water NEW ZEALAND
The New Zealand Water & Wastes Association Wai ora Aotearoa

WATER NEW ZEALAND
Good Practice Guide for the

SUPPLY OF POLYELECTROLYTES FOR USE IN DRINKING-WATER TREATMENT

Second Edition - July 2016

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The first edition of this document was produced for the Water Supply Managers Sub-Group of the New Zealand Water and Wastes Association and the Ministry of Health by Opus International Consultants in 1999. This edition of the document amalgamates that which were previously contained in the following documents;

- Standards for the Supply of Polyelectrolytes for Use in Drinking-Water Treatment
- Standard for the Supply of Polyacrylamides for Use in Drinking- Water Treatment
- Standard for the Supply of EPI-DMA Polyamides for Use in Drinking-Water Treatment
- Standard for the Supply of PolyDADMAC for Use in Drinking-Water Treatment

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Contents

1 GENERAL

1.1 Scope

This Guide covers requirements for ensuring the following polyelectrolytes are of a suitable quality for use in drinking water treatment: polyacrylamides, EPI-DMA polyamides, and PolyDADMAC

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 polyacrylamides, EPI-DMA polyamides, and PolyDADMAC 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 polyacrylamides, EPI-DMA polyamides, and PolyDADMAC, and can be used as a guide for testing the physical and chemical properties of samples. The stipulations of this Guide apply when this document has been referenced and only to polyacrylamides, EPI-DMA polyamides, and PolyDADMAC when used for the dosage of water supplies. It does not cover the use of any other filter aids, flocculants and/or coagulants.

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 (Subsidiary Hazard) Group Standard 2006* (Environmental Protection Authority, 2006).

1.4 Legal Requirements

This Guideline is not attended to address supplier or operator legal responsibilities and should be considered alongside other requirements of New Zealand law. Principal legislation that relates to the supply and use of polyelectrolytes in drinking water supplies are:

- The Hazardous Substances and New Organisms (HSNO) Act 1996 (Ministry for the Environment, 2014)
- The 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 hazards associated with the use of hazardous

substances are outlined in the HSNO Act. At the time of the production of these guidelines, polyacrylamides, EPI-DMA polyamides, and PolyDADMAC had yet to receive HSNO classifications.

Polyelectrolytes are, however, listed on the New Zealand Inventory of Chemicals (NZIoC) and approved for use under the *Water Treatment Chemicals (Subsidiary Hazard) Group Standard 2006* (Environmental Protection Authority, 2006). The Group Standard lists all the controls or conditions that apply to water treatment chemicals.

The NZIoC is a list of chemicals allowed as components in products covered under group standard approvals. Approvals for polyacrylamides, EPI-DMA polyamides, and PolyDADMAC can be found by using the following CAS codes:

CAS 26062-79-3 PolyDADMAC (Polydiallyldimethylammonium chloride)

CAS 25988-97-0 EPI-DMA polyamines (Epichlorohydrin dimethylamine)

CAS 9003-05-8 Polyacrylamides

1.5 Uses in Water Treatment

Polyacrylamides, EPI-DMA polyamides, and PolyDADMAC are coagulants and coagulant aids (secondary coagulants) used in the treatment of drinking-water supplies.

The purpose of a coagulant is to promote the coagulation of colloidal and smaller particles in raw water and thereby aid in their removal in subsequent treatment steps.

Polyacrlamides are also used as filter aids and flocculants. Filter aids improve the performance of filters used in the treatment of drinking water-supplies. Flocculants promote the agglomeration of destabilised particles.

1.6 Description of Polyelectrolytes Compounds

1.6.1 **Polyacrylamides** are a family of polymers which use acrylamide as their basic monomer. Polyacrylamides can either be nonionic, anionic, or cationic. The nonionic polymer is made solely from acrylamide monomer, while the anionic form also uses an acrylic acid monomer, and the cationic form also uses a cationic acrylamide based salt monomer (e.g. ethanaminium, N,N,N-trimethy1-2-[(1-oxo-2-propenyl)oxy]-, chloride).

