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# Assessment of Toxic, Essential, and Other Metal Levels by ICP-MS in Lake Eymir and Mogan in Ankara, Turkey: An Environmental Application

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## INTRODUCTION

Air, water, and soil contamination are the basis of many environmental problems. The increase in population, urbanization, and industrial development has caused further contact with heavy metals not only for living species (1, 2) but also for the overall environment. In aquatic environments, the presence of heavy metals has gained much attention because they dissolve in water and bio-accumulate in all living organisms (3-5) by way of geogenic, atmospheric, industrial, pharmaceutical, mining wastes and domestic discharge (6-10). Thus, low levels of metals in water can become toxic (11, 12) such as As, Cd, Pb, and Hg,(10), while others such as Zn, Cu, Fe, and Mg (10, 13) are fundamental and natural components of aquatic life. Nonetheless, these essential metals can become toxic when taken at very high concentrations (14).

Although there are alternative atomic absorption spectrometry (AAS) methods, inductively coupled plasma mass spectrometry (ICP-MS) is the leading analytical technique because of its excellent sensitivity, simultaneous measurement of numerous metals at ultra-trace levels in various sample matrices, sample input, plasma, sampling interface, ion optics, quadrupole (mass separation), and detector (15-16).

Biomonitoring of metals is necessary to evaluate environmental health (17). The main goal of this study was to develop and validate

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## ABSTRACT

The goal of this study was to develop and validate a sensitive ICP-MS method for the determination of some toxic metals (Al, As, Hg, Pb, Cd, Ni, Cr, and Sb), along with essential and other elements (Fe, Cu, Zn, Mn, Se, Co, and Ti) in water samples collected from 20 sites of Lake Eymir and Lake Mogan in Ankara, Turkey. The mean metal concentrations, except for As, in the water samples of the two lakes were found at safe levels. The As levels in Lake Mogan (12.15±0.41 μg/L) and Lake Eymir (11.49±0.66 μg/L) were higher than the permissible limits recommended for drinking water of 10.0 μg L$^{-1}$ As. The "significance" of this paper fundamentally addresses the assessment of general signal optimization for multi-element analysis and reducing interferences during validation and optimization of this ICP-MS method. Good linearity with a correlation coefficient between 0.9911 and 1.000 was obtained, respectively. Imprecision was measured as the coefficient of variation (CV), which ranged between 1.16% and 4.79%. Recovery of the method was between 97.3% and 103.6% for all elements, which supports the accuracy of the method. The procedure described is relatively simple, precise, and applicable for routine environmental metals analysis in natural water samples.

a sensitive ICP-MS method for the multi-element determination of Al, As, Hg, Pb, Cd, Ni, Cr, Sb, Fe, Cu, Zn, Mn, Se, Co, and Ti in natural water samples of Lake Mogan and Lake Eymir, located in Ankara, Turkey. Although, there are many studies on this topic, the major significance and novelty of the present investigation is on the assessment of the general signal optimization for multi-elemental analysis and reducing the interferences during validation and optimization of the method. Last but not least, this work yielded environmental data in terms of metal content in the above-mentioned lakes.

## EXPERIMENTAL

### Instrumentation

All quantifications of the metal concentrations were performed using a Model 7700x ICP-MS (Agilent Technologies, USA). Ultra-pure water used for the experimental process was obtained with a model Direct-Q8 (Merck-Millipore, Germany) with a resistivity of 18MΩ·cm. The ICP-MS operating parameters for this study are listed in Table I.

### Standard Solutions and Reagents

Multi-element calibration standards containing 10 mg/L of each element were obtained from VHG LABS (Manchester, NH, USA). The ICP-MS Internal Standard Multielement mix, containing $^7$Li, $^{45}$Sc, $^{72}$Ge, $^{115}$In, $^{175}$Lu, $^{103}$Rh $^{159}$Tb, and $^{209}$Bi at a concentration of 1000 mg/L, was purchased from Agilent® (USA). Nitric acid (HNO$_3$, 65% v:v) was obtained from Merck (Darmstadt, Germany). For validation of the method, the certified reference material (CRM) ERM-CA713 Wastewater was used (Sigma-Aldrich, Germany). Argon gas with a purity of 99.999% was bought from a local supplier (Linde Gaz, Diyarbakir, Turkey).

