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Speciation of Soluble Selenium in Agricultural Drainage Waters and Aqueous Soil-Sediment Extracts Using Hydride Generation Atomic Absorption Spectrometry

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There are few methods to effectively measure organic selenium [Se(–II)] in natural water and soil-sediment extracts. A method has been developed to determine organic Se(–II) in soil-sediment extracts and agricultural drainage water by using persulfate to oxidize organic Se(–II) and using manganese oxide as an indicator for oxidation completion. This method was used to determine Se speciation in eleven soil-sediments and four agricultural drainage water samples collected from the western United States. Results showed that organic Se(–II) can be quantitatively oxidized to selenite without changing the selenate concentration in the soil-sediment extract and agricultural drainage water and then quantified by hydride generation atomic absorption spectrometry. Recoveries of spiked organic Se(–II) and selenite were 96–105% in the soil-sediment extracts and 96–103% in the agricultural drainage water. Concentrations of soluble Se in the soil-sediment extracts were 0.0534–2.45 $\mu\text{g/g}$, of which organic Se(–II) accounted for 4.5–59.1%. Selenate is the dominant form of Se in agricultural drainage water, accounting for about 90% of the total Se. In contrast, organic Se(–II) was an important form of Se in the wetlands. These results showed that wetland sediments are more active in reducing selenate compared to evaporation pond sediments.

Introduction

The fate of selenium (Se) in natural environments is affected by a variety of physical, chemical, and biological factors which are associated with changes in its oxidation state (1, 2). Selenium can exist in four different oxidation states (–II, 0, IV, and VI) and as a variety of organic compounds. The different chemical forms of Se can control Se solubility and availability to organisms. Selenate [Se(VI)] is the most oxidized form of Se, is highly soluble in water, and is generally considered to be the most toxic form (3). Selenite [Se(IV)] occurs in oxic to suboxic environments and is less available to organisms because of its affinity to sorption sites of sediment and soil constituents (4–8). Under anoxic condi-

tions, elemental Se and selenide(–II) are the thermodynamically stable forms (9). Elemental Se is relatively insoluble, and selenide(–II) precipitates as metal selenides(–II) of very low solubility. Organic Se(–II) compounds such as selenomethionine and selenocystine can accumulate in soil and sediments or mineralize to inorganic Se (10). Therefore, Se(VI), Se(IV), and organic Se(–II) are the most important soluble forms of Se in natural environments (1, 11–16).

Hydride generation atomic absorption spectrometry (HGAAS) is widely used to determine the speciation of Se in natural water, and soil-sediment extracts because of its low detection limits. Speciation of Se is determined by subdividing sample solutions into selective treatments. Selenite is determined by directly analyzing aliquots of samples without any treatments (17, 18) or by analyzing samples acidified to pH 2 with concentrated HCl or samples in 4–7 N HCl solutions (1, 13, 19–23). Selenate plus Se(IV) are determined after reduction of Se(VI) to Se(IV) in 4–7 N HCl at high temperatures (80–100 °C) (1, 13, 17, 19–23) and analysis for Se to obtain Se(VI+IV) concentrations. Selenate is determined by the difference between a determination of Se(VI+IV) and a determination of Se(IV) in another subsample. Total Se is determined by oxidizing all Se species [organic Se(–II) and Se(IV)] to Se(VI) with H_2O_2 or persulfate [$\text{K}_2\text{S}_2\text{O}_8$ or $(\text{NH}_4)_2\text{S}_2\text{O}_8$] (1, 13, 17–23), then reducing Se(VI) to Se(IV) with 4–7 N HCl at a high temperature (80–100 °C) and analyzing for total Se in the samples. Determination of organic Se(–II) is calculated as the difference between the Se(VI+IV) and total Se analyses. To separate organic Se(–II) from inorganic Se, a technique was developed by passing an acidified sample (pH 1.6–2.2) through an XAD-8 resin column to remove hydrophobic and neutral organic-Se(–II) compounds before Se species analysis (11, 13, 23, 24). These methods have provided valuable information about Se speciation in natural water and soil-sediment extracts.

