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# GUIDELINES FOR DRINKING-WATER QUALITY MANAGEMENT FOR NEW ZEALAND

## APPENDIX 3: SAMPLING REQUIREMENTS, REFEREE METHODS AND ALTERNATIVE ANALYTICAL METHODS FOR DETERMINANDS

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*E. coli*, faecal coliforms, presumptive coliforms

The *E. coli* referee method is:

- APHA 9223 B – Enzyme Substrate Coliform Test
- Presence / Absence
- Multi-Well MPN (Quantitray)
- MPN (multiple tube technique).

Faecal coliforms

APHA 9221 E – Multiple Tube Fermentation (MPN) Technique (EC Medium)

Total or Presumptive Coliforms

APHA 9221 B – Multiple Tube Fermentation (MPN) Technique (Lauryl Tryptose Broth)

Protozoa

The *Cryptosporidium* enumeration procedure that is to be used for assessing the protozoal risk category of a raw water for the purposes of section 5.2.1 is a modified EPA 1623. Protozoal recovery must be assessed by the addition of colour seed to every sample. Both *Cryptosporidium* and *Giardia* are to be recorded.

The sample size shall be a minimum of 10L and the entire pellet must be analysed.

The full method description is given in Appendix 8 of the *Guidelines*.

Turbidimeters

Turbidimeters used for compliance monitoring must comply with:

- ISO 7027, or USEPA Method 180.1, or USEPA Method 10133, or GLI Method 2: and/or
- be approved by the USEPA for drinking-water monitoring.
- The separation between data records is not to be more than one minute for measurements.

- The signal averaging time is to be one minute or less.

Primary calibration must be undertaken by personnel approved to do so by the DWA, and in accordance with the manufacturer's recommended procedures and frequency or three-monthly whichever is the most frequent. Primary calibration must be performed using StablCal (Hach) or PrimeTime (HF Scientific) (or other MoH-approved stabilised formazin preparation); or AMCO-AEPA-1 styrene divinylbenzene microsphere suspensions (Advanced Polymer Systems), except in the following circumstances under which user-diluted formazin preparations may be used.

1. The calibration point is 20 NTU or greater.
2. The 4000 NTU formazin preparation is obtained from a quality certified manufacturer.
3. The dilution is done immediately prior to use for calibration.
4. The quality assurance procedures are approved by the DWA.

Verification of online turbidimeters must be carried out weekly using the manufacturer's secondary standard. If the instrument reading is outside the limits specified for the secondary standard, then that instrument must be recalibrated using the primary calibration method.

### pH

The pH referee method is APHA 4500-H<sup>+</sup>B/electrometric method. The pH electrode must be calibrated before each set of measurements is made, and the manufacturer's instructions must be followed for the storage of the electrode when not in use. Calibration solutions used must be prepared by an analytical laboratory using the formulations given in the above method, or purchased from a chemical manufacturing company as a certified solution.

Two buffers (about 7 then 4) must be used to calibrate and set the slope of the pH meter. Finally a pH 9 buffer must be used to check that the calibration holds over the whole range.

For potable waters (which are often only weakly buffered in New Zealand waters), the laboratory must note the time taken for the pH to return from measuring the 9 buffer to reading the pH of an unbuffered potable water. If this has become slow, then the electrode needs attention or is unsuitable.

Meters being used for potable water require special thin glass electrodes to work properly on unbuffered waters. "Robust" electrodes are not suitable.

### Temperature

A thermometer that has been calibrated according to TELARC technical guide no 3 Working Thermometers Calibration Procedures August 1986 must be used. Checks against another similarly calibrated thermometer must be made at least once every six months. If the readings diverge by more than 0.5°C both thermometers must be recalibrated.

### Continuous monitoring analysers

For validation of on line continuous monitoring analyser records used to demonstrate compliance with these Standards, the value of the determinand recorded at a specified time must be checked to be the same as that obtained by from a grab sample that has been taken at the same time from the designated sampling point for that determinand and that has been analysed by the referee method [or a subordinate method that has been verified against the referee method]. If the monitor is checked using a subordinate method, the subordinate method must be validated against the referee method at least once every six months by a Ministry of Health approved laboratory.

The result, together with any adjustments that are made to the instrument and the identity of the operator(s), must be recorded. The frequency of checking for each class of instrument must be at least the greater of that specified below or that recommended by the manufacturer, and must be increased if this is found necessary to ensure that the rate of “drift” of the instrument reading is insignificant.

