

Aluminum Fractionation in the Water of Karakaya Dam Lake (Malatya, Turkey)

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A method was developed for the determination of trace amounts of Al species in water samples using the amberlite type XAD-4 resin. For this purpose, total dissolved Al, organically bonded Al and particulate Al in water samples taken from Karakaya dam lake (Malatya, Turkey) were determined by flame atomic absorption spectroscopy (FAAS) or graphite furnace atomic absorption spectroscopy (GFAAS) after an enrichment procedure. The total dissolved Al in the water samples was determined using 8-hydroxyquinoline as complexing reagent at pH 8 and amberlite type XAD-4 resins for the enrichment. The organically bonded Al species in the water samples were destroyed by the use of a photodecomposition apparatus and their levels were determined by FAAS after an enrichment procedure using amberlite type XAD-4 resin. The particulate Al in the water samples was determined by GFAAS after filtering them through a 0.45 μm membrane filter. According to our results, levels of total dissolved Al, organically bonded Al and particulate Al were between 1.98 and 3.76 mg/L, 55.3 and 67.1 $\mu\text{g/L}$, and 12.4 and 30.9 $\mu\text{g/L}$, respectively.

Key Words: Aluminum speciation and fractionation, atomic absorption spectroscopy, enrichment, trace element.

Introduction

Aluminum (Al) is the third most abundant element in the earth's crust and it is also one of the trace inorganic metals present in drinking water. An understanding of the chemistry of Al in water is crucial and useful for water science practitioners. After the discovery of a link between high Al levels in tap water used for renal dialysis equipment and the accumulation of the element in human brain tissue and possibly with dialysis dementia, research related to Al has been stimulated¹⁻³. The speciation and fractionation of Al during drinking-water treatment is essential for understanding the behavior of Al and Al species removal

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during water treatment⁴. Al in water has received increased attention, both in relation to toxicity to water organisms and in relation to drinking water and health. Increased Al concentrations are a secondary effect of acid rain, and it has been shown that a part of this Al is toxic^{5,6}. Al concentrations ranging from 0.1 to 0.2 mg/L may be toxic to fish and other aquatic organisms. The toxicity, however, depends upon the chemical form; hydrolyzed species are highly toxic, whereas organic and inorganic complexed species exhibit few toxic effects^{7,8}. There are various Al speciation and fractionation methods in the literature such as fluorometric^{9,10}, size-exclusion chromatographic^{11,12} and ion chromatographic^{13,14} methods, equilibrium dialysis¹⁵ and using chelating resin, Chelex-100¹⁶⁻¹⁸ and XAD-7¹⁹. The aim of this study was to describe Al species levels in the water of Karakaya dam lake and investigate whether XAD-4 resin rather than Chelex-100 resin is useful for the enrichment of Al.

Experimental

Apparatus

The determination of Al species was carried out with a Philips model PU 9100 X flame atomic absorption spectrometer or a Hitachi model 170-70 graphite furnace atomic absorption spectrometer with Zeeman background correction. The optimum conditions for the two instruments are shown in Tables 1 and 2, respectively. The pH values were measured with a Hanna Instruments HI 8314 membrane filter pH meter. A photodecomposition apparatus (Grantzel, Karlsruhe, 100 W) with a mercury lamp was used to destroy the organically bonded Al species. In the enrichment work, an Electro-Mag mixer was used.

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

Parameter	Al
Wavelength/nm	309.2
Hollow cathode lamp current/mA	10
Slit-width/nm	2.2
Drying temperature/°C	100
Drying time/s	30
Ashing temperature/°C	1500
Ashing time/s	20
Atomization temperature/°C	2800
Atomization time/s	8

Table 2. Operating parameters for the flame atomic absorption spectrometer.

Parameter	Al
Wavelength/nm	309.3
Hollow cathode lamp current/mA	10
Slit-width/nm	0.5
Acetylene flow rate/L min ⁻¹	55
Dinitrogen oxide flow rate/L min ⁻¹	35

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.