Polyacrylamides come in three forms: powders, emulsions and solutions. The powders are generally white or colourless, and the liquids are generally white. Polyacrylamides are not considered hazardous either by contact, inhalation or by ingestion. However, there may be impurities present in the polyacrylamide solution, either unreacted ingredients, or by-products formed from further reactions, which may be hazardous. There is evidence that unreacted acrylamide is likely to be present in many polyacrylamide products. Acrylamide is an established neurotoxin, and studies indicate that it is a probable human carcinogen.

1.6.2 **EPI-DMA polyamines** are straw- to amber-coloured liquids. They are polyquaternary polymers produced from the reaction of dimethylamine and epichlorohydrin. Polyquaternary means that the nitrogen atom in the structure is fully alkylated, and

thus has very strong positive charge. It is therefore a cationic polyelectrolyte. The polymers have a low to medium molecular weight and a high charge density.

EPI-DMA polyamines are not considered hazardous either by contact, inhalation or by ingestion. However there may be impurities present in the polyamine solution, either unreacted ingredients, or by-products formed from further reactions, which may be hazardous. There is evidence that unreacted epichlorohydrin is likely to be present in many EPI-DMA polyamine products. Epichlorohydrin can be acutely toxic, and is classed by USEPA as a probable human carcinogen.

1.6.3 **PolyDADMAC** is a colourless to pale yellow liquid. It is a polyquaternary polymer produced from the reaction of an aqueous solution of DADMAC monomer. Polyquaternary means that the nitrogen atom in the structure is fully alkylated, and thus has very strong positive charge. It is therefore a cationic polyelectrolyte. The polymers have a low to medium molecular weight and a high charge density.

PolyDADMAC is not considered hazardous either by contact, inhalation or by ingestion. There is very little literature on the toxicity of both PolyDADMAC, and the DADMAC monomer, but it is generally regarded as low.

1.7 Manufacture of Polyelectrolytes Compounds

1.7.1 **Polyacrylamides** are manufactured in one of three ways:

Free radical polymerisation: The oxidising component of a redox reaction is added to the acrylamide monomer. The reducing agent is then added slowly to control the rate of polymerisation.

Inverse emulsion polymerisation: Acrylamide, in an aqueous phase, is dispersed as small droplets in an organic medium.

Reaction with precipitation: This process involves using a reaction medium in which the monomer is soluble, but the polymer is not. As the polymer forms it precipitates out from the reaction medium.

Most polyacrylamides used in New Zealand for drinking-water treatment are manufactured in the USA, Europe and Australia. The three forms of polyacrylamides are manufactured as follows:

Powder: droplets of monomer are usually first polymerised to form a gel, which is then dried and ground.

Emulsion: droplets of monomer(s) are first emulsified in hydrocarbon oil before polymerisation is initiated.

Solution: manufactured either by aqueous polymerisation of the monomer(s), or by dissolving emulsion or powdered form in water.

1.7.2 **EPI-DMA polyamides** used in New Zealand for drinking-water treatment are mostly manufactured in the USA, Europe and Australia.

Less than the required amount of epichlorohydrin is added to a solution of dimethylamine in a pressurised reactor. Once this has all been reacted the rest of the

epichlorohydrin is added to maximise polymerisation. The reaction is terminated by the addition of a small amount of dimethylamine. There are actually two reactions taking place: the formation of the monomer 2-hydroxy-3-dimethylaminopropyl, and then the formation of the polymer.

The finished product may be diluted with water to achieve the desired concentration.

1.7.3 **PolyDADMAC** manufacturing involves two sequential steps: formation of the monomer, and its polymerisation. The monomer is usually formed by a reaction of a stoichiometric excess of allyl chloride with dimethyl amine in an aqueous solution. After the DADMAC monomer is purged of various by-products and stabilised, it is then polymerised using an initiator compound.

Most PolyDADMAC used in New Zealand for drinking-water treatment is manufactured in the USA, Europe and Australia.

1.8 Methods of Dosing

Polyacrylamides, EPI-DMA polyamides, and PolyDADMAC are normally dosed directly to water from a mixing tank or day tank via a positive displacement metering pump.

