transmitted to SCADA (supervisory control and data acquisition). SCADA is a name for software-based operator interfaces that use symbols and icons for indicating the operational status of a plant as well as facilities to initiate controls.

Usually the SCADA will reside in a PC. However, the logic for the controls usually resides in the PLC or in dedicated controllers, with the SCADA software communicating with the PLC. The SCADA software packages can allow considerable transfer and storage of data for process monitoring. The operator interface is the screen display that may incorporate sophisticated graphics to illustrate the plant components and status of the components/processes. Similarly there may be a facility to demonstrate historic trends. Generally the screen will display alarms that are generated by unacceptable deviation of process variables from set points that have been determined by the operator.

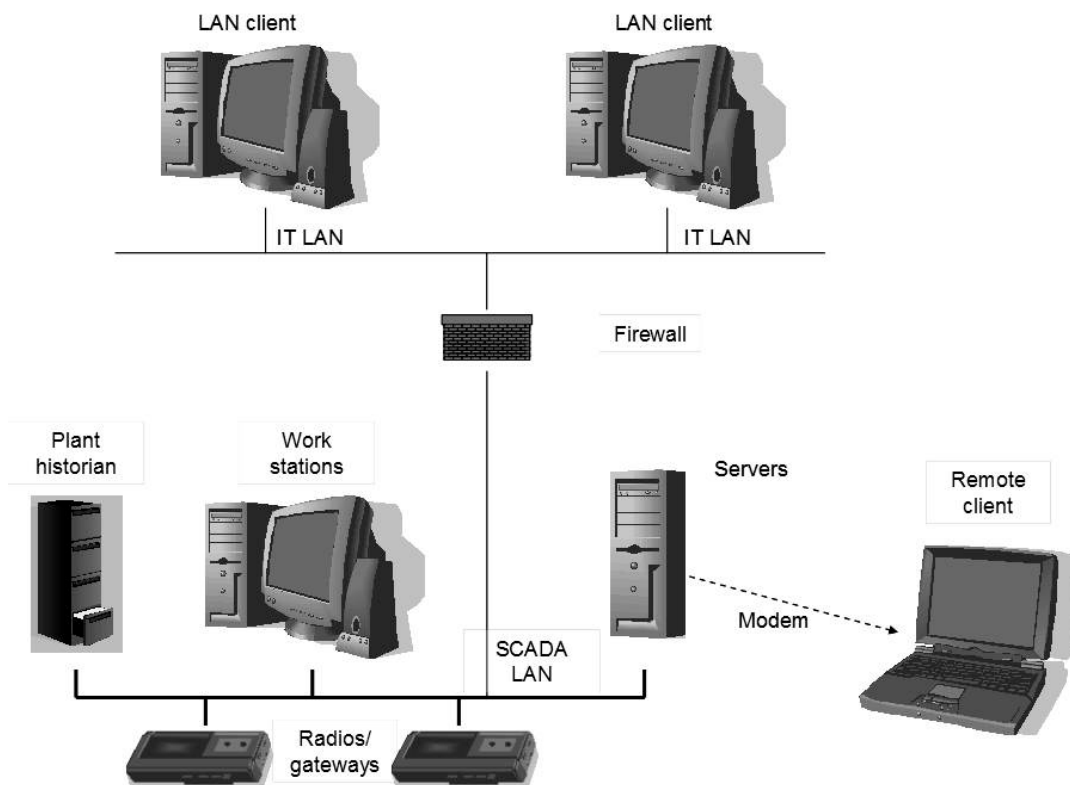
The process monitor that displays alarms may also connect directly to further devices that serve as alarm warning devices: hooters, sirens, lights, auto-diallers and pagers. Remote connection to the SCADA system can be provided through a number of techniques (see telemetry).

In some cases the system enables the manager/operator to dial in to the plant to turn equipment on and off and make changes to set points (usually from an internet enabled laptop). Sometimes this can mean that site attendance in response to alarms is not necessary. Very often the operator can stabilise the system or call in additional resources prior to attending the site.

Generally SCADA systems cover a large geographic area, automatically collecting data from remote sites such as pump stations, service reservoirs and dams. Typical data collected is pump flow, reservoir level and water main pressure.

The software provided with many of the data acquisition systems, which can be custom designed for SCADA/DCS systems, also allows operators to trend and analyse data. Easy-to-use software provides clear graphics for operators to evaluate. Typically, data can be exported to various spreadsheets or database programs for later analysis. Software is interactive, with the ability to change colours, and graph sizes.

Figure 17.4: An example of a SCADA arrangement



Having all this data at the fingertips of the operator is an extremely useful tool in quality management and trouble-shooting. For example, operators can analyse turbidity data to:

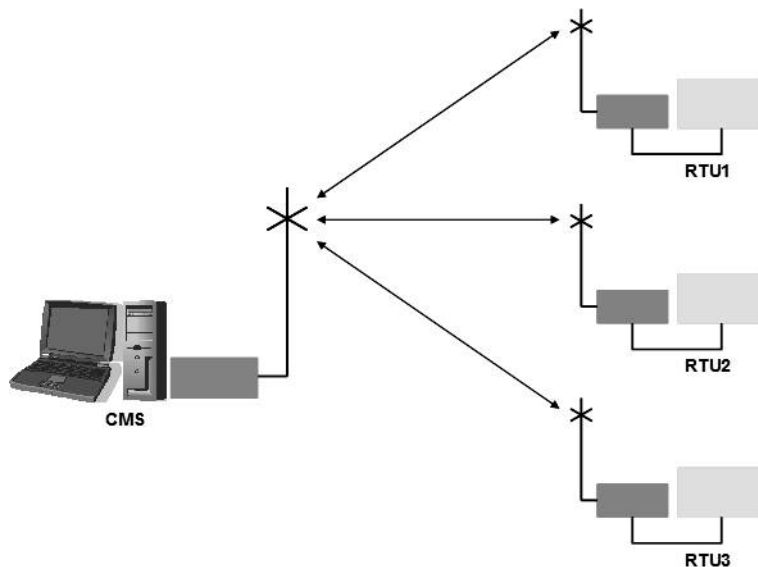
- evaluate peaks in filtered water turbidity for individual filters
- check how storm events affect the filtration capabilities
- examine the effect of various chemical dosages on filtered effluent
- check the setting on the streaming current meter
- compare different filters within a system
- assess the effect of different flow rates on filter performance.

Telemetry

Telemetry is the capability of transmitting or retrieving data over long distance communication links. This is generally by telephone or radio link, but can be by satellite link in remote locations.

To transmit information from a number of locations to a central monitoring station, different communication systems may be employed, including microwave, radio, telephone, dedicated land lines, or even the internet.

Figure 17.5: A telemetry system arrangement



In Figure 17.5, RTU stands for remote transmitter unit. These units can collect information from PLCs, controllers, or even sensors, and transmit to the central monitoring unit (CMS).

Problems that often occur with telemetry/SCADA systems include:

- lightning strikes, especially on radiotelephone antennae. Note that during some storms, high level service reservoir alarms may activate due to the reservoir transducers reacting to low atmospheric pressure
- signal loss in hard-wired communications links due to earthing or cable breaks, or moisture ingress
- radio link loss due to atmospheric conditions or physical damage, especially to repeater stations.

17.4 Continuous monitoring for compliance

Section 3.2 of the DWSNZ specifies the minimum requirements for continuous (online) monitoring to demonstrate that public health is being protected. The minimum requirements vary depending on the determinand, the method of treatment, source, and population served. While standards are different for lesser populations for reasons of affordability, monitoring is equally important, regardless of size. The situations requiring continuous monitoring in DWSNZ appear in Table 17.3, and are discussed further in section 17.5.3.

See section 17.3 for general information about process control monitoring, much of which applies to this section as well.

Current guidance in the UK for drinking water compliance monitoring allows the use of online monitors for data collection; DWI (2014). The DWI publication specifies the extent to which online and laboratory data can differ for the online data to be acceptable; it sets limits on the mean difference between data pairs of online and laboratory data, and on the 95 percent confidence range of the difference between online and laboratory data pairs. The report finds that there are some important differences between online and laboratory measurements of chlorine and turbidity; these are discussed. UK water companies use duplication and triplication of instruments as a means of detecting instrument problems and of achieving high availability of key measurements.

17.4.1 Priority 1 determinands

The regulatory requirements for continuous monitoring relate primarily to Priority 1 determinands. For protozoa, an alternative parameter must be used to demonstrate compliance because measuring infectious protozoa directly in drinking-water is impractical at present. This is because tests can take days to complete, cannot be measured continuously, require very large samples, highly trained staff are needed, and the tests are very expensive.

Protozoa

Continuous turbidity monitoring is used to indicate the likelihood of *Giardia* cysts and *Cryptosporidium* oocysts being present in water leaving filters. This is based on evidence correlating turbidity with (oo)cyst numbers, documented in USEPA (2003/2006). See also Chapter 8: Protozoa Compliance.

As an example, for a plant serving more than 10,000 people, which is treating a surface water or a non-secure bore water by chemical coagulation and filtration, continuous turbidity monitoring on each filter is required in order to meet the protozoal compliance criteria in the DWSNZ. Continuous measurement of the individual filter turbidity provides operators with the basis for understanding what the filter is doing. For example:

- poor performance of an individual unit can be detected because the effect is not diluted by the other filters
- short term deterioration is detected
- ripening times and the optimum time to wash the filter become clearer
- by measuring at the filter the effect of subsequent processes such as post filter lime dosing is excluded.

Particle counting is an increasingly common method for monitoring the performance of filtration systems. Particle counters are more sensitive than turbidimeters although they are relatively expensive, susceptible to spikes in turbidity and are difficult to calibrate on-site (see Chapter 8: Protozoa Compliance, section 8.6.2.2). These units indicate particle numbers and sizes, including particles that are in the size range of protozoa. A particle counter is frequently recommended to ensure compliance as it will often detect deterioration in filter performance before detection by a conventional turbidimeter. Laser turbidimeters are now available with greatly improved sensitivity over conventional units. When turbidity and particle counts are both measured it is good practice to supply the instruments from a common sample stream.

Another method for demonstrating protozoal compliance is direct integrity testing (DIT), used for membrane filtration plants. There are no continuous DIT methods suitable for compliance testing at present.

Methods for monitoring compliance for protozoal inactivation rely on disinfectant dose rates (chlorine dioxide, ozone and UV dose) along with the monitoring of parameters that affect the performance of the disinfectant, such as temperature, UVT, turbidity, contact time and the residual remaining after treatment (chlorine dioxide, ozone).

See Chapter 8: Protozoa Compliance, sections 8.4.4.3 and 8.6.2.6 for discussion relating to operation and standardisation of UV intensity meters, and section 8.4.4.3 re UV transmission.

