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# Selenium Speciation Analysis in Waters– Meeting the Challenges of Environmental Contamination and Regulatory Compliance

## Part 1: Regulations and Standard Methods

Paramee Kumkrong, Kelly L. LeBlanc, Patrick H.J. Mercier, Zoltán Mester

*Selenium is released into the aquatic environment through anthropogenic activities such as agricultural irrigation, coal mining, and metallurgical activities, where it acts as a reproductive toxin with detrimental effects on predatory fish and water fowl. Waterborne selenium concentrations are closely regulated worldwide, and various standardized methods are implemented by regulatory bodies to allow for the monitoring of selenium concentrations in different types of waters. In the first part of this two part review, we discuss worldwide regulations relating to concentration limits of selenium in drinking, natural, and industrial waters. Focussing specifically on North America, we look at some standardized analysis methods and discuss the fact that many of these methods are not adequately sensitive to measure selenium in the concentrations outlined by the associated regulations for natural waters. We look in detail at the limitations of these methods with regards to both detection limits and interfering sample matrix components and establish the need for more sensitive and robust methods of analysis for regulatory compliance.*

### **Introduction**

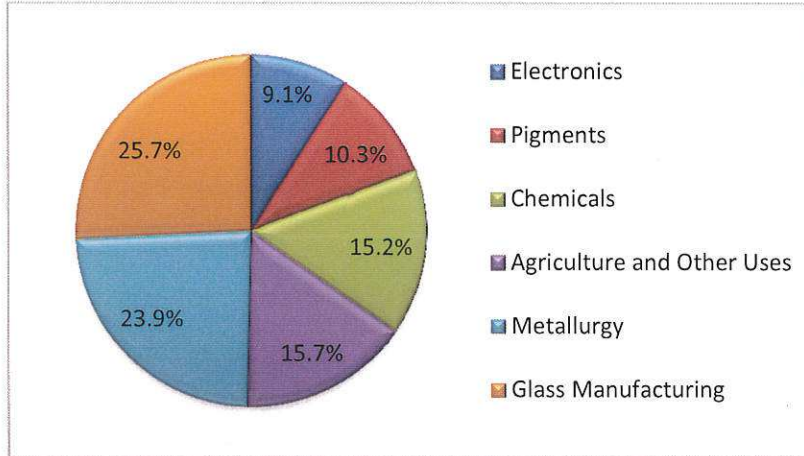
Selenium (Se) is a naturally occurring element, present in the earth's crust with a relative abundance of 0.3 to  $10 \times 10^{-6}$  %, depending on geographical region (Fleischer, 1953), which is mobilized through various anthropogenic activities. Over the last several decades, interest in Se has increased significantly, particularly in North America, due to its severe impact on aquatic ecosystems. As a result, regulations controlling maximum permissible Se concentrations in drinking waters, industrial effluents, and natural surface waters have become increasingly stringent, which has posed challenges to analysts measuring Se in these types of samples. In this review, we discuss these challenges in terms of the regulations/guidance by various governmental and non-governmental bodies and outline the analytical methods accepted by these regulators. We then critically examine the outcomes of such methods and discuss challenges that will likely be faced in the future of Se analysis, specifically in terms of the increasing need for speciation analysis in environmental monitoring.

### **Selenium in the Environment**

#### **Occurrence, Production and Uses of Selenium**

The United States Geological Survey (USGS) Mineral Commodity Profiles of Se estimated its production was approximately 2,200 - 2,300 tonnes between 2013 and 2016, with the largest producers including the United States, Canada, Peru, the European Union (EU), Russia, China, and Japan (United States Geological Survey, 2018). Se is classified as economic minor metal and it is produced and sold in the

form of pure  $\text{SeO}_2$  powder (>99%) and Se ingot. Se is used in variety industries, as illustrated in Figure 1. Among the “other uses” of Se are pharmaceuticals, cosmetics (though selenium sulfide is prohibited, except in anti-dandruff shampoos where its limited quantity is labelled (European Parliament and of the Council on Cosmetic Products, 2009)), and food and feed additives (Yukon Zinc Corporation, 2005).



**Figure 1:** World consumption of selenium, adapted from Yukon Zinc Corporation (Yukon Zinc Corporation, 2005)

While Se has been classified as a non-metal (Rumble, 2016), environmental chemists typically consider it to be a metalloid due to its chemical behaviour. In naturally-occurring minerals, Se often coexists with iron, lead, zinc, cadmium, copper, or silver, but upon mobilization via contact with water Se forms the soluble oxyanions selenite ( $\text{Se(IV)}$  or  $\text{SeO}_3^{2-}$ ) and/or selenate ( $\text{Se(VI)}$  or  $\text{SeO}_4^{2-}$ ) (Howard, 1977). Se in the water column can also be present in two additional oxidation states: elemental  $\text{Se}^0$ , and  $\text{Se}^{2-}$  (selenide) which is typically found as an organic Se species such as selenomethionine (SeMet) or selenocysteine (SeCys) (Maher *et al.*, 2010).

Background concentrations of Se in uncontaminated surface waters are generally below  $1 \mu\text{g/L}$  (Seiler *et al.*, 1965), but in areas where the weathering and erosion of seleniferous soils is augmented by anthropogenic activities such as agricultural irrigation, environmental Se concentrations have been shown to be significantly elevated. For example, early studies of the San Joaquin Valley region noted Se concentrations up to  $100 \text{ mg/kg}$  in the sediments of evaporation ponds (Dungan and Frankenberger, 1999; Saiki and Lowe, 1987). Other anthropogenic activities known to mobilize Se include petroleum refining, certain mining operations (e.g. Cd and Zn), and the combustion of fossil fuels. In particular, coal mined from high-sulphur areas such as the southeastern United States contains elevated levels of Se, which is released via vapour- and particulate-phase emissions as  $\text{SeO}_3$  or trapped along with sulphur in flue gas desulphurization (FGD) waters, producing a Se-contaminated wastewater that must be treated before release back into the environment (Electric Power Research Institute., 2008; Maher *et al.*, 2010).

#### Selenium Contamination in Aquatic Environments – The Issue and Proposed Regulations

While it has been demonstrated that 0.1 – 0.3 mg/kg Se in the diet is generally nutritionally adequate (Mayland, 1994), elevated intake is cause for significant concern, particularly in oviparous animals such as predatory fish and waterfowl where it results in teratogenic effects that can devastate entire populations in contaminated ecosystems (Janz *et al.*, 2010). However, one of the most significant challenges being faced by those attempting to manage environmental Se toxicity lies in the fact that there is no apparent correlation between the total Se concentration in a water body and the associated effects observed in the animal population within that ecosystem. These inconsistencies arise from the mechanisms by which Se enters the aquatic food web, where the majority of the bioconcentration occurs between the water and the lowest trophic level (usually algae). The extent of this bioconcentration varies over several orders of magnitude and is dependent on both the species of algae and the species of Se present in the water (Baines and Fisher, 2011). For example, the algal uptake of the organic Se species SeMet has been shown to occur much more quickly and to a greater extent than the uptake of Se(IV) or Se(VI) (Besser *et al.*, 1989; Riedel *et al.*, 1991; Sandholm *et al.*, 1973). Additionally, inhibitory effects on the uptake of Se(IV) and Se(VI) by algae have been observed in the presence of phosphate and sulphate, respectively (Riedel and Sanders, 1996).

Due to this inconsistency between waterborne Se concentration and observed toxic effects, the United States Environmental Protection Agency (U.S. EPA) has recently released new guidelines for Se in the environment which consider fish egg/ovary Se as the primary indicator when examining a body of water, rather than looking at the water column concentration alone, as has been done historically (U.S. EPA., 2016). This type of monitoring and regulation can provide a better indication of Se's effects as a reproductive toxin than whole-body or muscle-based concentrations (Hamilton, 2002), although those values are to be monitored when egg/ovary concentrations are not available (U.S. EPA., 2016) because they are still more relevant than water column concentrations (Hamilton, 2002), which are used as a last resort (U.S. EPA., 2016).

### **Water Quality Guidelines for Selenium**

Se and Se-containing compounds are classified by the International Agency for Research on Cancer (IARC) as Group 2B - "Possibly carcinogenic to humans" with some evidence that they can cause cancer in humans, though at present this evidence is far from conclusive (reference?). Se is of concern in the areas of seleniferous soils from which Se could accumulate in plants and livestock and become released to aquatic environment. Seleniferous soils are present in many areas of the world such as in North America: Great Plains of the U.S. and Canada, in South America: Chili, Venezuela, in Asia: Enshi County Hubei Province China, northwestern India, and Turkey, in Europe: Denmark, Norway, Finland, Sweden, Poland, Germany, Ireland, Spain, and Greece, and parts of Australia and New Zealand (Comb, 2001; Dhillon and Dhillon, 2014; Oldfield, 2002; Sasmaz *et al.*, 2015).

Due to the evidence showing the detrimental effects of Se on aquatic life (Hamilton and Buhl, 2003; Hume, 2014; May *et al.*, 2008; Muscatello *et al.*, 2008), the maximum permissible concentration of Se in habitat waters is, on average, 10 times lower than in drinking water, at values of 1 – 5 µg/L and 10 – 50 µg/L, respectively (Lemly, 2007). While overall, these guidelines for Se in freshwater for aquatic life are very low level, they do vary from country-to-country. The Se toxicity criteria for aquatic life (fish and

birds) is a controversial issue because there are several factors involved such as vulnerable aquatic life species, type of water (lentic and lotic water), water temperature, fish diet source, age of aquatic animals and other co-contaminants (Lemly, 2007).

This section describes Se concentration limits proposed by national and international bodies for drinking water, water intended for (human) consumption, fresh water for irrigation, for livestock and for aquatic life, effluents, and marine water. The guidelines for Se outlined in Table 1 are organized by country or region and are divided into drinking water, groundwater, marine water, water supplies for communities, effluent discharged into waterways, and waters with various intended uses including recreation, irrigation, livestock watering, and for protection of aquatic life.

#### World Health Organization Water Quality Guidelines

In 1958, the World Health Organisation (WHO) established the International standard for drinking water after a questionnaire had circulated among members of the WHO in 1953 and revealed a problem and the need for standard criteria for water quality. As a minimum requirement, drinking water for human consumption must be physically accepted as free from chemical substances and micro-organisms. The first edition of “WHO - Standard Drinking Water Quality” identified and regulated a few toxic substances: arsenic, chromium, lead, Se and cyanide (World Health Organization, 1958). Five years later, the second edition of “WHO - Standard Drinking Water Quality” was published with more stringent regulations of maximum allowable concentrations of toxic substances, including Se where the allowable limit was decreased from 50 µg/L to 10 µg/L, and also added barium and cadmium into the list of toxic substances (World Health Organization, 1963).

The chemical and physical requirements for water were classified into four groups including: (1) toxic chemical substances, (2) specific chemicals which may affect health, (3) chemicals affecting the potability of water, and (4) chemical and physical indicators of pollution (World Health Organization, 1958, 2011a). Among these classifications, Se falls into the toxic chemical substances category, with the maximum allowable limit closely regulated. Later in “WHO - Guideline for Standard Drinking Water Quality” (2011, 4<sup>th</sup> Edition), the chemical substances requirement categories were further classified according to source categories including: 1) natural occurring chemicals, 2) chemicals from industrial sources and human dwellings, 3) chemicals from agricultural activities, and 4) chemicals used in water treatment or from materials in contact with drinking water. The presence of any of these substances in excess of the allowable concentrations result in the water being prohibited in use as a public supply. In WHO – 2011, Se is classified as a “naturally occurring chemical” (World Health Organization, 2011a).