### Sampling requirements, referee method and alternative analytical methods for water properties and inorganic determinands listed in Table 2.2 of DWSNZ

Name	Sampling location		Container	Referee method	Alternative methods
	TW	DZ			
high plumbosolvency		✓	P(A)	[Determine Pb on first flush sample]	See Guidelines
antimony		✓	P(A), G(A)	GFAA (APHA 3113) (pre-concentration may be necessary)	ICP-MS (EPA 200.8)
arsenic	✓	✓	P(A), G(A)	GFAA (APHA 3113)	HGAA (APHA 3114) ICP-MS (EPA 200.8)
barium	✓	✓	P(A), G(A)	GFAA (APHA 3113)	FAA (APHA 3111) ICP (APHA 3120) ICP-MS (EPA 200.8)
beryllium	✓	✓	P(A)	ICP-MS (EPA 200.8)	
boron	✓	✓	P	Colorimetric method (Department of Environment 1980, 1981)	Colorimetric method (APHA 4500-B B) ICP-MS (EPA 200.8) ICP (APHA 3120)
bromate		✓	P	IC (EPA 300.0)	IC (JAWWA (1992), 84(11): 88)
cadmium		✓	P(A), G(A)	GFAA (APHA 3113)	ICP (APHA 3120) ICP-MS (EPA 200.8)
chloramines (mono-chloramine, dichloramine, trichloramine)		✓	G	TITR (APHA 4500-CI F) DPD	TITR (APHA 4500-CI D) Amperometric Colorimetric DPD (APHA 4500-CI G)
chlorate	✓	✓	P	IC (EPA 300.0)	IC (JAWWA (1992), 84(11): 88)
chlorine		✓	G	TITR (APHA 4500CI F)	TITR (APHA 4500CI D)
chlorite		✓	P	IC (EPA 300.0)	IC (JAWWA (1992), 84(11): 88)
chromium		✓	P(A), G(A)	GFAA (APHA 3113)	FAA (APHA 3111) ICP (APHA 3120) ICP-MS (EPA 200.8)
copper		✓	P(A), G(A)	GFAA (APHA 3113)	FAA (APHA 3111) ICP (APHA 3120) ICP-MS (EPA 200.8)
cyanide (total)	✓	✓	P	Total cyanide (APHA 4500-CN C)	
cyanogen chloride		✓	G(S)	(APHA 4500-CN J)	[Hydrolyses rapidly, testing must be done on-site. If no cyanide pre-chlorination then no cyanogenchloride possible]
fluoride	✓	✓	P	Ion selective electrode (APHA 4500-F C)	IC (APHA 4110) Colorimetric method, SPADNS (APHA 4500-F D)
lead		✓	P(A), G(A)	GFAA (APHA 3113)	ICP (APHA 3120) (pre-concentration may be needed) ICP-MS (EPA 200.8)
lithium	✓	✓	G(A)	Flame emission (APHA 3500-Li B)	ICP-MS (EPA 200.8)

Name	Sampling location		Container	Referee method	Alternative methods
	TW	DZ			
manganese		✓	P(A), G(A)	GFAA (APHA 3113)	FAA (APHA 3111) ICP (APHA 3120) ICP-MS (EPA 200.8)
mercury	✓	✓	G(A)	CVGAA (3112 B)	ICP-MS (EPA 200.8)
molybdenum	✓	✓	P(A), G(A)	GFAA (APHA 3113)	ICP (APHA 3120) ICP-MS (EPA 200.8)
nickel		✓	P(A), G(A)	GFAA (APHA 3113)	ICP (APHA 3120) ICP-MS (EPA 200.8)
nitrate		✓	P, G	Cadmium reduction (APHA 4500-NO <sub>3</sub> -E)	IC (APHA 4110) Ion selective electrode (APHA 4500- NO <sub>3</sub> -D)
nitrite		✓	P, G	Colorimetric method (APHA 4500-NO <sub>2</sub> -B)	IC (APHA 4110)
selenium	✓	✓	P(A), G(A)	GFAA (APHA 3113)	HGAA (APHA 3114) ICP (APHA 3120) ICP-MS (EPA 200.8)
silver	✓	✓	P(A)	GFAA (APHA 3113)	ICP-MS (EPA 200.8)
tin		✓	P(A)	GFAA (APHA 3113)	ICP-MS (EPA 200.8)
uranium	✓	✓	P(A)	ICP-MS (EPA 200.8)	