NH₃-NH₄ buffer solution was used to achieve pH 8.0. Al standards were prepared from the mixed sulfate salt, KAl(SO₄)₂.12H₂O. Amberlite XAD-4 resin (Sigma 37380-42-0) was dried at 110 °C for 1 h. The dried resin was ground to 0.180-0.250 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 1 M HNO₃, 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-4 column consisted of 2 cm of washed resin in a 0.8 cm i.d. glass column and, before use, the XAD-4 column was sequentially rinsed with acetone and plenty of water.

Chelex-100 (50-100 mesh), a styrene-divinylbenzene copolymer with iminodiacetate functional groups, was supplied in 75% sodium form (Sigma C-7901). The resin was first converted to hydrogen form with 2 M HNO₃ according to the supplier's instructions, and then conditioned with Ca(NO₃)₂ (1 x 10⁻³ M) and MgSO₄ (2.5 x 10⁻³ M). The resin was then recovered by decantation and stored in deionized water until use. Both resins were loaded into the columns by gravitational force.

Al-humic acid model solutions were prepared to provide a similar natural environment while working with XAD-4 resin to choose the optimum conditions.

Al-humic acid model solutions were prepared as follows: 1 g of humic acid (Fluka 53680) was added to 500 mL of deionized water including 5 µg of Al. The mixture was then stirred at room temperature for 8 h. The other concentrations (20, 30, 40, 50, 100 and 250 µg Al/L) of the Al-humic acid model solutions were prepared similarly. The formation of humic acid-Al complex was followed by FAAS. For this purpose, a necessary amount of each Al-humic acid model solution was taken every hour and the free aluminum concentration was determined by FAAS. This continued for up to 10 h; after 8 h, it was observed that the free aluminum concentration was no longer changing considerably. From these measurements, it was determined that about 85% of aluminum formed the complex with humic acid, and that about 85% of Al formed the humic acid-Al complex after FAAS measurements.

In order to minimize Al contamination from glassware, laboratory manipulations were carried out in polyethylene containers. The labware was soaked in 10% HNO₃ for at least 24 h and then rinsed carefully with deionized water before use.

Procedures

In this study, total dissolved Al, organically bonded Al and particulate Al in water samples taken from three different sampling sites at Karakaya dam lake (Malatya, Turkey) were determined by FAAS or GFAAS after an enrichment procedure. To determine total dissolved Al in the water samples, 8-hydroxyquinoline was used as complexing agent at pH 8 and XAD-4 type amberlite resins were used for enrichment. The organically bonded Al species in the water samples were destroyed by photodecomposition and their levels were determined by FAAS after an enrichment procedure using XAD-4 resin. Particulate Al in the samples was determined by GFAAS after filtering the water samples through a 0.45-µm filter and treating with concentrated HNO₃ first, and then diluting to 1 M HNO₃. Before using the Al enrichment procedure with the XAD-4 resin, the optimum working parameters such as recovery (97-98%), appropriate complexing reagent (8-hydroxyquinoline), pH (8), sample volume (300 mL), eluent (acetone), amount of resin (900 mg) and amounts of reagents (1-250 µg) were determined using the model samples.