Se concentrations in drinking water of “WHO –1<sup>st</sup> Edition” in 1958 were set at 50 µg/L, which was revised to 10 µg/L in “WHO –2<sup>nd</sup> Edition” in 1963. The current “WHO – 4<sup>th</sup> Edition, Standard for Drinking Water Quality”, Se has been revised again to 40 µg/L. The limit of Se in drinking water was calculated using an average total daily intake (TDI of 0.005 mg/kg/day (Canadian International Development Agency, 2017) or 400 µg/day/man (World Health Organization, 2011b)) of water consumed per day, by an adult male (average weight of 70 kg) and a fraction of the TDI allocated to drinking-water (20% of TDI). The TDI of Se at 400 µg per day is recommended by The Food and Agricultural Organization (FAO), the WHO (1998), and the United Kingdom Expert Group on Vitamins and Minerals (EGVM) (World

Health Organization, 2011a). However this guideline for Se may be modified according to variable factors such as the weight of the average adult, and the fraction (%) of the TDI represented by Se intake from the diet. While these factors vary by country and/or geographical region, where these factors are not known, the WHO guideline may be considered (World Health Organization, 2011a).

#### North American Water Quality Guidelines

Preliminary surveys of Se (to establish the background data) were conducted on soil, plant, and water samples from areas in the U.S. Great Plains during the period 1928-1933 (Durrell and Cross, 1944; Lambert, 1947). The survey of water in South Dakota, found 8% of the 586 samples collected from seleniferous regions had Se concentrations exceeding 10 µg/L (Stach, 1978). The U.S. Public Health Service (U.S. PHS) first developed the drinking water standard in 1946 and Se was regulated at a concentration limit of 50 µg/L. In 1962, the U.S. PHS revised the maximum limit of Se in drinking water to 10 µg/L (Department of Health Education and Welfare, 1962; Write, 1962).

In 1972, U.S. Federal Government enforced requirements under the Clean Water Act (CWA) regulating the discharge of pollutants into waters as well as quality standards for surface waters, and the Safe Drinking Water Act (SDWA) to regulate the quality of drinking water. The regulations on water quality are mentioned in 40 CFR Part 131 - Water quality standard, Part 132 - Water quality guidance for the great lake system, Part 141 - National primary drinking water, and 40 CFR Part 264 - Standard for owners and operators of hazardous, waste treatment, storage and disposal facilities. In Canada, drinking water standard guidelines are the responsibility of Health Canada, and natural water quality and aquatic system guidelines across Canada are under the control of the Environment and Climate Change of Canada (ECCC) and the individual provinces.

Both the U.S. and Canada regulate the maximum limit of Se in drinking water at 50 µg/L as a minimum requirement. However states/provinces can modify the value to satisfy their needs, as long as the value is not greater than that imposed by the Federal Government's requirement. Many states in the U.S. and provinces in Canada have revised the Se maximum allowable limit to 10 µg/L, as seen in Table 1.

Researchers in the U.S. and Canada have conducted many studies on the toxicity of Se to aquatic fish and birds (Hamilton and Buhl, 2003; Hume, 2016; May *et al.*, 2008). The U.S. and Canada have established the concentration limit of Se in fresh water to protect aquatic life at the low level of 1 to 5 µg/L (Lemly, 1996). The low limit of Se in freshwater is set according to the chronic effect of Se in water column to vulnerable aquatic habitats. Many protocols for assessing the toxicity of Se use models to calculate the daily allowable intake of Se in aquatic habitats and therefore the safe total maximum daily loads for mining effluents, based on data proposed by many researchers (Lemly, 1995, 2002; Peterson and Nebeker, 1992).

Recently, oil sands, coal, metal and mineral mining in Canada have been in the focus of much attention, as a result of proposed, new more stringent regulations for Se in discharge waters from mining operations. In a consultation document issued by Environment and Climate Change Canada (ECCC), it is being recommended that Se be monitored and controlled in mining permits through proposed Amendments to the Metal Mining Effluent Regulations (MMER) (Government of Canada, 2017). MMER

were initially promulgated in 2002 under Canada’s Fisheries Act, which prohibits the deposit of deleterious substances into fish frequented waters unless authorized by regulations. The MMER currently require metal mines to monitor the concentration of selenium in their effluent as part of the Effluent Characterization provisions of the Environmental Effects Monitoring requirements. This obligates metal mines to report on hardness, alkalinity, electrical conductivity and temperature of effluent water samples, and also on the concentrations, in total values, of aluminum, iron, mercury, molybdenum, selenium, ammonia and nitrate. In addition to metal mines, the proposed Amendments to MMER would extend regulatory controls to diamond mining and potentially coal mines, and would also expand the list of substances monitored to include chloride, chromium, cobalt, sulphate, thallium, uranium, phosphorous and manganese. Additionally, the proposed Amendments would also add mandatory fish tissue study for Se, if the annual average of the concentrations reported under the Effluent Characterization are equal to or greater than 5 µg/L or if any single grab or composite sample is equal to or greater than 10 µg/L.

The United States Environment Protection Agency (U.S. EPA) limits the level of Se in effluent at point source in specific industries, including inorganic chemicals (40 CFR Part 415), waste treatment (40 CFR Part 437), steam electric power generation (40 CFR Part 423) and waste combustors (40 CFR 444). Furthermore U.S. EPA has strictly controlled limits for Se in a variety of water resources and a database of Se background concentrations in soils and waters of specific geological areas; these values are available from the USGS.

The U.S. EPA has recently released a new “Aquatic Life Ambient Water Quality Criterion for Selenium” (U.S. EPA., 2016). These new regulations not only examine water-column Se, as has been historically monitored, but also use fish tissue Se concentrations to determine whether an ecosystem is contaminated. Since Se is a reproductive toxin, the primary factor considered is the egg/ovary Se, which is not to exceed 15.1 mg/kg (dry weight) at any given time of measurement. When egg/ovary Se is not (or cannot be) monitored, fish whole body or muscle tissue values are used and cannot exceed 8.5 mg/kg or 11.3 mg/kg (dry weight), respectively. Water column Se criteria differ depending on the ecosystem, with average monthly exposure not to exceed 1.5 µg/L in lentic (standing) or 3.1 µg/L in lotic (flowing) waters more than once in a three year period. Intermittent Se water concentration limits are not given as specific values, but are calculated based on the system, as follows:

$$WQC_{int} = \frac{WQC_{30\ day} - c_{bkg}(1 - f_{int})}{f_{int}} \quad \text{(Equation 1)}$$

where  $WQC_{int}$  is the intermittent exposure criterion,  $WQC_{30\ day}$  is the water column monthly exposure criterion for either lentic (1.5 µg/L) or lotic (3.1 µg/L),  $c_{bkg}$  is the average background Se concentration, and  $f_{int}$  is the fraction of a 30-day period during which Se concentrations are elevated ( $f_{int} \geq 0.033$ ; for 1 day) (U.S. EPA., 2016).

To complicate matters, the areas of concern relating to environmental Se contamination are typically those that involve the release of Se into aquatic ecosystems, usually as (treated) wastewaters. The U.S. EPA regulations account for these scenarios, classifying them as “new inputs” to acknowledge that

higher concentrations in both fish tissue and in the water column will be observed until a quasi-steady-state is reached; this may take several months (lotic system) to several years (lentic systems). In these systems, fish-tissue Se concentrations do not take priority over water column concentrations as is the case in general, but instead rely on site-specific criteria (U.S. EPA., 2016).

#### European Union Water Quality Guidelines

The EU established the water policy framework Directive 2000/60/EC and Directive 2008/105/EC to avoid long term deterioration of surface water, groundwater and marine water quality (The European Parliament and the Council of the European Union, 2000, 2008). Se is only regulated under Directive 98/83/EEC on the quality of water intended for human consumption which controlled the maximum level at 10 µg/L (The European Parliament and the Council of the European Union, 1998). This value is endorsed by EU members (e.g. Ireland, UK, Germany, Poland, Romania, and Bulgaria, as noted in Table 1). Another Directive that involves metals and their compounds is Directive 2006/118/EC (The European Parliament and the Council of the European Union, 2006b); other priority substances regulated under EU water policy can be explored in Decision No. 2455/2001/EC (The European Parliament and the Council of the European Union, 2001). Interestingly, Se is not specifically mentioned in this document, unlike Directive 80/68/EEC on the release of certain dangerous substances into groundwater and Directives 76/464/EEC and 2006/11/EEC on pollution caused by certain dangerous substances discharged into the aquatic environment – regulations which are no longer enforced (The European Parliament and the Council of the European Union, 1976, 1979, 2006a).

#### Asian Water Quality Guidelines

The exposure of Se to humans (selenosis) was discovered in Enshi District, Hubei Province China between 1958-1963 and at the same time, 150 km away, Keshan disease (Se deficiency) was reported in Zhangjikou District, Hubei Province (Li *et al.*, 2012; Yin *et al.*, 2013). Clearly, soil chemistry plays an important role in the release of Se from different types of soil. Agricultural plants and livestock samples from Zhangjikou and Shadi, Enshi district were sampled and analysed for Se concentrations and it was concluded that the major source of Se exposure to human was from food (rice, corn, vegetable, chicken and egg). Therefore the recommendation was to change daily diets and manage soils to increase Se uptake into plants in the Keshan disease-affected areas. Conversely, the trend of Se in agricultural plants in selenosis-affected areas decreased from 1963 to 2010, due to the loss of Se through natural volatilization (Johnson *et al.*, 1996; Li *et al.*, 2012). Another area in Asia where seleniferous soils have been reported is Northwestern India (Dhillon and Dhillon, 2014). There is little English information available relating to standards for Se in waters in Asia, though the drinking water standard in many Asian countries is set at 10 µg/L.

**Table 1: Waters quality guidelines for selenium**

Matrix	Limit (µg/L)	Country or Organisation <sup>Ref</sup>	Reference
Drinking Water	10	Canada: British Columbia Ontario Quebec Saskatchewan New Brunswick United States: Oklahoma Australia  Brazil China European Union  Germany Ireland Japan India Malaysia Mexico Poland Russia Singapore United Kingdom Thailand	(British Columbia Ministry of Environment, 2017b) (Ontario Ministry of the Environment, 2002) (Government of Québec, 2017) (Government of Saskatchewan, 2002) (Government of New Brunswick, 2018)  (Oklahoma Administrative Code, 2016) (Australian National Health and Medical Research Council and Australian National Resource Management Ministerial Council, 2016) (Brazilian Ministry of the Environment, 2012) (Ministry of Health of China, 2006) (The European Parliament and the Council of the European Union, 1998) (Bartel, 2007) (Hayes <i>et al.</i> , 2012) (Japan Ministry of Health Labour and Welfare, 2004) (Bureau of Indian Standards, 1991) (Ministry of Health Malaysia, 2010) (Martell <i>et al.</i> , 2016) (Polish Ministry of Health, 2010) (Ministry of Health of Russia, 2002) (National Environment Agency Singapore, 2008) (Government of the United Kingdom, 2016) (Ministry of Industry Thailand, 1968)
Drinking water	40	World Health Organization Abu Dhabi	(World Health Organization, 2011a) (The Regulation and Supervision Bureau for the water wastewater and electricity sector in the Emirate of Abu Dhabi, 2014)
Drinking water	50	Canada: Federal Government Alberta Newfoundland and Labrador  Manitoba Nova Scotia Prince Edward Island Yukon United States: U.S. EPA Arizona  California Colorado  Minnesota	(Health Canada, 2017) (Government of Alberta, 2016) (Newfoundland Department of Environment and Conservation, 2013)  ??? (Province of Nova Scotia, 2017) (Government of Prince Edward Island, 2015) (Commission of Yukon, 2007)  (U.S. EPA, 2009) (Arizona Department of Environmental Quality, 2009) (Government of California, 2017) (Colorado Department of Public Health and Environment, 2005) (Minnesota Pollution Control Agency, 2017)