## Sample Collection and Sample Preparation

A 10-mL amount of sample was collected from 20 different parts of Lake Eymir and Lake Mogan in Göl-basi, Ankara, Turkey (see Figure 1). The samples were put into 50-mL polypropylene tubes. The samples were filtered with Acrodisc® Min-ispike syringe filters PTFE mem-brane with a pore size 0.45 μm (Merck, Germany) and pretreated by addition of 10 mL of 8% (v/v) nitric acid [prepared manually from 65% (v/v)], then stored in 50-mL polypropylene tubes at 4 ℃ in the refrigerator until the day of analysis. Multi-element stock solutions (VHG LABS, Manchester, NH, USA) con-taining 10 μg/mL of each element were diluted in 4% (v:v) $HNO_3$ in order to prepare calibration stan-dards at the concentrations of 1.0, 5.0, 10.0, 25.0, 50.0 and 100.0 μg/L. To avoid possible contamina-tions, all glassware (Analitik Kimya, Istanbul, Turkey) was kept in 10.0% (v:v) nitric acid for at least one night before analysis.

## RESULTS AND DISCUSSION

### Optimization

In order to achieve the best per-formance from this ICP-MS analysis, a number of problems were over-come. To avoid high values of stan-dard deviation, an Agilent Internal Standard Mixture containing [7]Li, [45]Sc, [72]Ge, [115]In, [175]Lu, [103]Rh, [159]Tb, and [209]Bi at a concentration of 1000 mg/L was manually diluted with nitric acid 4% (v:v) until final con-centration of 100 μg/L. To measure the concentration of Al, Cr, Mn, Fe, Co, Ni, and Cu, [45]Sc was chosen as the internal standard. Similarly, [72]Ge was selected as the internal standard for analysis of As, Se, and Zn. For Hg and Pb, [209]Bi was used, while [175]Lu and [115]In were the inter-nal standards for Ti and Cd, respec-tively. The final solution of the internal standard was automatically pumped to all solutions. The inter-nal standard recoveries ranged between 95% and 105%, and the stability of the internal standard can be observed in Figure 2.

The analysis of natural water samples is very demanding since the trace element levels are mostly remarkably low, and often cause a sensitivity effect due to Na, Mg, Ca, K, and Cl as the matrix elements. To reduce matrix effects, the water samples were diluted with 10 mL of 8% (v:v) nitric acid. In order to achieve the optimum signal inten-sity during multi-element determi-nation at trace and ultra-trace levels, it is required to examine the optimization for mass range since optimum parameters can change from element to element in ICP-MS. General signal optimization for multi-element quantification can be accomplished by using three ele-ments from low to high mass. From this point of view, [7]Li at low mass, [89]Y at medium mass, and [205]Tl at high mass were used at 10 mg/L in a multi-element calibration standard (VHG LABS, Manchester, NH, USA). The peak resolutions and signal sen-sitivities of these three elements are shown in Figures 3 and 4, respec-tively.