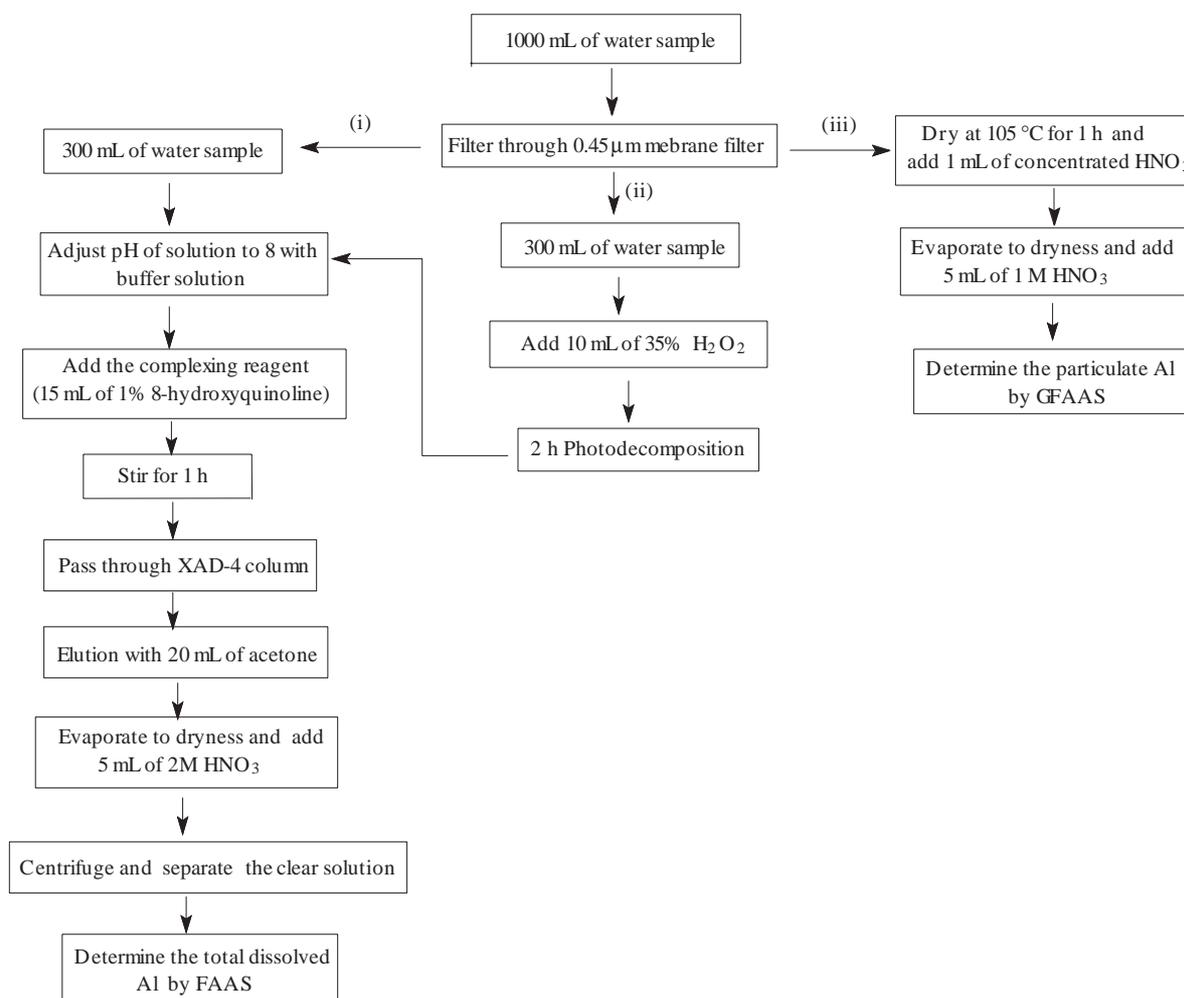


Figure 1. Analytical procedure for the separation of (i) dissolved Al, (ii) organically bonded Al and (iii) particulate Al.

Determination of total dissolved Al in the water of Karakaya dam lake

A 300-mL water sample was filtered through a 0.45- μm membrane filter (Schleicher & Schuell BA 85/21). The pH of the filtrate was adjusted to 8 with buffer solution. After adding 15 mL of 1% complexing reagent (8-hydroxyquinoline), the solution was stirred mechanically for 1 h. The solution was submitted to an amberlite type XAD-4 column and the column was then eluted with 20 mL of acetone. The eluate was heated to dryness and 5 mL of 2 M HNO_3 was added to the residue. After centrifuging twice at 2000 rpm, the solution was separated for measurements. The total dissolved Al concentration of the solution was determined by FAAS.

Determination of organically bonded Al in the water of Karakaya dam lake

A 300-mL water sample was filtered through a 0.45- μm membrane filter (Schleicher & Schuell BA 85/21). Then 10 mL of 35% H_2O_2 solution was added to the filtrate. The filtrate was then irradiated in a photodecomposition apparatus with a mercury lamp at room temperature for 2 h. After this stage, the procedure reported above for the total dissolved Al was followed. The level of total Al (organically bonded +

inorganic) was determined by FAAS. The organically bonded Al levels were then calculated as the difference between total Al (organically bonded + inorganic) and total dissolved Al (inorganic).

