

# Selenium Speciation in Karakaya Dam Lake's Water (Malatya-Turkey)

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Concentrations of total inorganic selenium, Se(IV), Se(VI) and organically bonded selenium from samples of Karakaya dam lake's water were determined using ammonium pyrrolidine dithio carbamate (APDC) as a chelating agent and subsequent adsorption on amberlite type XAD-8 resins. Eluted analytes are taken up in a matrix free acidic solution suitable for graphite furnace atomic absorption spectroscopy (GFAAS).

According to our results, levels of the total inorganic selenium, Se(IV), Se(VI) and organically bonded selenium were found to be between  $0.11 \pm 0.01$  and  $0.17 \pm 0.01$   $\mu\text{g/L}$ ,  $0.07 \pm 0.01$  and  $0.12 \pm 0.01$   $\mu\text{g/L}$ ,  $0.02 \pm 0.01$  and  $0.05 \pm 0.01$   $\mu\text{g/L}$ , and  $0.05 \pm 0.01$  and  $0.08 \pm 0.01$   $\mu\text{g/L}$ , respectively.

**Key Words:** Selenium speciation; Atomic absorption spectroscopy; Enrichment; Trace element.

## Introduction

Selenium can be a cumulative toxic substance when found in high concentrations in food and water. However at low concentrations it is recognized as a trace element in animal nutrition<sup>1</sup>. Selenium speciation has been attracting much attention in recent years because selenium compounds have been reported to have anticarcinogenic activity and prevent heavy metal toxic effects. On the other hand, the biological effects of selenium are dependent upon its chemical form. The most important inorganic species of selenium in water are selenate ( $\text{SeO}_4^{2-}$ ) and selenite ( $\text{SeO}_3^{2-}$ ). Knowledge of the chemical speciation of trace elements in natural waters is essential to an understanding of the toxicity and bio-availability of these elements, and so special attention is also paid to the content of the different forms of selenium in water samples<sup>2,3</sup>.

Although there are various selenium speciation studies such as selective volatilization with organic species and inorganic species selectively reduced to the hydride<sup>4,5</sup>, ion chromatography<sup>1,6,7</sup>, inductively coupled plasma<sup>8,9</sup>, sequential extraction<sup>10</sup>, gas chromatography<sup>11</sup>, cathodic stripping voltametry<sup>12</sup>, chromatographic and spectroscopic coupled technique<sup>13</sup> and colorimetry<sup>14</sup>, most of the selenium speciation studies are

based on using amberlite type XAD-8 resin for the enrichment stage<sup>15-18</sup>. In the present study, amberlite XAD-8 resin was also used for the selenium enrichment of the Karakaya dam lake's water.

The purpose of this study was to assess the trace selenium species in Karakaya dam lake's water and report the results obtained.

## Experimental

### Apparatus

The determination of selenium species were carried out with a Hitachi model 170-70 graphite furnace atomic absorption spectrometer with Zeeman background correction. Pyrolytic graphite coated graphite tubes with a pyrolytic graphite platform were employed throughout the experiment. Nickel nitrate was used as a matrix modifier for the selenium determination. The optimum conditions for the GFAAS are given in Table 1. The pH values were measured with a Hanna Instruments, HI 8314 membrane filter pH meter.

The photodecomposition apparatus (Grantzel, Karlsruhe, 100 W) with a mercury lamp was used to destroy the organically bonded selenium species. In the enrichment work, an Electro-Mag mixer was used.

**Table 1.** Operating parameters for the graphite furnace atomic absorption spectrometer.

Parameter	Selenium
Wavelength/nm	196.0
Hollow cathode lamp current/mA	10
Slit-width/nm	3
Drying temperature/°C	150
Drying time/s	20
Ashing temperature/°C	500
Ashing time/s	20
Atomisation temperature/°C	2400
Atomisation time/s	5

### Reagents

Deionized water for the preparation of stock solution was obtained from a Fistream water purification system (Sanyo Gallenkamp, UK). All chemicals were of analytical-reagent grade, unless otherwise stated. Selenium standards were prepared from analytical reagent grade Na<sub>2</sub>SeO<sub>4</sub> (Sigma S-0882) and Na<sub>2</sub>SeO<sub>3</sub> (Sigma S-1382), using 1% HNO<sub>3</sub> and 1% HCl as the solvent, respectively.

