



## **Water New Zealand Good Practice Guide**

# **Supply of Fluoride for Use in Water Treatment**

**May 2014**

**Third Edition**



Edition	Date	Author	Revisions
1.0	1995	Works Consultancy Services	
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Revision	21/5/2015	Water New Zealand	Section 2.2.1 of the Guide amended to read " <i>Hydrofluosilic acid shall contain between 17% and 25% (w/w) hydrofluosilicic acid.</i> " In line with Ministry of Health advice letter included in Appendix C.

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## GENERAL

### 1.1 Scope

This Guide covers hydrofluosilicic acid<sup>1</sup>, sodium fluoride and sodium silicofluoride<sup>2</sup>, for the addition to water supplies.

### 1.2 Purpose

The main purpose of this Guide is to provide purchasers, manufacturers and suppliers with the minimum requirements for hydrofluosilicic acid, sodium fluoride and sodium silicofluoride, including physical, chemical and testing requirements.

### 1.3 Application

This Guide can be referenced in specifications for purchasing and receiving hydrofluosilicic acid, sodium fluoride and sodium silicofluoride, 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 hydrofluosilicic acid, sodium fluoride or sodium silicofluoride when used for the dosage of water supplies.

### 1.4 Uses in Water Treatment

Fluoride is added to the water supply to reduce the incidence of dental caries. Hydrofluosilicic acid, sodium fluoride and sodium silicofluoride are the fluoride compounds that are commonly used for this purpose.

### 1.5 Manufacture of Fluoride Compounds

1.5.1 Hydrofluosilicic acid is produced as a co-product in the manufacture of phosphate fertilisers. Phosphate rock, which contains fluoride and silica, is treated with sulphuric acid. This produces two gases: silicon tetrafluoride and hydrogen fluoride. These gases are passed through scrubbers where they react with water to form hydrofluosilicic acid.

1.5.2 Sodium fluoride is generally produced by neutralising hydrofluosilicic acid with caustic soda (sodium hydroxide) or soda ash.

1.5.3 Sodium silicofluoride is generally produced from the addition of sodium carbonate or sodium chloride to hydrofluosilicic acid.

### 1.6 Description of Fluoride Compounds

1.6.1 Hydrofluosilicic acid is a strong, corrosive, pale yellow liquid with a characteristic sour odour.

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<sup>1</sup> Synonyms include: hydrofluorosilicic acid, hexafluorosilicic acid, hexafluosilicic acid, fluorosilicic acid and fluosilicic acid.

<sup>2</sup> Synonyms include: sodium fluorosilicate and disodium hexafluorosilicate.

- 1.6.2 Sodium fluoride is white, odourless, free-flowing, powder or crystals.
- 1.6.3 Sodium silicofluoride is a white, odourless, free-flowing crystalline powder.

## 1.7 Methods of Dosing

- 1.7.1 Hydrofluosilicic acid is normally fed directly into water by means of various liquid feeding devices and metering pumps. Dilution of the acid in the range of 10 to 1 and 20 to 1 (parts water to parts acid) before feeding is not recommended due to the possible formation of an insoluble silica precipitate.
- 1.7.2 Sodium fluoride is proportionally added to water either as a dry powder, or as a solution of varying strengths. A saturated solution tank eliminates the necessity of weighing the compound, but does require a water meter to measure the amount of water that is used to make up a solution of known strength.
- 1.7.3 Sodium silicofluoride is fed into water by means of mechanical dry feeders equipped with solution tanks, which should completely dissolve the compound before its introduction into the water. Sodium silicofluoride is less soluble than sodium fluoride, so liquid proportioning of solutions is rarely used and feeding of slurries is not recommended.