		Missouri Montana  Nevada North Dakota Nebraska  New Mexico Tennessee  Texas West Virginia  Wisconsin Wyoming  South Africa Tanzania	(Missouri Department of Natural Resources, 2015) (Montana Department of Environmental Quality, 2015)  (Nevada Administrative Code, 2016) (North Dakota Centruy Code, 2001) (Nebraska Department of Environmental Quality, 2015)  (New Mexico Administrative Code, 2013) (Tennessee Department of Environment and Conservation, 2008)  (Texas Commission on Environmental Quality, 2014) (West Virginia Department of Environmental Protection, 2015)  (Wisconsin Department of Natural Resources, 2017) (Wyoming Department of Environmental Quality, 2016)  (Department of Water Affairs and Forestry, 1996a) (Energy and Water Utilities Regulatory Authority of Tanzania, 2014)
Water for human consumption	20	South Africa	(Department of Water Affairs and Forestry, 1996b)
Water supply used and human consumption	120	United States: Oregon	(Oregon Department of Environmental Quality, 2011)
Water supply used and human consumption	170	United States: Idaho Kansas  Iowa South Carolina  Vermont  Virginia	(Idaho Department of Environmental Quality, 2011) (Kansas Department of Health and Environment, 2017)  (Iowa Department of Natural Resources, 2017) (South Carolina Department of Health and Environmental Control, 2014) (Vermont Department of Environmental Conservation, 2014) (Virginia State Water Control Board, 2011)
Natural mineral water	10	Codex	(Codex Alimentarius, 2001)
Water for livestock	20	Australia and New Zealand	(Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Austraila and New Zealand, 2000)
Water for livestock	30	Canada: British Columbia	(British Columbia Ministry of Environment, 2017a)
Water for livestock	50	Canada: Federal Government  Ontario Arizona  Nevada Brazil	(Canadian Council of Minister of the Environment, 2017) (Ontario Ministry of the Environment, 1994) (Arizona Department of Environmental Quality, 2009) (Nevada Administrative Code, 2016) (Brazilian Ministry of the Environment, 2012)

		South Africa	(Department of Water Affairs and Forestry, 1996b)
Water for irrigation	10	Canada: British Columbia	(British Columbia Ministry of Environment, 2017a)
Water for irrigation	20	Canada: Alberta Ontario United States: Arizona  Colorado  Nebraska  Nevada South Africa United Nations Food and Agriculture Organization	(Government of Alberta, 2016) (Ontario Ministry of the Environment, 2011)  (Arizona Department of Environmental Quality, 2009) (Colorado Department of Public Health and Environment Water Quality Control Commission, 2017) (Nebraska Department of Environmental Quality, 2015) (Nevada Administrative Code, 2016) (Department of Water Affairs and Forestry, 1996b) (Ayers and Westcot, 1994)
Water for irrigation	50	United States: Utah	(Utah Administrative Code, 2017)
Water for irrigation (Long term, 100 years)	20	Australia and New Zealand	(Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, 2000)
Water for irrigation (short term, 20 years)	50	Australia and New Zealand	(Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand, 2000)
Water for irrigation (intermittent)	50	Canada: Federal Government	(Canadian Council of Minister of the Environment, 2017)
Fresh water for aquatic life	1	Canada: Federal Government  Alberta	(Canadian Council of Ministers of the Environment, 2017) (Alberta Environment and Sustainable Resource Development, 2014)
Fresh water for aquatic life	2	Canada: British Columbia United States: Arizona  South Africa	(British Columbia Ministry of Environment, 2017a)  (Arizona Department of Environmental Quality, 2009) (Department of Water Affairs and Forestry, 1996a)
Fresh water for aquatic life	4.6	United States: Colorado  Pennsylvania Utah	(Colorado Department of Public Health and Environment Water Quality Control Commission, 2017) (Pennsylvania Code, 2012) (Utah Administrative Code, 2017)
Fresh water for aquatic life	5	United States: Alabama	(Alabama Department of Environmental Management, 2017)

		Florida Georgia Maine  Nebraska  New Hampshire  North Carolina  North Carolina  North Dakota South Carolina  South Dakota Virginia Tennessee  Vermont  Washington West Virginia	(Florida Administrative Code, 2015) (Georgia Department of Natural Resources, 2016) (Maine Department of Environmental Protection, 2005) (Nebraska Department of Environmental Quality, 2015) (New Hampshire Code of Administrative Rules, 2015) (North Carolina Department of Environmental Quality, 2016) (North Carolina Department of Environment and Natural Resources, 2007) (North Dakota Centruy Code, 2001) (South Carolina Department of Health and Environmental Control, 2014) (South Dakota Legislative Research Council, 1999) (Virginia State Water Control Board, 2011) (Tennessee Department of Environment and Conservation, 2008) (Vermont Department of Environmental Conservation, 2014) (Washington State Legislature, 2016) (West Virginia Department of Environmental Protection, 2015)
Fresh water for aquatic life	10	Australia and New Zealand	(Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Austraila and New Zealand, 2000)
Fresh water for aquatic life	35	United States: Oregon	(Oregon Department of Environmental Quality, 2011)
Fresh water for aquatic life	100	Canada: Ontario	(Ontario Ministry of the Environment, 1994)
Fresh water	3	Germany	(Irmer <i>et al.</i> , 2013)
Fresh water (Lentic, chronic 30 day)	1.5	United States: U.S. EPA	(U.S. EPA., 2016)
Fresh water (Lotic, chronic 30 day)	3.1	United States: U.S. EPA	(U.S. EPA., 2016)
Fresh water (continuous concentration)	5	United States: U.S. EPA	(U.S. EPA, 2017c)
Surface water	10	Ireland Bulgaria Romania	(Hayes <i>et al.</i> , 2012) (Stoimenova <i>et al.</i> , 1998) (Popovici <i>et al.</i> , 1998)
Marine water	10	Australia and New Zealand  Brazil	(Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Austraila and New Zealand, 2000)  (Brazilian Ministry of the Environment, 2012)

Marine water (chronic)	71	United States: U.S. EPA	(U.S. EPA, 2017c)
Groundwater	1	Canada: British Columbia	(British Columbia Ministry of Environment, 2017b)
Groundwater	10	Brazil Japan Thailand	(Brazilian Ministry of the Environment, 2012) (Japan Ministry of the Environment.) (Thailand Ministry of Industry, 1978)
Groundwater	50	Canada: Alberta Newfoundland and Labrador	(Government of Alberta, 2016) (Water Resources Management Division, 2009)
Groundwater (Full depth background site condition standards)	5	Canada: Ontario	(Ontario Ministry of the Environment, 2011)
Groundwater; generic site, full depth generic and stratified site condition standards in a potable groundwater condition, and generic site condition standards for use within 30 m of a water body in a potable groundwater condition)	10	Canada: Ontario	(Ontario Ministry of the Environment, 2011)
Groundwater; Generic site condition standards for shallow soils in a non-potable groundwater condition and Generic site condition standards for use within 30 m of a water body in a non-potable groundwater condition)	50	Canada: Ontario	(Ontario Ministry of the Environment, 2011)
Groundwater (Full depth generic and	63	Canada: Ontario	(Ontario Ministry of the Environment, 2011)

Stratified site condition standards in a non-potable groundwater condition)			
Groundwater for livestock	10	Brazil	(Brazilian Ministry of the Environment, 2012)
Groundwater for irrigation	50	Brazil	(Brazilian Ministry of the Environment, 2012)
Effluent	20	Thailand	(Thailand Ministry of Science Technology and Environment, 1996)
Effluent	50	India	(000check; Bureau of Indian Standards, 1981)
Effluent	300	Brazil	(Brazilian Ministry of the Environment, 2012)
Effluent	100	United Nations World Bank Group United States: Florida	(The World Bank Group, 1999)  (Florida Department of State, 2014)
Effluent	500	Singapore	(National Environment Agency of Singapore, 2017)
Effluent into controlled water	10	Singapore	(National Environment Agency of Singapore, 2017)
Effluent into controlled water	20	Thailand	(000check)
Effluent into groundwater	20	United States: New York	(New York Department of State-Division of Administrative Rules, 2016)
Effluent into harbor and irrigation	20	Dubai	(Government of Dubai, 2013)
Effluent into the environment or to storm sewers	50	Canada: Newfoundland and Labrador	(Ryan, 2003)
Effluent into coastal	50	India	(Bureau of Indian Standards, 1981)
Effluent into municipal or industrial effluent treatment	100	Canada: Newfoundland and Labrador	(Ryan, 2003)
Effluent into seawater (instantaneous)	150	United States: California	(California State Water Resources Control Board, 2015)

## Analytical Methods for Selenium in Waters Used by U.S. Regulatory Bodies

This section will focus on the analytical methods for the determination of Se in waters used by U.S. Federal Departments and will also discuss other “standard methods” that are recognised worldwide. These standard methods for water and wastewater analysis are published by highly respected scientific organisations, though they are not mandatory standard test methods based on any official legislation. However, the local regulatory authority under the Nation Acts has endorsed and approved the standard methods for nationwide or regional use.

### Selenium Determination by Gravimetric Methods

Following Swedish scientist Jacob Berzelius’ initial discovery of Se in 1818 (Trofast, 2011), he collaborated with Heinrich Rose to develop the first method for the quantitative analysis of Se based on a gravimetric method (László Erdey *et al.*, 1965). Later, a similar concept of gravimetric measurement was developed, but with titration to quantify Se in seleniferous materials and geological samples (Dudley and Byers, 1934; Norris and Fay, 1896; Noyes and Bray, 1924; Scott, 1917). AOAC International (unofficially, the “Association of Analytical Communities”) modified these two methods to analyze Se in biological samples as method “AOAC 936.04 - Se in plants”, and “AOAC method 939.09 - Se in food” (Horwitz, 2000; Robinson *et al.*, 1934). The sample preparation to separate Se from the sample matrix was modified for Se determination in water by the U.S. PHS in 1946 and the USGS in 1960 (Rainwater and Thatcher, 1960).

For this analysis, Se is oxidised by hydrogen peroxide, sulfuric and nitric acid, then reduced to  $\text{H}_2\text{SeO}_4$  with hydrogen bromide-bromine to liberate Se tetra-bromide in a distillate. The collected distillate is then reduced by hydroxylamine hydrochloride or sodium bisulphite and oven dried to precipitate Se for quantification by weighing. This technique is not appropriate for Se concentrations less than 1 mg/kg. The quantitative analysis of Se in water can be achieved by the precipitation of elemental  $\text{Se}^0$  in a gum arabic solution and matching the colour against standard Se solutions (Robinson *et al.*, 1934).

### Selenium Determination by Visual Colorimetric Comparison

The colorimetric comparison of elemental Se suspensions was first used by the U.S. PHS in 1946. At the time, Se was regulated at a maximum level of 50  $\mu\text{g}/\text{L}$  (World Health Organization, 1958), and the gravimetric method was not sufficient to measure Se at the low concentrations present in drinking water. Therefore, the method of analysis for Se was modified to use a colorimetric comparison. The sample is prepared in the same way as the gravimetric method, mentioned above. The distillate is collected in hydrogen bromide-bromine solution. The fine pink to red Se particulate can be observed after the colour interference of bromine is removed. The pink particles are suspended in the solution of gum arabic in a Nessler tube and ready for visual colour matching against Se standard solution. The visual colour comparison was claimed to be able to detect Se present in concentration from 5 to 10  $\mu\text{g}/\text{L}$ . The colorimetric comparison appeared in the Standard test methods for the examination of water, sewage and industrial wastes (American Public Health Association (APHA), in 1955) and WHO during the period from 1958 to 1971 (World Health Organization, 1958, 1963, 1971). The disadvantages of this

method include the fact that it requires a large amount of sample (up to 10 L), the long time required for the distillation process, and the toxicity of the bromine solution.