For the chelate formation with trace selenium species, 5% analytical grade reagent APDC (Aldrich 14,269-7) solution was used. The labware was soaked in 10% HNO<sub>3</sub> for at least 24 h and then rinsed carefully with deionized water before use.

Amberlite XAD-8 resin (Sigma 11104-40-8), was dried at 110°C for 1 h. The dried resin was ground to 0.1-0.2 mm (60-80 mesh) and stirred with analytical grade reagent methyl alcohol for 30 min on a mechanical mixer. After this step, the resin was washed sequentially with 1M HNO<sub>3</sub>, water, 1 M NaOH, water and acetone. The washed resin was dried again at 105°C for 1 h and stored in a desiccator until use. The XAD-8 column consisted of 2 cm of washed resin in a 0.8 cm-i.d. glass column and, before use, the XAD-8 column was sequentially rinsed with acetone and plenty of water.

## Procedures

In this study, total inorganic selenium, selenite, selenate and organically bonded selenium species of Karakaya dam lake (Malatya-Turkey) were determined by the GFAAS after an enrichment procedure. To determine selenite and selenate levels in the water samples, ammonium pyrrolidine dithio carbamate (APDC) was used as a complexing reagent at pH 1.2 and amberlite type XAD-8 resins for the enrichment. The organically bonded selenium species in the water samples were destroyed by using the photodecomposition technique and their levels were determined by GFAAS after an enrichment procedure using the XAD-8 resins. Before using the selenium enrichment procedure with the XAD-8 resin, the optimum working parameters such as recovery (96-97%), appropriate complexing reagent (5% APDC), pH (1.2), sample volume (500 mL), eluent (MeOH), and amount of the reagents (900 mg of XAD-8) were determined using the model samples.

The values of the organically bonded selenium species obtained from different sites were compared statistically. The significance of the differences between the groups was evaluated by Student's t-test<sup>19</sup>.

### Determination of selenite levels in Karakaya dam lake's water

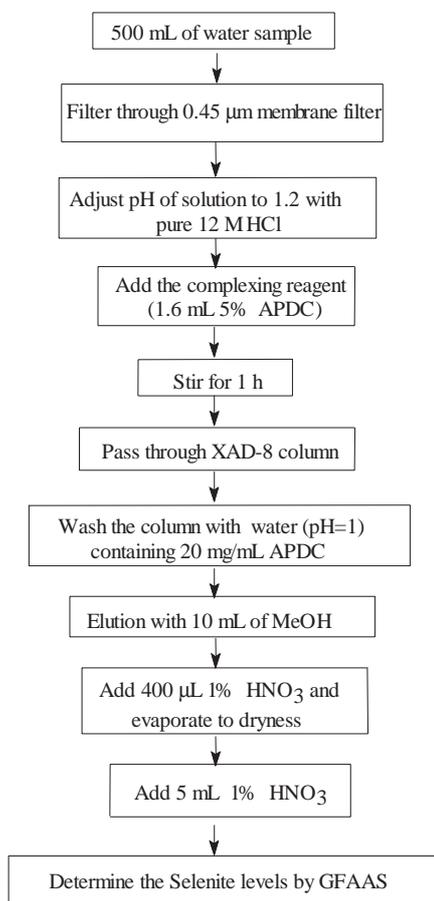
A 500 mL water sample was filtered through a 0.45  $\mu\text{m}$  membrane filter (Schleicher & Schuell BA 85/21). The pH of the sample was adjusted to 1.2 with HCl and the complexing reagent (1.6 mL of 5% APDC) was added. The sample was then passed through the amberlite type XAD-8 resin column. The flow rate of the water sample from the column was adjusted to 10 mL/min. The column was then washed with 10 mL of water (pH = 1) containing 20 mg/mL APDC. The retained selenium species in the column were eluted with 10 mL of pure methyl alcohol. 400  $\mu\text{L}$  of 1%  $\text{HNO}_3$  solution was added to the elution solution and the solution was evaporated to dryness. 5 mL of 1%  $\text{HNO}_3$  solution was added to the residue and the trace selenite levels in the water samples were determined by GFAAS using the injection method.