Bacteria

The DWSNZ require bacterial compliance monitoring of water leaving the treatment plant to be measured directly (*E. coli*) at regular intervals, or by continuously monitoring the free available chlorine equivalent (FACE) or chlorine dioxide residual, or by a combination of *E. coli* and continuous ozone monitoring if disinfecting with ozone. *E. coli* testing is covered in Chapter 6.

When the water has a residual of at least 0.2 mg/L chlorine or chlorine dioxide (allowing for the effect of pH when using chlorine) after a minimum of 30 minutes' contact time, it is assumed (based on years of experience) that the bacteria will have been inactivated. Because free available chlorine and pH (and hence FACE) can be measured continuously, the reliability of disinfection can be demonstrated. Refer to Chapter 6: Bacterial Compliance, section 6.3.7 and Chapter 15: Treatment Processes: Disinfection, section 15.2.9). Continuously recording FAC and pH analysers will generally be more economical than the daily *E. coli* monitoring required. For water treatment plants serving fewer than 10,000 people, less than daily *E. coli* monitoring is required, so continuous FAC and pH analysers may become less economic as an alternative monitoring option. In practice, however, this level of process control is desirable for any sized plant. It also assists to reduce the amount of monitoring for *E. coli* in the distribution system.

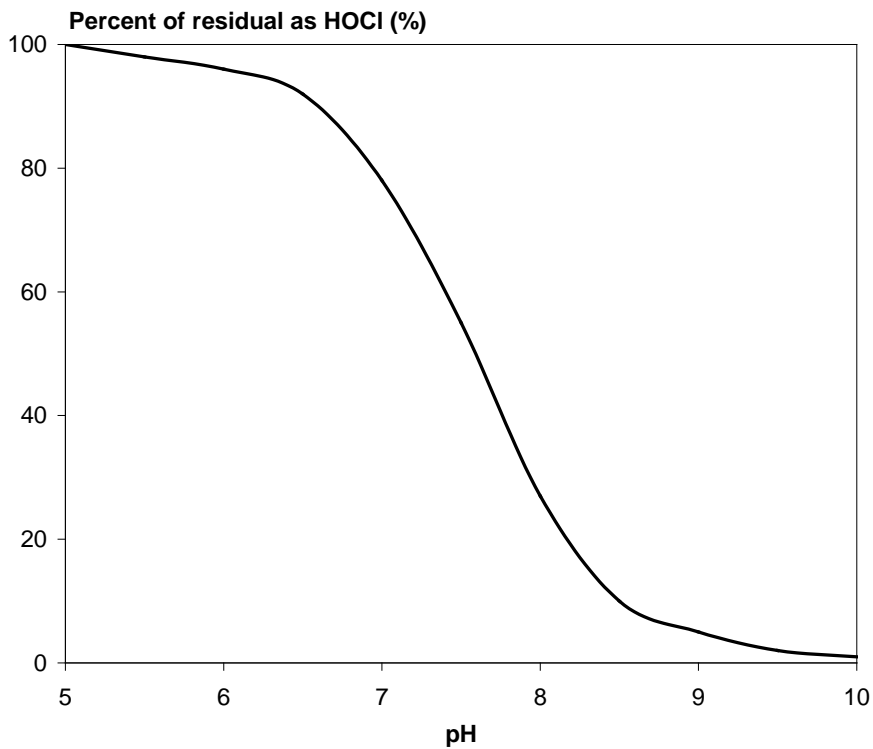
The reliability of chlorine and chlorine dioxide monitoring is such that some *E. coli* monitoring of water in the distribution system can be substituted with FAC or chlorine dioxide monitoring (section 4.4.4.2 of the DWSNZ). Bulk water suppliers can measure FAC or chlorine dioxide continuously in lieu of *E. coli* testing (section 4.4.7 of the DWSNZ). Refer also to Chapter 6 for details of compliance issues.

Most FAC instruments are designed to indicate the total of two forms of FAC, ie, hypochlorite ion and hypochlorous acid (HOCl). In general they are only sensitive to the form that is prevalent at low pH values (hypochlorous acid). For this reason a buffer is often added to the sample to lower the pH and convert both forms of FAC to the detectable form (HOCl) and the sensor simply reads the total FAC.

Some instruments indicate the FAC without adding a buffer. They can do this by measuring the amount of hypochlorous acid and calculating the proportion it makes of the total using a relationship based on sample pH. These instruments allow the waste from the meter to be recycled more easily but depend heavily on the accuracy of both the FAC and pH calibration. This is a problem at a pH approaching 8 as the proportion of hypochlorous acid becomes very small, magnifying any error. Refer also to Chapter 15: Disinfection, section 15.5.1.1.

A spreadsheet method for converting FAC concentrations to FACE when the pH is greater than 8 appears in Chapter 6: Bacterial Compliance, section 6.3.7.

Figure 17.6: Hypochlorite ion vs hypochlorous acid at various pH values



17.4.2 Priority 2 determinands and indirect indicators

The MAV for fluoride is 1.5 mg/L. The fluoride concentration in the water leaving most water treatment plants that fluoridate is around the 0.8 mg/L level, thereby making fluoride a priority 2A determinand, requiring weekly analysis. It is possible to monitor fluoride continuously for both process control and compliance purposes.

Most monitoring requirements for Priority 2 determinands are satisfied by manual sampling and laboratory analysis. Nevertheless it is good practice to monitor selected parameters online to confirm that the water treatment plant operates well within compliance limits.

Absorbance (A_{254}), also sometimes measured as transmittance, is a useful indication of the level of natural organic matter (mainly humic and fulvic substances) that may give rise to disinfection by-products following disinfection. In organic-rich waters, A_{254} should be measured prior to chlorination. This test (reported as UVT) is also needed when using UV light for disinfection.

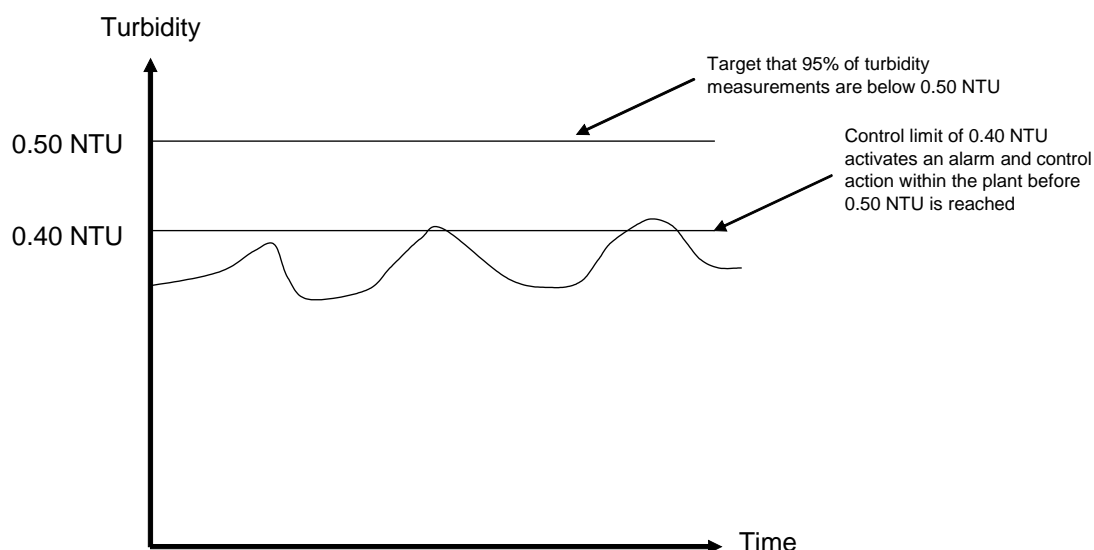
17.4.3 Control limits

To comply with the DWSNZ, a water supply should be operating within any MAVs or operational requirement limits set by the DWSNZ. The DWSNZ recommend that water suppliers establish control limits. Control limits warn that the water supply or treatment process is approaching transgression level. These should always be chosen conservatively to raise alerts and/or undertake corrective action before the MAVs or operational requirements are reached. It is recommend that water suppliers decide on a control limit for every MAV and operational requirement that relates to their system. Then they are to plan preventive measures that will come into play when the measured determinand reaches the control limit; these control limits and preventive measures are to be included in their WSP.

On occasions when water quality moves outside the acceptable range an operator alarm should be raised. Ideally the alarm limits should be set well below the 'not to exceed' limits in the DWSNZ; a limit set at about two-thirds the standard or requirement is quite common. Process control limits should be set to ensure that supply of non-compliant water is prevented.

A formal approach, aimed at laboratories, to establishing control charts, and how to use them, appears in APHA (2005), in section 1020. The Australian Drinking-water Guidelines Information Sheet 3.4 (NHMRC 2011) offers a useful summary (in three pages) for water suppliers. Further guidance is offered in DWI (1999).

Figure 17.7: Example of use of control limits



17.4.4 Recording and storing results

In order to prove compliance with DWSNZ there must be a continuous record of the relevant processes whilst in use. Clearly with digital data the record is actually a series of discrete data points. Continuous monitoring requirements for bacterial and protozoal compliance are defined in section 3.2 of the DWSNZ. As an example, records of filtered water turbidity are required to be no more than a minute apart, whereas five-minute intervals are acceptable for FACE in the water leaving the treatment plant. Obviously signal averaging time cannot exceed the recording period of one or five minutes, whichever applies.

The data are reported as the percent of time each condition was exceeded (or met) during the monitoring compliance period. Minimum measurement frequency and monitoring compliance periods are listed in the DWSNZ. There are also limits on the amount of time that instruments can be offline, see section 3.2 of DWSNZ.

Drinking water assessors will want to see a record showing that water quality complies with DWSNZ. Reliable storage of the data is an essential part of compliance. Maintaining data points for future analysis can pose a problem due to the amount of storage required. For example if turbidity is recorded every minute on each filter in a bank of four filters for one year, more than 2 million records are created for this parameter alone! It is permitted to compress the data if accuracy is maintained. In some plants this is achieved by only recording a value where that value has changed from the previous one, including recording if the instrument goes offline.

Water suppliers should consider the use of DVDs, CDs, USB memory sticks, external hard drives, Zip-drives or tape-drives for storage of data. Hard drives can be used to store data while manipulating or evaluating the data, but loss of data is likely to occur during a PC crash. Use of the above storage media types can overcome or minimise this problem.

The data must be stored in a usable format. Operators should have the ability to download data from their acquisition equipment into a usable and manageable format. Data is typically placed in one of many different formats such as Excel, Access, dBASE, and Lotus 123. Data should be converted into a format that can be used by the facility and by the assessor. Many water suppliers use software as above. The key to selecting a format is the ease with which the data can be viewed, manipulated, and or converted. Some software packages allow users to create reports, tables, or graphs based on the data.