#### Selenium Determination by Titration

Improved analysis of Se was achieved by titrimetric method. Following distillation and Se precipitation, as described above, the Se particles are re-dissolved with hydrogen bromide-bromine solution to form  $\text{H}_2\text{SeO}_3$  and an excess of 0.001 N sodium thiosulfate is added. The solution is then back titrated with a standard iodine solution using a starch solution as the indicator. The back titration is calculated as 1.00 mL of 0.001 N sodium thiosulfate being equivalent to 0.0198 mg of Se. This method can provide a low detection limits for Se when using larger volumes of water (maximum of 100 mL) containing Se in amounts less than 0.5 mg. With careful work, results are accurate and reproducible to  $\pm 0.002$  mg. Potential sources of interference include the presence of oxidizing compounds in solution. This titration of Se with excess sodium thiosulfate is known as Norris-Fay titration and has been used since 1896 (Coleman and McCrosky, 1937). The quantitative analysis of Se using distillation and titration appeared in "Methods for Collection and Analysis of Water Samples" published by the USGS in 1960 as method D:33a-1: Norris-Fay Titration Method, which was modified from the Association of Official Agricultural Chemists in 1945 (Rainwater and Thatcher, 1960).

#### Selenium Determination by Colorimetry (Spectrophotometry)

A spot test for Se was first developed for qualitative purposes, using the redox reaction of  $\text{H}_2\text{SeO}_3$  with reducing agents (hydriodic acid or thiourea).  $\text{Se}^0$  obtained from this step is further reacted with sulfuric acid to form a blue coloured complex with codeine. This method was used for biological samples and good results were achieved at concentrations above 1 mg/kg. The colorimetric-basis of this complexing method gave it the potential for development into a quantitative method (Frank *et al.*, 1936; Horn, 1934; Stahl, 1969).

In 1962, the American Water Works Association (AWWA) / American Public Health Association (APHA), joint committee considered a new method proposed for the determination Se in water by colorimetry using 3,3-diaminobenzidine as a complexing agent. Here, following sample digestion, complexation is completed under alkaline conditions and the resulting red-coloured 5,5-dipiazselenol is extracted into an organic phase (typically toluene) for spectroscopic measurement against a standard solution which is prepared in the same manner. However, other metals interfere with this complexation, and must be removed through chelation with ethylenediamine tetra-acetic acid (EDTA) to ensure accurate Se analysis (U.S. EPA., 1971a). It should be noted that 3,3-diaminobenzidine is carcinogen and therefore stringent regulations are in place regarding its commercial availability.

The tested method and results of Se concentrations in waters from a collaborative study had been proposed by the AWWA/APHA. There was an agreement in results among the participating laboratories with accurate and precise data (AWWA Editorial Board, 1963; Skougstad and Fishman, 1963). This method replaced the visual colour comparison method and was published in "Standard Method of Analysis in Water and Wastes" by APHA, 12<sup>nd</sup> Edition in 1965. This method was used for Se in surface water by the U.S. Federal Water Pollution Control Administration in 1968(Federal Water Pollution

Control Administration, 1968; U.S. EPA., 1971b). The USGS also endorsed this method in "Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases" in 1970 (Brown *et al.*, 1970). This colorimetric method with 3,3-diaminobenzidine was able to detect as little as 10 µg Se with an absorbance of 0.093 observed at wavelength 420 nm.

U.S. Federal Water Pollution Control and USGS had specified the terms "dissolved Se", "suspended Se", and "total Se" in their test reports. Dissolved Se is obtained when the sample is filtered through a 0.45 µm membrane prior to analysis, total Se is the amount present in the water without filtration, and suspended Se is the difference between the first two measurements (Federal Water Pollution Control Administration, 1968; Wallschläger and Roehl, 2001). At present, the determination of Se can be specified as "dissolved Se" and "total recoverable Se"

Alternatively, other complexing agents such as 2,3-Diaminonaphthalene (DAN) can be used and produce brightly coloured and strongly fluorescent selenol compounds which can be measured at 480 nm with detection limits around 10 µg/L. The DAN colorimetric method for Se appeared in APHA-Standard Method, 22<sup>nd</sup> Edition in 2012 as Standard Method 3500-Se(C) (Rice *et al.*, 2012). The development of new complexing agents is still an active field of research (Krishnaiah *et al.*, 2003; Narayana and Mathew, 2006; Soruraddin *et al.*, 2011). Commercial test kits for the determination of Se in water based on this type of chemistry are capable of detecting Se in the 0.01 to 1.0 mg/L range when used with a 1 cm absorption cell (Xu *et al.*, 1997).

#### Selenium Determination by Fluorometry

Similar to the 3,3-diaminobezidine colorimetric method for Se analysis, a fluorescent complexing agent, 2,3-diaminonaphthalene (DAN), was developed and provides better sensitivity than conventional colorimetric reagents. The distillation process for sample preparation is omitted in these procedures, making this method significantly faster. However, DAN does need to be prepared freshly prior to analysis due to its sensitivity to air and light. Similarly, the use of EDTA is often required to complex metals which interfere with Se complexation.

For this method, the sample is acid digested with strong acid and reduced to H<sub>2</sub>SeO<sub>3</sub> by hydrochloric acid. EDTA is added to mask interfering metals (tellurium, copper, zinc and aluminum) and the DAN solution is added. The 4,5-benzopiazselenol formed through this reaction is extracted into toluene, hexane, decahydronaphthalene, or cyclohexane (cyclohexane is recommended due to its low background interference). The colour of 4,5-benzopiazselenol depends on pH, reaction time and light conditions. The measurement is done at an excitation wavelength of 375nm and a fluorescent emission wavelength of 525 nm (Lott *et al.*, 1963). The fluorometric method had been used for Se in geological surveys of waters by the U.S. Water Research Institute and claimed to be able to analyse Se at concentration as low as 1 µg/L (Stach, 1978).

#### Selenium by Hydride Generation – Atomic Absorption Spectrometry

It has long been known that distinctive colours are produced when compounds of certain metals are vaporized in flames. Since 1955, flame atomic absorption spectrometry (FAAS) has taken advantage of this phenomenon and has been widely used for the quantitative analysis of many elements; however, it

is still not suitable for metalloids including Se (L'Vov, 1961; Walsh, 1955). Direct measurement of Se by FAAS is not recommended because the absorption line of Se at 196 nm is interfered by hydrocarbon molecules generated from air-acetylene in the flame. Other types of gas (i.e. propane-air, argon-hydrogen and nitrogen-hydrogen) have been studied to reduce the spectral absorption of hydrocarbons below 200 nm. Moreover, increasing the intensity of the light source by using an electrodeless discharge lamp was examined, but the detection limit of 200 µg/L was not suitable for the analysis of Se in most natural waters (Thompson and Thomerson, 1974; Winefordner and Vickers, 1972).

Due to the limited sensitivity for metalloids (Se, As, Hg) analysis by hydride generation (HG) FAAS has been developed. HG for Se involves two reducing steps: first reducing Se(VI) in digested solutions to Se(IV) using hydrochloric acid, stannous chloride, potassium/sodium iodide, or potassium bromide. The second step involves the reduction of Se(IV) to Se<sup>-2</sup> using zinc powder, or magnesium or sodium borohydride in acidic solution to form volatile selenides (typically H<sub>2</sub>Se). HG is widely used for the analysis of Se in waters due to its sensitivity, specificity, and affordability; therefore, the research on reducing reagents to increase the efficiency of hydride formation are still active and recently there has been a trend to move from inorganic to organic reducing agents (Limchoowong *et al.*, 2015; Musil and Matoušek, 2008; Welz and Šucmanová, 1993; Yamamoto and Kumamaru, 1976).

The HG reaction is prepared by batch or continuous (flow injection) systems. Samples must be digested to ensure that all Se is present as inorganic species before proceeding with the two reduction steps mentioned above. Later, H<sub>2</sub>Se is purged into a quartz tube placed on a furnace or burner and atomised by flame or flameless AAS. The measurement is taken as a transient signal and integrated by peak area or peak height. The method of batch HG has the advantage of being able to handle large sample volumes (up to 100mL), but it is time consuming to reach the equilibrium required for hydride reaction and diffusion to the flame. Continuous flow injection HG coupled to AAS (FI-HG-AAS) was developed with automated systems, reducing time, and improving precision; however, these methods are rather expensive (Chan and Sadana, 1992; Limchoowong *et al.*, 2015; Piston and Knochen, 2012).

In 1974, the utilization of batch HG-AAS for Se analysis was issued by the U.S. EPA as Method 270.3 for dissolved, suspended, and total Se in drinking water, freshwater, and marine waters and the USGS published a HG-AAS protocol for total Se analysis as Method number I-3667-85 for batch HG-AAS and FI-HG-AAS (Fishman and Friedman, 1989; U.S. EPA., 1983). The USGS used the HG-AAS technique for a Se survey of selected streams in regions with mineable coal reserves in Eastern Kentucky in 1980; at the time, Se in waters was regulated at 5 µg/L. Most of the water samples from the sampling sites were reported at 0-2 µg/L (detection limit was 1 µg/L); only two samples were found to contain higher concentrations of Se, at 5 and 6 µg/L (Downing-Kunz *et al.*, 2005). HG-AAS for Se analysis appeared in APHA-Standard Method 301A in 1975, which later become Standard Methods 3114B (manual HG-AAS) and 3114C (continuous HG-AAS) (Rand *et al.*, 1976; Rice *et al.*, 2012). The capability to detect Se by HG-AAS below 1 µg/L was reported with sample volumes of 50-100 mL for batch systems (Fishman and Friedman, 1989; International Organization for Standardization, 2013).

The current version of WHO-Guidelines for Drinking Water Quality references HG-AAS for Se analysis. U.S EPA 40 CFR 136 (Clean Act Water) and 40 CFR 141 (Safe Drinking Water Act) have approved

mandatory methods for Se analysis by HG as follows: APHA-Standard Method 3114B, 3114C, ASTM D3859-A and USGS Method I-3667-85. The USGS Method I-3667-85 is not mentioned for Se analysis in drinking water by 40CFR 141 (ASTM International, 2008; U.S. EPA, 2017a, b, d). However, there is a concern based on the sample preparation by acid digestion using perchloric acid, which is not recommended by the U.S. EPA because of its potential danger (U.S. EPA., 1994).

#### Selenium Determination by Graphite Furnace Atomic Absorption Spectrometry

Graphite furnace (GF)-AAS, also known as electro-thermal atomization (ETA)-AAS, electro-thermal vaporization (ETV)-AAS, or flameless AAS, was developed at the same time as FAAS. GF-AAS affords the determination of most metallic elements with a smaller amount of sample consumed (10-50  $\mu\text{L}$ ), excellent sensitivities and detection limits, and direct analysis without sample preparation. However, the disadvantage is the cost of GF-AAS itself, which includes the consumption of a graphite tube and additional inert gas (Ashino *et al.*, 2010). However, an important advantage of GF-AAS over FAAS is that GF-AAS can analyse metalloid species with satisfactory sensitivity.

As the GF-AAS is working with a transient signal, the use of a modifier to assist pyrolysis/atomization, a temperature program, and purging gas maintain the retention time of atom vapor to enhance the absorption and to remove spectral interferences (e.g. iron, chloride, sulfate). The graphite tube has been specifically designed in terms of its shape as well as through the development of a pyrolytic coating material to assist in temperature homogeneity during atomisation and to expand a lifetime of the graphite tube under high temperatures in corrosive solutions (Moreira *et al.*, 2007). The use of background correction (i.e. Zeeman or Deuterium background correction) to overcome the matrix spectral interferences can significantly increase the capability of GF-AAS to determine metal contaminants in low the  $\mu\text{g/L}$  range. For Se analysis, the interferences in water samples include chloride, sulfate, sodium and potassium. Palladium nitrate or nickel nitrate modifiers are preferred. The detection limit of Se by GF-AAS has been published recently at less than 1  $\mu\text{g/L}$  (Greenberg *et al.*, 1992; Hergenreder; Niedzielski and Siepak, 2003).

