

WATER NEW ZEALAND  
**Good Practice Guide for the**

# **Supply of Chlorine for use in Drinking-Water Treatment**



**Revision history:**

The first edition of this document titled “Standard for the Supply of Chlorine for Use in Drinking Water Treatment” was prepared for the Water Supply Managers’ Group of the New Zealand Water & Wastes Association and the Ministry of Health by Opus International Consultants Ltd in 1997.

The second edition was revised with the assistance of the following Technical Review Committee for their contribution to the development of this revision of the Guide: Andrew van Bussell of Rangitikei District Council, Craig Freeman of Filtec, Duncan Leigh of Chemiplas, Graeme Colquhoun of Ixom, Jason Colton of Lutra, Tom Surrey of Watercare, Phil Eberhard of Aquacare and Chris Nokes of ESR on behalf of Ministry of Health. During the review, concerns were raised about levels of chlorate exceeding Specific Impurity Limits. This edition was issued with SIL’s for chlorate redacted pending a review of chlorate in drinking water supplies commissioned by the ministry.

The contents of the third edition reinstates the chlorate limit for Sodium Hypochlorite and increases testing of chlorate in Sodium Hypochlorite from annual to per batch. The revision also elaborates on risk and mitigation actions to maintain chlorate within limits specified in the Drinking Water Standards. Updates to this edition of the guide are based on the recommendations made based on outcomes of the Ministry of Health commissioned survey which found potentially health-significant chlorate concentrations do arise in New Zealand’s reticulated waters as the result of the use of hypochlorite. The outcomes of this study are published in the paper *Water Supply Risk Assessment - Preliminary survey of chlorate concentrations in drinking-water* (Ashworth, Cressey, & Pattis, 2018).

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# 1 GENERAL

## 1.1 Scope

This Guide covers requirements for ensuring liquefied chlorine gas (commonly known as liquid chlorine) sodium hypochlorite and calcium hypochlorite are of a suitable quality for use in drinking water treatment.

This Guide does not cover:

- Chlorine products for use in swimming pool water treatment or other applications.
- Environmental protection or health and safety measures associated with the use of chlorine including labelling, site and storage, transportation, packaging or disposal requirements.
- Operational procedures for using chlorine.

## 1.2 Purpose

The main purpose of this Guide is to provide purchasers, manufacturers and suppliers with the minimum physical, chemical and testing requirements for chlorine to meet safe limits for drinking water supplies. The requirements align with requirements for drinking-water safety outlined in the *Drinking Water Standards for New Zealand* (Ministry of Health, 2008).

## 1.3 Application

This Guide can be referenced in specifications for purchasing and receiving liquefied chlorine gas, sodium hypochlorite and calcium hypochlorite, and can be used as a guide for testing the physical and chemical properties of samples of them. The stipulations of this Guide apply when this document has been referenced and only to the above chemicals when used for the treatment of drinking water. It does not cover the use of any other product.

The guide does not cover information requirements, packaging, equipment, transportation, disposal, safety or issues. Requirements for these aspects of water treatment chemical use are stipulated under New Zealand law and contained in the *Water Treatment Chemicals (Corrosive) Group Standard 2006* (Environmental Protection Authority, 2006).

## 1.4 Legal Requirements

This Guideline is not intended to address supplier or operators legal responsibilities and should be considered alongside other requirements of New Zealand law. Principle relevant legislation that relates to the supply and use of chlorine in drinking water supplies is:

- The Hazardous Substances and New Organisms (HSNO) Act 1996 (Ministry for the Environment, 2015)
- Health (Drinking Water) Amendment Act 2007 (Ministry of Health, 2008)
- Land Transport Act 1998 (Ministry of Transport, 2012)
- Health and Safety at Work Act 2015 (Ministry of Business, Innovation, and Employment, 2015)

- Resource Management Act 1991 (Ministry for the Environment, 2015)

There may also be other legislation that needs to be complied with.

Legislated requirements for protecting the environment and the health and safety of people and communities from the use of hazards associated with chlorine are outlined in the HSNO Act. HSNO hazard classification and controls specific to chlorine can be found in the *Controls for Approved Hazardous Substances Database* available on the Environmental Protection Authority website: <http://www.epa.govt.nz/>

They are also contained in the *Water Treatment Chemicals (Subsidiary Hazard) Group Standard 2006* (Environmental Protection Authority, 2006).

## 1.5 Uses in Water Treatment

Chlorine products are oxidising agents used for disinfection of water supplies. Chlorination can also reduce colour, tastes and odours in water and oxidise metallic substances to facilitate their removal during filtration, known as pre-chlorination.

Liquefied chlorine gas, sodium hypochlorite and calcium hypochlorite are the chlorine products commonly used in treatment of drinking-water supplies for this purpose.

## 1.6 Manufacture of Chlorine Compounds

- 1.6.1 In New Zealand chlorine gas for use in drinking-water treatment is manufactured at Kinleith in a membrane cell chlor-alkali plant. The process is an electrolytic one, but with a titanium anode separated from a steel cathode by a cation exchange membrane. The electrolyte used is very pure brine (solution of NaCl).