### Sampling requirements, preferred method and alternative analytical methods for cyanotoxins of health significance listed in Table 2.3 of DWSNZ

Name	Sampling location		Container	Referee method	Alternative methods
	TW	DZ			
anatoxin-a	✓	✓	G(S) P(S)	LC-MS (Namikoshi <i>et al.</i> 2003; Dell'Aversano <i>et al.</i> 2004; Furey <i>et al.</i> 2003)	HPLC-FLD (James <i>et al.</i> 1998) HPLC-UV (Wong and Hindin 1982)
anatoxin-a(S)	✓	✓	G(S) P(S)	ChE Inhibition Assay (Mahmood and Carmichael 1987; Barros <i>et al.</i> 2004.)	Mouse Bioassay (Falconer 1993)
cylindrospermopsin	✓	✓	G(S) P(S)	LC-MS (Eaglesham <i>et al.</i> 1999; Dell'Aversano <i>et al.</i> 2004)	HPLC-PDA (Harada <i>et al.</i> 1994; Torokne <i>et al.</i> 2004)
homoanatoxin-a	✓	✓	G(S) P(S)	LC-MS (Namikoshi <i>et al.</i> 2003; Dell'Aversano <i>et al.</i> 2004; Furey <i>et al.</i> 2003)	HPLC-FLD (James <i>et al.</i> 1998) HPLC-UV (Wong and Hindin 1982)
microcystins (expressed as MC-LR toxicity equivalents)	✓	✓	G(S) P(S)	HPLC-UV/PDA (Lawton <i>et al.</i> 1994; Meriluoto 1997)	LC-MS (Zweigenbaum <i>et al.</i> 2000; Barco <i>et al.</i> 2002; Spooof <i>et al.</i> 2003) ADDA-ELISA (Fisher <i>et al.</i> 2001) PP2A (An and Carmichael 1994; Meriluoto 1997; Ward <i>et al.</i> 1997)
nodularin	✓	✓	G(S) P(S)	HPLC-UV/PDA (Lawton <i>et al.</i> 1994; Meriluoto 1997)	LC-MS (Zweigenbaum <i>et al.</i> 2000; Barco <i>et al.</i> 2002; Spooof <i>et al.</i> 2003) ADDA-ELISA (Fisher <i>et al.</i> 2001) PP2A (An and Carmichael 1994; Meriluoto 1997; Ward <i>et al.</i> 1997)
saxitoxins (as STX-eq)	✓	✓	G(S) P(S)	HPLC-FLD (Lawrence and Niedzwiadek 2001; Oshima <i>et al.</i> 1989; Thomas <i>et al.</i> 2004)	LC-MS (Quilliam <i>et al.</i> 2001; Dell'Aversano <i>et al.</i> 2004) Mouse Bioassay (Falconer 1993; AOAC 1996) Receptor Binding Assay (Powell and Doucette 1999; Doucette <i>et al.</i> 1997; Ruberu <i>et al.</i> 2003)

### Sampling requirements, referee method and alternative analytical methods for organic determinands of health significance listed in Table 2.3 of DWSNZ