Determination of particulate Al in the water of Karakaya dam lake

A 1000-mL water sample was filtered through a 0.45- μm membrane filter (Schleicher & Schuell BA 85/21). The residue was dried at 105 °C for 1 h. Then 1 mL of concentrated HNO_3 was added to the residue in a Teflon beaker and evaporated to dryness. Then 5 mL of 1 M HNO_3 solution was added to the beaker and the particulate Al level was determined by GFAAS.

Results and Discussion

This study was undertaken to assess Al species such as total dissolved Al, particulate Al and organically bonded Al in the water of Karakaya dam lake. The effect of pH on the recovery of Al is shown in Figure 2. The optimum pH for recovery of up to 98% was 8, by using 8-hydroxyquinoline as a complexing agent.

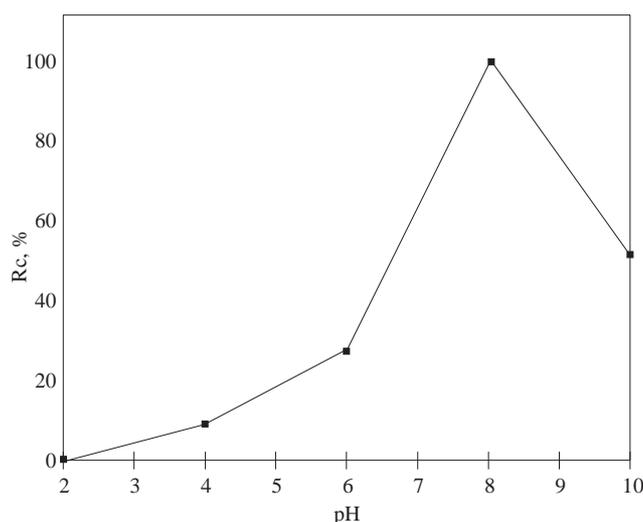


Figure 2. Effect of pH on recovery of Al using 8-hydroxyquinoline as a complexing agent.

The results of the speciation studies in Karakaya dam lake are shown in Tables 3 and 4. Al concentrations were found to increase with increasing depth. Similar observations were also obtained for selenium speciation studies in seawater^{20,21}. It was also observed that Al species levels were affected by the changing of the seasons; among the seasons, Al levels were found to be high in the summer. High Al concentrations in the summer samples may be due to the high evaporation rate of the lake water during hot days. The concentration of some Al species in natural samples is low, in the $\mu\text{g/L}$ range, and therefore very sensitive detection techniques and an enrichment step are required. Although FAAS and GFAAS are important techniques for the determination of metal ions at trace levels in natural waters, because of the low Al concentration, direct determination of the Al in dam lake water by these techniques is difficult. For this reason, it is necessary to employ a preconcentration method in order to increase the concentration of Al in the water samples. For this purpose, in the present study, an enrichment step using XAD-4 resin was improved.

Table 3. Levels of Al species in the water of Karakaya dam lake. The results are mean values \pm standard deviation; $n = 3$.

Sample no.* (depth)	Total dissolved Al (mg/L)	Particulate Al ($\mu\text{g/L}$)	Organically bonded Al ($\mu\text{g/L}$) XAD-4
1 (1 m)	3.63 \pm 0.03	23.6 \pm 0.2	65.2 \pm 0.5
1 (3 m)	3.74 \pm 0.03	25.2 \pm 0.2	65.7 \pm 0.4
1 (5 m)	3.76 \pm 0.03	24.8 \pm 0.3	66.8 \pm 0.5
1 (6 m)	3.76 \pm 0.03	24.7 \pm 0.3	67.1 \pm 0.5
2 (1 m)	2.33 \pm 0.02	29.3 \pm 0.3	62.3 \pm 0.4
2 (3 m)	2.47 \pm 0.03	31.7 \pm 0.4	63.5 \pm 0.5
2 (5 m)	2.49 \pm 0.02	30.9 \pm 0.4	63.9 \pm 0.4
2 (6 m)	2.52 \pm 0.02	30.9 \pm 0.4	64.1 \pm 0.4
3 (1 m)	1.98 \pm 0.02	29.8 \pm 0.3	55.7 \pm 0.4
3 (3 m)	2.11 \pm 0.02	24.6 \pm 0.3	55.3 \pm 0.4
3 (5 m)	2.19 \pm 0.02	23.3 \pm 0.3	56.4 \pm 0.4
3 (6 m)	2.30 \pm 0.03	22.4 \pm 0.3	56.8 \pm 0.4

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

Table 4. The variation of Al concentrations in the water of Karakaya dam lake with the changing of the seasons. The results are mean values \pm standard deviation; $n = 3$.