Table 17.3: Drinking-water Standards for New Zealand: requirements for continuous online monitoring

Treatment process	Turbidity	Flow/ dose ²	Temperature	pH	Disinfectant residual	Other
Bacterial disinfection criteria	Required ¹	Required ¹	Or manual	Required ¹	Required ¹	
Protozoal compliance criteria						
Bank filtration	Required ¹					
Coagulation, sedimentation, filtration	Required ¹					
Coagulation, direct filtration	Required ¹					
Second stage filtration	Required ¹					
Combined filtration	Required ¹					
Individual filtration	Required ¹					
Diatomaceous earth filtration	Required ¹					
Slow sand filters	Required ¹		Or manual			
Membrane filtration	Required ¹					Direct integrity
Cartridge filtration	Required ¹					Differential pressure
Bag filtration	Required ¹					Differential pressure
Chlorine dioxide	Required ¹	Required ¹	Or manual		Required ¹	
Ozone	Required ¹	Required ¹	Or manual		Required	
UV	Required ¹	Required ¹			UV intensity	UV transmittance

1 Refer to DWSNZ for specific requirements, as requirement varies depending on population served, etc; some manual testing may be acceptable.

2 Flow and dose calculated to enable C.t to be calculated. Refer to DWSNZ for specific online testing requirements for UV.

17.5 Testing

17.5.1 Introduction

This section discusses testing in a general sense. Obtaining a satisfactory test result presupposes a correct sample collection technique, and that the sample was placed in a container prepared for the purpose, or sterile container for microbiological testing. Some of these requirements are discussed generally in earlier sections of this chapter. A discussion on the use of statistics appears in the Appendix in Chapter 1. More specific sampling, preservation, transportation and testing procedures are provided elsewhere in these *Guidelines*, in appropriate chapters as follows:

- Chapter 2: Management of Community Supplies, section 2.4.3 Sampling frequency (for compliance)
- Chapter 4: Selection of Water Source and Treatment, sections 4.4.1 Where to sample, 4.3.2 When to sample and how often, and 4.4.3 What to sample
- Chapter 6: Bacterial Compliance (throughout most of the chapter)
- Chapter 8: Protozoa Compliance, section 8.6 Sampling and testing
- Chapter 10: Chemical Compliance, sections 10.3 Monitoring programme design, 10.4 Sampling procedures and techniques, and 10.5 Analytical details
- Chapter 18: Aesthetic Considerations, sections 18.4 Monitoring programme design, and 18.6 Analytical details.

Recommended test protocols are available, in detail, in publications such as *Standard Methods for the Examination of Water and Wastewater* (APHA). The requirements for a laboratory to be recognised by the Ministry of Health for compliance testing are outlined in Chapter 1: Introduction, section 1.3.10 Register of recognised laboratories.

This section deals with the process of testing in broader terms (eg, quality control) and the concepts and practices necessary to ensure that the testing is meaningful. This is important due to the time, effort and cost obtaining samples, the level of confidence needed in the results, as well as the public health risks a water supply can present. Some areas of repetition from previous sections have been inevitable. However, given the critical requirement of competency, such repetition is not amiss.

17.5.2 Appropriate testing

The critical requirement of any water testing protocol is that the testing be appropriate and competent. The monitoring and sampling efforts necessary to comply with the *Drinking-water Standards for New Zealand* (DWSNZ) are onerous and considerable in time, labour and expense. Such effort is wasted if the subsequent testing does not meet these requirements. It is implicit in the entire rationale of the monitoring process imposed by the DWSNZ that the samples collected are not just tested, but that they are tested properly.

Testing must not just be competent (ie, reliable, accurate and repeatable), but also appropriate. This means not just doing the tests right, but doing the right tests. This is necessary to ensure not just that the test process remains valid, but that test results (between time, place and laboratory) can be compared, and that it is possible to use the data for trend analysis if so desired.

There are several aspects to the concept of appropriate testing:

- testing only on valid samples, ie, samples having had proper sampling, transportation, storage and pretreatment procedures
- testing the exact parameter required. This is important, for example, in metals testing, where a number of forms of the metal can exist (total, soluble, particulate, acid digest, acid soluble) which require specific pretreatment and test methodologies to distinguish. It is important in microbiological testing too where options exist to distinguish various coliform types

- using a method with an appropriate limit of detection, see section 17.6. For example, the MAV for *E. coli* is less than 1 per 100 mL, so there is no point in testing a 50 mL aliquot for compliance purposes
- testing to the appropriate accuracy. This accuracy is essentially predetermined by the compliance values provided in the DWSNZ. For example, the MAV for lead is 0.01 mg/L, so testing with a method that has an uncertainty of measurement of 0.005 mg/L does not provide a very meaningful result, see also section 17.6.

The objective of the testing will usually indicate the determinand's form of interest, but it is often an area where experience and appropriate skill of the analyst will come into play, and where thought and consideration must be given to test options.

A number of determinands need to be tested on-site. This is usually because of determinand stability and the transportation time to reach the testing laboratory. The common example is testing of chlorine residuals where on-site testing is the only real option. The nature of such testing, sometimes with the use of simple test kits, may suggest a regime of testing where different standards apply. That is not the case. As far as compliance with the DWSNZ is concerned, such on-site testing is not just a screening procedure, or a rough check. It may lack the inherent accuracy of many laboratory tests but the same quality control requirements should apply. On-site results must be of known reliability, and they too must be traceable back to known reference standards.

If a laboratory's results are to be used to assess compliance with the DWSNZ, the laboratory must be a Ministry of Health recognised laboratory, ie, IANZ accredited, or a level 2 laboratory. Supplementary Criteria for Accreditation No. 1.2/2.2 defines the specific criteria for the approval of laboratories for entry into the Ministry of Health Register of Water Testing Laboratories; see IANZ (2007) for details. An accredited test report suggests that the laboratory met the requirements of IANZ, which does not necessarily include sampling. It is recommended that a document accompanying the test report include useful information such as the laboratory staff told the sampler how to collect and deliver the sample and provided the sampler with the correct equipment, and that the sample appeared to arrive in good condition; although that statement does not say the sample was handled correctly throughout the process, it does lend the test report a little more credibility.

17.5.3 Online monitoring

There can be obvious advantages in online instrumental monitoring:

- the immediacy of testing and of obtaining results
- the ability to use the results for direct plant control
- the ability to collect data without having to collect samples or to man sites
- the provision of continuous and recordable results.

Such monitoring can be more appropriate than manual methods, for example:

- where highly time-variable water quality fluctuations occur
- where and when it is difficult to sample manually
- where it is difficult to maintain the required sampling frequency
- variations between analysts are not a problem
- results can be more accurate when the manual method is difficult.

There can be economic advantages as well, despite what may be a fairly large capital outlay. Thus a wide range of on-site monitoring equipment is now available, and widely used, for an increasing number of test parameters.

However, while such testing can replace a degree of dependence on laboratory testing resources, the automated results should have a similar credibility to a result subject to the rigorous quality control regime that should prevail in an accredited laboratory environment. Thus a requirement exists that online monitoring equipment must be standardised properly and professionally certified at the time of installation, see section 17.3.3.

Also, because such instrument sensors can change over time (as a result, for example, of fouling, breakage, electronic drift, aging of electrodes), there must be sufficient regular standardisations and checks to ensure consistent and accurate performance. The verification process typically involves either instrument performance testing (essentially having the instrument read an independent standard), or by independent separate testing of a sample from the instrument against which its reading can be checked. Following the instrument manufacturer's instructions is a minimum requirement of the DWSNZ; this covers installation, operation, standardising with a zero and at least one other standard, and maintenance.

Instrument accuracy must be consistent with that required for any compliance monitoring function. Measurements from online instruments must agree with calibration or reference values within the predetermined uncertainty of measurement required.

Note that a record of each instrument standardisation (and indeed each maintenance and service event) must be retained as a retrievable, and auditable, document. Individual equipment requirements vary widely, though in all cases proper adherence to the manufacturer's instructions (as a minimum) is essential. Readers are directed to White (1997 and 1999) for an example (available on the internet) of a comprehensive field manual for automated water quality monitoring.

A public water supply in Portugal operated online monitoring equipment to monitor several parameters, including chlorine, pH, turbidity and conductivity. However, the quality of monitoring results was such that operators lacked confidence in readings and relied instead on manual sampling and laboratory testing. Through the WSP process, the WSP team focused on increasing the quality of data generated by the online instrumentation through improved calibration and maintenance, which resulted in greater confidence in readings and reduced reliance on laboratory testing. Also, the WSP risk assessment process revealed that some online instrumentation was unnecessary and could be removed from service. In addition, the frequency of

laboratory testing for other parameters (ie, those not monitored with the online equipment) was reduced on the basis of the outcomes of the risk assessment and prioritisation. As a result of WSP implementation, a 56 percent reduction in the cost of water quality monitoring was achieved through O&M costs avoided for the online instrumentation removed from service as well as reduced frequency of laboratory analysis (WHO 2018).

UK Guidance for online monitors used for compliance testing appeared in DWI (2010). In general, online monitors at water treatment works or service reservoirs may be used for regulatory analysis provided it can be shown that the particular monitor is:

- i. capable of providing fit for purpose data (as defined in regulation 16 or this Guidance)
- ii. sited to ensure that results are representative of the water being supplied
- iii. maintained and operated to a demonstrably high standard at all times
- iv. calibrated in a way that is valid, appropriate and traceable
- v. subject to reliable quality checks at an appropriate frequency
- vi. the date and time of each compliance reading is specified in advance of the start of the compliance year
- vii. there is a traceable means of demonstrating that the recorded reading is the true reading of the instrument at that time; and
- viii. there are robust and effective means for sampling and analysis whenever the monitor is out of service or performing unreliably.

Existing monitors for total chlorine, free chlorine, turbidity and conductivity may be demonstrated as meeting requirements (i) and (ii) above by comparing results of analysis using the current regulatory method with the instrument readings at the times of sampling. Provided the difference between the means is not greater than 10 percent of the result or 5 percent of the PCV, whichever is the greater, and the 95 percent confidence interval for the difference of an individual pair of results (difference between paired instrument result and compliance method result) is not greater than 20 percent of the result or 10 percent of the PCV, whichever is the greater, the results will be acceptable. Not fewer than 20 pairs of results covering at least one year should be used for the comparison. Only installations which satisfy these requirements may be used for compliance monitoring purposes.

DWI (2014) reports:

There is a paucity of dependable test data where online and laboratory measurements are compared in situations relevant to final water measurements at water treatment works. Based upon literature the following numerical conclusions were drawn.