A GF-AAS technique was first issued by the U.S. EPA in 1969 under "atomic absorption methods" and in 1978 became Method 270.2 for dissolved, suspended and total Se analysis in water and waste. A detection limit of 2  $\mu\text{g/L}$  was reported for Se and the method remained in effect until 1996 (U.S. EPA., 1983, 1994). Later, the U.S. EPA revised methods for all elements, including Se, by GF-AAS and the analysis of 15 trace elements together became EPA Method 200.9. EPA Method 200.9 specifies the type of graphite platform to be used as a stabilised temperature graphite platform or a transverse heated graphite platform (U.S. EPA, 1994c).

In 1985, the determination of Se by GF-AAS was appeared as APHA-Standard Method 304 (Greenberg *et al.*, 1985) which was later revised to Standard Method 3113B and is still active in the current version published in 2017 (Rand *et al.*, 1976; Rice *et al.*, 2012). The use of GF-AAS for Se analysis in water has been seen in the USGS as Method I-2668-98 with a method detection limit of 1  $\mu\text{g/L}$  for Se (Jones and Garbarino, 1998). The USGS recommended the GF-AAS instrumentation has a Zeeman background correction system, the transverse heated graphite atomizer (THGA), and analyse individual elements to achieve detection limits of 1  $\mu\text{g/L}$ . Methods for GF-AAS analysis of Se in water are also published in

ASTM D3859-B and ASTM D3919, but in ASTM D3919 it is only mentioned as a general practice of GF-AAS for trace elements analysis including Se (ASTM International, 2004, 2008).

U.S EPA 40 CFR 141 (Safe Drinking Water Act) has approved test methods for Se from EPA 200.9, ASTM D3859-B and APHA 3113B, while EPA 40 CFR 136 (Clean Act Water) accepts only EPA 200.9 (U.S. EPA, 2017a, b).

#### Selenium by Inductively-Coupled Plasma Atomic Emission Spectrometry

The simultaneous multi-elemental nature of inductively-coupled plasma atomic emission spectrometry (ICP-AES), which is also known as ICP optical emission spectrometry (ICP-OES), has clear advantages over AAS-based methods for multi-element analysis, with a large dynamic linear range and refractory element removal in the high-temperature plasma. ICP-AES was introduced to the U.S. EPA in order to improve instrumentation for identification and quantification of environmental pollutants. Using the prominent lines of the ICP emission of 70 elements, each spectral line of elements was studied by the Ames Laboratory under the sponsorship of the U.S. EPA from 1977 to 1978. For Se, the spectral lines were reported at 196.026, 203.985, 206.279, 207.479 and 199.511 nm, noted here in order from highest to lowest sensitivity. The estimated detection limit using the 196.026 nm line (as is generally used for Se analysis) was calculated to be 75 µg/L (Winge *et al.*, 1979). The U.S. EPA method for the analysis of 33 elements in water and wastes by ICP-AES was published in 1982 as a new method called Method 200.7 and it is still active in the current version of the guide (U.S. EPA, 2015). However, with typical ICP-AES, the detection limit for Se raises questions of whether the method can be used to analyze the concentrations below 10 µg/L present in drinking water. The development of an ultrasonic nebulizer (USN) to obtain a larger amount of fine aerosol was published in EPA Report-600/R-94/111 in 1994 as method 200.15 (U.S. EPA, 1994b). The detection limit for Se using USN-ICP-AES decreased significantly to below 8 µg/L from 75 µg/L using a conventional pneumatic nebulizer (International Organization for Standardization, 2007).

The criteria of ICP-AES instrumentation in EPA Method 200.7 only specifies a general ICP-AES system with background-correction, meanwhile EPA Method 200.15 added "Section 6.1.5 UNS - A radio-frequency powered oscillating transducer plate capable of providing a densely populated, extremely fine desolvated aerosol" (U.S. EPA, 1994b). However, the sensitivity for some elements, including Se, by ICP-AES was still not adequate for natural water analysis. The idea of axially viewed (AV) ICP-AES was introduced to the U.S. EPA for multi-elemental analysis because of its improved sensitivity. The changing of the torch position and viewpoint configuration of the spectrometer from radially to axially provided larger emission signals and more stability during the entire measurement process (U.S. EPA, 2003).

Nobrega *et al.* (Nobrega *et al.*, 2002) evaluated the performance of ICP-AES between axially and radially viewed configurations and observed that an ICP-AES axial configuration can increase sensitivity 20-30 times for Se analysis. The study demonstrated detection limits ranging from of 4 to 6 µg/L in waters with varying carbon content. Meanwhile, EPA Method 200.5 (Determination of trace elements in drinking water by AV-ICP-OES) claimed a detection limit of 2 µg/L for Se (U.S. EPA, 2003). Some AV-ICP-AES instruments are configured such that the emitted signal can be viewed alternately or simultaneously in a radial manner, called "dual view ICP" in which the user can obtain both sets of results in a single

analysis. Therefore, the radially viewed signals can be used for the determination of major matrix elements such as Ca, Mg, Na, and silica. EPA Methods 200.5 (using AV-ICP-AES) and 200.7 (ICP-AES) are accepted for Se analysis in the Clean Water Act (U.S. EPA, 2018a). However, for drinking water, EPA Method 200.5 is accepted as an alternative test method.(U.S. EPA, 2018b) EPA Methods 200.7 and 200.15 are not referred to as accepted methods for Se analysis in drinking water (U.S. EPA, 2018c).

An ICP-AES method for multi-elemental analysis, including Se, is also published in ISO 11885 – 2007; the detection limits for Se at 196.026 and 203.985 nm are stated to be 100 µg/L for radial viewing and 2 µg/L for axial viewing. The UNS is also possible for the analysis of selenium in water samples in the low concentration range (International Organization for Standardization, 2007). An ICP-AES method is also published in APHA Method 3120B (Greenberg *et al.*, 1992) and ASTM D1976 (ASTM International, 2012a).

### Selenium Analysis by Inductively-Coupled Plasma Mass Spectrometry

Mass spectrometry (MS) has become widely used by researchers as a powerful tool for analytical chemistry. ICP-MS is able to analyse a most elements in the ppt (ng/L) to ppb (µg/L) range and can be applied to a higher precision measurements through the application of isotope dilution mass spectrometry (IDMS), which is discussed in further detail in the next section. The advantage of its sensitivity makes ICP-MS is applicable to the analysis of ultra-trace elements in natural waters. While single quadrupole-ICP-MS is by far the most commonly used, the presence of isobaric interferences on the masses of Se isotopes present some challenges.

Se has naturally-occurring stable isotopes at masses 74, 76, 77, 78, 80 and 82 amu. In the high temperature plasma, argon (Ar) becomes ionized and forms positively charged polyatomic ions ( $^{40}\text{Ar}_2^+$ ,  $^{38}\text{Ar}_2^+$ ) and also with other matrix elements such as chlorine, sulfur, nitrogen, and calcium, all of which interfere with various Se isotopes (see Table 2). Further interference arises from elements which have the same isotope as Se, such as krypton, which is a common impurity in argon. Table 2 shows isotope interfering Se analysis (De Bièvre and Barnes, 1985; May and Wiedmeyer, 1998).

Table 2: Isobaric and polyatomic interferences for selenium analysis by ICP-MS

Se Isotope	Isotope Abundance (%)	Isobaric Interferences	Polyatomic Interferences	Recommended Mass
$^{74}\text{Se}$	0.87	$^{74}\text{Ge}$	$^{37}\text{Cl}_2^+$ , $^{36}\text{Ar}^{38}\text{Ar}^+$ , $^{38}\text{Ar}^{36}\text{S}^+$ , $^{40}\text{Ar}^{34}\text{S}^+$	
$^{76}\text{Se}$	9.02	$^{76}\text{Ge}$	$^{40}\text{Ar}^{36}\text{Ar}^+$ , $^{40}\text{Ar}^{36}\text{S}$	
$^{77}\text{Se}$	7.58	$^{154}\text{Gd}^{2+}$	$^{36}\text{Ar}^{40}\text{Ar}^1\text{H}^+$ , $^{38}\text{Ar}_2^1\text{H}^+$ , $^{40}\text{Ar}^{37}\text{Cl}^+$ , $^{12}\text{C}^{19}\text{F}^{14}\text{N}^{16}\text{O}_2^+$	AOAC 993.14, APHA 3125B, ISO 17294-1(for low Cl)
$^{78}\text{Se}$	23.52	$^{78}\text{Kr}^+$ , $^{156}\text{Gd}^{2+}$	$^{40}\text{Ar}^{38}\text{Ar}^+$ , $^{38}\text{Ar}^{40}\text{Ca}^+$	USGS,(Garbarino, 1999) ISO 17294-1(for high

				Cl and Br)
<sup>80</sup> Se	49.82	<sup>80</sup> Kr <sup>+</sup> , <sup>160</sup> Gd <sup>2+</sup>	<sup>40</sup> Ar <sub>2</sub> <sup>+</sup> , <sup>40</sup> Ar <sup>40</sup> Ca <sup>+</sup> , <sup>32</sup> S <sup>16</sup> O <sub>3</sub> <sup>+</sup>	AOAC 993.14
<sup>82</sup> Se	9.19	<sup>82</sup> Kr <sup>+</sup>	<sup>40</sup> Ar <sub>2</sub> <sup>1</sup> H <sup>+</sup> , <sup>40</sup> Ar <sub>2</sub> <sup>1</sup> H <sub>2</sub> <sup>+</sup> , <sup>81</sup> Br <sup>1</sup> H <sup>+</sup> , <sup>12</sup> C <sup>35</sup> Cl <sub>2</sub> <sup>+</sup> , <sup>34</sup> S <sup>16</sup> O <sub>3</sub> <sup>+</sup>	EPA 200.8(must be monitored), APHA 3125B, USGS, ISO 17294-1(for low Br), ASTM D5673

Some isobaric interference, such as <sup>82</sup>Kr, can be removed using background subtraction. A mathematical correction model (Equation 2) is recommended by APHA Method 3125 and ISO 17294-1 (Rice *et al.*, 2012; Wiel, 2003). However the U.S. EPA Method 200.8 does not specify the correction factor for <sup>82</sup>Kr, but stated that if the correction factor is used then a record of this correction process should be included in the report of the data. The correction factor is dependent on the accuracy of isotope abundance used for calculation (U.S. EPA, 1994a).

$$^{82}\text{Se} = ^{82}\text{C} - (1.008696 \times ^{83}\text{C}) \quad (\text{Equation 2})^*$$

where C is the calibrated blank-corrected counts at indicated masses, and

$$1.008696 = \frac{\text{Abundance of } ^{82}\text{Kr}}{\text{Abundance of } ^{83}\text{Kr}} = \frac{11.6}{11.5} **$$

\*\*1.008696 is derived from (Equation 2) using isotope abundance from spectroscopyonline.com (Neubauer, 2010; Rice *et al.*, 2012)

However, this type of mathematical correction model does not work when the signal from the interference is higher than that of the analyte. Instead, advanced technologies using a collision reaction cell (CRC) or dynamic reaction cell (DRC) have been developed to eliminate these types of interferences (Koppelaar *et al.*, 2004; Rottmann *et al.*, 2012; Salazar *et al.*, 2011; Tanner and Baranov, 1999). These reaction cells operate as rf-only multipoles, situated before the mass analyzer, which can be pressurized with a gas to induce various ion-molecule reactions in one of two scenarios. In the first, a gas is chosen to react with the analyte ions, changing the mass and allowing for detection without interference; for example, O<sub>2</sub> gas can react with ion X<sup>+</sup> to form XO<sup>+</sup> which can then be monitored at mass x + 16. Alternately, the cell gas can react with the interference to change its mass, allowing the analyte ion to be measured at its native m/z. The latter scenario is more commonly employed for Se, for example CH<sub>4</sub> will react with <sup>40</sup>Ar<sub>2</sub><sup>+</sup> allowing for the analysis of <sup>80</sup>Se (Tanner *et al.*, 2002). The application of collision and reaction cells in ICP-MS significantly lowered detection limits for difficult-to-analyze elements such as Se, where even in the early days of the technology detection limits in the low- or sub-ng/L range were obtained (Sloth and Larsen, 2000; Tanner *et al.*, 2000).