## 1.8 Definitions

The following definitions shall apply in this Guide:

- 1.8.1 *Fluoride Compounds:* A group of chemical compounds, consisting of hydrofluosilicic acid, sodium fluoride and sodium silicofluoride, presently used for fluoridation of water.
- 1.8.2 *Hydrofluosilicic Acid:* Hydrofluosilicic acid (HFA), or hydrofluorosilicic acid, or fluosilicic acid is an aqueous solution of  $\text{H}_2\text{SiF}_6$ .
- 1.8.3 *Sodium Fluoride:* Sodium fluoride is a powder, or crystals, or a combination of both, consisting essentially of NaF.
- 1.8.4 *Sodium Silicofluoride:* Sodium silicofluoride, or sodium fluosilicate, is a crystalline powder consisting essentially of  $\text{Na}_2\text{SiF}_6$ .
- 1.8.5 *Manufacturer:* The party that manufactures, fabricates, or produces materials or products.
- 1.8.6 *Purchaser:* The person, company or organisation that purchases any materials or work to be performed.
- 1.8.7 *Reception Point:* The point of physical transfer of materials from the supplier to the purchaser.
- 1.8.8 *Supplier:* The party who supplies material or services. A supplier may or may not be the manufacturer.
- 1.8.9 *w/w* weight per unit weight, for example g/kg.

## 2 MATERIALS

### 2.1 Physical Properties

Table 1 gives some physical properties of fluoride compounds.

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

Property	Fluoride Compound																				
	Hydrofluosilicic Acid	Sodium Fluoride	Sodium Silicofluoride																		
Appearance	Hydrofluosilicic acid is a clear pale yellow aqueous solution	Sodium fluoride is a fine dry powder or a dry crystalline material with no lumps	Sodium silicofluoride is a fine, dry powder containing no lumps																		
Molecular Formula	H <sub>2</sub> SiF <sub>6</sub>	NaF	Na <sub>2</sub> SiF <sub>6</sub>																		
Molecular Weight	144.09	41.99	188.06																		
pH	1.2 (25% w/w solution)	close to neutral (solution)	3.5 – 4.0 (solution)																		
Specific Gravity	1.18 – 1.20 (20°C) of 25% w/w solution	N/A	N/A																		
Bulk Density	N/A	about 1.4 kg/L	about 1.4 kg/L																		
Solubility in Water	Completely miscible	4.1 g/100 mL @ 15°C 4.3 g/100 mL @ 25°C	0.43 g/100 mL water (0°C) 0.65 g/100 mL water (17°C) 0.76 g/100 mL water (25°C) 0.94 g/100 mL water (35°C)																		
Particle Size	N/A	<table border="1"> <thead> <tr> <th>Mesh<sup>1</sup></th> <th>% Passing</th> </tr> </thead> <tbody> <tr> <td>No 200 (74 µm)</td> <td>90-99</td> </tr> <tr> <td>No 325 (43 µm)</td> <td>40-75</td> </tr> <tr> <td>No 400 (38 µm)</td> <td>30-45</td> </tr> </tbody> </table>	Mesh <sup>1</sup>	% Passing	No 200 (74 µm)	90-99	No 325 (43 µm)	40-75	No 400 (38 µm)	30-45	<table border="1"> <thead> <tr> <th>Mesh<sup>1</sup></th> <th>% Passing</th> </tr> </thead> <tbody> <tr> <td>No 32 (495 µm)</td> <td>100</td> </tr> <tr> <td>No 100 (147 µm)</td> <td>50-90</td> </tr> <tr> <td>No 200 (74 µm)</td> <td>15.50</td> </tr> <tr> <td>No 325 (43 µm)</td> <td>0-20</td> </tr> </tbody> </table>	Mesh <sup>1</sup>	% Passing	No 32 (495 µm)	100	No 100 (147 µm)	50-90	No 200 (74 µm)	15.50	No 325 (43 µm)	0-20
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<sup>1</sup> Tyler Mesh Size