- Chlorine – an uncertainty of about ± 0.1 mg/L Cl₂ against laboratory analysis is being achieved.
- Turbidity – uncertainty against laboratory analysis is better than ± 0.2 FTU, but due to the instrument-dependent nature of turbidity it may be more helpful to consider reproducibility and systematic error. The reproducibility is better than 0.1 FTU; the systematic error varies between instruments.

In all cases the performance derived from test data is significantly poorer than the suppliers' claimed performance.

17.5.4 Quality assurance, quality control and testing proficiency

The terms quality assurance and quality control are often used interchangeably. They have distinguishable meanings, particularly with regard to laboratory proficiency auditing and accreditation. Quality assurance (QA) refers to the system of operating protocols in a laboratory that, if strictly followed, will provide data of known and auditable quality. Separately, quality control (QC) is the laboratory's individual operational monitoring techniques and activities (within the QA system) used to check and ensure performance requirements.

A laboratory's QA system should be all-encompassing, and cover every aspect of laboratory activity including:

- management
- personnel
- equipment
- environment
- supplies
- test performance
- records
- reporting
- compliance with standards
- client relationships.

Such comprehensive (and auditable) quality assurance processes are a requirement of New Zealand's laboratory accreditation programme. This accreditation programme is intended to create a consistent and reliable level of laboratory testing performance nationally. Such performance is a necessity for good monitoring of any drinking-water standards and is supported by the system requirement of registered laboratories. Readers are referred to the referenced International Accreditation New Zealand (IANZ) publications for more detailed discussion of QA/QC, accreditation, and laboratory proficiency issues. Part 1000 of APHA (2005) contains useful information too.

IANZ accreditation provides confidence that:

- appropriate quality assurance systems are in place
- appropriate methods are being used for the tests the laboratory offers
- the methods used are either internationally recognised, or are properly validated in-house methods.

Through the site visits, IANZ assess whether the methods used are being carried out as stated. Site visits only 'sample' what is being done in the laboratory on an annual (or less frequently), so what accreditation cannot demonstrate is that the laboratory is following documented methodology on a daily basis. Even with accreditation in place, the production of reliable results from a laboratory, in the end, depends on the competence, diligence and integrity of the staff. The same is true of Level 2 labs.

Having a signatory, or head laboratory scientist, with appropriate expertise is important for ensuring that the correct response is made when dealing with situations that are not covered by the documentation. All that said, while accreditation does not guarantee the absence of inaccurate data, mistakes or corners being cut, it provides much greater assurance that such things are unlikely to happen than the lack of accreditation.

The outcome of the above is that a laboratory's test results should be of appropriate accuracy and reproducibility, and be able to be proven by audit to be so.

Laboratory accreditation bodies worldwide use proficiency testing schemes as part of the assessment process to validate the ability of laboratories to competently perform tests for which accreditation is held. Proficiency tests complement the traditional technique of an onsite laboratory review by technical experts.

IANZ operates the proficiency testing scheme in accordance to ISO/IEC Guide 43:1997, Proficiency testing by interlaboratory comparisons; Part 1: Development and operation of proficiency testing schemes.

The primary aims of proficiency testing schemes are:

- establishing the effectiveness and precision of test methods
- checking the individual testing performance of laboratory staff
- determining the characteristics of a material to a particular degree of accuracy (such as in the preparation of reference materials).

By participating in a proficiency testing scheme, laboratories will:

- identify any problem in the laboratory, eg, individual staff competence, method suitability, calibration of instrumentation, and initiate remedial action
- provide clients with additional confidence in the test results.

IANZ (2007) requires all laboratories in the MoH Register of Water Testing Laboratories to participate in suitable interlaboratory comparison programmes (ILCP) for those tests within their scope of recognition.

Ideally, ILCP samples should be part of a routine batch of analyses, all relevant determinands should be tested, and as many staff involved as possible. A very important part of ILCP is a timely follow-up, with a thorough investigation of all batches producing an unacceptable ILCP result. Outcomes should be available as part of staff training.

There may be occasions when a smaller scale interlaboratory comparison is appropriate, such as when establishing a new method, settling in new staff or equipment, or during problem solving. Splitting samples with an experienced nearby laboratory can be useful in such circumstances.

17.5.5 Accuracy, precision, uncertainty of measurement

An inherent part of a testing laboratory's QA and QC programme is prevention, detection and correction of errors in the measurement process. However, this aim is rarely completely achievable. The process can only minimise errors. Thus an extension of the quality control process is required to assess the errors remaining. In this way, a test result can be provided with an associated measure of its reliability. This is usually identified in terms of uncertainty of measurement or confidence limits that define the statistical certainty (often 95 percent) that the actual result lies within a given range, see section 17.6 for a more quantitative discussion.

Important components in limiting the uncertainty of a water test result may include some or all of the following:

- Method validation or verification (see section 17.5.6 for details)
 - analysis of reference standards or material
 - examination of published test performance data
 - appropriate limit of detection
 - eliminating interferences in the analysis
 - recovery of known additions
 - replicate analyses
 - independent method comparisons
- Laboratory analysis
 - testing samples in timely manner, or preserve them
 - calibration standards included with every batch
 - including appropriate sample and reagent blanks
- Quality control
 - internal performance audits
 - inter-laboratory proficiency testing programmes
 - control samples/charts
 - checking calculations
 - eliminating transcription errors.

Statistical data (usually in terms of standard deviation, or less commonly variance) from the above processes allow the measurement and monitoring of test method accuracy and precision. This reveals the basic reliability of a laboratory's test results, particularly in chemical testing. Microbiological testing has some differences in approach because of the absence of reference standard concentrations. Here methodology is primarily verified against both positive and negative control organisms.

The terms accuracy and precision have distinct meanings in the context of test results:

- accuracy refers to the proximity to the true or actual concentration value
- precision refers to the comparative similarity of repeat results.

IANZ (2004) defines three types of precision: repeatability, reproducibility and intermediate precision. These can be compared most easily in tabular form (Table 17.4).

Table 17.4: Types of precision associated with test results

Parameter	Repeatability	Intermediate precision	Reproducibility
Laboratory	Same	Same	Different
Sample	Same	Same	Same
Test method	Same	Same	Same*
Equipment	Same	Different	Different
Materials	Same	Different	Different
Time	Same	Different	Different
Staff	Same	Different	Different

* Note that by requiring test methods to be calibrated against a referee method or to be validated, acceptable reproducibility should be achievable nationally for purposes such as compliance testing.

When an analyst measures the concentration of a determinand in a sample several times in one batch, the repeatability can be calculated, which under these conditions will look rather good! Generally this will not reflect the precision obtained by a laboratory over time. A more realistic measure of the laboratory's precision is represented by intermediate precision. Reproducibility is more a measure of a test method's precision, as reflected by interlaboratory testing.

The test for precision, ie, measuring the standard deviation on one set of replicate samples (which is a measure of repeatability), can give misleading information in the situation where compliance with a national standard is being assessed over a very long period. A more reliable assessment of uncertainty of measurement includes a long-term assessment, or intermediate precision, which covers issues such as different analysts, the effect of new calibrations, new reagents, new equipment, etc. The situation may worsen if the water supplier uses more than one laboratory. On average, reproducibility has been found to be about double repeatability (Royal Soc Chem 2003).

A test method is said to be precise when repeated analyses on the same sample give similar results, but such results may not necessarily be accurate. An analogy with a dartboard is often made where a close cluster of darts represents precision, but with accuracy only being represented also when the cluster is around the bulls-eye, assuming that was the target.

Random errors (such as sample contamination, weight or volume uncertainties and calculation errors) are the main influence on precision, with a method being precise when random errors are small. Relatively small random error is advantageous in laboratory work since it allows reliably reproducible results to be obtained time after time. The results may still not represent the true value however. This depends on accuracy that is more derived from systematic errors (or bias) contributed by such factors as errors in standardising, interference, speciation and reagent contamination.

Ideally a test method should be both 100 percent precise and 100 percent accurate. However, given all the variables that can impact on test performance, this is very unlikely. Some systematic and random errors will still occur despite the minimisation of these through quality control measures. These will tend to be specific for any given test method and laboratory procedure, and they can be quantified by quality control components such as those listed above. Some (reference standards, independent method comparisons, inter-laboratory testing) identify systematic errors and accuracy, while others (sample replicates, different analysts, internal standards) identify random errors and precision.

Statistical treatment of the derived data (usually in terms of standard deviation) then quantifies total test performance error so that overall uncertainty of measurement can be available for any given result. This step of the quality control process is necessary before any result can be truly meaningful. Additionally, it can provide accept or reject criteria, used for example in test control charts, for individual test performance assessment.

It is not appropriate here to provide exact application guidelines for statistical treatment of test results. Various approaches are possible, and a brief summary is difficult. For examples of explanatory discussion of applications that are relevant to water testing, readers are directed to the very good IANZ Technical Guide (2004), APHA (2005), and Appendix 5 in ANZECC (2000).

When analysing a sample from a regular site for the first time, there are no previous results available for comparison. If all the major ions are analysed, the results can be checked by calculating the ion balance, or by comparing the measured conductivity with the calculated conductivity, see APHA (2005).

17.5.6 Referee methods, standards and traceability

For any given determinand, there is usually a range of test methods available. Sometimes this range is considerable. Different test methods might be preferred for a number of reasons such as:

- the concentration range of the determinand
- the form of the determinand
- presence of interfering substances
- accuracy required
- equipment available
- skill and qualifications of testing personnel
- sample stability
- time available before results needed
- cost
- convenience.

The overriding consideration must be that the method chosen can provide the required accuracy, limit of detection and uncertainty of measurement, and be 'fit for purpose'. The water supplier must define the objectives of the testing and discuss these with the analysts.

Referee methods

Because different test methods often give different results (differing test conditions, forms of the determinand, reaction mechanisms, etc), comparison of results can lead to contention. This is certainly not desirable when compliance with a standard is being sought. For this reason referee methods have been identified for most test determinands in the DWSNZ. Referee methods first appeared in the DWSNZ in 1995 when there were several laboratories testing water in New Zealand, not all accredited by IANZ.

The DWSNZ are not updated very often, so the referee methods tend to become outdated. Therefore, apart from coliforms/*E. coli*, referee methods will probably not appear in future DWSNZ. Although the use of referee methods is currently encouraged, alternatives will be considered but the laboratory must have calibrated (section 17.5.7) or validated the alternative methodology against the referee method (IANZ 2007).

Validation

Referee methods are usually taken from internationally accepted standard texts such as USEPA methods, APHA/AWWA/WPCF, ASTM, AOAC, ISO, etc. Methods that reach this 'status' have usually gone through a rigorous validation or peer review process. Individual laboratories can also validate a method, to the satisfaction of an accreditation body such as IANZ. They would normally do this when they have developed an analytical procedure of their own, or adapted a method not normally used for the same purpose.