More recently, further advancements in ICP-MS technology have resulted in the production of triple quadrupole ICP-MS (ICP-QQQ-MS) instruments, first introduced by Agilent Technologies in 2012 (Kuwabara *et al.*, 2012). Their design and operation is similar to collision/reaction cell instruments, but there is a mass analyzer both before and after the collision cell, allowing for extreme selectivity and elimination of most interferences. The application of ICP-QQQ-MS is especially beneficial for samples

containing relatively high concentrations of interfering components in the matrix, as is frequently the case in contaminated waters.

Since 1990, a method for multi-element analysis by ICP-MS has been published as U.S.EPA Method 200.8 (U.S. EPA, 1994a). Other ICP-MS methods that have been approved for Se determination in clean water include APHA 3125B, ASTM D5673, AOAC 993.14, and USGS Method I-4020-05. An ICP-MS method (EPA Method 200.8) for Se determination in drinking water is also mentioned in the National Primary Drinking Water Act (40 CFR 141.23) Appendix A to Subpart C (U.S. EPA, 2017b). International Food Standards CODEX STAN 108-1981 suggest several methods for Se analysis in natural mineral waters (maximum level of 10 µg/L); including ICP-MS methods ISO 17294-2 and EPA 200.8 (Codex Alimentarius, 1999).

#### Selenium Determination by Isotope Dilution Mass Spectrometry

IDMS represents the state-of-the-art in analytical chemistry and can be applied to both total element and speciation analysis. The method requires mass spectrometric measurements of the ratio abundance of two or more stable (or long-lived) isotopes of a given analyte and is based on the addition of a known amount of enriched isotope spike into a sample (Heumann, 1982, 1992). While sometimes rather expensive, these enriched isotope standards are commercially available, for example from LGC-UK and American Elements®, etc. Based on the measured ratios between the spiked isotope and a reference isotope in a sample and knowledge of the enrichment of the spike and the exact amount used, the concentration of analyte in the sample can be calculated as shown in Equation 3.

$$C_x = C_y \cdot \frac{m_y}{m_x} \cdot \frac{A_y - B_y \cdot R_n}{B_x \cdot R_n - A_x} \cdot \frac{M_x}{M_y} - C_b \quad (\text{Equation 3})$$

where:

$C_x$  is the concentration of analyte in the sample,

$C_y$  is the concentration of the analyte in the spike solution,

$m_y$  is the mass of the spike solution used in the spike/sample mixture,

$m_x$  is the mass of the sample,

$A_y$  is the abundance of the reference isotope in the spike solution,

$B_y$  is the abundance of the spike isotope in the spike solution,

$A_x$  is the abundance of the reference isotope in the sample,

$B_x$  is the abundance of the spike isotope in the sample,

$R_n$  is the reference/spike isotope ratio in the spike/sample mixture,

$M_x$  is the atomic weight of the reference isotope,

$M_y$  is the atomic weight of the spike isotope,

$C_b$  is the concentration of the analyte in the blank

One of the greatest advantages of IDMS is its high level of accuracy and precision due to its ability to account for analyte losses and/or changes during sample preparation because factors affecting the native analyte will affect the spike to an equal degree.

An important factor in the accuracy of IDMS measurements is the mass resolution achieved by the instrument; there are a variety of types of mass spectrometers, each with different capabilities. For the analysis of metal(loid)s, there are five basic types of ICP-MS instruments: single quadrupole (SQ-ICP-MS, which may contain a CRC or DRC), triple quadrupole (ICP-QQQ-MS), time of flight (ICP-TOF-MS), and sector field (magnetic and electric) instruments which may contain single collector, or multi-collector (MC-ICP-MS) detection systems.

A report on the analysis of Se in groundwater, river water and lakes samples by IDMS was published in 1991 by Heumann *et.al.* using a Negative Thermal Ionization Mass Spectrometer (NTI-MS) measuring ratio of enriched  $^{82}\text{Se}$  isotope and most abundant isotope  $^{80}\text{Se}$ . Total Se was reported from 0.2 to 15.6  $\mu\text{g/L}$  where Se(VI) was the major species (Tanzer and Heumann, 1990).

The U.S. EPA, under the Clean Water Act and National Primary Drinking Water Regulation, does not require IDMS for the analysis of any metal, including Se. However, IDMS method is recommended by the U.S. EPA for evaluating of solid wastes (known as SW-846) to comply with the Resource Conservation and Recovery Act (RCRA). EPA Method 6800 covers 20 elements, including Se, all of which have more than one isotope (U.S. EPA, 2014b; Vogl and Pritzkow, 2010).

### **Method Requirements for Selenium analysis**

#### **Sample Collection**

Similar approaches for sample collection are described in U.S. EPA-600/4-82-029 (general sampling) and ISO 5667-3 (International Organization for Standardization, 2012; U.S. EPA., 1982); both of which are used as a general sampling guideline for a variety analytes in waters. AWWA Section 3010-B and EPA Method 1669 are related to sampling for metals analysis. EPA Method 1696 covers 13 metals (including Se) to comply with clean water regulations as these metals are regulated at very low concentrations (ppt to ppb levels). This standard has a stringent measure to control contamination generated from sampling, transportation, and analysis (Greenberg *et al.*, 1985; U.S. EPA, 1996a). Water samples can be collected in a container made of quartz, borosilicate glass, propylene (PP), high density polyethylene (HDPE), fluoroethylenepolymer (FEP), polycarbonate (PC), or polytetrafluoroethylene (PTFE). The container needs to be washed with detergent, cleaned, rinsed with nitric acid (from 20-50 %v/v) or mixture of nitric and hydrochloric acid, and soaked in or filled with dilute nitric or hydrochloric acid for at least 24 hours before being rinsed with ultrapure water. When sampling, water samples must be filtered through (at least) 0.45  $\mu\text{m}$  membrane filters (polycarbonate or cellulose esters) immediately upon collection. The container is completely filled with sample, without headspace, and keep as cool as possible after collection. It has been noted that exposure of a sample to air during filtration can cause co-precipitation of Se with iron and manganese oxide (Wu and Pichler, 2015).

#### **Sample Preservation**

The purpose of preservation is to maintain the integrity of a sample, through the prevention of interactions with microorganisms, the reduction of co-precipitation and complexation of the analyte of interest and other matrix components, and to minimize adsorption of the analyte onto the sample

container's surface. For (total) metals analysis, a water sample is typically preserved in nitric acid to achieve a final pH less than 2 (Rice *et al.*, 2012; U.S. EPA, 1996a). However nitric acid preservation has caused difficulty when the subsequent analysis is performed via a reaction with sodium borohydride as the nitric acid can diminish the Se hydride signal (Campbell, 1992).

There is no standard method detailing guidelines for sample storage for the preservation of Se speciation; however, EPA Method 1632 discusses the preservation of arsenic species in water, during which hydrochloric acid is added and the recommended maximum storage time to preserve speciation is 28 days at 0-4°C (U.S. EPA, 1998). Conversely, Se species are not stable in the presence of microorganisms or reducing or oxidising compounds, therefore immediate analysis is generally recommended (Eswayah *et al.*, 2016). There are several studies examining various storage conditions for Se species in waters (Héninger *et al.*, 1997; Wiedmeyer and May, 1993; Wu and Pichler, 2015). For example, Wu and Pichler (Wu and Pichler, 2015) found that the speciation was preserved for small concentrations of Se (from 5 ppb) in the presence of rich iron and manganese through the addition of 0.5M EDTA when the samples were stored in PE bottles at 4°C in the dark for up to 11 weeks.

#### Sample Preparation and Quality Control

Many standard methods of analysis have been discussed in this section. In these methods, sample preparation for Se and other metals categorized based on three pools of Se: dissolved, suspended, and total recoverable metals. AWWA section 3010 (A) adds an additional group – acid-extractable metals – and associated methods are applied to extract Se from suspended particulates and solid samples. The analysis of Se in waters is typically reported in two pools: dissolved Se and total recoverable Se (Rice *et al.*, 2012).

Direct analysis of water samples is fairly uncommon and is only recommended for drinking water analysis where turbidity is less than 1 NTU (U.S. EPA, 2015). The dissolved fraction is defined as the amount of Se recovered after filtration a 0.45 µm membrane. Lastly, total recoverable Se measures all of the analyte in a sample for acid preserved waters and samples analyzed after acid digestion. Total recovery digestions typically acid use either nitric acid or aqua regia and can be conducted under closed (microwave or autoclave) or open (hot block, water bath, or hot block) conditions. For USN-ICP methods, hydrogen peroxide is added during digestion to enhance aerosol capability.

To ensure the integrity of acquire data, various quality control measures are implemented during sample collection, preparation, and analysis. These quality control measure are stated with acceptance criteria for various standard methods and include:

1. Maintenance of data generated from analysis
2. Demonstration of laboratory capability and proficiency participation
3. Routine quality control
  - a. Multi-point calibration using standard solutions
  - b. Analysis of a variety of types of blanks (field blank, rinsed/equipment blank, calibration blank, reagent/method blank)

- c. Accuracy and precision
- i. Lower limit of quantification measurement
  - ii. Internal standardization
  - iii. Recovery check using LFB, LFM, LCS, and/or CRM
  - iv. Repeatability (duplicate samples, and duplicate spike fortified samples)
  - v. Interval checks of system stability using continuing calibrations blanks, continuing calibration verifications (at a mid-point concentration)

The use of specific reference materials are not stated in any standard methods, and can therefore be chosen based on availability. There is a wide variety of water certified reference materials certified for total metals, but many are not certified for Se. Table 3 provides some examples of waters certified for total Se which are currently (as of writing date) available for purchase. Table 4 provides a list of standard methods which are widely used for routine analysis of total Se.