During the analysis of Cd, Sb, Hg, Ti, and Pb, no gas mode was

### TABLE I
### ICP-MS Operational Parameters Used
### for the Determination of Elements

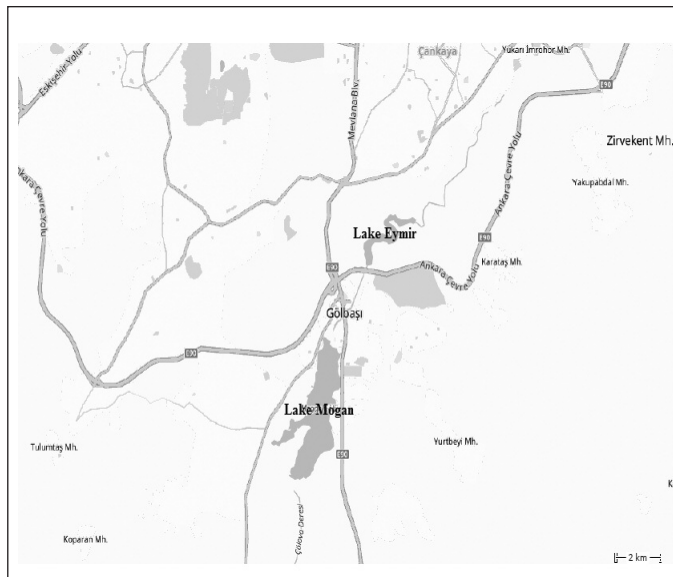| Agilent ICP-MS 7700x | Instrumental Parameters at Analysis Mode and Operating Conditions |
|---|---|
| Ar Gas Delivery Pressure | 540 kPa |
| Forward Power | 1300 W |
| Reflected Power | 7 W |
| Cooling Water Flow Rate (RF/WC/IF) | 2.0 L/min |
| Interface/Backing Pressure (IF/BK ) | 252 Pa |
| RF Power (W) | 1550 |
| Sampling Depth (mm) | 8.0 |
| Omega Lens (V) | 7.3 |
| S/C Temp (oC) | 2 |
| Scanning Mode | Peak hopping |
| Internal Standard | [45]Sc, [72]Ge, [115]In, [175]Lu, and [209]Bi |
| Nebulizer | Meinhard |
| Spray Chamber | Cyclonic |
| Sampler and Skimmer Cones | Ni |
| Shield Torch | Platinum |
| The Autosampler | ASX-500 Series |
| Bottle 1 | With fresh doubly deionized water (DDW) |
| Bottle 2 | With fresh 1% $HNO_3$ %(v:v) |
| Bottle 3 | With tuning solution (1 μg/L [7]Li, [89]Y, [205]Ti, and [140]Ce, in 2% $HNO_3$) |
| Water of Chiller Temperature | 14 ℃ |
| Low Matrix Mode | < %0.1 |
| Ar Gas Flow Rates (L/min): | |
|    Plasma | 16 |
|    Auxiliary | 1.0 |
|    Nebulizer | 1.0 |

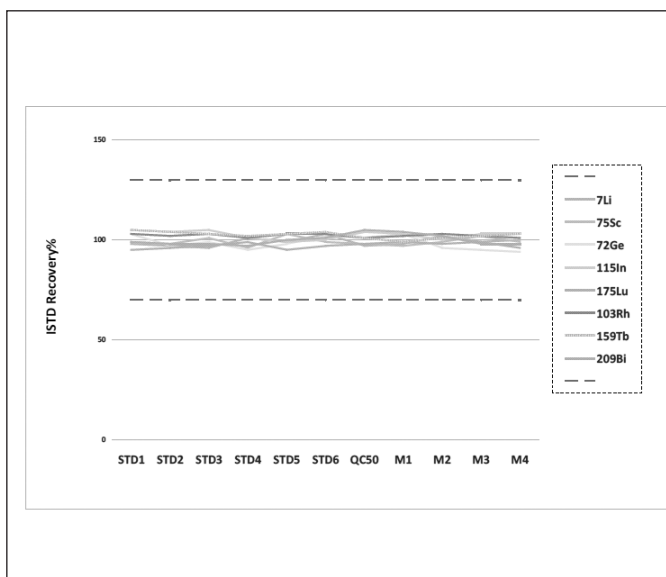Fig 1. Map of Lake Eymir and Lake Mogan located in Gölbasi, Ankara, Turkey.



Fig 2. Graph of internal standard recovery.

applied. However, the remaining elements of Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, and Al were analyzed in the helium collision mode because all elements, except for Al, have at least one analytically useful isotope causing a polyatomic overlap in the no gas mode for the lake water matrix. The samples were injected (60 s, 0.3 rps) with a Meinhard® nebulizer and a chilled spray chamber. No flow injection valve was utilized, and the autosampler was directly set up to stay in the sampling position for the defined time. The argon plasma conditions were adjusted as forward power at 1300 W and reflected power at 7 W. The nebulizer gas flow rate, auxiliary and plasma gas flow rates were selected as 1.0, 1.0, and 16.0 L/min, respectively. Nickel interface cones were used. The instrument was run in peak jumping mode, while the metals and internal standards were scanned at three points per peak.