1.9 Definitions

The following definitions shall apply in this Guide:

1.9.1	*Coagulant:*	A substance added during water treatment to bring about destabilisation of colloidal particles. Refer also to Primary Coagulant and Secondary Coagulant.
1.9.2	*Guideline Value:*	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 *Drinking-water Standards of New Zealand* (Ministry of Health, 2008).
1.9.3	*EPI-DMA polyamides:*	DMA polyamides are straw to amber coloured liquids used as coagulants and coagulant aids in the treatment of drinking-water.
1.9.4	*Flocculant:*	A polymer added to promote the agglomeration of destabilised particles.
1.9.5	*Filter Aid:*	A polymer added immediately upstream of the filters which strengthens the attachment of particles to the filter media.
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

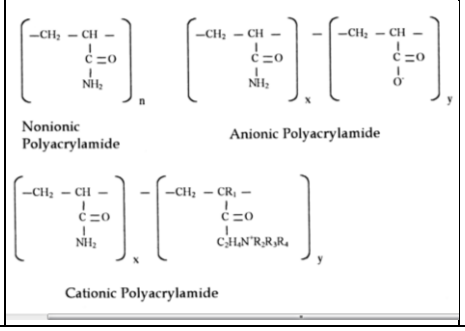
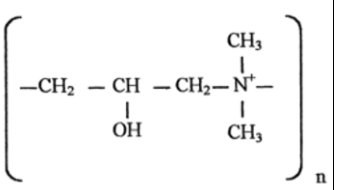
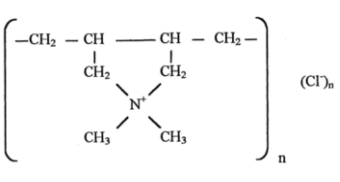
		considered not to cause any significant risk to the health of the consumer over 70 years of consumption of that water. Maximum acceptable values are specified in the *Drinking-water Standards of New Zealand* (Ministry of Health, 2008).
1.9.8	*Polyacrylamides:*	Polyacrylamides are either white or colourless powders, or white liquids, used as coagulants, flocculants or filter aids in the treatment of drinking-water.
1.9.9	*PolyDADMAC:*	PolyDADMAC (polydiallyldimethylammonium chloride) is a colourless to pale yellow liquid used as a coagulant and a coagulant aid in the treatment of drinking water.
1.9.10	*Polyelectrolyte:*	A polymer in which some or all of the monomeric units contain ionisable groups (eg, carboxyl or amino). Depending upon the type of ionisable group, a polyelectrolyte may be cationic or anionic, although amphoteric types (containing both positive and negative groups) also exist. Polymers without ionisable groups are termed nonionic (and therefore are not strictly speaking polyelectrolytes). However, the word polyelectrolyte is commonly used to include cationic, anionic and nonionic products. Polyelectrolytes are used in water treatment as coagulants, flocculants and filter aids.
1.9.11	*Polymer:*	A large molecular weight natural or synthetic compound formed into a chain from low molecular weight simple molecules (monomers). Some polymers are made from only one monomer; others contain two or three different monomers.
1.9.12	*Primary Coagulant:*	A coagulant taking the sole or primary role in the coagulation process. Normally refers to either: (i) a cationic polyelectrolyte used as the sole coagulant, or (ii) a metal salt coagulant when used with a polymer, when the polymer acts as a secondary coagulant.
1.9.13	*Secondary Coagulant:*	A coagulant assisting in the coagulation process (also called a coagulant aid). Normally refers to a polymer when used in combination with a metal salt, when the metal salt acts as primary coagulant.
1.9.14	*Purchaser:*	The person, company or organisation that purchases any materials or work to be performed.
1.9.15	*Reception Point:*	The point of physical transfer of materials from the supplier to the purchaser.
1.9.16	*Specific Impurity:*	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.
1.9.17	*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.
1.9.18	*Supplier:*	The party who supplies material or services. A supplier may or may not be the manufacturer.
1.9.19	*w/w*	Weight per unit weight, for example g/kg.