### 2.2 Chemical Requirements

- 2.2.1 Hydrofluosilicic acid shall contain between 17% and 25% (w/w) hydrofluosilicic acid, H<sub>2</sub>SiF<sub>6</sub>.
- 2.2.2 Sodium fluoride shall have a minimum of 97% w/w sodium fluoride, NaF, corresponding to approximately 43.9% fluoride ions. Moisture shall not exceed 0.3% w/w on delivery at the reception point.
- 2.2.3 Sodium silicofluoride shall have a minimum of 98% w/w sodium silicofluoride, Na<sub>2</sub>SiF<sub>6</sub>, corresponding to approximately 59.4% fluoride ions. Moisture shall not exceed 0.3% w/w on delivery at the reception point.

## 2.3 Impurities

### 2.3.1 Specific Impurity Limits

2.3.1.1 For the purposes of this Standard the term “specific impurities” refers to the following substances, which have maximum acceptable values (MAVs) assigned to them in the Drinking-water Standards for New Zealand 2005 (Revised 2008); antimony, arsenic, barium, boron, cadmium, chromium, copper, lead, manganese, mercury, molybdenum, nickel, selenium and uranium.

2.3.1.2 The levels of specific impurities in commercially available hydrofluosilicic acid, sodium fluoride and sodium silicofluoride shall not exceed the specific impurity limits (SILs) given in Appendix A1, which also specifies the equation and parameter values used for the calculation of the SILs.

2.3.1.3 Specific impurity limits shall be given as weight of impurity by weight of product (mg of impurity / kg of product).

### 2.3.2 Insoluble Matter

2.3.2.1 Insoluble matter in hydrofluosilicic acid shall not exceed 0.2% w/w.

2.3.2.2 Insoluble matter in sodium fluoride shall not exceed 0.6% w/w.

2.3.2.3 Insoluble matter in sodium silicofluoride shall not exceed 0.5% w/w.

### 2.3.3 Colour

2.3.3.1 Colour of hydrofluosilicic acid shall not exceed 200 Colour Units.

### 2.3.4 Free acid content

2.3.4.1 The hydrofluosilicic acid shall contain no more than 1% free acids (other than hydrofluosilicic acid) expressed as hydrofluoric acid.

### 2.3.5 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.

## 3 DELIVERY

### 3.1 Packaging and Shipping

- 3.1.1 Fluoride compounds are toxic and should be handled with care. Suppliers of fluoride compounds must comply with the relevant regulations for classification, marking, packaging, labelling and transporting of material, currently including the Hazardous Substances and New Organisms Act 1996 and Regulations and their amendments, Land Transport Rule 45001/1 and NZS 5433.1&2: 2012, Transport of Dangerous Goods on Land.
- 3.1.2 Hydrofluosilicic acid may be shipped in bulk in road tankers and trailers. Sodium fluoride and sodium silicofluoride may be shipped in multi-wall paper bags with polyethylene inner coating.
- 3.1.3 Tanks for transporting hydrofluosilicic acid shall comply with all conditions as required under the Land Transport Act 1998, and shall not contain any substances that might affect the quality of the hydrofluosilicic acid added to water supplies as specified by this Standard. Refer also to Section 4.1.1.

### 3.2 Labelling

Each shipment of material shall comply with the New Zealand Standard NZS 5433.1&2 :2012, *Transport of Dangerous Goods on Land, Parts 1 & 2*.and specifically must be clearly identifiable and be marked and/or accompanied by clear means of giving the following information:

Contents: (Proper Shipping Name)

UN Number:

Hazardous Chemical Classification:

Name of Manufacturer:

Net weight:

### 3.3 Unloading and Storage

- 3.3.1 Bulk hydrofluosilicic acid shall be unloaded at the purchaser's premises using either a gravity discharge or a pump into an appropriate receiving vessel. The supplier shall provide an appropriate "camlock" or other type of coupling as agreed with the purchaser for connection to the storage tank inlets, if required, which should prevent an incorrect discharge.
- 3.3.2 Bagged sodium fluoride and sodium silicofluoride shall be transported on pallets for unloading with a forklift or by hand. Bags shall be stored in a dry covered designated storage area. Bagged product shall have an expected shelf life on delivery in dry storage conditions of two years minimum.
- 3.3.3 Bags damaged prior to delivery will be the responsibility of the supplier, and bags damaged during unloading at the purchaser's premises will be the responsibility of the agent undertaking the unloading.
- 3.3.4 The condition on delivery of the paper outers of the bags shall not have deteriorated to any extent so as to impede handling or emptying of the bags.