**Method Validation Using CRM**

For validation of the method based on accuracy, precision, and recovery, the CRM ERM-CA713 Wastewater was analyzed 10 times with triplicate measurements. The



**Peak Resolution**

| Mass | Peak Height | Axis | W-50% | W-10% |
|------|-------------|--------|-------|-------|
| 7 | 8008.96 | 7.00 | 0.63 | 0.73 |
| 89 | 25804.65 | 88.95 | 0.61 | 0.74 |
| 205 | 17058.21 | 205.00 | 0.60 | 0.77 |
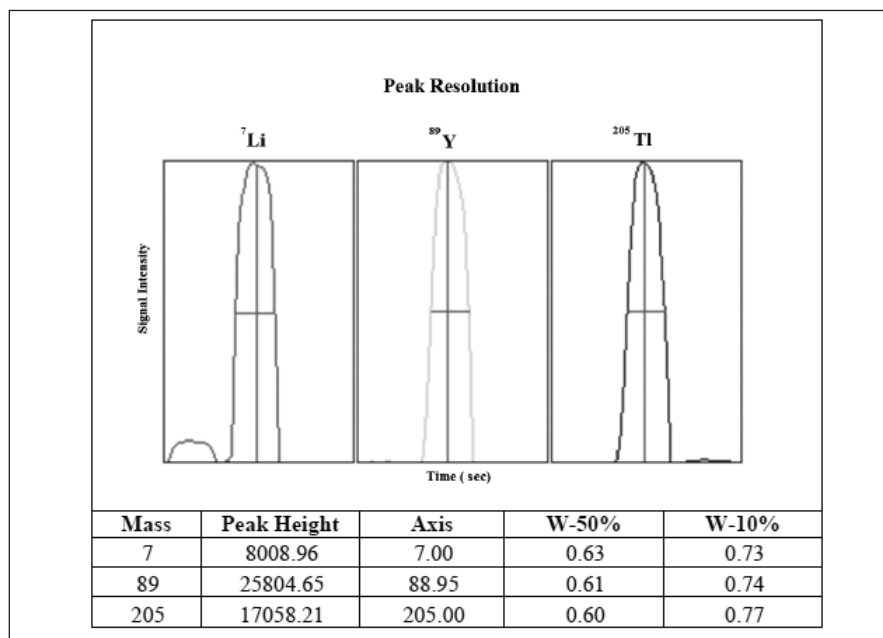
Fig. 3. Graph of peak resolutions for $^6Li$, $^{89}Y$, $^{205}Tl$. (Integration time and acquisition time were 0.1 and 22.74 s, respectively. W-50% and W-10% represent the widths of the peak measured at a specified fraction of the peak height 50% and 10%.).

precision of the method was expressed using the coefficient of variation (CV) of 10 independent analyses of the CRM, and accuracy was assessed by means of relative error (RE). The results of the analyses were compared to the certified values for accuracy and precision of the method. Good agreement was obtained for the certified values and the measured metal concentrations. The CV values ranged between 1.16 and 4.79% and were below the maximum CV

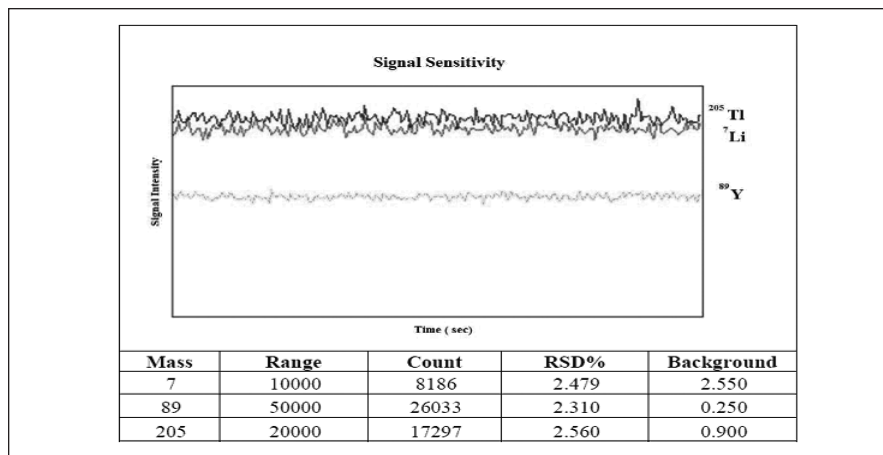| Mass | Range | Count | RSD% | Background |
|---|---|---|---|---|
| 7 | 10000 | 8186 | 2.479 | 2.550 |
| 89 | 50000 | 26033 | 2.310 | 0.250 |
| 205 | 20000 | 17297 | 2.560 | 0.900 |