2 MATERIALS

2.1 Physical Properties

Table 1: Some Physical Properties of Polyelectrolytes Compounds

Property	Polyelectrolytes Compound		
	Polyacrylamides	**EPI-DMA polyamides**	**PolyDADMAC**
Appearance	Polyacrylamides are either slightly hydroscopic white or colourless powders, or viscous white or translucent solutions or emulsions. They are supplied in a wide range of active polymer concentrations. Each form of polyacrylamide can be described generically as follows: *Powders*: polyacrylamide, moisture (water), may contain inert inorganic salts or inert organic compounds. Density is typically 0.5-0.9 kg/L. Soluble in cold water, with a gel being formed at concentrations of approximately 20 g/L and above. *Emulsions:* polyacrylamide, hydrocarbon oil (typically 20-50% w/w), water, surfactants. *Solutions*: usually diluted, viscous solutions of powder or emulsion.	The aqueous polymer solution is a viscous, clear, straw- to amber-coloured liquid, free from visible foreign matter, sediment and turbidity. EPI-DMA polyamines are sold as aqueous solutions in concentrations from less than 10% to greater than 65 % (w/w) active polymer, in a wide range of molecular weights.	The aqueous polymer solution is a viscous, clear, colourless to pale yellow liquid, free from visible foreign matter, sediment and turbidity. PolyDADMAC is sold as aqueous solutions in concentrations equal to or greater than 10%, and less than or equal to 50% (w/w) active polymer, in various molecular weight ranges.
Impurities	The product is likely to contain impurities such as acrylamide monomer, stabilisers, antioxidants, and emulsifiers.	EPI-DMA polyamine products may contain measurable amounts of inorganic salts (such as NaCl). The product is likely to contain impurities such as epichlorohydrin monomer, dimethylamine, 3 chloro-1,2 propanediol, 1,3-dichloro-2-propanol, 2,3-dichloro-1-propanol stabilisers, antioxidants, and emulsifiers.	As a result of the manufacturing process, sodium chloride or another chloride-containing salt will be a constituent of the product solution. The amount of salt present will vary, depending on the weight percent of PolyDADMAC in each product. The product is likely to contain other impurities such as dimethylamine, allyl chloride, diallyl ether, 5-hexanal, as well as initiators, stabilisers, antioxidants, and emulsifiers.
Molecular Formula			

Property	Polyacrylamides	EPI-DMA polyamides	PolyDADMAC
Molecular Weight	Low to high (10^3 -$\geq 10^7$ Da).	Medium (10^5 -10^6 Da).	Medium (10^5 -10^6 Da)
pH		Typically 4-7	Typically 4-7.
Density	Typically 1.19 kg/L at 25°C.	Typically 1.16 kg/L for 50% w/w polyamine at 20°C.	Typically 1.09 kg/L for 40% w/w PolyDADMAC at 20°C.
Solubility in Water	Soluble	Miscible at all concentrations.	Miscible at all concentrations
Charge Type	Anionic, cationic and nonionic	Cationic	Cationic
Charge Density	Anionic and cationic forms can range from low to high. Nonionic form has no charge.	High	High

2.2 Chemical Requirements

2.2.1 **Polyacrylamides** minimum specifications for determining specific product properties should be:

i. Visual inspections
ii. Total solids/percent moisture
iii. Solution Brookfield viscosity

2.2.1.1 The standard test for total solid/percentage moisture and solutions Brookfield viscosity are outlined in section 3.4.1. The total solids/percent moisture relates to the active polymer content, and is needed to interpret other tests. When the total solids/percent moisture is related to the concentration of active polymer content, the concentration of active polymer shall be within 90-105% of the manufacturer's claimed concentration.

2.2.1.2 The measurement of Brookfield viscosity of any polyacrylamide product at a specific concentration is a relatively easy way to determine whether product quality variation exists. The test can be applied to any of the three forms of polyacrylamide.

2.2.1.3 The visual inspection shall be carried out by the purchaser and the other two tests shall be carried out by the supplier.