Table 3: Examples of commercial certified reference materials for Se in water

Material	Producer	Matrix/sample type	Certified Se Concentration
SRM 1640a	National Institute of Standards & Technology	Trace Elements in Natural Water	20.13+0.17 µg/L
SRM 1643f	National Institute of Standards & Technology	Trace Elements in (Pure) Water	11.700+0.081 µg/L
CRM 7202-b	National Metrology Institute of Japan	Trace Elements in River Water (Elevated Level)	1.00+0.06 µg/kg
MX014	National Metrology Institute of Australia	Trace Elements in Sea Water	3.17+0.28 µg/L
ERM-CA011	European Reference Materials	Hard Drinking Water - Metals	11.13+0.47 µg/L
ERM-CA713	European Reference Materials	Wastewater – Trace Elements	4.9+1.1 µg/L
NWTM-35 TM-35	Environment and Climate Change Canada	Lake Ontario water (fortified)	3.70+0.46 µg/L
TMDA-51.5	Environment and Climate Change Canada	Lake Ontario water (fortified)	14.4+2.2 µg/L
TM-DWS.3	Environment and Climate Change Canada	Lake Ontario water (fortified)	9.20+1.17 µg/L
SPS-SW1	Spectrapure Standards-Norway	Trace Elements in Surface Water	2.0+0.02 µg/L
SPS SW2	Spectrapure Standards-Norway	Trace Elements in Surface Water	10.0+0.05 µg/L

Table 4: Standard method detail and quality control criteria for drinking water, waters and wastewater

Method	Standard Method	Digestion Method for Each Se Fraction	IDL-Se	MDL or LOQ -Se	Method Performance Indicators to be Reported	Reference
HG-AAS (Batch)	ASTM D3859-A (Se only)	<p><u>Dissolved:</u></p> <ul style="list-style-type: none"> <li>-filter sample (0.45 µm)</li> <li>- process filtrate as total recoverable fraction</li> </ul> <p><u>Total recoverable:</u></p> <ul style="list-style-type: none"> <li>-50 mL sample without filtration</li> <li>-add methyl orange, 0.5 mL CaCl<sub>2</sub> (3%w/v), 0.5 mL HCl (1%v/v), and 3 drops KMnO<sub>4</sub></li> <li>-boil, evaporate to 25 mL, add 2mL NaOH (0.4%w/v)</li> <li>-heat until dryness, cool, add 15 mL HCl, heat for 20 min, cool, add HCl (50% v/v) to make 50 mL</li> <li>-analyze</li> </ul>	No Data	No Data	<p>Working Range: 1-20 ppb</p> <p><u>Accuracy and Precision:</u></p> <ul style="list-style-type: none"> <li>-Overall precision: <math>0.146X+0.49</math> (X= Se concentration)</li> <li>-reagent water: bias 93 to 106% at 3 to 17 ppb</li> <li>-sample: bias 90 to 108% at 3 to 17 ppb</li> </ul> <p><u>Demonstration of Capability:</u></p> <ul style="list-style-type: none"> <li>-7 replicates of standard solution with matrix matching solution at midpoint</li> <li>-criteria as above for precision and bias for % recovery and STDEV</li> </ul> <p><u>Quality Control:</u></p> <ul style="list-style-type: none"> <li>- calibration curve: ≥6 calibration points</li> <li>-IPC at midpoint of calibration curve, 85-115% accuracy</li> <li>-CCB analyzed between every sample set*</li> <li>-CCV every 10%, 85-115% accuracy</li> <li>-reagent blank &lt; ½ of the lowest calibration concentration</li> <li>-LCS at midpoint calibration 85-115% accuracy</li> <li>-matrix spike, once per sample set; accepted as criteria in Guide ASTM D5810 - Table 1</li> <li>-matrix spike duplicate n=1/batch</li> <li>-use independent reference material</li> </ul>	<p>(ASTM International, 2008)</p> <p>(ASTM International, 2012b)</p> <p>ASTM D10-96</p>
HG-AAS	EPA 7741A (Se only)	<p><u>Total recoverable:</u></p> <ul style="list-style-type: none"> <li>-50 mL sample, add 10 mL HNO<sub>3</sub> and 12 mL H<sub>2</sub>SO<sub>4</sub></li> <li>-heat until white fumes produced, cool</li> </ul>	No Data	2 ppb	<p><u>Accuracy and Precision:</u></p> <ul style="list-style-type: none"> <li>-recovery at 5, 10 and 15 ppb 100-101%</li> <li>- RSD: 0.6-2.9 %</li> </ul> <p><u>Quality Control:</u></p>	(U.S. EPA, 1994d)

GF-AAS	ASTM D3859-B (Se only)	<p>-add 25 mL DIW, heat until white fumes produced, add H<sub>2</sub>O and evaporate until observing SO<sub>3</sub> fumes are observed, cool</p> <p>-add 40 mL HCl and make up to 100 mL with DIW</p>	No Data	No Data	(refer to EPA Method 7000)
GF-AAS	ASTM D3859-B (Se only)	<p><u>Dissolved:</u> -filter sample (0.45 μm) -add 2 mg NiNO<sub>3</sub> and inject sample</p> <p><u>Total-recoverable:</u> 100 mL sample without filtration -add 5 mL H<sub>2</sub>O<sub>2</sub> and 5 mL HNO<sub>3</sub> -heat at 95°C until volume reaches 15 to 20 mL, cool and filter (0.45 μm)</p>	No Data	No Data	<p><u>Accuracy and Precision:</u> -reagent water overall precision: 0.1072X+0.54 (X= Se concentration) -reagent water bias: 85-90% at 3 to 14 ppb -sample overall precision: 0.2658X-0.03 -sample bias: 76-93% at 3 to 14 ppb</p> <p><u>Demonstration of Capability:</u> See ASTM D3859-A</p> <p><u>Quality Control</u> -calibration curve ≥3 points -instrument check at midpoint of calibration curve, 85-115% accuracy -CCB, CCV between each sample set; 85-115% accuracy on CCV -reagent blank &lt; 1/2 of the lowest calibration concentration -LCS at a midpoint of calibration curve, 85-115% accuracy -recovery for matrix spike and matrix spike duplicate: see ASTM D3859-A -use independent reference material</p> <p>(ASTM International, 2008)</p>
GF-AAS	AWWA 3113B (Se only)	<p><u>Dissolved:</u> -filter acid preserved sample (0.45 μm) -add 3 mL H<sub>2</sub>O<sub>2</sub> per 100 mL sample and NiNO<sub>3</sub></p> <p><u>Total Recoverable:</u> -100 mL sample, unfiltered</p>	2 ppb	No Data	<p><u>Accuracy and Precision:</u> -Se in waters at 10 ppb: 6-12% error, 17-48 %RSD (overall precision) -Se in effluent at 10 ppb: 17-36% error, 30-51 %RSD (overall precision)</p> <p><u>Demonstration of Capability</u> -method detection limit</p> <p>(Rice et al., 2012)</p>

AV-ICP-OES	EPA 200.5 (multi-element)	<p><u>Total recoverable:</u></p> <ul style="list-style-type: none"> <li>-50 mL sample</li> <li>-add 1 mL HNO<sub>3</sub> (50%v/v), 0.5 mL HCl (50%v/v)</li> <li>-heat via block digester at 95 °C to volume of 25 mL, reflux 30 min, cool - dilute to 25 mL with DIW</li> </ul>	2 ppb	2.9 ppb	<p>-linear dynamic range,</p> <p><u>Quality Control:</u></p> <ul style="list-style-type: none"> <li>-calibration curve</li> <li>-CCV at midpoint of calibration curve, 90-110% accuracy</li> <li>-CCB at the beginning, during and end of analysis</li> <li>-LCS</li> <li>-matrix blank or reagent blank every 20 samples</li> <li>-LFB at midpoint of calibration curve, analyst to set criteria and record on control chart</li> <li>-replicate sample analyzed each sample set</li> <li>-LFM and LFM duplicate every 20 samples</li> <li>-10-fold diluted sample value within 10% of original value</li> </ul>	
AV-ICP-OES	ISO 11885 (multi-elements)	<p><u>Direct Analysis:</u></p> <ul style="list-style-type: none"> <li>-sample must be colorless with turbidity &lt;1.5 NTU</li> <li><u>Dissolved:</u></li> <li>-filter acid preserved sample (0.45 µm)</li> <li>-matrix match standards</li> </ul> <p><u>Total Recoverable (Aqua Regia Digestion):</u></p> <ul style="list-style-type: none"> <li>-25 mL sample (unfiltered)</li> </ul>	No Data	7 ppb	<p><u>Accuracy and Precision:</u></p> <ul style="list-style-type: none"> <li>-NIST SRM 1643 (12.7 ppb): 94% accuracy and 5.9 %RSD</li> <li>-surface water, well water, Tank storing water (Se &lt;2.9 ppb) : spiked at 50 ppb, 95-104% recovery and 1.2 - 2% RSD</li> <li>-well water (Se 4.1 ppb) : spiked at 50 ppb: 100% recovery and 1.1 % RSD</li> </ul>	(U.S. EPA, 2003)
AV-ICP-OES					<p><u>Quality Control:</u></p> <ul style="list-style-type: none"> <li>-IPC drift &lt;10%</li> <li>-independent calibration check 90-110% accuracy at the beginning and every 25 samples</li> <li>-reagent blank every 25 samples</li> <li>-spikes recovery:</li> </ul>	(International Organization for Standardization, 2007)

		<p>-add 6 mL HCl and 2 mL HNO<sub>3</sub>, heat (opened or closed system), cool, make up volume</p> <p><u>Total Recoverable (Nitric Acid Digestion)</u></p> <p>-25 mL sample (unfiltered)</p> <p>-add 6.25 mL HNO<sub>3</sub></p> <p>-heat (opened or closed system), cool and make up volume</p> <p><u>Suspended:</u></p> <p>-use particulates collected on 0.45 μm filter from "dissolved" fraction</p> <p>-add 4 mL HNO<sub>3</sub> and 4 mL H<sub>2</sub>O<sub>2</sub>, reflux</p> <p>-add 3 mL HNO<sub>3</sub> and 3 mL H<sub>2</sub>O<sub>2</sub> heat until digestion complete (evaporated to 2 mL), cool</p> <p>-add 10 mL HCl, 15 mL DIW, warm, cool, and filter (0.45μm)</p>			
<p>USN-ICP-AES</p> <p>EPA 200.15 (multi-element)</p>		<p><u>Direct Analysis:</u></p> <p>-sample must have turbidity &lt;1 NTU (unfiltered, acid preserved)</p> <p><u>Dissolved:</u></p> <p>-filter acid preserved sample (0.45 μm)</p> <p>-add HNO<sub>3</sub>, HCl and H<sub>2</sub>O<sub>2</sub> to obtain 2%, 1% and 4%, respectively</p> <p><u>Total Recoverable:</u></p> <p>-100mL filtered, acid preserved sample</p> <p>-add 2 mL HNO<sub>3</sub> (50%v/v) and 1 mL HCl (50%v/v)</p> <p>-heat at 85°C., evaporate to 20 mL</p> <p>-gently reflux for 30 min, cool</p>	<p>5 ppb (direct analysis)</p> <p>3 ppb (total recoverable)</p> <p>8 ppb</p>	<p><u>Accuracy and Precision:</u></p> <p>-tap water: 94-119% spike recovery (50 ppb) and 0.3-6.4% RSD</p> <p>-river water: 97% spike recovery (25 ppb) and 1.4% RSD</p> <p><u>Demonstration of Capability:</u></p> <p>-linearity dynamic range</p> <p>-QCS to verify calibration, 95-105% accuracy</p> <p>-MDL stated at 99% confidence level</p> <p><u>QC Requirements:</u></p> <p>-LRB every 20 samples (LRB &lt; MDL)</p> <p>-LFB analyzed between every sample set 85-115% accuracy</p> <p>-LFM (spiked at same level as LFB) analyzed between every sample set, 70-130%</p>	<p>(U.S. EPA, 1994b)</p>