Bags with deteriorated paper outers on delivery shall be replaced by the supplier at no cost to the purchaser.

- 3.3.5 Fluoridation chemicals should be stored under weatherproof conditions e.g. in a dry environment elevated from the ground. The chemicals must be stored separately from any other water treatment chemicals in a separate building or room. Chemical storage areas should have appropriate bunding and/or Secondary Containment Systems.

### **3.4 Disposal of packaging**

- 3.4.1 When the product is supplied in bags, the purchaser shall bag and label the used bags (which may contain residual product). The supplier shall have responsibility for the disposal or recycling of this material.

## 4 SAFETY

### 4.1 Health and Safety and Environmental Protection

4.1.1 Suppliers of fluoride compounds must comply with the requirements of the following documents and their amendments:

- Health and Safety in Employment Act 1992
- Land Transport Act 1998
- Resource Management Act 1991
- Land Transport Rule: Dangerous Goods 2005
- NZS 5433.1&2: 2012, *Transport of Dangerous Goods on Land*, Parts 1 & 2.

They shall also take all practicable steps to protect the purchaser and others, and the environment, from hazards rising from the transportation, delivery, and supply of fluoride compounds.

During the tendering process, the supplier shall provide the purchaser with records of their health and safety incidents and ACC claims.

4.1.2 Within two weeks of award of a contract to supply product, and prior to delivery, the supplier shall provide to the purchaser the following information:

(a) An updated copy of the Material Safety Data Sheet, which as a minimum shall include the following information, as detailed in *National Code of Practice for the Preparation of Material Safety Data Sheets*, [NOHSC:2011 (1994)]:

- Introductory and Company Details
  - Page numbers and total
  - Date of issue
  - Company, address, and phone numbers
- Identification
  - Product names, codes and numbers
  - Physical description/properties
  - Chemical properties
  - Other properties
  - Uses
- Health Hazard Information
  - Health effects
  - First aid
- Precautions for Use
- Safe Handling Information
- Other Information and Emergency Contacts

(b) Evidence that drivers have been adequately trained and have adequate knowledge and experience in the handling and delivery of fluoride compounds, including an endorsement on their licence as required under the Land Transport Act 1998.

- 4.1.3 A copy of the purchaser's Health and Safety Management Plan shall be made available to the supplier of fluoride compounds. Any practices by the supplier which do not comply with the Health and Safety Management Plan may be grounds for the termination of a supply contract. Health and Safety Management Plans are discussed in the National Guidelines for Occupational Health and Safety in the New Zealand Water Industry (2001).

## 4.2 Protective Equipment

The purchaser and the supplier will be responsible for providing their respective personnel or agents with any necessary safety and protective equipment identified in their Health and Safety Management Plans and ensuring it is used as required.

## 4.3 Spills

The supplier, their agent, or the authorised purchaser's representative responsible for unloading the fluoride compounds, shall immediately attend to and report any spills within the grounds of the property in which the fluoride compound reception point is located. Clean-up and reporting procedures should be specified in Health and Safety Management Plans; they may also be specified in the water treatment plant Consent issued by the Regional Council.