### Determination of selenate levels in Karakaya dam lake's water

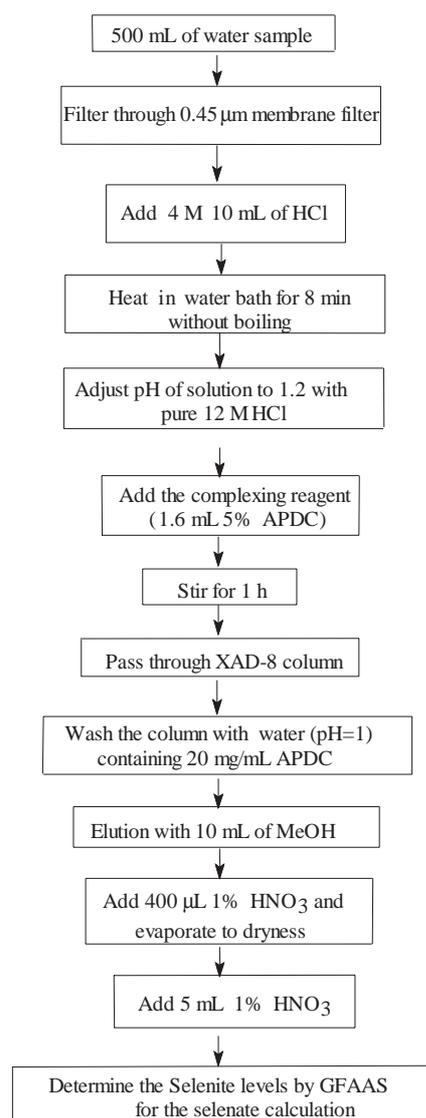
A 500 mL water sample was filtered through a 0.45  $\mu\text{m}$  membrane filter (Schleicher & Schuell BA 85/21). 10 mL of 4 M HCl solution was added to the filtrate and the solution was heated in a water bath for 8 min, without boiling, to convert the selenate to selenite form. After this stage, the procedure for the selenite determination as described above was followed. The levels of the total inorganic selenium (selenite and selenate) were determined by GFAAS with the injection method as a selenite. The selenate levels were then calculated as the difference between total inorganic selenium and selenite levels.

### Determination of organically bonded selenium species in Karakaya dam lake's water

A 500 mL water sample was filtered through a 0.45  $\mu\text{m}$  membrane filter (Schleicher & Schuell BA 85/21). The clear water sample was irradiated with a mercury lamp for 2 h in a photodecomposition apparatus. After this stage, the procedure for the selenite determination as outlined above was followed. The levels of the organically bonded selenium were then calculated as the difference between total selenium and the sum of selenite and selenate levels.



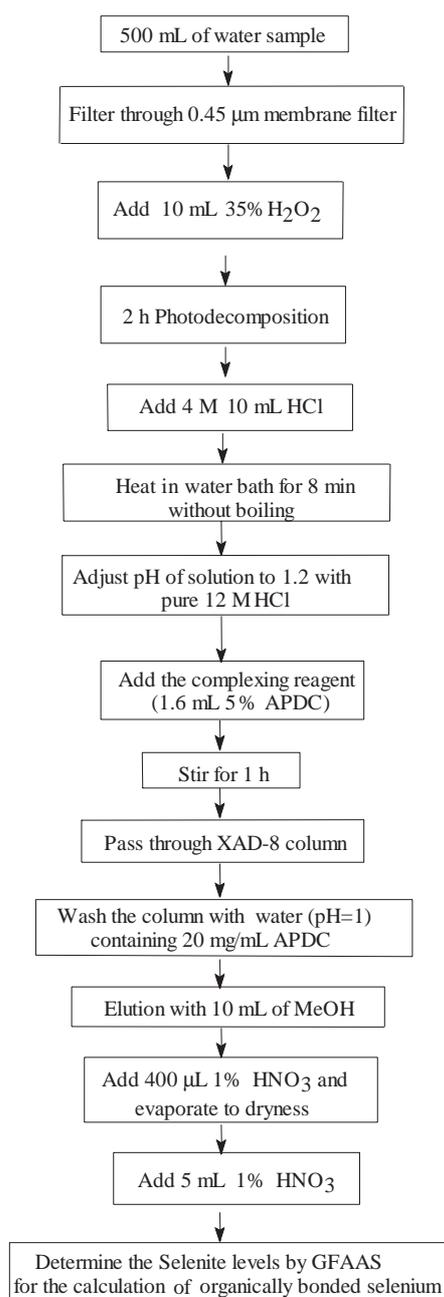
**Figure 1.** Analytical scheme of the enrichment procedure for the selenite ( $S_e^{4+}$ ) in water samples.