Some drawbacks for the speciation of Se using HGAAS have been found by some researchers. Weres et al. (18) studied Se speciation in groundwater and surface water and found that Se(VI) was recovered poorly from many samples after a reduction with 6 N HCl at 100 °C. They reported that the addition of ammonium persulfate increased the recovery of Se(VI). However, part of the organic Se(–II) was included in the value reported for Se(VI) due to the oxidation of organic Se(–II) by persulfate. Martens and Suarez (10) found that the reduction of Se(VI) to Se(IV) in soil extracts with 6 N HCl oxidized organic Se(–II) present in the sample resulting in an overestimation of Se(VI) concentration. XAD-resin has been used to separate hydrophobic and neutral organic Se(–II) compounds. However, hydrophilic organic Se(–II) compounds in solution, such as selenomethionine which was found in soil extracts (25, 26), will be detected as part of Se(VI). Moreover, Gustafsson and Johnsson (26) found that a considerable fraction of Se(IV) was removed due to a complexation of Se(IV) with humic substances when an acidified sample was passed through an XAD-8 column, thus resulting in overestimation of organic Se(–II) or Se(VI) concentration in the samples. All of these studies have showed that the present methods for determination of Se speciation by using HGAAS may be possible only in solutions with little or no organic Se(–II) and humic substances, but this situation is rarely found in natural environments. Therefore, to overcome these drawbacks, it is important to develop a new accurate method to determine Se speciation in water and soil-sediment extracts.

In this study, we developed a new method to determine organic Se(–II) concentration in soil-sediment extracts and

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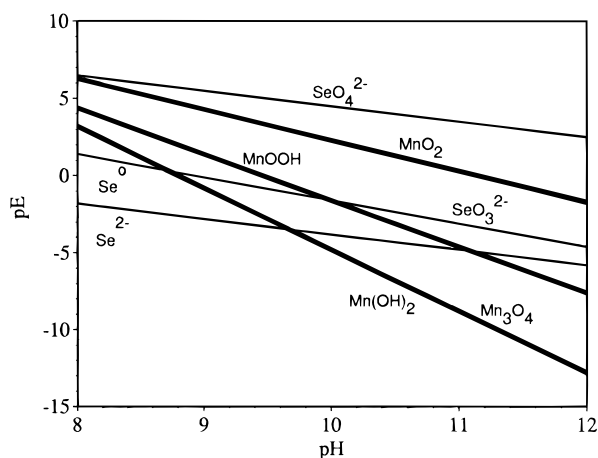
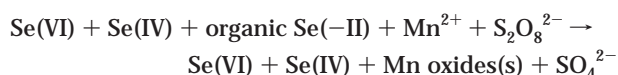


FIGURE 1. Redox potential of Mn and Se. Data from Blaylock and James (30) and Elrashidi et al. (9).

agricultural drainage waters by using persulfate ($\text{S}_2\text{O}_8^{2-}$) to oxidize organic Se(–II) and using manganese (Mn) oxide as an indicator for oxidation completion.

Theory

Redox reaction systems of Se and Mn in solution are presented in Figure 1. Selenium and manganese species are highly dependent on solution pE and pH. In alkaline solution (e.g., pH 10), redox potentials follow a trend: $\text{SeO}_4^{2-}/\text{SeO}_3^{2-} > \text{MnO}_2/\text{MnOOH} > \text{SeO}_3^{2-}/\text{Se}^{2-}$. Therefore, when an oxidant such as $\text{S}_2\text{O}_8^{2-}$ is added in solution, organic Se(–II), such as selenomethionine, is first released by cleaving the Se–carbon bond, and then oxidized to Se(IV). During this oxidation, the initially formed manganese hydroxide [$\text{Mn}(\text{OH})_2$] in the alkaline solution rapidly reacts with $\text{S}_2\text{O}_8^{2-}$ to produce Mn_3O_4 (hausmannite), MnOOH (manganite), and then MnO_2 (pyrolusite). Because the redox potential of $\text{MnO}_2/\text{MnOOH}$ is higher than $\text{SeO}_3^{2-}/\text{Se}^{2-}$, but lower than $\text{SeO}_4^{2-}/\text{SeO}_3^{2-}$, a mixture of precipitated dark brown MnO_2 and MnOOH would indicate the complete oxidation of organic Se(–II) to Se(IV) and also would consume surplus $\text{S}_2\text{O}_8^{2-}$ to prevent oxidation of Se(IV) to Se(VI). An overall oxidation reaction is summarized below:



If we can stop the oxidation reaction after a complete oxidation of organic Se(–II) to Se(IV) by using a MnO_2 – MnOOH indicator, we can determine organic Se(–II) concentration based on the difference between Se concentration in solution and Se(IV) concentration directly measured in another subsample.