## 5 TEST METHODS

### 5.1 General

- 5.1.1 The manufacturer or supplier shall test the materials at their own cost in order to provide a Certificate of Compliance as required in Section 6.1.
- 5.1.2 The purchaser may randomly take samples of the material and have these samples analysed for conformance with this Guide, at the cost of the purchaser. 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.
- 5.1.3 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 material, which shall be so conducted as not to interfere unnecessarily with the operation of the plant. When on site, the purchaser must follow the manufacturing site's safety policies and procedures when taking the sample, or allow the manufacturer to take the sample itself while under supervision of the supplier's representative.
- 5.1.4 Analytical methods shall be as specified in this Guide in Section 5.3. A request for the specific gravity of the product, where appropriate, will also provide data useful for dosing control.
- 5.1.5 Laboratories undertaking analyses to show that a product complies with the requirements of this Guide shall be suitably accredited for the tests being undertaken. A New Zealand laboratory shall be IANZ accredited and overseas laboratories shall have ISO 17025 accreditation.
- 5.1.6 If the analysis of a sample taken at the point of delivery shows the material does not comply with the requirements of this Guide, a notice of non-conformance must be provided by the purchaser to the supplier in accordance with Section 6.1.

### 5.2 Sampling

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

### 5.3 Standard Tests

- 5.3.1 For standard tests for the properties of fluoride compounds, refer to the following ANSI/AWWA Standards.

Hydrofluosilicic Acid                      ANSI/AWWA B703-11

- Hydrofluosilicic acid content
- Insoluble matter
- Colour

Sodium Fluoride                              ANSI/AWWA B701-11

- Size of particles
- Insoluble matter



## 6 QUALITY ASSURANCE

### 6.1 Certificate of Compliance

- 6.1.1 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.
- 6.1.2 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.
- 6.1.3 On written request from the purchaser, 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 5.3 have been met.
- 6.1.4 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 standard. A copy of the certificate of compliance shall be provided to the purchaser.

### 6.2 Weight Certificate

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

### 6.3 Rejection

#### 6.3.1 Notice of Non-conformance

If the fluoride compound delivered does not meet the requirements of this Guide or the additional impurity limits notified by the purchaser (Section 2.3.4), 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 5. 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.

### 6.3.2 **Material Removal**

- 6.3.2.1 If the material does not meet the impurity limit requirements of this Standard, 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.
- 6.3.2.2 If the material meets the impurity limits but not the fluoride 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.
- 6.3.2.3 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.
- 6.3.2.4 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

Commercially available hydrofluosilicic acid, sodium fluoride, and sodium silicofluoride are not known to contribute significant quantities of contaminants that adversely affect the potability of drinking water.

### A 1 Specific Impurity Limits based on a maximum dose of 1.0 mg of fluoride per litre of water, and a safety factor of 10

**Table A 1** Specific Impurity Limits for metallic and metalloid determinands and boron with MAVs set in the Drinking-water Standards for New Zealand 2005 (Revised 2008)

Determinand	MAV (mg/L)	mg of Determinand per kg of Product		
		<i>hydrofluosilicic acid</i> <sup>1</sup>	<i>sodium fluoride</i>	<i>sodium silicofluoride</i>
Antimony	0.02	270	880	1,190
Arsenic	0.01	130	440	590
Barium	0.7	9,400	30,700	41,600
Boron	1.4	18,800	61,400	83,200
Cadmium	0.004	50	180	240
Chromium	0.05	670	2,190	2,970
Copper	2	26,900	87,800	119,000
Lead	0.01	130	440	590
Manganese	0.4	5,400	17,600	23,800
Mercury	0.007	90	310	420
Molybdenum	0.07	940	3,070	4,160
Nickel	0.08	1,080	3,500	4,800
Selenium	0.01	130	440	590
Uranium	0.02	270	880	1,190

<sup>1</sup> The specific impurity levels for hydrofluosilicic acid are calculated using the lowest permitted percentage purity of the commercial product, i.e. 17%.