2.2.2 **EPI-DMA Polyamine** minimum specifications for determining specific product properties should be:

i. visual inspection
ii. concentration of active polymer

2.2.2.1 Concentration of active polymer shall be within 90-105% of manufacturers claimed concentration.

2.2.2.2 The visual inspection shall be carried out by the purchaser, and the concentration by the supplier.

2.2.3 **PolyDADMAC** minimum specifications for determining specific product properties should be:

i. visual inspection
ii. concentration of active polymer

2.2.3.1 Concentration of active polymer shall be within 90-105% of manufacturers claimed concentration.

2.3 Impurities

2.3.1 General

Polyacrylamides, EPI-DMA polyamides, and PolyDADMAC products shall be free of any impurities which would require the product to be strained prior to dilution or dosing.

2.3.2 Specific Impurity Limits (SIL)

2.3.2.1 For the purposes of this Guide the term “specific impurity” refers to the following substances that have maximum acceptable values (MAVs) and guideline values (GVs) assigned to them in the *Drinking-water Standards for New Zealand 2005 (Revised 2008)* (Ministry of Health, 2008) and are shown in Table 2. The term also includes the following substances, which do not have MAVs: 1,3-dichloro-2-propanol (CAS #: 96-23-1), 2,3-dichloro-1-propanol (CAS #: 616-23-9), 3 chloro-1,2-propanediol (CAS #: 96-24-2) and DADMAC monomer (CAS #: 7398-69-8).

2.3.2.2 The levels of specific impurities in commercially available polyelectrolytes shall not exceed the specific impurity limits (SILs) shown in Table 2, which also specifies the Maximum Allowable Values used for the calculation of the SILs.

2.3.2.3 Where there are likely to be multiple sources of the contaminant entering into the water system that will impact on human health, SILs have been determined using the equation shown in Appendix A1, which applies a Safety Factor of 10.

2.3.2.4 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.

2.3.2.5 Where the impurity is specific to the chemical treatment being used and no other sources of the contaminant exist, SILs have been adopted directly from standards or guidelines from other jurisdictions. The associated standards are noted in the footnotes of Table 2.

2.3.3 Other impurity Limits

2.3.3.1 The *Drinking-water Standards for New Zealand 2005 (rev. 2008)* does not contain Maximum Allowable Values (MAV) for several of the possible impurities in polyelectrolytes. Where MAVs do not exist, standards or guidelines for allowable concentrations in drinking-water from other jurisdictions are stated. Where more than one possible value is available from another jurisdiction, the value most protective of public health is selected.

2.3.3.2 Further information about the impurities for which there are no maximum acceptable values can be found in datasheets contained in *Guidelines for Drinking-water Quality Management* (Ministry of Health, Updated 2015).

2.3.3.3 No MAV is available for 3 chloro-1,2-propanediol. The Drinking-Water Inspectorate has set a maximum concentration at which 3 chloro-1,2-propanediol may be present in EPI-DMA polyamides. This concentration is used directly as the SIL.

Table 2: Impurity Limits of Polyelectrolytes Compounds

Determinand	MAV (mg/L)	mg of Determinand per kg of active polymer		
		Polyacrylamides	*EPI-DMA polyamides*	*PolyDADMAC*
Maximum Dose of active polymer		***0.5 mg/L***	***5 mg/L[1]***	***10 mg/L[2]***
Antimony	0.02	4,000	400	200
Arsenic	0.01	1,000	100	50
Barium	0.7			7,000
Cadmium	0.004	800	80	40
Chromium	0.05		1,000	500
Iron8	0.2		4,000	2,000
Lead	0.01	1,000	100	50
Manganese8	0.04	8,000	800	400
Mercury	0.007	1,400	100	70
Molybdenum	0.07		1,400	700
Nickel	0.08		1,600	800
Selenium	0.01	2,000	200	100
Uranium	0.02	4,000	400	200
Acrylamide	0.0005	200[3]		
Epichlorohydrin	0.0005		100[4]	
1,3-dichloro-2-propanol + 2,3-dichloro-1-propanol	0.009[5]		1800	
3-chloro-1,2 propanediol			40[6]	
DADMAC monomer	0.05[7]			5000[7]