Validation involves a successful examination of at least the following:

- i) repeatability, intermediate precision, with differences between the batches listed
- ii) recoveries from spiked and/or real samples, describing how this was carried out
- iii) matrix effects included for all matrices in the intended scope
- iv) comparison with alternative methods, interlab proficiency, reference materials
- v) method robustness, acceptance criteria established for conditions found to be critical
- vi) effect of determinand levels: acceptable ranges should be determined
- vii) uncertainty of measurement, method limits of detection, limits of quantitation etc
- viii) selectivity (interferences from other determinands)
- ix) linearity (over the intended range).

Method verification

A laboratory using a referee method (sometimes called reference method) for compliance testing needs to demonstrate their competence in performing that method. This is called verification. The laboratory needs to show that it is fully compliant with the reference method. To claim it follows a particular reference method does, however, imply that it can match any method performance criteria given in the reference method, and this needs to be demonstrated and included in the report. This will include, at least, operating a QC programme, including satisfactory participation in an interlaboratory proficiency testing programme, and measuring detection limits and uncertainty.

Standard materials

Ideally standard materials should be independent and certified, have known concentrations of determinands that, by analysis in the laboratory, allow the accuracy of test methods and procedures to be established. This is simply achieved by comparing the known value of the determinand in the standard material with the results obtained by the laboratory from its performed analysis of the standard material. Results should lie within the confidence limits identified for the reference standard material. Obviously the standard materials need to be in a similar concentration and matrix to the normal laboratory samples being processed.

A range of standard materials may be used:

- the most desirable are independently certified reference materials with stated determinand concentrations and confidence limits traceable to national or international standards. For water analyses, these can be obtained in a number of appropriate matrices, and with multi-determinand components. They are however relatively expensive and sometimes a lesser degree of certification may suffice
- the next level down is standard material prepared from (reputable) proprietary analytical grade chemicals
- a lesser form can be a large reservoir of a stable sample with known determinand concentrations from previous and confirmed analysis.

Important factors are that the reference material is certified to have a known true concentration and has not exceeded its warranty period, and is independent of the laboratory's calibration standards used in the routine test procedure. They should be used wherever possible. Use of standard materials, particularly certified reference materials, also provides testing laboratories with the added attribute of traceability. See Rienitz et al (2007) for a description of a technique for drinking-water interlaboratory comparisons.

Traceability

Traceability can have two meanings within a water laboratory environment:

- the traceability of analytical results from the test report back to where the sample was collected. This traceability depends on such things as chain of custody records, sample identity, analyst identity, and test data and calculations

- the traceability of analytical results from the test report back to reference materials or calibrations, which can link ultimately with national or international standards.

Both are important test quality control requirements and are prerequisites for certification and accreditation of analytical laboratories.

Chain of custody

The use of correct chain of custody procedures becomes very important when testing samples that may lead to a dispute or court appearance. Chain of custody traces the entire process of sample collection, delivery, storage, and the handling, testing and reporting procedures in the laboratory. Accredited laboratories should have adopted approved chain of custody practices for such occasions and they should be contacted for advice if required. The USEPA has produced a chain of custody 'procedure' which is available on the internet at:

http://www.epa.gov/region6/qa/qadevtools/mod5_sops/misc_docs/r1_chain-of-custody.pdf.

Utah State (2013) developed a Standard Operating Procedure (SOP) for sample Chain-of-Custody (CoC) based on the USEPA primer.

17.5.7 Calibrating a method against the referee method

The 2008 DWSNZ defined this as:

Demonstrating that an alternative method will reliably give the same result to an acceptable strength-of-agreement (NIWA 2007) as the referee method, under the same range of circumstances, within a known uncertainty considered acceptable by independent peer review, thus demonstrating that the alternative method is fit for purpose.

Section 3.1.1 of the DWSNZ stated that:

The referee methods specified in Appendix 2 are the definitive methods for demonstrating compliance with the DWSNZ. Alternative methods are acceptable but must have been calibrated against the referee methods, to the satisfaction of International Accreditation New Zealand (see NIWA 2007). In the event of any dispute about differences in analytical results, results obtained using the referee method will be deemed to be correct.

Infrequent revisions of the DWSNZ mean that the concept of referee methods is difficult to implement. The procedure for the approval of new test(s) used for drinking-water sample compliance was altered in December 2010; see

<http://www.health.govt.nz/publication/ministry-health-procedure-approval-new-test-methods-bacteriological-compliance-testing-drinking>:

Laboratories conducting tests for drinking-water compliance are either accredited by International Accreditation New Zealand (IANZ) or are recognised Level 2 laboratories. Laboratories conducting chemical tests may use the test methods for which they have been assessed by IANZ and found to be competent to perform, for the above compliance testing. Laboratories conducting bacteriological tests for drinking-water compliance need to use a referee method specified in the DWSNZ, or a method that has been calibrated against a referee method.

For new presence/absence bacteriological test methods, refer to the Ministry of Health procedure for approval of new test methods for bacteriological compliance testing of drinking-water samples using presence/absence methods (doc, 31.5 KB).

For numeric methods, refer to NIWA's 2007 report to the Ministry of Health: Equivalence measures for comparing the performance of alternative methods for the analysis of water quality variables (pdf, 246 KB).

The NIWA Concordance Calculator – a method for assessing agreement between alternative methods is recommended.

The NIWA report includes a calculator that allows users to determine the 'strength of agreement', which is classified into 'almost perfect', 'substantial', 'moderate' and 'poor'. The 'strength of agreement' must be fit for purpose. Ideally chemical methods will be 'almost perfect', but this will not always be possible, for example, when a MAV is close to the limit of detection.

Method validation and method verification are covered by IANZ in their *Specific Criteria for Accreditation*.

17.5.8 Reporting the results

Obviously there can't be a design or standard form because laboratories will be using different software packages, paper sizes, orientations, etc. But it is possible to say what should be included on the reports.

Some of the reporting requirements are specified in ISO 17025; for example, section 5.10.3 states that:

Test reports shall, where necessary for the interpretation of the test results, include the following:

- a. deviations from, additions to, or exclusions from the test method, and information on specific test conditions, etc, bearing in mind that reports need to contain all information necessary for the interpretation of the results (ISO 17025 section 5.10.1).

As a guide, Table 17.5 has been included to show the sort of information that should appear on a test report.

17.5.9 Records

Section 13 of the DWSNZ (2005, revised 2008) stated that:

The duty to keep records and make them available is covered in section 69ZD of the HDWAA (2007). See Health Act: <http://www.legislation.govt.nz/>.

This begins:

Every drinking-water supplier and every temporary drinking-water supplier who is required to prepare a WSP must ...

Section 69ZD(2)(g) states that the records kept must include details of the monitoring of that drinking-water; and (h) covers customer complaints.

Water suppliers only need to store information on the compliance monitoring results and the method used, not the field sheets, chain of custody documents, work sheets, QA/QC data, etc. The required information should appear on the laboratory result sheet.

The above applies to water suppliers, and does not apply to testing laboratories – their requirements are covered by their accreditation or conditions related to being a 'recognised laboratory', ie, covered by IANZ. *Supplementary Criteria for Accreditation No. 1.2/2.2* (IANZ. 2007) which covers laboratories recognised by the MoH states in section 12.1:

The laboratory shall maintain a record system to suit its particular circumstances and comply with any particular regulations. It shall retain on record all original observations and calculations and a copy of the test report for an appropriate period. The records for each test shall contain sufficient information to permit their repetition. Where appropriate, records of derived data and of calibration records shall also be retained for an appropriate period.

There is no reference to how long records should be retained. There had previously been some indication that a minimum of 10 years was required as stated in The Health (Retention of Health Information) Regulations 1996; however, these Regulations only relate to health services provided to, and information about, individuals.

Table 17.5: Suggested report form

WAIRARAPA TECHNICAL SERVICES LTD
PO Box 125, Masterton

Analytical Services Division
Chief Chemist: Brian Jones
phone 06 235 1457
fax 06 235 1458
b.jones@wts.co.nz

Report dated 12.11.06

Space for IANZ 'stamp' if appropriate

A Ministry of Health recognised laboratory

Number of pages: 2

b) Sample information area

Client: South Wairarapa District Council
Water supply: Martinborough MAR003

Samples	WINZ	Lab no	Sampled
Treatment plant	TP01234	2006/11/06	1015, 8 November 2006
17 High Street	MAR001HS	2006/11/07	1030, 8 November 2006
Rugby Club	MAR001RC	2006/11/08	1045, 8 November 2006

Samples collected by G Brown, Swimming Pool Services Ltd, Carterton.

Sample(s) arrived at laboratory at 1130, 8 November.

Sample details

- E. coli*: in sterile borosilicate bottles with thiosulphate, 5.2°C on arrival
- For other tests: each sample in 2 x 2 L PE bottles supplied by lab, one sample straight from the tap, the other pre-acidified with 5 mL 50 percent HNO₃.

Sampler's comments: fine this am, 35 mm rain fell previous day.

Analyst's comments: samples arrived in satisfactory condition for compliance testing purposes.

c) Analytical information area

Test	Test method	Detection limit	Uncertainty
<i>E. coli</i>	APHA 9223B	NA	NA
pH	APHA 4500-H ⁺ B	NA	NA
Turbidity	APHA 2130 B	0.05	0.05
Manganese	APHA 3111 B	0.005	0.01
FAC	APHA 4500-Cl G	0.02	0.03

d) Test results area

Sample	Test tested	Unit result	Date	Test	MAV
TP01234	<i>E. coli</i>	per 100 mL	8 November	<1	<1
TP01234	pH	8 November	7.95	–	
TP01234	Turbidity	NTU	9 November	0.25	–
TP01234	Manganese	g/m ³ Mn	11 November	0.12 * ¹	0.4
TP01234	FAC	g/m ³	8 November	0.35 * ²	5
MAR001HS	etc ...				
MAR001RC	etc ...				

* 1 Less than the MAV but exceeds the GV (0.04 mg/L).

* 2 Tested in the field by Swimming Pool Services Ltd, a MoH recognised laboratory.

Signed (Brian Jones – IANZ signatory)
Wairarapa Analytical Services Limited

17.6 Comparing test results against a MAV

17.6.1 Uncertainties of measurement

ISO 17025 requires:

Testing laboratories shall have and shall apply procedures for estimating uncertainty of measurement. In certain cases the nature of the test method may preclude rigorous, metrologically and statistically valid calculation of uncertainty of measurement. In these cases the laboratory shall at least attempt to identify all the components of uncertainty and make a reasonable estimation, and shall ensure that the form of reporting of the results does not give a wrong impression of the uncertainty. Reasonable estimation shall be based on knowledge of the performance of the method and on the measurement scope and shall make use of, for example, previous experience and validation data.