Name	Sampling location		Container	Referee method	Alternative methods
	TW	DZ			
acrylamide	✓	✓	G(S)	LLE/GC-ECD (EPA 8032)	HPLC/UV (Department of Environment 1988) LSE/HPLC-UV (EPA 8316)
benzene	✓	✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2)
benzo[a]pyrene		✓	G(S)	LSE/GC-MS (EPA 525)	LLE/HPLC (EPA 550) LSE/HPLC (EPA 550.1)
bromodichloromethane		✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-ECD (EPA 551)
bromoform		✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-ECD (EPA 551)
carbon tetrachloride		✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-ECD (EPA 551)
chloroform		✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-ECD (EPA 551)
di(2-ethylhexyl)adipate		✓	G(S)	LSE/GC-MS (EPA 525.2)	LLE or LSE/GC-PID (EPA 506)
di(2-ethylhexyl)phthalate		✓	G(S)	LSE/GC-MS (EPA 525.2)	LLE or LSE/GC-PID (EPA 506)
dibromoacetonitrile		✓	G(S)	LLE/GC-ECD (EPA 551)	
dibromochloromethane		✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC (APHA 6230D, EPA 502.2) LLE/GC-ECD (EPA 551)
dichloroacetic acid		✓	G(S)	LSE/GC-ECD (EPA 552.1)	LLE/GC-ECD (APHA 6251)
dichloroacetonitrile		✓	G(S)	LLE/GC-ECD (EPA 551)	
1,2-dichlorobenzene		✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)
1,4-dichlorobenzene	✓	✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)
1,2-dichloroethane		✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2)
1,1-dichloroethene	✓	✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2)
1,2-dichloroethene (cis/trans)	✓	✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2)
dichloromethane		✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2)
2,4-dichlorophenol		✓	G(S)	LLE/GC-MS (APHA 6410B)	
EDTA	✓	✓	G(S) P(S)	Reverse phase ion pair liquid chromatography (Bergers and De Groot 1994)	
epichlorohydrin	✓	✓	G(S)	P&T/GC-MS (EPA 8260)	GC/ECD (Pesselman and Feit 1988)
ethylbenzene	✓	✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2)

Name	Sampling location		Container	Referee method	Alternative methods
	TW	DZ			
fluoranthene		✓	G(S)	LSE/GC-MS (EPA 525)	LLE/HPLC (EPA 550) LSE/HPLC (EPA 550.1)
formaldehyde		✓		LSE/HPLC (EPA 554)	LLE/HPLC-UV (EPA 8315)
hexachlorobutadiene	✓	✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2)
monochloroacetic acid		✓	G(S) P(S)	LSE/GC-ECD (EPA552.1)	
monochlorobenzene	✓	✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2)
nitritotriacetic acid	✓	✓	G(S)	GC-MSD (Malaiyandi et al 1979; Aue et al 1972)	
styrene	✓	✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2)
tetrachloroethene		✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-ECD (EPA 551)
toluene		✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2)
tributyltin oxide	✓	✓	G(S)	LLE/GC-FPD (Greaves and Unger 1988)	
trichloroacetaldehyde/ chloral hydrate		✓	G(S)	LLE/GC-ECD (EPA 551)	
trichloroacetic acid		✓	G(S)	LSE/GC-ECD (EPA 552.1)	LLE/GC-ECD (APHA 6251)
trichloroacetonitrile		✓	G(S)	LLE/GC-ECD (EPA 551)	
trichlorobenzenes	✓	✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2)
1,1,1-trichloroethane	✓	✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-ECD (EPA 551)
trichloroethene		✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-ECD (EPA 551)
2,4,6-trichlorophenol		✓	G(S)	LLE/GC-ECD (APHA 6251)	LLE/GC-ECD & FID (APHA 6420) LLE/GC-MS (APHA 6410B) Acetylation/LLE/GC-MS (EPA 1653)
vinyl chloride		✓	G(S)	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2)
xylenes		✓	G(S)	P&T/GC-MSD (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2)