Chlorine gas is produced at the anode, and sodium hydroxide produced at the cathode. Chlorine gas is collected, dried, compressed and cooled to a point where it liquefies. Cylinders are filled so that liquid chlorine occupies about 90% of the cylinder when the temperature is about 60°C.

- 1.6.2 Sodium hypochlorite solutions for use in drinking-water treatment in New Zealand are manufactured at Kinleith, Tasman and Timaru by passing chlorine gas through a solution of caustic soda (known as the Lavel process). Generation of sodium hypochlorite is achieved by using brine solutions and purpose-built generating plants on-site and in Timaru. The strength of sodium hypochlorite generated in Timaru is typically 0.95% free available chlorine (FAC).

The strength of sodium hypochlorite produced on-site is about 0.8% FAC. This Guide is not intended to cover on-site generation.

- 1.6.3 Calcium hypochlorite is generally produced by passing chlorine gas through a solution of calcium hydroxide (lime slurry). This produces calcium hypochlorite, calcium chloride and water. The calcium hypochlorite is dried by a special process with the inert calcium chloride substantially removed before packaging. All calcium hypochlorite used in New Zealand is imported.

## 1.7 Description of Chlorine Compounds

- 1.7.1 **Liquefied chlorine gas ( $\text{Cl}_2$ )** is a greenish-yellow gas/amber liquid with a pungent and irritating odour. As a greenish-yellow gas, the chlorine is present at a concentration many times greater than the level dangerous to humans. Chlorine gas at low concentrations is colourless but may still be present at toxic concentrations. It is about 2.5 times heavier than air so will seek the lowest level in an area of leakage.

Chlorine gas is acidic and oxidising. It is corrosive to metals and other substances, particularly when moisture is present.

Chlorine gas is a respiratory irritant. A tolerance to odour can be built up by regular exposure and therefore the sense of smell should not be relied upon to detect harmful levels. High concentrations (above  $90 \text{ mg/m}^3$ ) in air cause coughing, laboured breathing and irritation of the eyes. At very high concentrations the difficulty in breathing may cause death by suffocation due to build-up of liquid in the lungs. Liquefied chlorine causes skin and eye burns on contact.

- 1.7.2 **Sodium hypochlorite ( $\text{NaOCl}$ )** is generally a clear light-yellow/green aqueous solution, free from deposits or suspended matter, with a faint chlorinous odour. It is typically manufactured at between 13.0% and 16.5% (and can be up to 18%) free available chlorine by volume (i.e. 14.8 to 16.5 kg FAC/100 L of product).

Light, heat, organic matter and certain heavy metal cations such as copper, nickel and cobalt accelerate the decomposition of sodium hypochlorite, with a loss in chlorine strength. Sodium hypochlorite undergoes a reaction which results in a decrease in the strength of the free available chlorine and the formation of chlorate ion ( $\text{ClO}_3^-$ ). Sodium hypochlorite typically has a shelf life of 130 days, but the Free Available Chlorine (FAC) content will decrease during this time because of this reaction.

- 1.7.3 **Calcium hypochlorite  $\text{Ca}(\text{OCl})_2$**  is a white or yellowish-white granular powder, generally produced in granular or tablet form. It has a chlorinous odour and approximately 60 to 70% free available chlorine by weight (i.e. 60 to 70 kg FAC/100 kg of product). When mixed to practical solubility levels (30g  $\text{Ca}(\text{OCl})_2/\text{L}$  water) the expected level of FAC would be 1.8 to 2.1 kg FAC/100 L. The same factors for sodium hypochlorite decomposition apply. The presence of moisture appreciably decreases the life of metal containers due to its corrosive nature. Calcium hypochlorite has an expected shelf life in cool dry storage conditions of about 18 months to 2 years but loses 2 to 3% FAC per year. Due to its oxidising properties, contact with flammable materials such as oil, grease, glycerine is highly reactive.

## 1.8 Methods of Dosing

Chlorine gas is normally fed directly into water, via an injector and automatic shutdown regulator, by means of a vacuum or positive pressure chlorinator. Pressure piping and connections should be minimised to decrease the possibility of leaks occurring.

Sodium Hypochlorite is dosed from a Polyethylene tank via PVC or polyethylene pipe and corrosion resistant dosing pump and polyethylene or PVC injector. Polypropylene is not suitable.

Potentially health-significant chlorate concentrations do arise in New Zealand's reticulated waters as the result of the use of hypochlorite. There is evidence that chlorinating solutions prepared by electrolysis, online and as a batch product at low hypochlorite concentration, are less likely to contain chlorate at concentrations exceeding the proposed SIL, and that the SIL is achievable, although this is more difficult for higher strength hypochlorite products.

Several steps have been identified for reducing the chlorate concentration in chlorinating solutions. The most important is dilution of the hypochlorite solution strength. Further recommendations to minimise the formation of chlorate (and other oxyhalides) are included in section 2.3.2.