Measurements are not exact. They are attempts at establishing the true value of a determinand, but because of numerous factors that influence the measurement in random ways (ie, excluding factors that bias the results), the measured value can only be an approximation of the true value. The statement of a test result alone, therefore, is incomplete. Information about the uncertainty in the measurement is needed in order to provide an understanding of how close to the true value the test result is likely to be. A good estimate of uncertainty of measurement allows laboratories and their clients to:

- establish that results are fit for purpose
- confirm that results are traceable to international or national standards
- properly compare results between laboratories
- compare results with specifications, legal tolerances or regulatory limits
- make informed decisions.

The uncertainty in a test result is stated as a \pm value, termed the confidence interval. The bounds of this interval are called the upper and lower confidence limits, respectively. Usually the interval is symmetrical about the test result (and is assumed always to be so in this section). So the limits are the test result \pm the 'confidence interval half-width'.

The size of the half-width depends on experimental factors, such as the sensitivity of the instrument, the analytical method used, the skill of the analyst etc, the required level of confidence, and the number of measurements made on the sample (see section 17.5). An estimate of the spread in the values caused by the experimental factors can be obtained by making repeated measurements of a determinand. This spread is often expressed as the standard deviation, and is one of the parameters used to calculate the confidence limits.

The level of confidence determines the likelihood that the true value will be within the confidence interval. The greater the confidence required, the larger that interval will be. Conversely, replicated analyses will tend to have smaller confidence intervals. The DWSNZ requires a 95 percent level of confidence where possible for the purposes of evaluating compliance.

Note that there is never 100 percent certainty that the true value will lie within the confidence limits; from time to time the true value will lie outside these limits. For example, if the level of confidence is set at 95 percent, this implies that there is a 5 percent probability that the true value will lie either below the lower limit or above the upper limit.¹

The confidence limits (CL) can be determined from Equation 17.1:²

$$CL = \bar{y} \pm 1.960 q \frac{s_r}{\sqrt{n}} \quad \text{Equation 17.1}$$

where:

- \bar{y} = the laboratory result for a particular sample; there is usually just one result, so usually $\bar{y} = y$ (a single result is its own mean)
- s_r = the standard deviation of a set of quality control samples³
- n = the number of independent measurements made on the sample
- $q = \sqrt{\frac{n+m}{m}}$ where m is the number of independent blank determinations used to obtain the result.

Often, a sample result is obtained by subtracting a reading of one or more blanks from a reading of one or more measurements on a sample. Frequently, there is a single sample analysis, and a single blank, so that $n = m = 1$. When an analysis does not involve a blank subtraction (eg, instrumental turbidity measurements, or when it is believed that the analytical technique will not produce a non-zero result if the determinand is absent). In that case $m = 0$ and so the q correction factor is simply $q = 1$.

For example, say we have previously performed a number low-level replicates of lead analyses, obtaining a standard deviation of $s_r = 0.0010$ mg/L. If the result is based on a single sample analysis, from which a blank result is subtracted, then $q = \sqrt{[(1+1)/1]} = \sqrt{2} = 1.414$ and the confidence interval lies a distance of 0.0028 mg/L on either side of the sample result.⁴

¹ Strictly, this is taking a Bayesian interpretation of probability, using uniform prior distributions (McBride 2005). The details need not concern us further.

² The approach given here is based on material in Hunt and Wilson (1984, section 8.3). It assumes that: (a) the standard deviation s_r equals the 'population' standard deviation and is known from an historical set of results for blank (or low level) samples, and (b) the distribution of the population of blanks and/or low level samples are 'normal'. The '1.960' factor is the value of the abscissa of the unit normal distribution that cuts off an area of 0.025 in each tail of that (symmetrical) distribution. (The 'unit normal distribution' is the ordinary normal, bell-shaped, distribution, with zero mean and unit standard deviation.) Note that some authors (eg, IANZ 2004) advocate the use of the t distribution in place of the unit normal distribution. However there are some conceptual difficulties in that approach (see Hunt and Wilson 1984, p 295).

³ These repeated measurements are not made on the sample in question.

⁴ Calculated as $1.960 \times (0.0010/\sqrt{1}) \times 1.414 = 0.0028$.

IANZ accredited and MoH recognised laboratories will routinely make quality control measurements that allow them to calculate their measurement methods' limits of detection and uncertainties. The most balanced measurement of uncertainty uses intermediate precision; see section 17.5.5 and IANZ (2004). Factors involved in calculating the measurement of uncertainty vary depending on the nature of the analysis, see (IANZ 2004). A discussion on how to avoid underestimating uncertainty appears in RSC (2012). For some other helpful discussion, see <http://www.rsc.org/Membership/Networking/InterestGroups/Analytical/AMC/TechnicalBriefs.asp/>.

Uncertainty of measurement can vary with concentration. In terms of compliance with the DWSNZ, it is important to know the uncertainty of measurement for concentrations near the MAV. With respect to compliance, the importance of uncertainty of measurement reduces when the test result is small compared with the MAV.

With respect to the DWSNZ, uncertainty of measurement does not have to be reported with results of operational requirements used for compliance testing. This is because of the wide range of instruments in use, and because the concept of uncertainty in this field is still developing. The DWSNZ simply require that 'equipment used to demonstrate compliance must be suitable for that purpose'. Operational requirements include online or manual testing of pH, turbidity, temperature, FAC, pressure differential, chlorine dioxide, ozone, UV irradiance (sensor reading), UV transmission, and direct integrity (as used on MF plants).

17.6.2 Comparison of a measurement with a fixed value

The calculation of the confidence limits for a measurement is important for the reasons discussed above. However, Equation 17.1 has to be modified slightly if upper or lower confidence limits are to be calculated for comparing test results against a fixed value. This is what is required when establishing if a MAV or operational requirement has been transgressed.

Either a precautionary or a permissive approach can be taken when making this comparison. Just which approach is followed depends on the stance taken by the regulatory authority on the burden of proof. This is discussed in the following sections (and more fully by McBride 2005).

The precautionary approach, which is taken by most public health authorities around the world, assumes 'guilty until proven innocent beyond reasonable doubt', ie, there must be 95 percent confidence that the fixed value has not been exceeded, for compliance to be inferred. For this requirement to be met, the upper confidence limit must not exceed the fixed value.

The permissive approach, on the other hand, assumes 'innocent until proven guilty beyond reasonable doubt', ie, it seeks 95 percent confidence that the fixed value has been exceeded, before it is classed as having been exceeded. Thus exceedence is only deemed to have occurred once the lower confidence limit (*LCL*) exceeds the fixed value.

The upper confidence limit (*UCL*) is calculated using Equation 17.2:

$$UCL = \bar{y} + 1.645 q \frac{s_r}{\sqrt{n}} \quad \text{Equation 17.2}$$

The parameters are the same as in Equation 17.1, but because a comparison is being made with a fixed value this is a 'one-sided' limit. That is why the value '1.960' in Equation 17.1 has been changed to '1.645' in Equation 17.2.⁵

The lower confidence limit (*LCL*) is calculated in a similar manner, simply replacing the plus sign by a minus sign. That is:

$$LCL = \bar{y} - 1.645 q \frac{s_r}{\sqrt{n}} \quad \text{Equation 17.3}$$

Continuing the lead example above (section 17.6.1), the one-sided confidence limits would lie a distance of 0.0023 mg/L from the sample result.⁶ The *UCL* would be above the sample result and the *LCL* would be below that result.

17.6.3 Approaches considered in developing the method used in the DWSNZ

Three approaches to the way in which results can be compared against MAVs and operational requirements were considered in establishing the requirements of the DWSNZ.

Approach 1: Ignore uncertainty in the test measurement

In this approach the face value (ie, the result without uncertainty of measurement considered) is compared directly with the MAV. No attempt is made to take the uncertainty of measurement into account. So, for example, a result for lead of 0.012 mg/L is a transgression, because it exceeds the MAV of 0.01 mg/L. If the uncertainty in the test measurement were, say, ± 0.003 mg/L, the true result could occasionally be below 0.009 mg/L, but this would make no difference to the finding that the result transgresses the MAV.

This approach relies on the balance of probabilities, taking an even-handed approach to swings and roundabouts for fairness. So when the measured value is just above a MAV, there is about a 50:50 chance that the true value is below it, and vice versa in the case that the measured result is just below the MAV.

⁵ An abscissa of 1.645 cuts off an area of 0.05 in the right tail of the unit normal distribution.

⁶ Calculated as $1.645 \times (0.0010 / \sqrt{1}) \times 1.414 = 0.0023$.

A major advantage of the approach is its simplicity.

Approach 2: Round up or down

This approach compares test results with MAVs and operational requirements using the same number of significant numbers, so, using the example in Approach 1, the test result of 0.012 mg/L can be rounded down to 0.01 mg/L, which is not greater than 0.01, so it is not a transgression.

This is effectively a permissive approach. That is, the result has to be some way over 0.01 mg/L before it fails the MAV. For example, a lead result of 0.0149 mg/L in this approach would comply with a 0.01 mg/L MAV, despite being 49 percent greater than the MAV. A result of 0.0151 mg/L would be a transgression. This rounding approach also ignores uncertainty in test measurement.

Approach 3: Accept uncertainty in the test measurement

To be implemented properly this approach requires the uncertainty of measurement to be based on either the upper or lower one-sided 95 percent confidence limit to be calculated using Equation 17.2, and for a decision to be made whether a precautionary or permissive approach should be taken, as discussed in section 17.6.2. Considering an example of a measured lead concentration being 0.012 mg/L, then, using the results we have already calculated, the two approaches would have the following consequences:

- a) **Permissive:** If this approach is taken, we use the result we calculated earlier (that the LCL lies 0.0023 below the result), to obtain $LCL = 0.0097$ mg/L. Therefore, the result is not classed as a transgression, because LCL is less than the MAV (0.01 mg/L). For simplicity, in this example it is assumed that the uncertainty of measurement and LCL have the same value.
- b) **Precautionary:** If this approach is taken, we use the result we calculated earlier (that the UCL lies 0.0023 above the result), so that $UCL = 0.0143$ mg/L. Or had the measured lead concentration been 0.0085 mg/L, then the $UCL = 0.0108$ mg/L, which is above the MAV despite the test result being below the MAV of 0.01 mg/L. For simplicity, in this example it is assumed that the uncertainty of measurement and UCL have the same value.

The precautionary approach has been used in all previous editions of the DWSNZ for *E. coli* or faecal coliforms. This approach has been continued in the DWSNZ 2005 (revised 2008). For example, Table A1.4 in the DWSNZ expresses the permissible number of exceedances of a MAV, given the need to have 95 percent confidence that the MAV is exceeded for no more than 5 percent *of the time*. The proportion of allowable exceedances *among the samples* is always less than 5 percent, as it must be in a precautionary approach.⁷ For example, one exceedance is allowed among 100 samples, a proportion of 1.0 percent, and six exceedances are allowed among 240 samples, a proportion of 2.5 percent.