### Sampling requirements, referee method and alternative analytical methods for pesticides listed in Table 2.3 of DWSNZ

Name	Sampling location		Container	Referee method	Alternative methods
	TW	DZ			
alachlor	✓	✓	G	LSE/GC-MS (EPA 525.2)	LLE/GC-NPD (EPA 507) LLE/GC-ECD (EPA 505)
aldicarb	✓	✓	G	RP HPLC (EPA 531.1)	HPLC/FLD (APHA 6610)
aldrin/dieldrin	✓	✓	G	LLE/GC-MS (APHA 6410B)	LLE/GC-ECD (EPA 505)
atrazine	✓	✓	G	LSE/GC-MS (EPA 525.2)	LLE/GC-NPD (EPA 507)
azinphos-methyl			G	LLE/GC-ECD (EPA 8141 <sup>a</sup> )	
bentazone	✓	✓	G	LSE/GC-ECD (EPA 515.2)	LLE/GC-ECD (APHA 6640B) HPLC/UVD (EPA 555)
bromacil			G	LLE/GC-NPD (EPA 507)	
carbofuran	✓	✓	G	RP HPLC (EPA 531.1)	HPLC-FLD (APHA 6610)
chlordane	✓	✓	G	LLE/GC-MS (APHA 6630C)	LLE/GC-ECD (EPA 508)
chlorpyrifos	✓	✓	G	LSE/GC-MS (EPA 525.2)	LLE/GC-MS (EPA 8270) LLE/GC-NPD or FPD (EPA 8140)
chlortoluron	✓	✓	G	LLE/LSE/HPLC (EPA 553)	LLE/LSE/HPLC-UV or HPLC-MS (EPA 8321B)
cyanazine			G	LLE/GC-ECD (EPA 551.2)	
2,4-D	✓	✓	G	LSE/GC-ECD (EPA 515.2)	LLE/GC-ECD (APHA 6640B) HPLC/UVD (EPA 555)
2,4-DB	✓	✓	G	LSE/GC-ECD (EPA 515.2)	LLE/GC-ECD (APHA 6640B) HPLC/UVD (EPA 555)
DDT + isomers	✓	✓	G	LLE/GC-MS (APHA 6410B)	LLE/GC-ECD (APHA 6630B) LLE/GC-ECD (EPA 508)
diazinon	✓	✓	G	LSE/GC-MS (EPA 525.2)	LLE/GC-NPD (EPA 507) LLE/GC-NPD or FPD
1,2-dibromo-3-chloropropane	✓	✓	G	P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall&PID (APHA 6230D) LLE/GC-ECD (APHA 6231B) LLE/GC-ECD (EPA 551)
1,2 dibromoethane	✓	✓	G	P&T/GC-MS (APHA 6210D, EPA524.2)	P&T/GC-Hall&PID (EPA 502.2, APHA 6230D)
1,2-dichloropropane	✓	✓	G	P&T/GC-MS (APHA 6210D, EPA524.2)	P&T/GC-Hall&PID (EPA 502.2, APHA 6230D)
1,3-dichloropropene	✓	✓	G	P&T/GC-MS (APHA 6210D, EPA524.2)	P&T/GC-Hall&PID (EPA 502.2, APHA 6230D)
dichlorprop	✓	✓	G	LSE/GC-ECD (EPA 515.2)	LLE/GC-ECD (APHA 6640B) HPLC/UVD (EPA 555)
dimethoate	✓	✓	G		
diquat	✓	✓	G	LSE/HPLC-UV (EPA 549.2)	

Name	Sampling location		Container	Referee method	Alternative methods
	TW	DZ			
diuron	✓	✓	G	LLE/LSE/HPLC (EPA 553)	LLE/LSE/HPLC-UV or HPLC-MS (EPA 8321B)
endrin	✓	✓	G	LLE/GC-MS (APHA 6410B)	LLE/GC-ECD (EPA 505)
ethylene dibromide	✓	✓	G	LLE/GC-ECD (EPA 551.2)	
fenoprop	✓	✓	G	LLE/GC-ECD (EPA 515.2)	LLE/GC-ECD (APHA 6640B)
heptachlor and epoxide	✓	✓	G	LLE/GC-ECD (EPA 505)	LLE/GC-ECD (EPA 508)
hexachlorobenzene	✓	✓	G	LSE/GC-MS (EPA 525.2)	LLE/GC-ECD (EPA 505) LLE/GC-ECD (EPA 508)
hexazinone	✓	✓	G	LLE/GC-NPD (EPA 507)	
isoproturon	✓	✓	G	LSE/GC-MS (EPA 525.2)	RPHPLC/ED (electrochemical) LLE, HPLC-UV
lindane	✓	✓	G	LSE/GC-MS (EPA 525.2)	LLE/GC-ECD (EPA 508) LLE/GC-ECD (EPA 505) LLE/GC (APHA 6630B)
malathion	✓	✓	G	LSE/GC-MS (EPA 525.2)	LLE/GC-NPD (EPA 507)
MCPA	✓	✓	G	HPLC/UVD (EPA 555)	LLE/GC-ECD (APHA 6640B)
mecoprop	✓	✓	G	LSE/GC-ECD (EPA 515.2)	LLE/GC-ECD (APHA 6640B) HPLC/UVD (EPA 555)
methyl parathion	✓	✓	G	LSE/GC-MS (EPA 525.2)	LLE/GC-NPD (EPA 507)
metalaxyl			G	LLE/GC-NPD (EPA 507)	LSE/GC-MS (EPA 525.2) LSE/GC-MS (EPA 508.1)
methoxychlor	✓	✓	G	LSE/GC-MS (EPA 525.2)	LLE/GC (APHA 6630B) LLE/GC-ECD (EPA 508) LLE/GC-ECD (EPA 505)
metolachlor	✓	✓	G	LLE/GC-NPD (EPA 507)	LSE/GC-MS (EPA 525.2) LSE/GC-MS (EPA 508.1)
metribuzin	✓	✓	G	LLE/GC-NPD (EPA 507)	LSE/GC-MS (EPA 525.2) LSE/GC-MS (EPA 508.1)
molinate	✓	✓	G	LLE/GC-NPD (EPA 507)	LSE/GC-MS (EPA 525.2) LSE/GC-MS (EPA 508.1)
oryxalin	✓	✓	G	LLE/LSE/HPLC (EPA 553)	LLE/LSE/HPLC-UV or HPLC-MS (EPA 8321B)
oxadiazon	✓	✓	G	LLE/GC-NPD (EPA 507)	LSE/GC-MS (EPA 525.2) LSE/GC-MS (EPA 508.1)
pendimethalin	✓	✓	G	LLE/GC-ECD/NPD (EPA 8091)	
pentachlorophenol	✓	✓	G	LSE/GC-MS (EPA 525.2)	LSE/GC-ECD (EPA 515.2) Acetylation/LLE/GC-MS (EPA 1653)
permethrin	✓	✓	G	LLE/GC-ECD (EPA 508)	LLE/GC-ECD (EPA 8081)
picloram	✓	✓	G	LLE/GC-ECD (EPA 515.2)	HPLC/PDAUV (EPA 555)
pirimiphos methyl	✓	✓	G	LSE/GC-MS (EPA 525.2)	