Calcium hypochlorite (in powder, granular or tablet form) must be dissolved in water and dosed as a settled, clear solution. When calcium hypochlorite is dissolved in water some insoluble sludge remains - this must not enter the feed line to the hypochlorinator. Solutions need to be prepared in advance, commonly by use of two tanks, to allow time for settlement. A float is attached to the feed line to ensure the solution is drawn from near the top of the tank and the last 100 mm cannot be drawn out.

## 1.9 Definitions

The following definitions shall apply in this Guide:

- |       |                                |  |
|-------|--------------------------------|--|
| 1.9.1 | <i>Calcium Hypochlorite</i>    | Calcium hypochlorite $\text{Ca}(\text{OCl})_2$ is a white or yellowish-white granular powder, granule or tablet with a chlorinous odour containing from 60 to 70% free available chlorine by weight. A saturated solution will have up to 12.6 kg FAC/100L of $\text{Ca}(\text{OCl})_2$ solution at 25°C. It is often sold under a trade name.   |
| 1.9.2 | <i>Chlorine Products:</i>      | A group of chemicals or compounds, consisting of liquefied chlorine gas, sodium hypochlorite and calcium hypochlorite, used for chlorination/disinfection of water.  |
| 1.9.3 | <i>FAC:</i>                    | Free available chlorine.   |
| 1.9.4 | <i>Guideline Value:</i>        | Guideline values are the highest concentration of a determinand in the water that can be present without unduly impacting on the aesthetic properties of drinking water. Guideline values relate to determinands that do not pose a direct threat to public health, however, may affect the appearance taste or smell of water. Guideline values are specified in the <i>Drinking Water Standards of New Zealand</i> (Ministry of Health, 2008). |
| 1.9.5 | <i>Liquefied Chlorine Gas:</i> | Chlorine $\text{Cl}_2$ in its elemental state (commonly known as liquid chlorine), is normally packaged as a liquid  |

- under pressure in specially fabricated containers.
- 1.9.6 *Manufacturer:* The party that manufactures, fabricates, or produces materials or products.
- 1.9.7 *Maximum Acceptable Value:* The highest concentration of a determinand in the water that, on the basis of present knowledge, is considered not to cause any significant risk to the health of the consumer over 70 years of consumption of that water. Maximum acceptable values are specified in the Drinking Water Standards of New Zealand (Ministry of Health, 2008).
- 1.9.8 *Purchaser:* The person, company or organisation that purchases any products or work to be performed.
- 1.9.9 *Reception Point:* The point of physical transfer of products from the supplier to the purchaser.
- 1.9.10 *Sodium Hypochlorite:* Sodium hypochlorite solution NaOCl is a clear light-yellow liquid with a faint chlorinous odour containing up to 18 kg/100 L free available chlorine.
- 1.9.11 *Specific Impurity:* Substances which have a maximum acceptable value (MAV) or guideline value assigned to them in the *Drinking Water Standards of New Zealand* (Ministry of Health, 2008).
- 1.9.12 *Specific Impurity Limit:* Specific impurity limits are the maximum limit of an inorganic impurity given as weight of impurity by weight of product (mg of impurity/ kg of product) acceptable in a product.
- 1.9.13 *Supplier:* The party that supplies product or services. A supplier may or may not be the manufacturer.



## 2 MATERIALS

### 2.1 Physical Properties

**Table 1: Some Physical Properties of Chlorine Compounds**

Property	Chlorine Compound		
	<i>Liquefied Chlorine Gas</i>	<i>Sodium Hypochlorite</i>	<i>Calcium Hypochlorite</i>
<b>Physical Description</b>	An amber coloured liquid about 1.5 times denser than water. At high concentrations in the gaseous state, it is a greenish-yellow gas about 2.5 times denser than air.	A clear light yellow/green aqueous solution, free from deposits or suspended matter, with a faint chlorinous odour.	A white or yellowish-white granular powder, granules or tablets with a chlorinous odour.
<b>Molecular Formula</b>	Cl <sub>2</sub>	NaOCl	Ca(OCl) <sub>2</sub> (approx) <sup>*1</sup>
<b>Molecular Weight</b>	70.91	74.44	142.98
<b>pH</b>	N/A (but acidic when dissolved in water)	Timaru 9.6 On-site approx. 12-13	N/A (but alkaline when dissolved in water)
<b>Density</b>	1.408 kg/L @ 20°C <sup>*2</sup>	1.13-1.24 kg/L @ 20°C <sup>*3</sup>	Bulk density: loose granular – 0.8 kg/L tablets – 1.9 kg/L
<b>Solubility in Water</b>	7 g/L at 20°C and 100 kPa	Completely miscible	30 g/L <sup>*4</sup>
<b>Particle Size</b>	N/A	N/A	Granular powder – not more than 10% passing a 100 (147µm) mesh screen. Tablets – uniform in shape and weight variance no more than 5% from average; no more than 2% broken.