Materials and Methods

Selenium standards used in this study were purchased from Fisher Scientific for Se(IV) (selenite reference standard solution) and from Sigma for Se(VI) (Na_2SeO_4) and organic Se(–II) (selenomethionine). Manganese sulfate (MnSO_4), sodium hydroxide (NaOH), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), sodium acetate (CH_3COONa), and dextrose ($\text{CH}_2\text{OH}(\text{CH}-\text{OH})_4\text{CHO}$) were purchased from Fisher Scientific. Method development involved determining the effects of varying amounts of $\text{S}_2\text{O}_8^{2-}$, Mn^{2+} , and organic compounds and heating time on the recovery of all Se species. All treatments were performed with 6–6.5 mL of deionized water and 120 ng Se of different Se species [Se(VI), Se(IV), and organic

Se(–II)] in 40-mL Teflon centrifuge tubes. The samples were adjusted to pH 10 with 0.1 M NaOH , followed by sequentially adding Mn^{2+} and $\text{S}_2\text{O}_8^{2-}$. After the samples were well mixed, they were placed in a hot water bath (80 °C) for 20 min, and then transferred to a room temperature water bath for another 20 min. After the samples were cooled to room temperature, the volume of the samples was adjusted to 12 mL by adding 5 mL of concentrated HCl and deionized water. After manganese oxides were completely dissolved in 5 N HCl solution, Se concentration was determined directly using HGAAS in these samples. Three treatments included (1) the concentration ratio of Mn^{2+} (0.4–1.2 mM) to $\text{S}_2\text{O}_8^{2-}$ (0.4–8.4 mM) in the samples was adjusted between 1:1 to 1:7 to determine the effect of the amount of Mn^{2+} and $\text{S}_2\text{O}_8^{2-}$ on the recovery of all Se species; (2) ratio of acetate and dextrose (0.7–1.4 mM) to $\text{S}_2\text{O}_8^{2-}$ (3.5–6.3 mM) was adjusted from 1:5 to 1:9 to determine effect of the amount of acetate or dextrose and $\text{S}_2\text{O}_8^{2-}$ on the recovery of all Se species when Mn^{2+} was 0.6 mM; and (3) the concentrations of Mn^{2+} and $\text{S}_2\text{O}_8^{2-}$ in the samples were adjusted to 0.6 mM and 3.0 mM, respectively, to determine the effect of heating time (10–30 min) on the recovery of all Se species.

Eleven soil-sediment samples (0–10 cm) were collected from different wetlands and evaporation ponds in the western United States (Table 1). All soil-sediment samples were air-dried and ground to less than 100 mesh prior to extraction. Four agricultural drainage water samples were collected from the San Luis Drain near Kesterson Reservoir, CA, and Tulare constructed wetland, CA (Table 1). Water samples were filtered through a 0.45- μm membrane filter into clean polyethylene bottles and stored in a cold room at 4 °C before Se measurement.

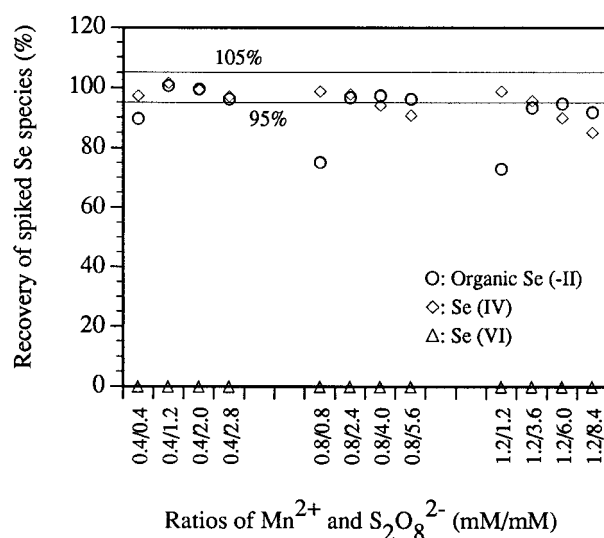
Soluble Se in soil-sediment samples was extracted using deionized water. In the extraction, 2–5 g samples of soil-sediment were placed in 40-mL Teflon centrifuge tubes, followed by 25 mL of deionized water. The centrifuge tubes were tightly capped and placed horizontally in a gyrotory shaker and shaken for 2 h. Then, the tubes were centrifuged at $17300 \times g$ (R.C.F) for 20 min. The supernatant from each tube was transferred to a polyethylene bottle. The soil-sediment sample was rinsed twice with 25 mL of deionized water and centrifuged. The final combined supernatant of the soil-sediment extract was adjusted to 75 mL with deionized water and then passed through a 0.45- μm membrane filter into another polyethylene bottle.