**Figure 2.** Analytical scheme of the enrichment procedure for the selenate ( $S_e^{6+}$ ) in water samples.

## Results and Discussion

This study was undertaken to assess the selenium species such as selenite, selenate, organically bonded selenium and total inorganic selenium in Karakaya dam lake's water. Selenium speciation of Karakaya dam lake's water was achieved after an enrichment procedure using XAD-8 amberlite resin, because direct determination of the selenium species in the samples by GFAAS is not possible due to insufficient instrumental sensitivity. The results of the speciation studies in Karakaya dam lake's water are shown in Tables 2 and 3. The values of the selenium concentrations were found to increase with increasing depth. It was also observed that the selenium species levels were affected by the changing of the seasons and, among the seasons, in the summer, selenium values were found to be high. High selenium concentrations in the summer samples may be due to the high evaporation rate of the lake's water during hot summer days.



**Figure 3.** Analytical scheme of the enrichment procedure for the organically bonded selenium in water samples.

The organically bonded selenium species in the water samples were obtained by subtracting the sum of selenite and selenate from the total selenium (selenite, selenate and organically bonded selenium) after decomposition of the organic structure by photodecomposition. Photodecomposition, a method known to be effective for the decomposition of organometallic species in natural waters, was preferred to an acid digestion step since it involved minimal additions to the sample matrix. The organically bonded selenium in the samples was within the range of  $0.05 \pm 0.01 \mu\text{g/mL}$  to  $0.08 \pm 0.01 \mu\text{g/mL}$ .

**Table 2.** Levels of selenium species of Karakaya dam lake's water. The results are mean values  $\pm$  standard deviation;  $n = 3$ 

Sample no* (depth)	Total inorganic Selenium ( $\mu\text{g/L}$ )	Se (IV) ( $\mu\text{g/L}$ )	Se (VI) ( $\mu\text{g/L}$ )	Organically bonded Selenium ( $\mu\text{g/L}$ )
1 (1m)	0.11 $\pm$ 0.01	0.08 $\pm$ 0.01	0.03 $\pm$ 0.01	0.07 $\pm$ 0.01
1 (3m)	0.11 $\pm$ 0.01	0.08 $\pm$ 0.01	0.03 $\pm$ 0.01	0.07 $\pm$ 0.01
1 (5m)	0.16 $\pm$ 0.01	0.11 $\pm$ 0.01	0.05 $\pm$ 0.01	0.08 $\pm$ 0.02
1 (6m)	0.17 $\pm$ 0.01	0.12 $\pm$ 0.02	0.05 $\pm$ 0.01	0.08 $\pm$ 0.01
2 (1m)	0.11 $\pm$ 0.01	0.08 $\pm$ 0.01	0.03 $\pm$ 0.01	0.07 $\pm$ 0.01
2 (3m)	0.11 $\pm$ 0.01	0.08 $\pm$ 0.01	0.03 $\pm$ 0.01	0.07 $\pm$ 0.01
2 (5m)	0.15 $\pm$ 0.01	0.10 $\pm$ 0.01	0.05 $\pm$ 0.01	0.07 $\pm$ 0.01
2 (6m)	0.16 $\pm$ 0.01	0.11 $\pm$ 0.01	0.05 $\pm$ 0.01	0.08 $\pm$ 0.01
3 (1m)	0.09 $\pm$ 0.01	0.07 $\pm$ 0.01	0.02 $\pm$ 0.01	0.05 $\pm$ 0.01
3 (3m)	0.10 $\pm$ 0.01	0.07 $\pm$ 0.01	0.03 $\pm$ 0.01	0.05 $\pm$ 0.01
3 (5m)	0.12 $\pm$ 0.01	0.09 $\pm$ 0.01	0.03 $\pm$ 0.01	0.05 $\pm$ 0.01
3 (6m)	0.14 $\pm$ 0.01	0.11 $\pm$ 0.01	0.03 $\pm$ 0.01	0.05 $\pm$ 0.01