[1] Maximum dose permitted by the Drinking Water Inspectorate of the UK (Drinking Water Inspectorate, September 2015)
[2] Maximum dose permitted by the Drinking Water Inspectorate of the UK (Drinking Water Inspectorate, September 2015)
[3] The maximum limit for free acrylamide monomer permitted by the Drinking Water Inspectorate of the UK (Drinking Water Inspectorate, September 2015)
[4] The *NSF/ANSI 60 – 2014a Drinking-water chemicals –Health effects* (NSF International, 2015) specify a value of 200 mg/kg based on dose of 10 mg/L and a maximum allowable concentration of 0.002 mg/L. Using the same calculation as NSF but adjusting to a max dose of 5 mg/L and an MAV of 0.0005 mg/L gives a value of 100 mg/kg, with no safety factor applied
[5] Neither 1,3-dichloro-2-propanol nor 2,3-dichloro-1-propanol has a MAV. This value is the single product allowable concentration[1] obtained from Table C1 of *NSF/ANSI 60 – 2014a Drinking-water chemicals –Health effects* (NSF International, 2015). The total concentration of 1,3-dichloro-2-propanol nor 2,3-dichloro-1-propanol should not exceed this value in the finished water.
[6] 3-chloro-1,2 propanediol does not have a MAV in the New Zealand Drinking Water Standards. This is the maximum concentration of 3-chloro-1,2 propanediol a batch of polyelectrolyte is permitted to contain (Drinking Water Inspectorate, September 2015)
[7] DADMAC monomer does not have a MAV in the New Zealand Drinking Water Standards. The MAV equivalent is the allowable concentration permitted in drinking water given in *NSF Fact Sheet on Polyelectrolytes and NSF/ANSI Standard 60* (NSF International, 2010) and the SIL is the NSF calculated by the NSF based on the allowable concentration.
[8] These determinands have only a guideline value in the Drinking Water Standards, which has been used in place of the Guideline Value.

2.3.4 General Impurities

There are other possible contaminants that may be present in some of these products. However, as these do not have MAVs (or equivalent values), SILs cannot be calculated for them. Should MAVs (or equivalent values) be developed for them subsequent to the preparation of this guide, the equation provided in Appendix A1 can be used to calculate SILs.

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 a determinand listed in Table 2 occurs in elevated levels in source water.

[1] Maximum concentration of a contaminant in drinking water that a single product is allowed to contribute.

3 TEST METHODS

3.1 Sampling

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

3.2 Testing

3.2.1 The manufacturer or supplier shall test the materials at their own cost in order to provide a Certificate of Compliance as required in Section 4.1.

3.2.2 The purchaser may take samples of the material at random and have these samples analysed for conformance with this Guide, at the cost of the purchaser.

3.2.3 Samples may be taken at the place of manufacture and/or at the delivery point, as agreed upon by the manufacturer or supplier and the purchaser.

3.2.4 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 conducted so 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.

3.2.5 Analytical methods shall be as specified in this Guide in Section 3.4.

3.2.6 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.

3.2.7 If the analysis of a sample 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 4.3.

3.3 Visual Inspections

3.3 Products are to be visually inspected by the purchaser as soon as possible after the product has been received.

3.3.1 **Polyacrylamide product** should be compared with a previously acceptable sample of the same product that has been stored properly and is within its shelf life.

3.3.1.1 *Emulsion Form Polyacrylamide*: The product shall be free from insoluble gel, visible foreign matter, and sediment. The product shall be shall be examined for coagulum/ agglomerates and contamination by rotating a glass container of the product in front of a light source to inspect for the coagulum (a globule) that adheres to the glass wall. Separation does not necessarily mean a bad product, but does indicate that mixing is required. Odour may reflect the presence of hydrocarbon oil.

3.3.1.2 *Powder Form Polyacrylamide*: The samples shall be inspected for discoloured particles or solid contaminants, especially for large particles that may indicate difficulty in solution preparation and would prevent the product from being free flowing. An ammonia smell may be present when the product is initially opened. A microscopic examination may be carried out to reveal changes in individual particle shape or appearance.

3.3.1.3 *Solution Form Polyacrylamide*: The product shall be free from insoluble gel, visible foreign matter, sediment and turbidity. The product shall be examined for coagulum/agglomerates and contamination by rotating a glass container of the product in front of a light source to inspect for the coagulum that adheres to the glass wall. Degradation of the product over time will be accompanied by a significant loss of viscosity and performance.