⁷ If 5 percent *of samples* exceed the MAV there would be about a 50 percent chance that the MAV would have been exceeded for more than 5 percent *of the time*. That is a 'face-value' stance to the burden-of-proof, not a precautionary approach.

17.6.4 Approach adopted in the DWSNZ

The DWSNZ 2005 (revised 2008) state that no account is to be taken of uncertainties of measurement in chemical test results when comparing them against MAVs. This is in line with previous practice.

However, NZS ISO/IEC 17025:2005 requires laboratories to calculate their uncertainty of measurement, which is explained in IANZ Technical Guide TG5 (IANZ 2004). When testing drinking-water for chemical compliance, laboratories must report their uncertainty of measurement (U) with the test result (T). A MAV has been exceeded when the test result (T) is higher than the MAV.

Most MAVs include a safety factor because of the uncertainty associated with the toxicological data. Consequently almost all are stated to only one significant figure. Despite this, MAVs are treated as exact numbers for the purposes of comparing them with test results. In other words, as many zeros as required can be placed after the last significant figure of the MAV when comparing it with a test result.

Roberts (2007) stated:

With the exception of some sections of the forensic fraternity, Australian regulators have not yet formally embraced the concept of measurement uncertainty (MU) or determined policies and rules for interpreting it with reference to regulatory limits. Some would argue that the limits established take MU into account, but in most cases the inaction is akin to adopting a policy to disregard MU. It is fair to say that to-date MU has had limited impact on regulatory standards in Australia. This is likely to change in the future. Both chemists and regulators would be well-advised to improve their understanding of MU.

In the future, the precautionary approach, ie, Approach 3(b) may well be used in determining whether a test result exceeds the MAV. The upper one-sided 95 percent confidence limit could be termed the adjusted result. Therefore it would be the adjusted result, and not the test result that will be compared against the MAV. If this adjusted result exceeds the MAV, a transgression will have occurred. For example:

If the uncertainty of measurement based on the upper one-sided 95 percent confidence limit (ie, adjusted result of $U + T$) in a lead measurement lies 0.002 mg/L units above the measured value, then the test result cannot exceed 0.008 mg/L, otherwise the true value may too often exceed the MAV of 0.01 mg/L.

17.6.5 Detection

Various techniques are used to describe the lowest meaningful concentration a test method can report. Sometimes the terminology is used rather loosely, so it is important to explain exactly what is meant when discussing detection.

APHA (2005) refers to instrument detection level, lower limit of detection, method detection level, and the level of quantification. The relationship among these levels is approximately 1:2:4:10.

IANZ (2004) refers to criterion of detection, limit of detection and limit of quantification. The relationship of these to the standard deviation of low-level results is approximately 1:1.7:3.4:8.

These seven different relationships vary depending on whether blanks are included and whether the sample is tested more than once. Most laboratories in New Zealand use the expressions in IANZ (2004), which tend to be based on UK and European practices.

The criterion of detection (*CofD*) is the minimum concentration that a single test result may have for the analyst to say that the determinand is present with 95 percent confidence. The limit of detection (*LofD*) is the upper confidence limit for a result that is exactly on the *CofD*.

The *CofD* is defined as $2.33s_r$, and the *LofD* is defined as $4.65s_r$.⁸ As an example, consider a determinand with $s_r = 1.2$ mg/L. Then *CofD* ≈ 2.8 mg/L and *LofD* ≈ 5.6 mg/L. The data series 4.5, 3.4, 3.0, 2.5 and 8.9 mg/L would be reported as 4.5, 3.4, 3.0, <5.6 and 8.9 mg/L. There is an apparent inconsistency here: some results are reported as less than the *LofD*, while some are (validly) censored and reported as numerical values less than that limit. What's happening is that the numerically-reported results are 'central estimates' of the true concentrations, whereas in the censored results the *LofD* is playing the role of an upper one-sided 95 percent confidence limit.

It should be noted that the censoring practice advocated in these *Guidelines* (in the preceding paragraph) is not followed routinely, it often being common to use only the *LofD*, often taken as $3s_r$ (eg, Eurachem 1988, Helsel 2005),⁹ or other multiples of s_r (APHA 2005, IANZ 2004). In such approaches, any data above this limit are reported at face-value, those below it are reported less than the *LofD*. The problem with that is that if the true concentration happens to equal the *LofD*, 50 percent of the time the result will be 'not detected', or less than the *LofD* value. In contrast, the approach adopted in these *Guidelines*, using both the *CofD* and *LofD*, avoids that problem and has a strong theoretical foundation, especially for reporting compliance data.¹⁰

⁸ These limits are based on keeping 'Type I' and 'Type II' statistical errors below 5 percent, for blank-corrected analyses. The rationale is as follows. If an analyst *observes* a blank-corrected value greater than *CofD* there is at least a 95 percent chance that it was in fact present. Furthermore, if the *true* concentration is greater than the *LofD* there is at least a 95 percent chance that the *observed* concentration will be above the *CofD*, thereby allowing detection to be claimed. Theoretical details can be found in Hunt and Wilson (1984), Ellis (1989) and McBride (2005). Note that if the analysis does not involve a blank-correction, the multipliers 2.33 and 4.65 for the *CofD* and *LofD* should be divided by $\sqrt{2}$, and so become 1.65 and 3.29 respectively. The latter figure is used in 'Standard Methods' (APHA 2005, pp 1–18), ie, ignoring the increased variability attributable to blank corrections.

⁹ This divergence of practice is made more complex by a lack of uniformity in nomenclature, with one writer's *CofD* being called a Limit of Detection by others.

¹⁰ The *CofD/LofD* approach given above involves 'informative censoring' (Helsel 2005). This can raise problems for some sophisticated data analyses (even for calculation of percentiles), but this is not an issue for compliance monitoring. Ellis (1989, Appendix 4B) presents some solutions to these difficulties.

Note also that this approach does not consider the Limit of Quantitation (LofQ), which is often taken as about 10s. Data above this limit can be held to have satisfactory measurement precision.

Finally, note that the *CofD* and *LofD* are independent of a particular test result. They refer to an expected performance of a laboratory or instrumental technique on average, not to any feature of a particular result.

MAVs and detection limits

Many chemical MAVs and operational requirements are close to common analytical limits of detection. The test methods need to be sensitive and precise enough to prevent large uncertainties. The detection limit needs to be less than the operational requirement or 50 percent of the MAV (to allow Priority 2 status to be assessed). That is, reporting a lead analysis as less than 0.1 mg/L, for example, is unsatisfactory because the result could be 0.09 mg/L, which is nine times its 0.01 mg/L MAV.

As far as possible, the limit of detection for tests should be *at most* a fifth of the MAV or operational requirement, eg, no more than 0.002 mg/L for lead, 0.06 NTU for a turbidity operational requirement of 0.30 NTU, or 0.02 NTU for an operational requirement of 0.10 NTU.¹¹ It is the responsibility of the water supplier to be vigilant when selecting a laboratory and/or method to ensure that *LofDs* are well below the MAV to eliminate the possibility of encountering an exceedance based on uncertain data. How to deal with “less than values” or “non-detects” is discussed in the Appendix of Chapter 1, and in Section 10.2.5.3 of the Guidelines.

Where a water supplier has control over a determinand such as turbidity, it would be wise to put control limits in place that signal a need for corrective action to be taken at levels well below the MAV or operational requirement; see section 17.4.3.

Measuring the limit of detection

Ideally, all water suppliers (and/or water laboratories) should use the same approach for estimating the criterion and limit of detection (*CofD* and *LofD*). The following is recommended.

Select a low level standard (for example, a standard at about five times the expected *LofD*) and test it many times, preferably over several days; large laboratories could conduct the test using different instruments and staff. This will need to be repeated when new staff conduct the test, and when new methods or instruments are introduced. Conducting repeat analyses on a single sample on a single occasion is called repeatability. Different people testing different samples, on different occasions etc is called intermediate precision; see section 17.5.5. Say the following results were obtained from testing a 0.001 mg/L standard (eg, lead or aldicarb):

¹¹ Making the detection limit one-10th of the detection limit is much more desirable.

0.0010	0.0012	0.0010	0.0010	0.0011	0.0018
0.0018	0.0014	0.0009	0.0009	0.0010	0.0019
0.0002	0.0011	0.0014	0.0014	0.0008	0.0018
0.0004	0.0008	0.0015	0.0015	0.0007	0.0015
0.0010	0.0005	0.0016	0.0016	0.0010	0.0013
0.0015	0.0004	0.0017	0.0017	0.0010	0.0011
0.0010	0.0006	0.0015	0.0015	0.0013	0.0008
0.0012	0.0009	0.0013	0.0013	0.0013	0.0006

Using a spreadsheet such as Excel, the above results have a standard deviation (s_r) of 0.00041 mg/L (mean 0.00116 mg/L). Therefore CofD = 0.00068 mg/L and LofD = 0.00134 mg/L, when using CofD = 1.65 s_r and 3.29 s_r respectively, ie, no blank corrections used. These could be rounded off to 0.007 and 0.0013 mg/L respectively.

Ideally the LofD should be a fifth of the MAV, or lower. There may be situations where the analytical technique of a determinand is not particularly sensitive, and may have a LofD that is close to the MAV. This may result in the reported value exceeding the MAV, thereby requiring a water treatment process that will reduce the concentration of the determinand to an unnecessary level.

There are some techniques that can be adopted that may overcome this problem. Some of these will increase the cost of analysis, but this cost will be very small compared with the cost of installing additional treatment. Some approaches include:

- using a different analytical technique with a lower LofD
- concentrating the sample, say by boiling 200 mL down to 20 mL
- running replicate tests on the water sample.

References

ANZECC. 2000. *Australian Guidelines for Water Quality Monitoring and Reporting*. Australia and New Zealand Environmental and Conservation Council.
<http://www.environment.gov.au/water/publications/quality/nwqms-monitoring-reporting.html>.

APHA. 2005. *Standard Methods for the Examination of Water and Wastewater* (21st edition). Washington: American Public Health Association, American Water Works Association, Water Environment Federation.

ANZECC/ARMCANZ. 2000. *Australian Guidelines for Monitoring and Reporting, National Water Quality Management Strategy Paper No 7*. Australia and New Zealand Environment and Conservation Council / Agriculture and Resource Management Council of Australia and New Zealand.
<http://www.environment.gov.au/water/policy-programs/nwqms/>.

AS/NZS 5667. 1998. *Water Quality – Sampling*. Homebush, NSW: Standards Australia, and Wellington: Standards New Zealand.