\*1 Ca(OCl)<sub>2</sub> is unstable and it is not possible to produce it in a pure form

\*2 at standard temperature and pressure

\*3 density varies with both FAC and excess NaOH content

\*4 30g/L is practical solubility; theoretical is 180 g/L at 25°C

### 2.2 Product Purity

- 2.2.1 Liquefied chlorine gas shall be a minimum of 99.5% pure by volume as determined by the *AWWA B301010 Liquid Chlorine Standard* (American Water Works Association, 2010).
- 2.2.2 Sodium hypochlorite shall contain not less than 13.0 kg FAC/100L of product (unless specified otherwise by the purchaser) on delivery at the reception point. All deliveries shall be clearly labelled to show the FAC content.
- 2.2.3 Calcium hypochlorite shall contain not less than 60 kg FAC/100 kg of product (unless specified otherwise by the purchaser) on delivery at the reception point. All deliveries shall be clearly labelled to show the FAC content.

## 2.3 Impurities

### 2.3.1 Impurity Limits

- 2.3.1.1 The limits of impurities in chlorine products shall be as set out in Table 2 (unless set otherwise by the purchaser) to ensure that the product supplied is suitable for drinking-water treatment.
- 2.3.1.2 Impurity limits shall be given as weight of impurity by weight of chlorine product (mg impurity/kg chlorine product), except for sodium hypochlorite which shall be weight by volume (mg impurity/L sodium hypochlorite solution).
- 2.3.1.3 The levels of specific impurities in commercially available liquefied chlorine gas, sodium hypochlorite and calcium hypochlorite shall not exceed the specific impurity limits (SILs) shown in Table 2. For the purposes of this Guideline the term “specific impurities” refers to the determinands shown in Table 2, which have maximum acceptable values (MAVs) assigned to them in the *Drinking-water Standards for New Zealand 2005 (Revised 2008)* (Ministry of Health, 2008). The MAV and Guideline Value (GV) used for determining SILs are also shown in Table 2. The equations for determining SILs are shown in Appendix A and have been based on a maximum dose rate of 5mg/L.
- 2.3.1.4 SILs have been calculated for all inorganic impurities with MAVs in the *Drinking-water Standards for New Zealand 2005 (Revised 2008)* (Ministry of Health, 2008), but some of these are not included in Table 2 because the levels are unrealistically high. Consequently, SILs constituting more than 1% of the product have been deleted.
- 2.3.1.5 Potentially health-significant chlorate concentrations do arise in New Zealand’s reticulated waters as the result of the use of hypochlorite. Chlorinating solutions containing chlorate concentrations less than the proposed specific impurity limit (SIL) of 2000 mg/kg are less likely to be associated with chlorate concentrations exceeding 50% of the MAV in the reticulation, however several factors can contribute to the presence of elevated chlorate (and other oxyhalides) concentrations in drinking water chlorinated using hypochlorite.

Water suppliers using hypochlorite need to be aware of these factors and ensure that this risk is managed in their water safety plans. This should include adequate monitoring as a check that their preventive measures are effective. Further recommendations to minimise the formation of chlorate (and other oxyhalides) are included in section 2.3.2.

- 2.3.1.5 In addition to the limits outlined in Table 2, calcium hypochlorite granular powder or granules shall be free from lumps and not contain any dirt or other foreign material.

### 2.3.2 Chlorate (and other oxyhalides)

The level of chlorate in sodium and calcium hypochlorite will increase over time. Purchasers of sodium hypochlorite need to be aware of factors influencing chlorate formation and ensure that this risk is managed in their water safety plans to ensure

that chlorate levels are meeting Maximum Acceptable Value specified by the Drinking Water Standards.

The formation of chlorate ion in a hypochlorite solution is influenced by storage conditions such as pH, temperature, length of time in storage, presence of ultraviolet light, concentration of solution and presence of transition metals.

There is evidence that chlorinating solutions prepared by electrolysis, online and as a batch product at low hypochlorite concentration, are less likely to contain chlorate at concentrations exceeding the proposed SIL, and that the SIL is achievable, although this is more difficult for higher strength hypochlorite products.

Because of the factors leading to elevated chlorate concentrations in chlorinating solutions, manufacturers and water suppliers share responsibility for taking steps to manage the risk associated with chlorate in water supplies.

Stanford et al (Stanford BD, 2011) have identified steps for minimising chlorate concentrations in chlorinating solutions. Manufacturers and water suppliers should be familiar with these steps and follow these recommendations when possible:

- Dilute stored hypochlorite solutions on delivery
- Store hypochlorite solutions at lower temperature
- Maintain the pH of the stored hypochlorite solution in the range pH 11–13, after dilution
- Use hypochlorite solutions generated on-site (and calcium hypochlorite solutions) as soon as possible after preparation.
- Use filtered hypochlorite solutions (to remove metals) if purchasing hypochlorite solutions, or low-metal feed waters if generating the hypochlorite on-site (this also applies to the feed waters manufacturers use).
- Avoid extended storage times and use fresh hypochlorite solutions where possible be used within a relatively short time frame after delivery (within 3 months); and
- be stored in a cool dry location where the temperature does not exceed 30°C, away from sunlight.

### 2.3.3 General Impurities

Additional impurity limits may be specified by the purchaser to ensure the material supplied is suitable for water treatment. If additional impurity limits are specified, the purchaser must specify the methods to be used to show that these limits have been met.