3.3.2 **EPI-DMA polyamines** shall be free from insoluble gel, visible foreign matter, sediment and turbidity.

3.3.3 **PolyDADMAC** shall be free from insoluble gel, visible foreign matter, sediment and turbidity.

3.4 Standard Tests

3.4.1 Standard tests for the properties of polyelectrolyte compounds are shown in Table 3.

Table 3: Standard tests for polyacrylamides, EPI-DMA polyamides and PolyDADMAC

Product		Test	Method Reference
Polyacrylamides	(i)	Total Solids/percent moisture	AWWA Standard B453-13 (American Water Works Association , 2013)
	(ii)	Brookfield Viscosity of Solution	AWWA Standard B453-13 (American Water Works Association , 2013)
	(iii)	Residual Acrylamide Monomer	Accepted industry methods
EPI-DMA polyamides	(i)	Concentration of active polymer	AWWA Standard B452-14 (American Water Works Association, 2014)
	(ii)	Residual epichlorohydrin	U.S. EPA Method 8260, or other accepted industry method (US EPA, 1996)
PolyDADMAC	(i)	Concentration of active polymer	AWWA Standard B451-10 (American Water Works Association, 2010)
	(ii)	Concentration of NaCl	

3.4.2 In all polyelectrolyte 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, 22nd Edition* (E.W. Rice, 2012). The purchaser must state which of the testing methods is to be used to determine compliance with the specific impurity limits.

3.5 Test Frequency

3.5.1 Base frequency of testing for impurities

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 impurities listed in Table 4. 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.

Table 4: Test frequency of product impurity (specified in section 2.3)

	Polyacrylamides	EPI-DMA Polyamine	PolyDADMAC
1,3-dichloro-2-propanol + 2,3-dichloro-1-propanol	-	For values in excess of 50% of the SIL, three monthly, or each delivery if longer than three months	-
3-chloro-1,2 propanediol	-	For values in excess of 50% of the SIL, three monthly, or each delivery if this is longer than three months	-
DADMAC Monomer	-	-	For values in excess of 50% of the SIL, three monthly, or each delivery if this is longer than three months
Fluoride	Per batch, or weekly if multiple batches are received per week	Per batch, or weekly if multiple batches are received per week	Per batch, or weekly if multiple batches are received per week
Other determinands listed in Table 2	Per batch, or monthly if multiple batches are received per month	Per batch, or monthly if multiple batches are received per month	Per batch, or monthly if multiple batches are received per month

3.5.2 Base frequency of testing chemical requirements

The sampling and certified analysis of chemical requirements specified in section 2.2 must occur at the frequencies listed in Table 5. Sampling and analysis must also be carried out whenever the process and/or raw materials changes.

Table 5: Test frequency of product chemical requirements (specified in section 2.2)

	Polyacrylamides	EPI-DMA Polyamine	PolyDADMAC
Visual Inspection	Each delivery	Each delivery	Each delivery
Acrylamide	Each delivery	-	-
Epichlorohydrin	-	Each delivery	-
Active polymer content	Three Monthly, or each delivery if this is longer than three months	Three Monthly, or each delivery if this is longer than three months	Three Monthly, or each delivery if this is longer than three months
Total Solids Percentage Moisture	Three Monthly, or each delivery if this is longer than three months	-	-
Brookfields Viscosity	Three Monthly, or each delivery if this is longer than three months	-	-

3.5.3 **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 4.1.

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.

4.1.2 For Products based on polyacrylamide an upper limit for the content of free acrylamide monomer must be stated by the supplier for every batch.

4.1.3 For EPI-DMA Polyamine products an upper limit for the content of Epichlorohydrin must be stated by the supplier for every batch.

4.1.4 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 section 3.5.

4.1.5 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.

4.1.6 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.

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 polyelectrolyte 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 polyelectrolytes 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 upon, 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

These calculations apply only to determinands where background concentrations of the impurity may occur in source water. Where the determinand is specific to water treatment chemicals used, Specific Impurity Limits have been based on limits applied in other jurisdictions. References for these determinands are provided in the footnotes of Table 2.