- AS/NZS 2031. 2001. *Selection of Containers and Preservation of Water Samples for Microbiological Analysis*. Standards Association of Australia.
- AWWA. 2001. *Concrete Pressure Pipe* (3rd edition). AWWA Manual M2. Denver CO: American Water Works Association.
- AWWA Manual. *Instrumentation and Control*. Denver CO: American Water Works Association. www.awwa.org.
- British Standards Institution. 2010. *Guide for the Auditing of Water Quality Sampling*. BS 8550:2010.
<http://shop.bsigroup.com/en/ProductDetail/?pid=00000000030169965>.
- Colton J. 2015. Online compliance, a decade of lessons. *Water* 191: 36–8. Water New Zealand, September/October.
- DWI. 1999. *Guidance on the Interpretation of Aspects of Analytical Quality Control (AQC)*. 8 pp. <http://dwi.defra.gov.uk/stakeholders/guidance-and-codes-of-practice/index.htm>.
- DWI. 2010. *Guidance on the Implementation of the Water Supply (Water Quality) Regulations 2000 (as amended) in England*. 99 pp.
[http://dwi.defra.gov.uk/stakeholders/guidance-and-codes-of-practice/WS\(WQ\)-regs-england2010.pdf](http://dwi.defra.gov.uk/stakeholders/guidance-and-codes-of-practice/WS(WQ)-regs-england2010.pdf).
- DWI. 2014. *A Critical Appraisal of Existing Guidance on Online Monitor Performance Data*. Report No: UC9882. 184 pp. <http://dwi.defra.gov.uk/research/completed-research/reports/DWI70-2-285.pdf> or <http://dwi.defra.gov.uk/>.
- DWI. 2016. *Private Water Supplies Sampling Procedures Manual*. Drinking Water Inspectorate (UK). 29 pp. <http://dwi.defra.gov.uk/private-water-supply/regs-guidance/Guidance/sampling/pws-sampling-procedures.pdf>.
- Ellis JC. 1989. *Handbook on the Design and Interpretation of Monitoring Programmes*. Medmenham, England: Water Research Centre Report NS29. Section 8.2.3 and Appendix 4-B. Revised in 1996 as *Water Quality Monitoring: A practical guide to the design and implementation of freshwater quality studies and monitoring programmes*. UNEP/WHO, 366 pp. <http://www.bvsde.paho.org/bvsacd/who/monito.pdf>.
- Eurachem. 1998. *The Fitness for Purpose of Analytical Methods: A laboratory guide to method validation and related topics*. Teddington, Middlesex, UK: Eurachem.
<http://www.eurachem.nl/images/eurachem/Fitnessforpurpose.pdf>.
- Helsel DR. 2005. *Nondetects and Data Analysis: Statistics for censored environmental data*. New York: Wiley. 288 pp.
- Hunt DTE, Wilson AL. 1986. *The Chemical Analysis of Water: General principles and techniques* (2nd edition). Section 8.3. London: The Royal Society of Chemistry.
<http://pubs.rsc.org/en/Content/eBook/978-0-85186-797-7>.
- IANZ. *Specific Criteria for Accreditation*. Lab C 1: Biological Testing. Lab C 2: Chemical Testing. For latest versions, see <http://www.ianz.govt.nz/>.
- IANZ. 2004. *Technical Guide: Uncertainty of measurement precision and limits of detection in chemical and microbiological laboratories*. Auckland: International Accreditation New Zealand. See <http://www.ianz.govt.nz/>.

IANZ. 2005. *General Requirements for the Competence of Testing and Calibration Laboratories*. (NZS/ISO/IEC 17025). Auckland: International Accreditation New Zealand. <http://www.ianz.govt.nz/>.

IANZ. 2007. *Supplementary Criteria for Accreditation No. 1.2/2.2* (2nd edition). Ministry of Health Register of Water Testing Laboratories. Auckland: International Accreditation New Zealand. August. See: <http://www.ianz.govt.nz/>.

ISO / VIM. 1993. *International Vocabulary of Basic and General Terms in Metrology*.

ISO/IEC Guide 43:1997. *Proficiency Testing by Interlaboratory Comparisons*. Part 1: Development and operation of proficiency testing schemes.

McBride GB. 2005. *Using Statistical Methods for Water Quality Management: Issues, options and solutions*. ISBN 0471733202 9780471733201; 344 pp. New York: Wiley.

Ministry of Health. *Public Health Risk Management Plan Guide PHRMP Ref: G2. General – Monitoring*. Available on: <http://www.health.govt.nz/water> then select publications and Water Safety Plans.

Ministry of Health. 2005. *Drinking-water Standards for New Zealand 2005*. Wellington: Ministry of Health. Revised 2008. <http://www.health.govt.nz/water>.

NHMRC. 2011. *Australian Drinking Water Guidelines 6*. 1244 pp. www.nhmrc.gov.au.

NIWA. 2007. *Equivalence Measures for Comparing the Performance of Alternative Methods for the Analysis of Water Quality Variables*. Report to the Ministry of Health. <http://www.health.govt.nz/publication/ministry-health-procedure-approval-new-test-methods-bacteriological-compliance-testing-drinking>; the calculator is also available.

Rienitz O, Schiel D, Guttler B, et al. 2007. A convenient and economic approach to achieve SI-traceable reference values to be used in drinking-water interlaboratory comparisons. *Accreditation and Quality Assurance* 12(12): 615–22. See abstract on <http://cat.inist.fr/?aModele=afficheN&cpsidt=19940494>.

Roberts G. 2007. Measurement uncertainty and its impact on regulatory standards. *Chemistry in Australia* 74(9): 24–6.

Royal Society of Chemistry. 2003. Is my uncertainty estimate realistic? *AMC Technical Brief* 15, December. UK: Analytical Method Committee. http://www.rsc.org/images/realistic-estimate-technical-brief-15_tcm18-214874.pdf.

Royal Society of Chemistry. 2012. Dark uncertainty. *AMC Technical Brief* 53, July. UK: Analytical Method Committee. http://www.rsc.org/images/brief_53_tcm18-221675.pdf.

Sundaram B, Feitz A, Caritat P de, et al. 2009. *Groundwater Sampling and Analysis: A field guide*. Commonwealth of Australia, Geoscience Australia, Record 2009/27, 95 pp. http://www.ga.gov.au/metadata-gateway/metadata/record/gcat_68901.

Sinton L. 1986. A guide to groundwater sampling techniques. *Water and Soil Miscellaneous Publication* 99. National Water and Soil Conservation Authority.

USEPA. *Chain of Custody for Samples and Data* (an online course).
<https://trainex.org/offeringlist.cfm?courseid=771>.

USEPA. 2002. *Standard Operating Procedure for Chain of Custody of Samples*. New England: Office of Environmental Measurement and Evaluation – Region 1. 11 Technology Drive, North Chelmsford, MA 01863. 10 pp. Available at:
http://www.epa.gov/region6/qa/qadevtools/mod5_sops/misc_docs/r1_chain-of-custody.pdf.

USEPA. 2003. *Long Term 2 Enhanced Surface Water Treatment Rule: Proposed Rule*. National Primary Drinking Water Regulations: 40 CFR Parts 141 and 142, August 11, 2003 – see USEPA (2006) for Final Rule.

USEPA. 2003. *IDEXX Colilert® - 18 Test Method for the Simultaneous Detection of Total Coliforms and E. coli in Water*. Draft. USEPA. 6 pp. Available at:
http://www.google.co.nz/search?hl=en&source=hp&q=%22IDEXX+Colilert%C2%AE-18+Test+Method+for+the+Simultaneous+Detection+of+Total+Coliforms+and+E.+coli+in+Water%22&btnG=Google+Search&meta=&aq=f&aqi=&aql=&oq=&gs_rfai=.

USEPA. 2006. *National Primary Drinking Water Regulations: Long Term 2 Enhanced Surface Water Treatment Rule: Final Rule*. (LT2ESWTR). Federal Register Part II, 40 CFR Parts 9, 141 and 142. Washington: National Archives and Records Administration. See
<http://www.epa.gov/fedrgstr/EPA-WATER/2006/January/Day-05/w04a.pdf>
<http://www.epa.gov/fedrgstr/EPA-WATER/2006/January/Day-05/w04b.pdf>
<http://www.epa.gov/fedrgstr/EPA-WATER/2006/January/Day-05/w04c.pdf>
<http://www.epa.gov/lawsregs/rulesregs/sdwa/lt2/compliance.cfm>.

USEPA. 2003. *Chemical/Name Index to EPA Test Methods* (April). 85 pp. Available at:
<http://www.google.co.nz/url?q=http://www.epa.gov/region1/info/testmethods/pdfs/testmeth.pdf&sa=U&ei=N-TyTMK3DpTksQPW8MnnCw&ved=0CBMQFjAA&usg=AFQjCNHKeIqQHKhmrPLHPwXCTeLXnJGhw>.

USEPA, USGS. National Environmental Methods Index. See <http://www.nemi.gov/>.

USEPA (regularly updated). *Analytical Methods Approved for Compliance Monitoring under the Enhanced Surface Water Treatment Rule*. 21 pp.
http://www.epa.gov/safewater/methods/pdfs/methods/methods_swtrules.pdf.

Utah State. 2013. *Standard Operating Procedure for Chain-of-Custody Samples*. 18 pp.
http://www.deq.utah.gov/Compliance/monitoring/water/docs/2014/05May/SOP_COCPcedures_7.1.13_Rev0.pdf.

WHO. 2004. *Guidelines for Drinking-water Quality 2004* (3rd edition). Geneva: World Health Organization. Available at:
www.who.int/water_sanitation_health/dwq/gdwq3/en/print.html see also the addenda.

WHO. 2011. *Guidelines for Drinking-water Quality 2011* (4th edition). Geneva: World Health Organization. Available at:
http://www.who.int/water_sanitation_health/publications/2011/dwq_guidelines/en/index.html.

WHO. 2017. *Guidelines for Drinking-water Quality: Fourth edition incorporating the first Addendum*. Geneva: World Health Organization. 631 pp.

http://www.who.int/water_sanitation_health/publications/drinking-water-quality-guidelines-4-including-1st-addendum/en/.

WHO. 2018. *Strengthening Operations and Maintenance through Water Safety Planning: A collection of case studies*. 20 pp. WHO/CED/PHE/WSH/18.69. WHO/IWA.

http://www.who.int/water_sanitation_health/publications/strengthening-om-thru-water-safety-planning/en/.

White ET. 1997. *Guidelines for Automated Water Quality Monitoring Equipment*. Ministry of Environ. Lands and Parks, Victoria, BC, Canada. See also *Automated Water Quality Monitoring* by same author, 1999, 73 pp. Available on website

http://www.geoscientific.com/technical/tech_references_pdf_files/BC%20RISC%20Automatic%20Water%20Quality%20Monitoring%20Manual.pdf.