The SILs in Table A1 are calculated using the following equation:

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

Where  
 SIL = Specific Impurity Limit  
 MAV = Maximum Acceptable Value of the impurity determinand set in the Drinking-water Standards for New Zealand 2005 (Revised 2008),



MD	=	Maximum Dose of fluoride
SF	=	Safety Factor
P	=	Percentage (w/w) of pure compound in the product
FF	=	Fraction of the weight of the pure compound due to fluoride (= (the atomic weight of F x the number of fluorine atoms in the molecule) / the molecular weight of the molecule)

The SILs are calculated based on:

1. the maximum acceptable value (MAV) for each determinand taken from the Drinking-water Standards for New Zealand 2005 (Revised 2008).
2. a maximum dose (MD) of 1 mg of fluoride ion/litre of water – the upper bound of the Ministry of Health’s recommended concentration range for fluoride in fluoridated water supplies
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.

Inclusion of a determinand in Table A.1 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 1 mg of fluoride ion/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 percent of a MAV should be contributed by a given impurity in a water supply chemical.

The SILs, expressed as the weight of impurity in mg per kg of product, are determined using the following equation:

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

Where	SIL	=	Specific Impurity Limit
	MAV	=	Maximum Acceptable Value of the impurity determinand set in the Drinking-water Standards for New Zealand 2005 (Revised 2008),
	MD	=	Maximum Dose of fluoride
	SF	=	Safety Factor
	P	=	Percentage (w/w) of pure compound in the product
	FF	=	Fraction of the weight of the pure compound due to fluoride (= (the atomic weight of F x the number of fluorine atoms in the molecule) / the molecular weight of the molecule)

An example calculation is as follows:

Arsenic:	MAV	=	0.01 mg/litre
	MD	=	1.0 mg/litre
	SF	=	10

For a 17% w/w H<sub>2</sub>SiF<sub>6</sub> (HFA) solution, this SIL equates as follows:

$$\begin{aligned}
 \text{SIL (As)} &= \frac{0.01 \times 10^6 \times 0.17 \times 113.99 \text{ (6 x atomic weight of F)}}{1.0 \times 10 \times 144.09 \text{ (molecular weight of HFA)}} \\
 &= 130 \text{ mg As/kg HFA product (rounded)}
 \end{aligned}$$

For a 97% NaF product, this SIL equates as follows:

$$\begin{aligned}
 \text{SIL (As)} &= \frac{0.01 \times 10^6 \times 0.97 \times 19.00 \text{ (atomic weight of F)}}{1.0 \times 10 \times 41.99 \text{ (molecular weight of NaF)}} \\
 &= 440 \text{ mg As/kg of NaF product (rounded)}
 \end{aligned}$$

For a 98% Na<sub>2</sub>SiF<sub>6</sub> product, this SIL equates as follows:

$$\begin{aligned}
 \text{SIL (As)} &= \frac{0.01 \times 10^6 \times 0.98 \times 113.99 \text{ (atomic weight of F)}}{1.0 \times 10 \times 188.06 \text{ (molecular weight of Na}_2\text{SiF}_6\text{)}} \\
 &= 590 \text{ mg As/kg of Na}_2\text{SiF}_6 \text{ product (rounded)}
 \end{aligned}$$

## 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 the minimum information as follows: 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 these steps.

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

#### B 1.2 Sodium Fluoride and Sodium Silicofluoride

B 1.2.1 If the sodium fluoride or sodium silicofluoride is packaged, a minimum of 2%, and preferably 5%, of the number of the packages shall be sampled. No sample shall be taken from a broken package. Samples from individual packages shall be combined to form a gross sample.

B 1.2.2 Care shall be taken to include a proportional amount of lumps and fines, to obtain representative material.

B 1.2.3 Sodium fluoride and sodium silicofluoride shall be sampled using a sampling tube or other effective device that measures at least 2 cm in diameter.