SILs were not able to be calculated on the basis of weight or volume of the product (as with the other guides) because the proportion of active polymer content varies and there is no commonly specified active polymer content range.

For this reason, the SILs are calculated per weight of active polymer content and the formula below has been modified to allow the calculation of any SILs to be calculated with respect to product weight/or volume (if they are needed).

Where a Specific Impurity Limit (SIL) for an MAV of a health related determinand is listed in Table 2 this has been calculated using the equation:

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

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 active polymer
	SF	=	Safety Factor

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),* or its equivalent where an MAV is unavailable.
2. 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.
3. a maximum dose (MD) of polyelectrolyte/litre of water as shown below:

Polyacrylamide MD	= 0.5 active polymer/litre
EPI-DMA polyamine	= 5 mg active polymer/litre
PolyDADMAC	= 10 mg active polymer /litre

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 the equation above.

An example calculation for polyacrylamide is as follows:

Antimony:

MAV	=	0.02 mg/litre
MD	=	0.5 active polymer/litre
SF	=	10

$$SIL = \frac{0.02\ (mg / litre) \times 10^{6}\ (mg / kg)}{0.5\ (mg / litre) \times 10}$$

$$SIL = 4{,}000\ mg\ of\ antimony / kg\ of\ active\ polymer$$

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 1.3 Powder polyelectrolyte

B 1.3.1 If the polyelectrolyte powder is packaged, a minimum of 2%, or 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 1.3.2 Care shall be taken to include a proportional amount of lumps and fines, to obtain representative material.

B 1.3.3 The powder shall be sampled using a sampling tube or other effective device that measures at least 2 cm in diameter.

B 1.3.4 The gross sample, of at least 8kg or as agreed, shall be mixed thoroughly and quartered and quartered again to provide eight 0.5kg 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 1.3.5 Each sample container shall be labelled for identification, dated, and signed by the sampler.

B 1.4 Liquid polyelectrolyte

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 3.3.More than one container may be required for each subsample.

B 1.4.3 Each sample container shall be labelled for identification and 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 upon by the purchaser and the supplier.

REFERENCES

American Water Works Association . (2013). *AWWA B453-13 Polyacrylamide.* American Water Works Association .

E.W. Rice, R. B. (2012). *Standard Methods for the Examination of Water and Wastewater, 22nd Edition.* American Public Health Association.

Environmental Protection Authority. (2006). *Water Treatment Chemicals (Subsidiary Hazard) Group Standard.* Wellington: Environmental Protection Authority.

Environmental Protection Authority. (n.d.). *Approved Hazardous Substances with Controls*. Retrieved August 17, 2015, from Environmental Protection Authority: epa.govt.nz

Ministry for the Environment. (2014). *Hazardous Substances and New Organisms Act 1996.* Wellington, New Zealand: New Zealand Government.

Ministry for the Environment. (2015). *Resource Management Act 1991.* Wellington, New Zealand: New Zealand Government.

Ministry of Business, Innovation and Employment . (2015). *Health and Safety at Work Act 2015.* Wellington, New Zealand: New Zealand Government.

Ministry of Health. (2008). *Drinking-water Standards for New Zealand 2005 (Revised 2008).* Wellington: Ministry of Health.

Ministry of Health. (2008). *Health (Drinking Water) Amendment Act 2007.* Wellington: New Zealand Government.

Ministry of Health. (Updated 2015). *Guidelines for Drinking-water Quality Management for New Zealand.* Wellington: New Zealand Government.

Ministry of Transport. (2012). *Land Transport Act 1998.* Wellington, New Zealand: New Zealand Government.

NSF International. (2010). *NSF Fact Sheet on Polyelectrolytes and NSF/ANSI Standard 60.* Arlington, Virginia, USA: NSF.

NSF International. (2015). *NSF/ANSI Standard 60: Drinking Water Treatment Chemicals – Health Effects.* Michigan, USA: NSF International.

USEPA (1996) *Method 8260B Volatile Organic compounds by gas chromatography/mass spectrometry (GC/MS*). USA

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