For determining Se(IV) concentration in a soil-sediment extract, 0.5–11 mL of the soil-sediment extracts was added to a 15-mL polypropylene centrifuge tube and then diluted to 12 mL with deionized water and 1 mL pH 7 phosphate buffer. This solution was analyzed for Se(IV) in triplicate using HGAAS. Extraction and analysis were completed on the same day. Selenite concentrations in four agricultural drainage water samples were also determined using the same method described above. All soil-sediment extracts and water samples were spiked with Se(IV) during measurement. Recovery of spiked Se(IV) ranged from 95 to 103% in all samples.

Determination of organic Se(–II) concentrations in the soil-sediment extracts were performed the day after extraction. Soil-sediment extracts (0.1–6.5 mL) were placed in a 40-mL Teflon centrifuge tube and diluted to 6–6.5 mL with deionized water and then adjusted to pH 10 with 0.1 M NaOH , 0.6 mM Mn^{2+} with 0.1 M Mn^{2+} , and 2–9 mM $\text{S}_2\text{O}_8^{2-}$ with 0.1 M $\text{S}_2\text{O}_8^{2-}$. The samples were placed in a hot water bath (80 °C) for 20 min and then transferred to a room temperature water bath for another 20 min. After the samples were cooled to room temperature, they were adjusted to 12 mL by adding 5 mL of concentrated HCl and deionized water for Se measurement. The organic Se(–II) concentration was calculated as the difference between Se in the solution and the Se(IV) concentration as determined in another subsample.

TABLE 1. Sampling Sites and Total Se Concentrations in Soil-Sediments ($\mu\text{g/g}$) and Agricultural Drainage Water ($\mu\text{g/L}$)

sampling sites	sample name	matrix	total Se
California soil-sediment			
Kesterson Reservoir, pond 4	KRP4 S1	old dried wetland	22.1
	KRP4 S2	old dried wetland	14.6
Losthill evaporation pond	LHS1	dried evaporation pond	11.2
	LHS2	evaporation pond	0.406
San Louis Drain	SLD		58.7
Benton Lake sediment, MT			
pond 1	BLP1	wetland	9.55
pond 4	BLP4	wetland	1.30
pond 5	BLP5	wetland	0.889
Stewart Lake sediment, UT			
sample 1	SLS1	wetland	8.32
sample 2	SLS2	wetland	24.7
sample 3	SLS3	wetland	35.3
San Louis Drainwater			
sample 1	SLDWS1		34.5
sample 2	SLDWS2		208
Tulare constructed wetland			
sample 1	TCWS1	inlet drainwater	20.5
sample 2	TCWS2	inlet drainwater	18.5

FIGURE 2. Recovery of spiked Se species at pH 10 with different concentration ratios of added Mn^{2+} to $\text{S}_2\text{O}_8^{2-}$. Selenite was not detected in samples spiked with only Se(VI).

Organic Se(-II) in agricultural drainage water was also determined using the same method described above.

Total Se in the soil-sediment extracts and agricultural drainage water was determined using a two-step digestion procedure. The first step is the oxidation of all Se species to Se(VI) using 30% H_2O_2 in a 90 °C hot water bath. After oxidation of all Se species to Se(VI), several drops of 1 N NaOH were added to the tubes to facilitate the decomposition of the surplus H_2O_2 . Then the solution was adjusted to 6 N HCl with concentrated HCl, followed by the addition of 0.2 mL of 0.1 M $\text{S}_2\text{O}_8^{2-}$. The solution was heated in a hot water bath at 90 °C for 20 min to reduce Se(VI) to Se(IV). The solution was analyzed for total Se in the soil-sediment extract and drainwater using HGAAS. Selenate concentration was calculated as the difference between total Se concentration and the Se(IV) plus organic Se(-II) concentration determined in another subsample. The instrument used was a Varian Spectra AA-10 atomic absorption spectrometer (Mulgrave, Victoria, Australia) with a VGA vapor generator assembly. The operational conditions were described elsewhere (27). The HGAAS was stabilized for 30 min and conditioned using