Additional impurity limits may be warranted in situations where impurities are impacting treatment plant operations, or, where determinands listed in Table 2 occur in elevated levels in source water.

**Table 2: Limits for product purity and impurities. Where these relate to parameters for metallic and metalloid determinands, boron, MAVs or guideline values (GV) in the *Drinking-water Standards for New Zealand 2005 (Revised 2008)* they are shown.**

Concentrations are rounded down to one significant figure for values less than or equal to 100 mg/kg (mg/L) and two significant figures

Determinand	MAV or GV (mg/L)	Impurity Limits expressed as mg of determinand per kg or L of product		
		99.5% pure Liquefied Chlorine Gas (mg/kg)	13% Sodium Hypochlorite Solution (mg/L)	60% Calcium Hypochlorite (mg/kg)
<b>Moisture Content</b>		150		
<b>Total non-volatile residue</b>		150		
<b>Carbon tetrachloride</b>		40		
<b>Chloroform</b>		300		
<b>Total free alkali (expressed as NaOH)</b>			3000 < NaOH < 18000	
<b>Insoluble matter</b>			1800	
<b>Cobalt<sup>√</sup></b>			0.05	
<b>Sodium chloride</b>				180,000
<b>Antimony</b>	0.02	390	50	240
<b>Arsenic</b>	0.01	90	10	60
<b>Barium</b>	0.7	13000	1800	8400
<b>Boron</b>	1.4		3600	
<b>Bromate</b>			20	120
<b>Cadmium</b>	0.004	70	10	40
<b>Chlorate</b>	0.8		2000	
<b>Chromium</b>	0.05	990	130	600
<b>Copper*<sup>√</sup></b>	1		0.05	
<b>Iron*<sup>√</sup></b>	0.1		3	
<b>Lead</b>	0.01	90	10	60
<b>Manganese*</b>	0.04	790	100	480
<b>Mercury</b>	0.007	130	10	80
<b>Molybdenum</b>	0.07	1300	180	840
<b>Nickel<sup>√</sup></b>	0.08	1500	0.05	960
<b>Selenium</b>	0.01	190	20	120
<b>Uranium</b>	0.02	390	50	240
<b>Zinc</b>	1.5		3900	

for values above 100 mg/kg (mg/L).

\* These determinands are either aesthetic determinands having only a guideline value or are health significant determinands having both an MAV and a guideline value. In the latter case, the lower of the two is given in the table.

<sup>√</sup>These determinands catalyse hypochlorite decomposition so sodium hypochlorite limits have been assigned lower values than the SILs required for human health.

## 3 TEST METHODS

### 3.1 Sampling

3.1.1 The sampling procedure set out in Appendix B of this Guide shall be followed.

### 3.2 Testing

3.2.1 The product shall be sampled and tested at the manufacturer's or supplier's own cost in order to provide a Certificate of Compliance as required in Section 4.1. Records of sampling and testing of representative samples, process monitoring results, and any other relevant records shall be made available to the purchaser on request.

3.2.2 The purchaser may randomly take samples of the product and have these samples analysed for conformance with this Guide. The cost of the analysis shall be paid by the supplier if the product does not meet the requirements of this Guide and shall be paid by the purchaser if the product does meet the requirements of this Guide. These samples shall be taken at the place of manufacture and/or at the delivery point, as may be agreed upon by the manufacturer or supplier and the purchaser.

3.2.3 When inspection and sampling are to be conducted at the point of manufacture, the manufacturer shall afford the inspector representing the purchaser all reasonable facilities for inspection and sampling of finished product, which shall be so conducted as not to interfere unnecessarily with the operation of the plant.

3.2.4 Analytical testing methods shall be as specified in this Guide in Section 3.3.

3.2.5 If the analysis of a sample taken at the place of manufacture shows the product does not comply with the requirements of this Guide, the purchaser may require that the manufacturer provide a certified analysis from an IANZ accredited laboratory (or equivalent) for successive deliveries. The cost of analysis shall be met by the manufacturer.

3.2.6 If the analysis of a sample taken at the point of delivery shows the product does not comply with the requirements of this Guide, a notice of non-conformance shall be provided by the purchaser to the supplier.

### 3.3 Standard Tests

3.3.1 Refer to Table 3 for the standard tests for chlorine products.

**Table 3: Standard tests for chlorine products**

Liquefied Chlorine Gas	
<b>Assay</b>	ASTM E 1746 (ASTM International, 2008)
<b>Moisture and residues</b>	ASTM E E410 (or for moisture, a method validated against ASTM E 410) (ASTM International, 2008)
<b>Arsenic</b>	AWWA B301 (American Water Works Association, 2010) & Food Chemicals Codex (The United States)