\*Sample numbers 1, 2 and 3 indicate the three different sites of the lake from which the water samples were taken.

**Table 3.** The variation of selenium concentrations in Karakaya dam lake's water with the changing of the seasons. The results are mean values  $\pm$  standard deviation;  $n = 3$ 

Sample no (season*)	Total inorganic Selenium ( $\mu\text{g/L}$ )	Se (IV) ( $\mu\text{g/L}$ )	Se (VI) ( $\mu\text{g/L}$ )	Organically bonded Selenium ( $\mu\text{g/L}$ )
1 (spring-1998)	0.12 $\pm$ 0.01	0.08 $\pm$ 0.01	0.04 $\pm$ 0.01	0.05 $\pm$ 0.01
2 (summer-1998)	0.18 $\pm$ 0.01	0.14 $\pm$ 0.01	0.04 $\pm$ 0.01	0.07 $\pm$ 0.01
3 (autumn-1998)	0.17 $\pm$ 0.01	0.14 $\pm$ 0.01	0.03 $\pm$ 0.01	0.06 $\pm$ 0.01
4 (winter-1998)	0.13 $\pm$ 0.01	0.10 $\pm$ 0.01	0.03 $\pm$ 0.01	0.05 $\pm$ 0.01

\*Mean value of the three different sites of the Karakaya dam lake from which the water samples were taken.

Among the three sample sites from which the water samples were taken, low organically bonded selenium levels were obtained from site 3. Organically bonded selenium levels obtained from the sample site 3 were found to be significantly lower than those of the other sample sites ( $P < 0.001$ ). On the other hand, there was no important difference in organically bonded selenium levels between sample sites 1 and 2 ( $P > 0.05$ ). The high organically bonded selenium levels of sample sites 1 and 2 may be due to settlement and agricultural facilities nearby. On the other hand, sample site 3 was far from the settlement and agricultural area.

The levels of the total inorganic selenium, Se(IV) and Se(VI) were found to be between  $0.11 \pm 0.01$  and  $0.17 \pm 0.01 \mu\text{g/mL}$ ,  $0.07 \pm 0.12$  and  $0.17 \pm 0.01 \mu\text{g/mL}$  and  $0.02 \pm 0.01$  and  $0.05 \pm 0.01 \mu\text{g/mL}$ , respectively.

According to the obtained results, total selenium (inorganic and organically bonded) content in Karakaya dam lake's water was within the range of  $0.16 \pm 0.01$  to  $0.25 \pm 0.01 \mu\text{g/L}$  (see Table 2).

The levels of the selenium species from the different lake waters are shown in Table 4 for comparison with the our results.

**Table 4.** The level of the selenium species ( $\mu\text{g/L}$ ) in some lake water and lake sediment extracts.

Sample place	Total inorganic selenium	Se(IV)	Se(VI)	Organically bonded selenium	Ref.
(Antwerp)					
Swimming pool	0.20-0.33	<0.04	0.17-0.30	—	2
California	—	0.018	<0.005	—	4
Benton lake, canal	1.90	0.60	0.28	1.02	10
Benton lake*, MT					
Pond 1	0.3660	0.1170	0.1310	0.1180	20
Pond 2	0,0558	0.0108	0.0183	0.0267	20
Pond 3	0.0534	0.0126	0.0174	0.6560	20
Stewart lake*, UT					
S1	0.192	0.086	0.034	0.072	20
S2	0.764	0.354	0.119	0.261	20
S2	1.110	0.404	0.050	0.656	20

\*These data were obtained from lake sediment extracts.

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