TABLE 2. Recoveries of Spiked Organic Se(-II), Se(IV) and Se(VI) in Deionized Water with an Addition of Acetate or Dextrose When Mn^{2+} Was 0.6 mM

organic soln	$\text{S}_2\text{O}_8^{2-}/\text{organic}^a$	organic Se(-II) (%)	Se(IV) (%)	Se(VI) ^b (%)
acetate	3.5/0.7	99.5 ± 1.44 ^c	100.5 ± 0.321	0
	4.9/1.4	101.4 ± 1.26	100.8 ± 1.26	0
dextrose	4.9/0.7	101.3 ± 0.734	98.6 ± 1.823	0
	6.3/1.4	98.5 ± 0.527	96.7 ± 2.90	0

^a Ratio of $\text{S}_2\text{O}_8^{2-}$ (mM) to acetate or dextrose (mM). ^b Selenite was not detected in samples spiked with only Se(VI). ^c Data showing means ± SD, $n = 3$.

blank and Se standard solution for 10 min before Se measurement. The detection limit was 0.5 μg Se(IV)/L in the water and aqueous soil-sediment extracts and 0.008 μg in the soluble Se(IV)/g soil-sediment.

Results and Discussion

Recovery of Spiked Se Species in Deionized Water. The method described here uses $\text{S}_2\text{O}_8^{2-}$, along with manganese oxides as an oxidation indicator, to oxidize organic Se(-II) to Se(IV) without changing the native Se(VI) and Se(IV) concentrations. The effect of concentration ratios of Mn^{2+} to $\text{S}_2\text{O}_8^{2-}$ on the recovery of Se species [Se(VI), Se(IV), and organic Se(-II)] with spike samples is shown in Figure 2. Recovery of organic Se(-II) was less than 90% in a 1:1 ratio and ranged from 97 to 101% in 1:3 and 1:6 ratios when the Mn^{2+} concentration was 0.4 or 0.8 mM. When the Mn^{2+} concentration was 1.2 mM, recovery of organic Se was below 95%. Recovery of spiked Se(IV) ranged from 96 to 101% in solution with 1:1 and 1:3 ratios when Mn^{2+} concentration was 0.4 or 0.8 mM, and was below 95% in solution with 1:5 and 1:7 when Mn^{2+} concentration was 0.8 or 1.2 mM. There was no detection of Se(IV) and organic Se(-II) in samples spiked with only Se(VI) at all ratios of Mn^{2+} to $\text{S}_2\text{O}_8^{2-}$, indicating that the addition of Mn^{2+} and $\text{S}_2\text{O}_8^{2-}$ in a basic solution does not affect Se(VI) concentration.

Soluble organic compounds are one of the most important components in natural waters and soil-sediment extracts. Oxidizing all soluble organic Se(-II) compounds by $\text{S}_2\text{O}_8^{2-}$ is the key for determining organic Se(-II) concentration in environmental samples. The effect of the amount of organic

TABLE 3. Selenite and Organic Se(–II) Concentrations ($\mu\text{g/g}$) and Recovery of Spiked Se Species in a Soil-Sediment Extract and Agricultural Drainage Water ($\mu\text{g/L}$)

samples	Se(IV) + organic Se(–II)	spiked organic Se(–II)	detected Se	recovery %	spiked Se(IV)	detected Se	recovery %	spiked Se(VI)	detected Se	recovery %
soil-sediment										
KRP4 S1	0.197 ± 0.005^a	0.6	0.802 ± 0.01	100.8	0.6	0.793 ± 0.012	99.3	0.6	0.204 ± 0.003	1.2
KRP4 S2	0.206 ± 0.001	0.55	0.782 ± 0.009	104.8	0.55	0.773 ± 0.005	103.2	0.55	0.214 ± 0.003	1.5
LHS1	0.101 ± 0.001	0.35	0.455 ± 0.003	101.3	0.35	0.451 ± 0.005	100	0.35	0.107 ± 0.002	1.9
SLD	1.56 ± 0.030	1.2	2.76 ± 0.024	100	1.2	2.74 ± 0.033	98	1.2	1.56 ± 0.013	–0.2
BLP1	0.235 ± 0.005	0.45	0.670 ± 0.008	96.8	0.45	0.694 ± 0.006	102.1	0.45	0.241 ± 0.007	1.4
SLS2	0.615 ± 0.005	0.6	1.192 ± 0.006	96.2	0.6	1.191 ± 0.008	96	0.6	0.619 ± 0.012	0.7
SLS3	1.06 ± 0.009	0.55	1.61 ± 0.014	98.4	0.55	1.63 ± 0.002	102.6	0.55	1.07 ± 0.008	1.3
water										
SLDWS1	3.79 ± 0.169	9	12.6 ± 0.682	97.8	9	12.74 ± 0.184	99.4	9	4.01 ± 0.127	2.4
SLDWS2	26.61 ± 0.330	16	42.05 ± 0.699	96.5	16	42.42 ± 0.111	98.8	16	26.83 ± 0.308	1.4

