

# Selenium

Dean A. Martens  
United States Department of Agriculture (USDA),  
Tucson, Arizona, U.S.A.

## INTRODUCTION

Selenium (Se) is an essential nutritional element, but excessive Se can be toxic to animals and humans. Selenium has an atomic number of 34, an atomic weight of 78.94 and occupies a position in Group VIA of the periodic table between the metal tellurium and the nonmetal sulfur. Selenium's chemical and physical properties are intermediate between those of metals and nonmetals (Table 1). Selenium has a valence of  $-2$  in combination with hydrogen or metals, and in oxygenated compounds it can exist as the  $+4$  or the  $+6$  oxidation states giving rise to an array of Se compounds.<sup>[1]</sup> Six stable Se isotopes occur with varying degrees of abundance:  $^{74}\text{Se}$  (0.87%),  $^{76}\text{Se}$  (9.02%),  $^{77}\text{Se}$  (7.58%),  $^{78}\text{Se}$  (23.52%),  $^{80}\text{Se}$  (49.82%), and  $^{82}\text{Se}$  (9.19%) and a short-lived isotope ( $^{75}\text{Se}$ ) used in neutron activation, radiology, and tracer applications.<sup>[2]</sup> The average Se concentration in the earth's crust is about  $0.05 \text{ mg kg}^{-1}$ – $0.09 \text{ mg kg}^{-1}$ .<sup>[3]</sup> Selenium concentrations range from  $0.004 \mu\text{g g}^{-1}$ – $1.5 \mu\text{g g}^{-1}$  in igneous rocks to  $0.6 \mu\text{g g}^{-1}$ – $103 \mu\text{g g}^{-1}$  in shales of the cretaceous period.

## FORMS OF SELENIUM

Important properties of elements, e.g., their bioavailability and toxicity, depend on their chemical form or speciation. Chemical speciation involves the quantification of chemical forms, or species that comprise the total element concentration. Selenium can exist in the  $(+6)$ ,  $(+4)$ ,  $(0)$ , and  $(-2)$  oxidation states, the major feature of Se chemistry that affects the Se solubility and movement in nature. The distribution of the valence states depends on microbial activity, solution pH, and redox conditions. Selenium in the  $(-2)$  oxidation state exists as hydrogen selenide ( $\text{HSe}^-$ ) and as a number of metallic selenides. Heavy metal selenides are the most insoluble forms of Se.  $\text{H}_2\text{Se}$  is a toxic gas at room temperature and is thermodynamically unstable in aqueous solutions. Elemental  $\text{Se}(0)$  exists as several allotropic forms and is very stable and highly water insoluble. Thermodynamic calculations show that  $\text{Se}(-2)$  should be found in reducing environments,  $\text{Se}(+4)$  species in moderately oxidized environments, and the  $\text{Se}(+6)$  species in oxidizing

environments.<sup>[4]</sup> In waters, dissolved inorganic Se is normally present as  $(+6)$  selenate ( $\text{SeO}_4^{2-}$ ) and as  $(+4)$  selenite ( $\text{SeO}_3^{2-}$ ).<sup>[4]</sup>

## Inorganic Se

The soluble inorganic Se forms, selenite and selenate, account for the majority of the total Se concentration of waters, although particulate  $\text{Se}(0)$  smaller than  $0.45 \mu\text{m}$  may also be present.<sup>[5]</sup> The proportion of selenate/selenite present in waters is generally predicted by the pH–redox status of the system. Selenate is stable under alkaline and oxidizing conditions and selenite is stable under mildly oxidizing conditions.<sup>[6]</sup> Although, measurement of pH–redox status is a good predictor of Se species,<sup>[7]</sup> actual speciation must be analyzed as exceptions to the thermodynamic predictable Se species have been reported<sup>[8]</sup> due to the influences of biological activity.

The ratio of selenate to selenite present in natural waters is also affected by the different adsorption kinetics of selenate vs. selenite. Selenite has a strong affinity for a variety of common minerals at pH values  $< 7$ , where as selenate does not;<sup>[9]</sup> selenite also has a strong affinity for particulate organic matter.<sup>[10]</sup> Constituents adsorbing selenite include Al and Fe oxides, clay minerals, and calcite. Also microbial populations selectively assimilate selenite over selenate.<sup>[11]</sup> Due to the many mechanisms for selenite removal from waters, selenate is the major soluble Se species in natural waters.<sup>[11]</sup>

Another important factor controlling the ratio of selenate to selenite in natural waters is the microbial activity. Microbial activity has been reported to quickly reduce selenite<sup>[12]</sup> and selenate<sup>[12]</sup> as well as tellurate, tellurite, vanadate, molybdate, arsenate, and chlorate<sup>[12]</sup> suggesting that microbial reductions are important for changing the solubility and availability of elements, especially Se.