	Pharmacopeial Convention, 2012)
<b>Carbon tetrachloride and chloroform</b>	ASTM E 806 (ASTM International, 2008) or ICI in-house procedure <sup>7</sup>
<b>Lead</b>	AWWA B301 (American Water Works Association, 2010) & Food Chemicals Codex (The United States Pharmacopeial Convention, 2012)
<b>Mercury</b>	AWWA B301 (American Water Works Association, 2010) & ASTM E506 (ASTM International, 2008)
<b>Heavy metals</b>	AWWA B301 (American Water Works Association, 2010) & Food Chemicals Codex (The United States Pharmacopeial Convention, 2012)
<b>Sodium Hypochlorite</b>	
<b>Free available chlorine</b>	AWWA B300 (American Water Works Association, 2010)
<b>Insoluble matter</b>	AWWA B300 (American Water Works Association, 2010)
<b>Free alkali</b>	AWWA B300 (American Water Works Association, 2010)
<b>Calcium Hypochlorite</b>	
<b>Free available chlorine</b>	AWWA B300 (American Water Works Association, 2010)
<b>Sodium chloride</b>	BS EN 900: 2014 (British Standards Institution, 2014)

3.3.2 In all chlorine products, the concentrations of the specific impurities listed in Table 2, shall be determined by test methods found in *Standard Methods for the Examination of Water and Wastewater, 22<sup>nd</sup> Edition* (E.W. Rice, 2012) unless methods have been otherwise stated in Table 3. The purchaser must state which of the testing methods is to be used to determine compliance with the specific impurity limits.

## 3.4 Frequency

### 3.4.1 Base frequency of testing

The sampling and certified analysis on which the Certificate of Compliance of a product is based (section 4.1) must occur at least annually for all of the properties listed in Table 2. Sampling and analysis must also be carried out:

- i. whenever the process and/or raw materials changes, in which case all impurities in Table 2 must be tested, and
- ii. at the frequency listed in Table 4 if any test shows the concentration of an impurity in the product exceeds 50% of its SIL, in which case only the impurities exceeding 50% of their SIL need be tested.

### 3.4.2 P2a determinands

Compliance with the chemical requirements of the *Drinking-water Standards for New Zealand* (Ministry of Health, 2008) for P2a determinands can be demonstrated using the alternative approach given in section 8.2.1.2 of the Standards. This requires a certified analysis stating the concentration of the P2a determinand in the product as provided for in section 4.

**Table 4: Test frequency of product purity (specified in section 2.2) and impurity limits (specified in section 2.3)**

	Liquefied Chlorine			Sodium Hypochlorite			Calcium Hypochlorite	
	<i>Supplied from the Kinleith plant</i>	<i>Other ISO19001 certified process</i>	<i>Other uncertified process</i>	<i>Continuous process</i>	<i>Continuous process ISO19901 certified</i>	<i>Other processes</i>	<i>Manufacturer testing*</i>	<i>Other</i>
<b>Purity</b>	Annually	Three Monthly	Monthly	Monthly	Three monthly	Per batch	Annually	2% of containers in each shipment
<b>Moisture Content</b>	Annually	Annually	Annually	-	-	-	-	-
<b>Total non-volatile residue</b>	Annually	Annually	Annually	-	-	-	-	-
<b>Carbon tetrachloride</b>	Annually	Annually	Annually	-	-	-	-	-
<b>Chloroform</b>	Annually	Annually	Annually	-	-	-	-	-
<b>Total free alkali (expressed as NaOH)</b>	-	-	-	Monthly	Three monthly	Per batch	-	-
<b>Insoluble matter</b>	-	-	-	Monthly	Three Monthly	Per batch	-	-
<b>Cobalt</b>	-	-	-	Annually	Annually	-	-	-
<b>Chlorate</b>	-	-	-	Per batch, or weekly if multiple batches are received in a week	Per batch, or weekly if multiple batches are received in a week	Per batch	-	-
<b>Sodium chlorate content</b>	-	-	-	-	-	-	Exempt	2% of containers in each shipment
<b>Fluoride</b>	Per batch, or weekly if multiple batches are received in a week			Per batch, or weekly if multiple batches are received in a week			Per batch, or weekly if multiple batches are received in a week	
<b>Specific Impurity Limits</b>	Per batch, or monthly if multiple batches are received in a month			Per batch, or monthly if multiple batches are received in a month			Per batch, or monthly if multiple batches are received in a month	

\* Calcium hypochlorite manufactured:

- (i) by a process which is certified to ISO 9002, and
- (ii) for which sampling and testing has been carried out on every batch to meet product purity and impurity requirements outlined in 2.2 and 2.3
- (iv) for which the certification links every container to a unique batch number

## 4 QUALITY ASSURANCE

### 4.1 Certificate of Compliance

- 4.1.1 The manufacturer or supplier shall provide the purchaser with a certificate of compliance with each delivery that states that the material furnished in accordance with the purchaser's order complies with all applicable requirements of this Guide. This is to include the concentrations of properties listed in section 2.3 and 2.2 using tests undertaken at frequencies outlined in section 3.4.
- 4.1.2 The purchaser shall not use a delivered product until a certificate of compliance for that delivery is received from the chemical supplier, and the supplier has demonstrated that there is a satisfactory system in place to ensure the quality of the product between the point of manufacture and point of delivery.
- 4.1.3 The chemical supplier shall provide a certified analysis of the material from a mutually agreed upon IANZ or ISO 17025 accredited laboratory showing that the requirements of Sections 2.3 and 2.3 have been met at test frequencies outlined in 3.4.
- 4.1.4 If the method of manufacture, source and/or quality of raw material used is changed during the contract period, additional samples shall be tested by the supplier to demonstrate that the changes have not affected conformance with this Guide. A copy of the certificate of compliance shall be provided to the purchaser.