Name	Sampling location		Container	Referee method	Alternative methods
	TW	DZ			
pirimisulphuron	✓	✓	G	[No New Zealand lab does this, cannot find a method]	
procymidone	✓	✓	G	LLE/GC-NPD (EPA 507)	LSE/GC-MS (EPA 525.2) LSE/GC-MS (EPA 508.1)
propanil	✓	✓	G	LLE/HPLC/UV (EPA 632.1)	
propazine				LLE/GC-NPD (EPA 507)	
pyridate	✓	✓	G		LLE/HPLC UV
pyriproxifen	✓	✓	G		
simazine	✓	✓	G	LSE/GC-MS (EPA 525.2)	LLE/GC-NPD (EPA 507)
2,4,5-T	✓	✓	G	LSE/GC-ECD (EPA 515.2)	LLE/GC-ECD (APHA 6640B) HPLC/UVD (EPA 555)
terbuthylazine	✓	✓	G	LLE/GC-ECD (EPA 1656)	LLE/GC-NPD (Department of Environment 1986)
thiabendazole	✓	✓	G	HPLC – Fluorescence (EPA 641)	
triclopyr	✓	✓	G	LSE/CD-ECD (EPA 515.2)	LLE/GC-ECD (APHA 6640B) HPLC/UVD (EPA 555)
trifluralin	✓	✓	G	LLE/GC-ECD (EPA 508)	LLE/GC-MS (EPA 8270)
1080	✓	✓	G	LSE/GC-ECD Ozawa and Tsukioka (1987) (proposed)	

Note: In the analysis of the organic determinands, it is the extraction method that is important. The choice of the final method of detection, for example, MSD or ECD affects the sensitivity and selectivity of the analysis.

### Sampling requirements, referee method and alternative analytical methods for radiological determinands listed in Table 2.4 of DWSNZ

Name	Sampling location		Container	Referee method	Alternative methods
	TW	DZ			
total alpha activity			[Kit supplied by NRL <sup>1</sup> ]	EPA 520/5-84-006 method 00-02	
total beta activity			[Kit supplied by NRL <sup>1</sup> ]	EPA Method 900.0 August 1980	
radon			[Kit supplied by NRL <sup>1</sup> ]	Gregory (1976)	

#### Notes

(S) NRL = National Radiation Laboratory, PO Box 25 099, Christchurch, phone 03 366 5059, fax 03 366 1156, www.nrl.moh.govt.nz

### Sampling requirements, referee method and alternative analytical methods for aesthetic determinands listed in Table A2.1 of DWSNZ