The season*	Total dissolved Al (mg/L)	Particulate Al ($\mu\text{g/L}$)	Organically bonded Al (XAD-4) ($\mu\text{g/L}$)
Spring	2.27 \pm 0.02	18.68 \pm 0.3	62.43 \pm 0.4
Summer	3.92 \pm 0.03	21.70 \pm 0.3	65.10 \pm 0.4
Autumn	2.42 \pm 0.03	22.56 \pm 0.3	63.40 \pm 0.4
Winter	2.34 \pm 0.02	22.73 \pm 0.3	60.10 \pm 0.4

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

XAD-4 type resins provide reversible absorption-desorption and they can be eluted by relatively cheap solvents such as acetone and methanol similar to Chelex-100 resins. XAD-4 type resins can be used several times, and their inert properties generally do not change during the work in acidic, basic or organic solvents. Because the required conditions for the analysis are not critical, XAD-4 resin was used in this work; it is easily adaptable for the separation-enrichment procedure in every laboratory. On the other hand, XAD-4 type resins are relatively cheaper than Chelex-100 resin, which is used in many Al speciation studies^{16–18} (e.g., 59.09 euros for a 25-g Chelex-100 package compared with 4.38 euros for the same quantity of XAD-4 [from the Sigma 2002-2003 catalog]).

The organically bonded Al species in the water samples were obtained by subtracting the dissolved Al from the total Al 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. We recently used this procedure for the decomposition of organometallic selenium species in the water of Karakaya dam lake²².

In order to explain the reliability of the method developed in terms of dissolved and organically bonded Al, the recovery of Al species was determined using Al standard solutions and humic acid-Al model solutions, respectively. It was also found that about 85% of Al was complexed with humic acid as a humic acid-Al complex. As can be seen from Tables 5 and 6, the recovery yields obtained for XAD-4 resin were always higher than 96%. The results show that the reliability of the method is quite good.

Table 5. Recovery of standard Al solutions for the evolved method. Resin and amount: XAD-4, 900 mg, pH 8, Complexing agent: 8-hydroxyquinoline, sample volume: 300 mL.

Amount of standard Al (μg)	Recovery, %
1.0	96
2.5	96
5.0	97
10.0	97
15.0	98
20.0	98
30.0	98
40.0	98
50.0	98
100.0	98
250.0	98

Table 6. Effect of resins type on recovery of organically bonded Al model solutions (Humic acid-Al standard solutions)

Amount of the Al in Humic acid-Al model solutions ($\mu\text{g/L}$)	Recovery, %	
	Chelex-100	XAD-4
10	96	97
20	96	98
30	97	98
40	98	98
50	98	98
100	98	98
250	96	98

The levels of organically bonded and total dissolved Al species in the samples were 55.3 to 67.1 $\mu\text{g/L}$ and 1.98 to 3.76 mg/L (see Table 3), respectively.

Al is considered a non-essential element for human health and development but interest in the potential link between high Al contents in tissues and various neurodegenerative disorders such as Alzheimer's disease has drawn attention to the intake of this element from different sources. Although the lake water is not used as drinking water, fish caught in the lake are consumed by people in this region and over prolonged periods the indirect intake of Al may be hazardous.

Conclusion

A method was developed for the preconcentration of trace Al in natural water. The short chromatographic column packed with amberlite XAD-4 examined in this paper provides a very simple, fairly rapid (about 30 min), precise, accurate and reliable technique for the preconcentration of trace Al separation from water

samples. The recovery yields obtained with standard Al solutions in deionized water were always higher than 96%, thus confirming the accuracy of the method. The relative error for the total Al measurements was within 2-4% and the lowest detection limit was about 3.3 µg/L.

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