### 4.2 Weight Certificate

The weight of bulk product delivered shall be determined by certified instrumentation, and a record from the instrumentation of the weight delivered provided to the purchaser.

### 4.3 Rejection

#### 4.3.1 Notice of Non-conformance

If the chlorine product delivered does not meet the requirements of this Guide or the additional impurity limits notified by the purchaser, a notice of non-conformance must be provided by the purchaser to the supplier within 30 working days after receipt of the shipment at the point of destination. The results of the purchaser's tests shall prevail unless the supplier notifies the purchaser within five working days after receipt of the notice of complaint that a retest or inspection is desired. On receipt of the request for a retest, the purchaser shall forward to the supplier one of the sealed samples taken in accordance with Section 3. In the event that the results obtained by the supplier upon retesting do not agree with the results obtained by the purchaser, the other sealed sample shall be forwarded, unopened, for analysis to a referee laboratory agreed upon by both parties. The results of the referee analysis or inspection shall be accepted as final.



The cost of the referee analysis shall be paid by the supplier if the material does not meet the requirements of this Guide and shall be paid by the purchaser if the material does meet the requirements of this Guide.

#### 4.3.2 **Material Removal**

- 4.3.2.1 If the material does not meet the impurity limit requirements of this Guide, the supplier shall remove the material from the premises of the purchaser when requested by the purchaser. Removal of material shall be at no cost to the purchaser.
- 4.3.2.2 If the material meets the impurity limits but not the chlorine content requirements of this Guide, a price adjustment may be agreed between the supplier and the purchaser. In the event that a price adjustment cannot be agreed, the supplier shall remove the material from the premises of the purchaser if required by, and at no cost to, the purchaser.
- 4.3.2.3 The material that shall be removed shall include the rejected material and any other material the rejected material may have contaminated, for example, contents of a tank into which a bulk delivery has been unloaded, if required by the purchaser.
- 4.3.2.4 All material removed shall be concurrently replaced with material conforming to this Guide with an appropriate compliance certificate at no cost to the purchaser.

## Appendix A: Specific Impurity Limits

### A 1 Equation for determining Specific Impurity Limits

Equations are based on a maximum dose of 5.0 mg of chlorine per litre of water, and a safety factor of 10.

Where SILs in Table 2 have stated MAV's and health related impacts, these are calculated using the following equation:

$$SIL (mg/kg) = \frac{MAV (mg/litre) \times 10^6 (mg/kg) \times P}{MD (mg/litre) \times SF \times 100}$$

Where	SIL	=	Specific Impurity Limit
	MAV	=	Maximum Acceptable Value of the impurity determinand set in the <i>Drinking-water Standards for New Zealand 2005 (Revised 2008)</i> ,
	MD	=	Maximum Dose of chlorine
	SF	=	Safety Factor
	P	=	Purity - minimum percentage of chlorine in the product

The SILs are calculated based on:

1. the MAV, or guideline value (GV), for each determinand taken from the *Drinking-water Standards for New Zealand 2005 (Revised 2008)* (Ministry of Health, 2008).
2. a maximum dose (MD) of 5 mg/L of chlorine as FAC – the MAV for chlorine.
3. a safety factor (SF) of 10, which reflects the view that no more than 10 percent of a MAV should be contributed by a given impurity in a water supply chemical. Arsenic and lead have been assigned a safety factor of 20, reflecting recent concern amongst some public health practitioners of the impact on these impurities on public health.

Note inclusion of a determinand in Table 2 is not an indication that the products are expected to contain the impurity, or, if present, that the impurity will occur near its calculated SIL.

### A 2 Example Specific Impurity Limit Calculations

Specific Impurity Limits (SILs) are calculated based on a maximum dose (MD) of 5 mg of chlorine as Cl<sub>2</sub> /litre of water and the maximum acceptable value (MAV) for each determinand taken from the *Drinking-water Standards for New Zealand 2005 (Revised 2008)*. The safety factor (SF) used in these calculations is 10, which reflects the view that no more than 10% of a MAV should be contributed by a given impurity in a water supply chemical.