^a Data shows means \pm SD, $n = 3$.

TABLE 4. Concentrations of Soluble Se Species in Soil-Sediment Extracts ($\mu\text{g/g}$) and Agricultural Drainage Water ($\mu\text{g/L}$)

soil-sediment and water	organic Se(–II)	Se(IV)	Se(VI)	total Se
soil-sediment				
KRP4 S1	0.045 (6.4) ^a	0.161 (23)	0.493 (70.5)	0.699
KRP4 S2	0.0262 (4.5)	0.0928 (15.9)	0.464 (79.6)	0.583
LHS1	0.054 (9.1)	0.087 (14.6)	0.453 (76.3)	0.594
LHS2	0.015 (4.6)	0.0824 (25.1)	0.2306 (70.3)	0.328
SLD	0.43 (17.6)	1.11 (45.3)	0.91 (37.1)	2.45
Benton Lake, MT				
BLP1	0.118 (32.2)	0.117 (32)	0.131 (35.8)	0.366
BLP4	0.0267 (47.8)	0.0108 (19.4)	0.0183 (32.8)	0.0558
BLP5	0.0234 (43.8)	0.0126 (23.6)	0.0174 (32.6)	0.0534
Stewart Lake, UT				
SLS1	0.0716 (37.3)	0.0864 (45)	0.034 (17.7)	0.192
SLS2	0.261 (35.6)	0.354 (48.2)	0.119 (16.2)	0.734
SLS3	0.656 (59.1)	0.404 (36.4)	0.05 (4.5)	1.11
Water				
SLDWS1	0.51 (1.5)	3.28 (9.5)	30.71 (89)	34.5
SLDWS2	1.74 (0.8)	24.86 (11.9)	181.53 (87.2)	208.1
TCWS1	0.09 (0.4)	1.55 (7.6)	18.9 (92.2)	20.5
TCWS2	0.23 (1.2)	1.06 (5.7)	17.2 (93)	18.5

^a Data in parentheses show the percentages of Se(VI), Se(IV), and organic Se(–II) concentrations.

acetate and dextrose and $\text{S}_2\text{O}_8^{2-}$ on the recovery of all Se species is presented in Table 2. Recovery of Se(IV) and organic Se(–II) in the basic solution with 0.7–1.4 mM sodium acetate and dextrose ranged from 97 to 101%. This showed that acetate and dextrose can be oxidized with the oxidation of organic Se(–II) to Se(IV) by adequate addition of $\text{S}_2\text{O}_8^{2-}$ in the sample. There also was no detection of Se(IV) and organic Se(–II) in samples spiked with only Se(VI).

Heating a sample to a high temperature is an important procedure to accelerate the oxidation of organic Se(–II) to Se(IV) by $\text{S}_2\text{O}_8^{2-}$. The effect of heating time on the recovery of Se species in a pH 10 solution with a concentration of 0.6 mM Mn^{2+} and 2.4 mM $\text{S}_2\text{O}_8^{2-}$ at 80 °C is shown in Figure 3. Recoveries of Se(IV) and organic Se(–II) ranged from 96 to 100% when the heating time was 15–20 min. Recovery of organic Se(–II) was less than 92% with 10-min heating. Also, there was no detection of Se(IV) and organic Se(–II) in samples spiked with only Se(VI) during oxidation with $\text{S}_2\text{O}_8^{2-}$. All results above showed that organic Se(–II) such as selenomethionine can be quantitatively oxidized by adequately adding the appropriate amount of $\text{S}_2\text{O}_8^{2-}$ in a basic sample with 0.6 mM Mn^{2+} and by heating the sample at 80 °C for 20 min.