	<p>-add 0.2 mL H<sub>2</sub>O<sub>2</sub> and make up 100mL with DIW.</p> <p><u>Direct analysis:</u>          -sample must have turbidity &lt;1 NTU (unfiltered, acid preserved)</p> <p><u>Dissolved:</u>          -filter acid preserved sample (0.45 μm)          -add HNO<sub>3</sub> to achieve 1% acid.</p> <p><u>Total Recoverable:</u>          -100mL acid preserved sample          -add 2 mL HNO<sub>3</sub> (50%v/v) and 1 mL HCl (50%v/v)          -heat at 85°C., evaporate to 20 mL          -gently reflux for 30 min, cool and make up to 50 mL with DIW          -let stand overnight and filter (0.45μm) if needed.          - add internal standard solution</p> <p><u>Total Recoverable (High Turbidity):</u>          -for samples with solid content &gt;1%          -evaporate to 10 mL          -add 4mL HNO<sub>3</sub> (50%v/v) and 10 ml HCl (25%v/v)          -reflux at 95°C for 30 minutes, evaporate to 4 mL, cool and dilute to 100 mL with DI          -prior to analysis, take 20 mL and dilute to 100 mL</p>	<p>5 ppb (scan mode)</p> <p>1.3 ppb (SIM mode)</p>	<p>7.9 ppb Scan mode and 0.5 ppb SIM mode for direct analysis and 2.1 ppb for total recovery</p>	<p>-IPC every 10 samples, 90-110% accuracy          -CCB every 10 samples (CCB &lt; IDL or within ±3δ of control limit)          -matrix spike recovery</p> <p><u>Accuracy and Precision:</u>          -reagent water bias (Se<sub>cal</sub>) =1.022X+0.14, reproducibility (S<sub>R</sub>)=0.056Se<sub>cal</sub>+2.10          -groundwater bias (Se<sub>cal</sub>)=1.045X-0.83, S<sub>R</sub>=0.091Se<sub>cal</sub>+2.03          -reagent water bias (Se<sub>cal</sub>)=1.036X+0.06, S<sub>R</sub>=0.051Se<sub>cal</sub>+3.24          -samples: 99-129.5% spike recovery (50 ppb) and 1.8- 10.9% RSD or as per equation (32-200 ppb)</p> <p><u>Demonstration of Capability:</u>          -linear dynamic range          -QCS to verify calibration, 90-110% accuracy          -MDL stated at 99% confidence level</p> <p><u>QC Requirements:</u>          -LRB every 20 samples (LRB&lt;MDL)          -LFB analyzed between every sample set, 85-115% accuracy          -IPC every 10 samples, 90-110% accuracy          -LFM (spiked at same level as LFB) analyzed between every sample set, 70-130% accuracy          -throughout analysis, internal standard response within 60-125% of the original response</p>	<p>(U.S. EPA, 1994a)</p>
<p>ICP-MS</p> <p>EPA 200.8 (multi-element)</p>					

ICP-MS	ASTM D5673 (multi- element)	<p><u>Dissolved:</u> -filter acid preserved sample (0.45 µm) -add HNO<sub>3</sub> to achieve 1% v/v HNO<sub>3</sub> -add internal standard</p> <p><u>Total Recoverable:</u> -100 mL acid preserved sample (unfiltered) -add 2 mL HNO<sub>3</sub> (50% v/v), 1 mL HCl (50%v/v) -heat, evaporate to 25 mL, cool, filter (0.45µm), dilute to 100 mL with DIW</p>	5 ppb	No Data	<p><u>Accuracy and Precision:</u> -see EPA 200.8</p> <p><u>Demonstration of Capability:</u> -IDL and MDL: spiked reagent water (n=7) at 2xDL<sub>estimated</sub> and 5xDL<sub>estimated</sub> -inter-laboratory comparison</p> <p><u>Quality Control:</u> -Cal curve: ≥3 points plus calibration blank -PC analyzed between every sample set and at the end of analysis, 90-110% accuracy -CCB analyzed between every sample set and at the end of analysis, (accepted CCB &lt; 2.2x MDL) -QCS analyzed between every sample set, 90-110% accuracy -internal standard 65-125% of the original response</p>	(ASTM International, 2016)
ICP-MS	EPA 6020B (multi- element)	<p><u>Dissolved:</u> -filter acid preserved sample (0.45 µm) -adjust acid content to match standards</p> <p><u>Total Recoverable (EPA 3005):</u> -100 mL acidified sample (unfiltered) -add 2 mL HNO<sub>3</sub> and 5 mL HCl -heat at 90-95°C, evaporate to 20 mL -cool, filter (0.45 µm) and dilute to 100 mL with DIW</p> <p><u>Total Recoverable (EPA 3010)</u> -100 mL acidified sample (unfiltered) -add 3 mL HNO<sub>3</sub> -heat, evaporate to 5 mL, cool</p>	No Data	No Data	<p><u>Demonstration of Capability:</u> -IDL: n= 10 (reagent blank) -LLOQ : n=7, 65-135 % recovery, &lt;20% RSD</p> <p><u>QC Requirements:</u> -calibration curve ≥3 points plus calibration blank -calibration blank less than ½ of LLOQ -ICV, 90-110% accuracy -low level verification 80-120% accuracy -mid level verification 90-110% Accuracy -CCV every 10 samples and at the end of analysis, 90-110% accuracy -matrix blank (&lt;LLOW) analyzed between every sample set -LCS or reference material every 20 samples, 80-120% recovery</p>	(U.S. EPA, 2014a) (U.S. EPA, 1992a) (U.S. EPA, 1992b)

ICP-MS	AWWA 3125 (multi-element)	<p>-add 3 mL HNO<sub>3</sub>, heat to gently reflux, add additional HNO<sub>3</sub> if necessary, evaporate to 3 mL</p> <p>-cool, add HCl (50%v/v) to make 10% acid in final solution</p> <p>-reflux for 15 min, cool, filter (0.45 µm) and dilute to 100 mL with DIW</p> <p><u>Total Recoverable:</u></p> <p>-10 mL acid preserved sample</p> <p>-add 0.5 mL HNO<sub>3</sub>, heat at 105°C for 2hrs</p> <p>- add more HNO<sub>3</sub>, heat until solution is clear</p> <p>-cool, dilute to 10 mL with DIW</p>	0.064 ppb	No Data	<p>-matrix spike, 75-125% recovery and matrix spike duplicate within 20% RPD</p> <p>-internal standard not less than 30% of original signal</p> <p>-5-fold dilution of test solution within 20% of original value</p> <p>-replicate sample analyzed every sample set</p>	
					<p><u>Accuracy and Precision:</u></p> <p>-total recoverable Se, 83.42% spike recovery (20 ppb), 4.73% RSD</p> <p>-dissolved Se, 105.36 % spike recovery (10 ppb), 10.75 %RSD</p> <p><u>Demonstration of Capability</u></p> <p>-IDL, MDL and linear dynamic range</p> <p><u>Quality Control:</u></p> <p>-calibration curve ≥5 points, plus calibration blank</p> <p>-calibration blank less than MDL</p> <p>-CVS at a midpoint of calibration curve, 90-110% accuracy</p> <p>-LFB or LCS at a midpoint of calibration curve, 70-130% recovery</p> <p>-replicate samples, &lt;20% RPD</p> <p>-check with NIST SRM 1643 or equivalent material</p> <p>-matrix spike analyzed between every sample set, 75-125% recovery</p> <p>-internal standard response 70-125% of original signal</p>	22 <sup>nd</sup> Ed.(Rice et al., 2012)

ICP-MS	EPA 1638 (multi-element)	<u>Dissolved:</u> -filter ≥20 mL acid preserved sample (0.45 μm) -add HNO <sub>3</sub> to 1%v/v -add internal standard(s)  <u>Total Recoverable (A):</u> 100mL acid preserved sample (unfiltered) -add 2 mL HNO <sub>3</sub> (50%v/v) and 1 mL HCl (50%v/v) -heat, evaporate to 20 mL, reflux -cool, dilute to 50 mL, add internal standard  <u>Total Recoverable (B):</u> -same as A, except heat for 2 hrs	No Data	1 ppb	<u>Demonstration Capability:</u> -MDL, linear calibration ranges -spiked reagent water: 63-145% Recovery, 41% RSD -quality control standards (standard solution from a different source) (n=3) 90-110% accuracy  <u>Quality Control:</u> -CCV at midpoint of calibration, 69-127% accuracy -matrix spike and matrix spike duplicate: 59-149 % recovery, <20% RPD -LRB 59-149% recovery -blanks	(U.S. EPA, 1996b)
ICP-MS	AOAC 993.14 (multi-element)	<u>Dissolved:</u> -filter acid preserved sample (0.45 μm) add HNO <sub>3</sub> to achieve 1%v/v  <u>Total Recoverable:</u> -100 mL acid preserved sample (unfiltered) -add 1 mL HNO <sub>3</sub> and 0.5 mL HCl -heat, evaporate to 20 mL, reflux -cool and dilute to 50mL, pipette 20 mL and dilute to 50 mL	No data	7.9 ppb	<u>Accuracy and Precision:</u> -reagent water, samples: 98.107.1% spike recovery (30-200 ppb) 4.2-9.8% RSD -standard solution: 103.5% recovery (100 ppb), 8.52% RSD  <u>Demonstration of Capability:</u> -MDL -LFB  <u>Quality Control:</u> -QCS 100 ppb=79-128 % recovery -LRB, CCB and rinse blank -LFB -QCS -internal standard 60-125% of original response -CCV/10 analyses	(AOAC International, 1993)

ICP-MS	ISO 17294-2 (multi-element)	<p><u>Total Recoverable (Aqua Regia Digestion):</u></p> <ul style="list-style-type: none"> <li>-25 mL sample (unfiltered)</li> <li>-add 6 mL HCl and 2 mL HNO<sub>3</sub>,</li> <li>-heat (opened or closed system), cool, and make up volume</li> </ul> <p><u>Total Recoverable (Nitric Acid Digestion)</u></p> <ul style="list-style-type: none"> <li>-25 mL sample (unfiltered)</li> <li>-add 6.25 mL HNO<sub>3</sub></li> <li>-heat (opened or closed system), cool and make up volume</li> </ul>	No Data	1 ppb	<p><u>Quality Control:</u></p> <ul style="list-style-type: none"> <li>-calibration blank <math>\leq 3 \times \text{IDL}</math></li> <li>-QCS 90-110% recovery</li> <li>-spike recovery, 75-125%</li> <li>-difference between results for the original sample and the fivefold-diluted sample <math>\leq 20\%</math>.</li> <li>-internal standard solution 70-130% of original count</li> <li>-interference check solution</li> <li>-correction <math>^{82}\text{Se} = ^{82}\text{Se} - 1.009(^{83}\text{Kr})</math> and <math>\leq 20\%</math> of uncorrected result</li> </ul>	<p>(International Organization for Standardization, 2016)</p> <p>(International Organization for Standardization, 2002b)</p> <p>(International Organization for Standardization, 2002a)</p>
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\* unless otherwise noted, a "sample set" is considered to be 1 10<sup>th</sup> of an entire batch of samples

**List of Acronyms Used in Table 4:**

STDEV: standard deviation, RDS: relative standard deviation, IPC: instrument performance check, CCB: continuing calibration blank, CCV: continuing calibration verification, LCS: laboratory control sample, LFM: laboratory fortified matrix, QCS: quality control sample, LRB: laboratory reagent blank, LFB: laboratory fortified blank, LLOQ: lower limit of quantification, MDL: method detection limit, IDL: instrumental detection limit

### Limitations of Total Selenium Analysis

Over the last few decades, methods for Se analysis have improved significantly in terms of their ability to quantify trace concentrations in natural and industrial waters. With regulations becoming increasingly strict, there is a need for analytical methods capable of accurately analyzing sub- $\mu\text{g/L}$  concentrations of Se in the presence of interfering matrix components. While some standard methods can handle this, others demonstrate detection limits near or above the allowable concentrations of Se in many types of waters, making it extremely difficult to properly monitor these waters for potential toxicity. It is important to keep detection limit-based restrictions in mind when selecting analytical methods for testing environmental waters, and note that in the near future it may be necessary to move towards more sensitive and robust techniques for Se analysis.

Thus far, the analysis methods discussed have all aimed to quantify the total concentration of Se in a given sample (sometimes distinguishing between dissolved and suspended), but have not examined the discrete species of Se present in said samples. Se speciation can have a significant effect on the overall toxicity of the element in an ecosystem. In freshwater systems, algal uptake (and therefore incorporation into the food chain) of Se(VI) occurs to a greater extent than uptake of Se(IV), though the opposite is true in saline waters (Baines and Fisher, 2011; Maher *et al.*, 2010). Additionally, algal uptake of the organic Se species SeMet is significantly greater than that of either Se oxyanion (Riedel *et al.*, 1991; Sandholm *et al.*, 1973), meaning its presence in a water body could significantly alter the bioavailability of Se in that system. Therefore, to begin to have a thorough understanding of the potential for Se toxicity in an aquatic environment, it is essential to know the speciation of Se within that water body and to be able to account for species present even at small fractions of the total Se concentration.

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