An example calculation is as follows:

$$\text{Antimony}^1: \quad \text{MAV} = 0.02 \text{ mg/litre}$$

<sup>1</sup> Note that antimony is not a known impurity in liquefied chlorine gas, but is used in this Standard as an indicator of

$$\begin{aligned} \text{MD} &= 5 \text{ mg/litre as Cl}_2 \\ \text{SF} &= 10 \end{aligned}$$

For 99.5% pure liquefied chlorine gas, this SIL equates as follows:

$$\begin{aligned} \text{SIL} &= \frac{0.02 \text{ ( mg / litre ) } \times 10^6 \text{ ( mg / kg ) } \times 99.5}{5 \text{ ( mg / litre ) } \times 10 \times 100} \\ \text{SIL} &= \frac{398 \text{ mg}}{\text{kg}} \quad \text{of liquefied chlorine gas} \end{aligned}$$

Rounding down to two significant figures, yields

$$\text{SIL} = \frac{390 \text{ mg}}{\text{kg}} \quad \text{of liquefied chlorine gas}$$

For a 13% NaOCl solution (13 kg Cl<sub>2</sub> per 100 L, or 130,000 mg/L) this SIL equates as follows:

$$\begin{aligned} \text{SIL} &= \frac{0.02 \text{ ( mg / litre ) } \times 10^6 \text{ ( mg / L ) } \times 13}{5 \text{ ( mg / litre ) } \times 10 \times 100} \\ \text{SIL} &= \frac{52 \text{ mg}}{\text{kg}} \quad \text{of sodium hypochlorite product} \end{aligned}$$

Rounding down to one significant figure, yields

$$\text{SIL} = \frac{50 \text{ mg}}{\text{kg}} \quad \text{of sodium hypochlorite product}$$

For a 60% Ca(OCl)<sub>2</sub> product (60 kg Cl<sub>2</sub> per 100kg of product) this SIL equates as follows:

$$\begin{aligned} \text{SIL} &= \frac{0.02 \text{ ( mg / litre ) } \times 10^6 \text{ ( mg / L ) } \times 60}{5 \text{ ( mg / litre ) } \times 10 \times 100} \\ \text{SIL} &= \frac{240 \text{ mg}}{\text{kg}} \quad \text{of calcium hypochlorite product} \end{aligned}$$

Rounding down to two significant figures, yields

$$\text{SIL} = \frac{240 \text{ mg}}{\text{kg}} \quad \text{of calcium hypochlorite product}$$

## Appendix B: Sampling Procedure

### B 1 Sampling Method

#### B 1.1 General

B 1.1.1 Sampling and preparation shall be conducted as expeditiously as possible in order to avoid undue exposure of the material to the air, thus avoiding contamination and evaporation.

B 1.1.2 The sampling method must give a gross sample that is representative of the material and which may be divided to provide representative samples for analysis. The quantity of sample required by the testing laboratory to carry out the desired tests must be known prior to the sample being taken.

B 1.1.3 Samples for analysis shall be provided in triplicate. One sample is for the immediate use of the purchaser for testing of the shipment. The other two samples shall be retained until it is known from the results of the laboratory examination that the shipment meets the requirements of this Guide. The second sample shall be delivered to the supplier if requested within five days of notification of the examination results of the first sample. The third sample is for the use of a referee laboratory if there is a controversy over the analyses.

B 1.1.4 Samples shall be sealed in airtight, moisture-proof containers supplied by the analysing laboratory.

B 1.1.5 Each sample shall be labelled with at least the following information: the material name, the name of the purchaser, the name of the sampler, package number, date sampled, and date received.

#### B 1.2 Risk Assessment and Management

B 1.2.1 Before collecting samples, the sampler shall assess the risks to their own safety, and to others in the vicinity, of taking the sample (e.g. the release of dust from powdered or crystalline material, splashing or spillage of liquid product), identify what measures can be taken to minimise these risks (e.g. different approach for taking the sample, dust masks, protective clothing), and take those steps.

B 1.2.2 Where possible, samples should be taken by an experienced laboratory technician.

#### B1.2 Liquefied Chlorine Gas

B 1.2.1 Samples shall be taken in 4.5 kg cylinders as set out in the appropriate test method given in Section 3.3.

#### B 1.3 Sodium Hypochlorite

B1.3.1 For safety reasons, samples shall be taken from the tanker after it has been filled. A gross sample shall be taken, the total volume of which shall be no less than three times the volume required for Section B1.4.3.

B1.3.2 The gross sample shall be thoroughly mixed and split into three subsamples as provided for in Section B1.1.3. The containers for the subsamples shall be supplied by the laboratory for the tests listed in Section 3.3, that is, more than one container may be required for each subsample.

B 1.3.3 Each sample container shall be labelled to identify it and shall be signed by the sampler.

B.1.3.4 The concentration of chlorate in the product will change over time. Samples for chlorate should therefore be taken on delivery at the reception point.

#### B1.4 Calcium Hypochlorite

B1.4.1 For powdered or granule forms, the product shall be sampled using a sampling tube that measures at least 20 mm in diameter.

B1.4.2 For tablet form, the tablets shall be selected at random from each container sampled.

B1.4.3 The gross sample, of at least 1.0 kg, or as agreed, shall be mixed thoroughly and divided to provide three 0.3 kg samples. These samples shall be sealed in airtight, moisture-proof, plastic or glass containers.

B1.4.4. No sample shall be taken from a broken container.

## B2 Sample Preparation

B2.1 The preparation of subsamples for testing may affect the results obtained from identical samples so appropriate and consistent preparation procedures are most important.

B2.2 Sample handling and test procedures for sodium and calcium hypochlorite are detailed in *AWWA B300-10 Standard for Hypochlorites* (American Water Works Association, 2010).

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