B 1.2.4 The gross sample, of at least 8 kg or as agreed, shall be mixed thoroughly and quartered and quartered again to provide eight 0.5 kg samples. Six of these samples shall be sealed in air tight, moisture-proof, plastic or glass containers. Two samples shall be for use by the purchaser. The other four shall be retained to be used for retesting as provided for in Section B1.1.3.

To quarter the sample, tip it on to a clean surface so that it forms a conical or hemispherical pile. With a clean knife, cut the pile vertically, dividing the pile into four equal parts. Make up a new pile with these four parts, and repeat the quartering process.

B 1.2.5 Each sample container shall be labelled to identify it, dated, and shall be signed by the sampler.

#### B 1.4 **Hydrofluosilicic Acid**

B1.4.1 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 B1.4.2.

B1.4.2 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 5.3, that is, more than one container may be required for each subsample.

B 1.4.3 Each sample container shall be labelled to identify it and shall be signed by the sampler.

## **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 Appropriate preparation techniques and test procedures must be agreed by the purchaser and the supplier.

## Appendix C: Ministry of Health Letter Outlining Guideline Updates



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21 May 2015

John Pfahlert  
Chief Executive  
Water New Zealand  
PO Box 1316  
**Wellington 6140**

Dear John

### **Water New Zealand Good Practice Guide Supply of Fluoride for Use in Water Treatment.**

As you will be aware, in May 2014, Water New Zealand published a *Good Practice Guide Supply of Fluoride for Use in Water Treatment* (Guide)

The Guide states in Section 2.1.1 that: '*Hydrofluosilicic acid shall contain between 17% and 21% (w/w) hydrofluosilicic acid, H<sub>2</sub>SiF<sub>6</sub>*'. This narrow concentration range relates to the product manufactured for the New Zealand market at the time the original *Standard for the Supply of Fluoride for Use in Water Treatment* was written (in 1995).

The American Water Works Association (AWWA) standard specifies a range of 20 - 30 percent w/w unless specified otherwise by the purchaser. The Victorian Code of Practice refers to the AWWA standard and the Queensland Water Fluoridation Code of Practice states that the concentration of hydrofluorosilicic acid (HFA) should be within a range of 20 – 30 percent w/w.

In New Zealand HFA is supplied to water suppliers at a bulk supply concentration of 18 percent w/w. Improvements in the manufacturing process since 1995 have lifted the concentration of HFA to around 22 percent, therefore dilution is required during manufacturing to achieve the 18 percent w/w concentration dosed into water supplies. The dilution of HFA from 22 percent to 18 percent w/w prior to dosing is causing silica scaling problems in HFA dosing lines which can cause blockages.

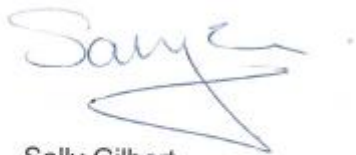
Section 1.7.1 of the Guide states that dilution of HFA in the range of 10:1 to 20:1 (parts water:parts acid) before feeding is not recommended due to the possible formation of an insoluble silica precipitate. A controlled trial conducted in New Zealand in early 2015 with undiluted 22 percent w/w HFA did not produce silica scale.

Ministry of Health officials have been advised that a change from 18 to 22 percent in the concentration of HFA supplied to water industry will not present an increased risk to public health, provided that water suppliers make the necessary adjustment to their dosing.

To address the reported dosing line clogging problem, Ministry of Health officials recommend that Section 2.2.1 of the Guide be amended to read: '*Hydrofluosilicic acid shall contain between 17% and 25% (w/w) hydrofluosilicic acid, H<sub>2</sub>SiF<sub>6</sub>*'.

I trust this is self-explanatory, but if you have any questions, please contact John Harding by email ([john\\_harding@moh.govt.nz](mailto:john_harding@moh.govt.nz)) or phone (04 816 3928).

Yours sincerely



Sally Gilbert  
Manager, Environmental and Border Health  
Clinical Leadership, Protection and Regulation Business Unit

## REFERENCES

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