Name	Sampling location		Container	Referee method	Alternative methods
	TW	DZ			
aluminium		✓		GFAA (APHA 3113)	ICP (APHA 3120) ICP-MS (EPA 200.8) Colorimetric method (APHA 3500-AI B)
ammonium		✓		Colorimetric – phenate (APHA 4500-NH3 F)	ISE (APHA 4500-NH3 D, E)
calcium	✓	✓		Flame AA (APHA 3111B)	ICP (APHA 3120) ICP-MS (EPA 200.8)
chloride	✓	✓		IC (APHA 4110)	
chlorine		✓		DPD FAS titrimetric (APHA 4500-CI F))	DPD FAS colorimetric (APHA 4500-CI G))
2-chlorophenol		✓		LLE/GC-MS (APHA 6410B)	
colour		✓		Nessleriser (APHA 2120B)	Spectrophotometric (APHA 2120C)
copper		✓		Flame AA (APHA 3111B)	ICP (APHA 3120) ICP-MS (EPA 200.8)
1,2-dichlorobenzene		✓		P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)
1,4-dichlorobenzene		✓		P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)
2,4-dichlorophenol		✓		P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)
ethylbenzene		✓		P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)

Name	Sampling location		Container	Referee method	Alternative methods
	TW	DZ			
hardness (total) (Ca + Mg) as CaCO <sub>3</sub>		✓		Calculation from Ca, Mg (APHA 2340B)	EDTA Titrimetric (APHA 2340 C)
hydrogen sulphide		✓		Calculation (APHA 4500-S2H)	
iron		✓		Flame AA (APHA 3111B)	ICP (APHA 3120) ICP-MS (EPA 200.8)
magnesium	✓	✓		Flame AA (APHA 3111B)	ICP (APHA 3120) ICP-MS (EPA 200.8)
manganese		✓		Flame AA (APHA 3111B)	ICP (APHA 3120) ICP-MS (EPA 200.8)
monochlorobenzene		✓		P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)
odour		✓		'Acceptable to most consumers'	Threshold Odor Test (APHA 2150B)
pH		✓		Electrometric (APHA 4500-H <sup>+</sup> B)	
sodium	✓	✓		Flame AA (APHA 3111B)	ICP (APHA 3120) ICP-MS (EPA 200.8)
styrene		✓		P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)
sulphate	✓	✓		IC (APHA 4110)	
taste		✓		'Acceptable to most consumers'	APHA 2160 B, C
temperature		✓		Field measurement (APHA 2550B)	
toluene		✓		P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)
total dissolved solids	✓	✓		Gravimetric (APHA 2540C)	
trichlorobenzenes (total)		✓		P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)
1,2,3-trichlorobenzene		✓		P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)
1,2,4-trichlorobenzene		✓		P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)
1,3,5-trichlorobenzene		✓		P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)
2,4,6-trichlorophenol		✓		LLE/GC-MS (APHA 6410B)	
turbidity		✓		Nephelometric (APHA 2130B)	
xylene		✓		P&T/GC-MS (APHA 6210D, EPA 524.2)	P&T/GC-Hall & PID (APHA 6230D, EPA 502.2) LLE/GC-MS (APHA 6410B)

Name	Sampling location		Container	Referee method	Alternative methods
	TW	DZ			
zinc		✓		Flame AA (APHA 3111B)	ICP (APHA 3120) ICP-MS (EPA 200.8)

Notes to tables

### Abbreviations

DZ distribution zone  
TW water leaving the treatment plant

### Container

(S) acid washed  
G glass  
P plastic  
(S) solvent washed

### Analytical method

BA bioassay  
ELISA Enzyme linked immunosorbent assay  
CVGA cold vapour atomic absorption method  
ECD electron capture detector  
FAA flame atomic absorption  
FID flame ionisation detector  
FLD fluorescence detector  
FPD flame photometric detector  
GC gas chromatography  
GFAA graphite furnace atomic absorption  
HGAA hydride generation atomic absorption  
HPLC high pressure liquid chromatography  
IC ion chromatography  
LC Liquid chromatography  
LSE liquid/solid extraction  
MS mass spectrometer  
ND nitrogen specific detector  
NPD nitrogen/phosphorus detector  
P&T purge and trap  
PDA Photo-diode array  
PID photoionisation detector  
RPHPLC reversed-phase HPLC  
TITR titrimetric method  
UVD ultraviolet detection

**Source:** APHA refers to APHA (1998) and EPA refers to USEPA (2003c).