Recovery of Spiked Se Species in Soil-Sediment Extracts and Agricultural Drainage Water. The selenite and organic Se(–II) concentration ranged from 0.101 to 1.56 $\mu\text{g/g}$ in seven

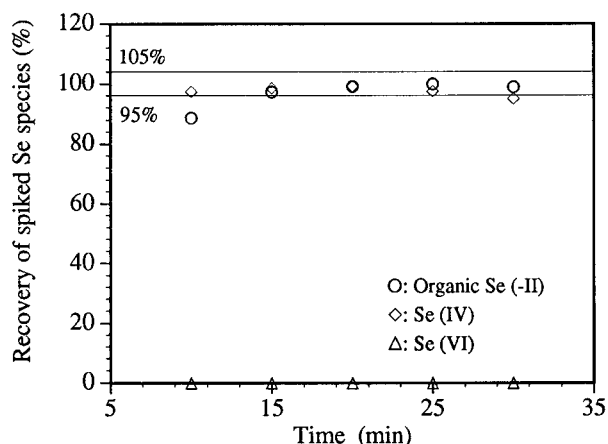


FIGURE 3. Effect of heating time at 80 °C on the recovery of spiked Se species in a basic solution (pH 10) with a concentration of 0.6 mM Mn^{2+} and 2.4 mM $\text{S}_2\text{O}_8^{2-}$. Selenite was not detected in samples spiked with only Se(VI).

soil-sediment samples and ranged from 3.79 to 26.61 $\mu\text{g/L}$ in San Luis Drain water (Table 3). Recoveries of spiked organic Se(–II) and Se(IV) in all tested samples were 96 to 105%. In samples spiked with only Se(VI), there was little detection (<2%) of Se(IV). These results show that organic Se(–II) can be quantitatively determined using $\text{S}_2\text{O}_8^{2-}$ to oxidize organic

Se(–II) and using Mn oxides as an oxidation indicator in the soil-sediment extract and agricultural drainage water.

Selenium Species in Soil-Sediment Extracts and Agricultural Drainage Water. Concentrations of Se species in the soil-sediment water extracts and agricultural drainage water are presented in Table 4. The speciation of Se in the soil-sediment extract differed with the soil-sediment samples. In the Kesterson Reservoir soil and Losthill evaporation pond sediments, Se(VI) was the dominant form of Se, accounting for 70–80% of the total soluble Se, and Se(IV) accounted for only 15–25%, while organic Se(–II) was less than 10%. In contrast, Se(IV) and organic Se(–II) were the important forms of Se in Stewart Lake sediment, accounting for 36–48% and 36–59% of the total soluble Se, respectively. In Benton Lake sediment, Se(VI) and organic Se(–II) were important forms of soluble Se, accounting for 33–36% and 32–48% of the total soluble Se, respectively, and Se(IV) was relatively low, accounting for 19–32%. In San Luis Drain sediment, Se(IV) concentration was higher than Se(VI) concentration, which was higher than organic Se(–II) concentration. In agricultural drainage water, Se(VI) was the dominant Se species in San Luis Drain water and the inlet water of Tulare constructed wetland, accounting for about 90% of the total Se.

Selenium contamination in wetlands and evaporation ponds in the western United States is caused by agricultural drainage water which has high Se concentrations. Selenate is the dominate form of Se in drainwaters in the San Luis Drain, Tulare constructed wetland, Benton Lake, and Stewart Lake (16, 28). The fate of Se(VI) that accumulates in the sediment appears to be related to the wetlands and evaporation ponds tested. Wetland sediments (Benton Lake, MT, and Stewart Lake, UT) are more active in reducing Se(VI), resulting in a low percentage of soluble Se(VI) concentration in the wetland sediments as compared to evaporation ponds (Losthill evaporation ponds, CA).

Although the method described can successfully determine the total organic Se(–II) concentration in agricultural drainage waters and aqueous extractions of soil-sediment, it cannot determine the identity of the individual organic Se species in the samples. A detailed study in the determination of different Se species in soil-sediment extracts by using ion exchange chromatography (29) combined with the method described in this study is being undertaken in our laboratory.

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