## Organic Selenium

Selenium is required as an essential micronutrient for a host of mammals, birds, fishes, algae, and bacteria.<sup>[13]</sup> The Se analog of cysteine, selenocysteine ( $\text{SeCys}$ ), plays a critical role in the enzyme glutathione peroxidase (EC



Table 1 Chemical properties of selenium<sup>[2]</sup>

Property	
Atomic number	34
Atomic mass	78.96
Density (g cm <sup>-3</sup> )	4.79
Melting point (°C)	217
Boiling point (°C)	685.4
Atomic radius (um)	0.117
Hardness, relative units	2
Electronegativity, relative units (Li = 1)	2.4
Latent heat of fusion, J g <sup>-1</sup> (cal g <sup>-1</sup> )	6.91 (16.5)
Heat of vaporization (J g <sup>-1</sup> )	272.98 (65.2)
Thermal conductivity, W (m °C)	0.293–0.766

1.11.1.9)<sup>[14]</sup> and regulates ribosome-mediated protein synthesis.<sup>[15]</sup> Selenium containing organic compounds noted includes selenomethionine, selenocystathionone, dimethylselenopropionic acid, methylselenomethionine, trimethylselenonium ion, and the volatile organics dimethyl selenide (DMSe) and dimethyldiselenide (DMDSe).<sup>[16,17]</sup> Selenium toxicity through enhanced incorporation of SeCys into protein disrupts the three-dimensional structure and impairs function due to pH differences between sulfhydryl and selenol bridges.<sup>[18]</sup> In a tragic event that emphasized the need to monitor Se levels in waters generated by agriculture, the inadvertent concentration of Se from agricultural drainage conveyed to evaporation ponds in San Joaquin Valley, California resulted in the formation of organic Se compounds from the assimilation of inorganic Se from the drainage waters<sup>[19]</sup> that resulted in death or impaired reproduction in aquatic wildlife<sup>[19]</sup> Selenomethionine has been reported to be the most toxic organic Se compounds ingested by waterfowl,<sup>[20]</sup> although no other organic Se compound has been tested for waterfowl toxicity.

### Volatile Species

A major mechanism for Se cycling in the environment is the biological volatilization of assimilated inorganic Se. Challenger and North<sup>[21]</sup> first confirmed microbial volatilization of DMSe and since, other Se gases as hydrogen selenide (H<sub>2</sub>Se), methaneselenol (CH<sub>3</sub>SeH), and dimethyl selenenyl sulfide (CH<sub>3</sub>SeSCH<sub>3</sub>) have been identified. The two major Se gases of environmental importance are DMSe and DMDSe<sup>[22]</sup> and are important in fossil fuel emissions, during plant growth<sup>[23]</sup> and from soil microorganism exposed to inorganic Se as selenate or selenite.<sup>[24]</sup> Atmospheric Se gases are subject to several important processes such as reaction with hydroxyl radicals and ozone,<sup>[25]</sup> converted into particles<sup>[26]</sup> and

then removed from the atmosphere by dry or wet deposition. The biological emissions of volatile Se forms are as great as emissions from anthropogenic sources<sup>[22]</sup> and are an important mechanism for Se cycling.

### Elemental Selenium

Elemental Se is allotropic, not measurably soluble in water, and can exist as gray hexagonal, red monoclinic, and vitreous amorphous forms. In reducing environments, Se speciation is predicted by thermodynamics to be H<sub>2</sub>Se, but this species is extremely unstable and is oxidized to elemental red Se. Microbial dissimilatory reduction of selenate or selenite to insoluble Se(0) forms can result in higher concentrations than predicted by the speciation and chemical reactivity of the soluble forms. Although anaerobic conditions have been reported to be necessary for the Se reduction to occur by facultative anaerobes,<sup>[27]</sup> recent research has found certain bacterium can reduce selenate under microaerophilic conditions to Se(0).<sup>[11]</sup>

In environmental systems, there are three major transformation mechanisms for Se: oxidation/reduction, mineralization/immobilization, and volatilization with the kinetics of each a function of the Se species, microbial activity, and pH–redox conditions. With the toxicity of Se at only approximately 50 times the dose required as an essential element, knowledge of the transformation mechanisms involved with cycling and processes of Se is vital for prevention of additional problem areas associated with water cycling.

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