*Fig. 4. Graph of signal sensitivities for $^{6}Li$, $^{89}Y$, $^{205}Tl$. (Sampling period and integration time were respectively, 0.311 and 0.1 s. RSD represents the relative standard deviation.*

### TABLE II.  Summary of CRM Analysis

| Metals | CRM | Certified Value (ppb) | Measured Value (ppb) | RE (%) | RSD or CV (%) |
|---|---|---|---|---|---|
| As | ERM-CA713 | 10.8±0.3 | 11.1±0.4 | 2.78 | 3.60 |
| Cd | ERM-CA713 | 5.09±0.20 | 5.17±0.22 | 1.57 | 4.26 |
| Cr | ERM-CA713 | 20.9±1.3 | 21.4±0.5 | 2.39 | 2.34 |
| Cu | ERM-CA713 | 101±7 | 102.4±1.7 | 0.69 | 1.67 |
| Fe | ERM-CA713 | 445±27 | 439.4±5.1 | 1.26 | 1.16 |
| Hg | ERM-CA713 | 1.84±0.11 | 1.88±0.09 | 2.17 | 4.79 |
| Mn | ERM-CA713 | 95±4 | 93.6±1.4 | 1.37 | 1.49 |
| Ni | ERM-CA713 | 50.3±1.4 | 51.2±0.9 | 1.79 | 1.75. |
| Pb | ERM-CA713 | 49.7±1.7 | 50.3±0.7 | 1.21 | 1.39 |
| Se | ERM-CA713 | 4.9±1.1 | 4.8±0.2 | 2.04 | 4.16 |

RE: relative error, RSD: relative standard deviation, CV: coefficient of variation.

### TABLE III.  Summary of Recovery Study

| Metals | Expected Value (ppb) | Measured Value (ppb) | Recovery (%) | RE (%) | RSD or CV (%) |
|---|---|---|---|---|---|
| Cr | 100.0 | 98.3±3.1 | 98.3 | 1.7 | 3.15 |
| Mn | 100.0 | 101.2±0.9 | 101.2 | 1.2 | 0.89 |
| Co | 100.0 | 99.1±1.1 | 99.1 | 0.9 | 1.11 |
| Ni | 100.0 | 97.6±2.5 | 97.6 | 2.4 | 2.56 |
| Cu | 100.0 | 99.4±2.1 | 99.4 | 0.6 | 2.21 |
| As | 100.0 | 102.6±3.2 | 102.6 | 2.6 | 3.1 |
| Fe | 100.0 | 101.4±2.2 | 101.4 | 1.4 | 2.16 |
| Zn | 100.0 | 98.2±1.7 | 98.2 | 1.8 | 1.73 |
| Al | 100.0 | 98.4±2.3 | 98.4 | 1.6 | 2.34 |
| Se | 100.0 | 102.6±4.1 | 102.6 | 2.6 | 4.0 |
| Cd | 100.0 | 99.2±1.1 | 99.2 | 0.8 | 1.11 |
| Sb | 100.0 | 103.6±2.9 | 103.6 | 3.6 | 2.80 |
| Hg | 100.0 | 97.3±2.3 | 97.3 | 2.7 | 2.36 |
| Ti | 100.0 | 102.8±1.9 | 102.8 | 2.8 | 1.84 |
| Pb | 100.0 | 101.5±2.1 | 101.5 | 1.5 | 2.07 |

RE: relative error, RSD: relative standard deviation, CV: coefficient of variation.

(15%) calculated according to Horwitz's 1982 study (18). Therefore, the results of the present work indicate that the proposed method is precise (see Table II).

In order to assess the recovery of the method, multi-element calibration standards (VHG LABS, Manchester, NH, USA) containing 10 mg/L of each element analyzed were spiked with the appropriate amount of nitric acid (4%, v:v) until the total concentration of each element was 100 μg/L, then was analyzed 10 times with triplicate measurements. The recoveries for all elements ranged between 97.3% and 103.6% and showed the method to be accurate (see Table III).

**Limit of Detection, Quantification, and Linearity**

After primary calibration, a series of 10 analytical blank quantifications were performed to compute the standard deviation. Next, according to ICH guidelines (19-22), the limit of detection (LOD) and lowest limit of quantification (LOQ) were determined based on the standard deviation of the response and the slope of the calibration curve (LOD = 3.3 σ/S, LOQ = 10 σ/S, where σ is the standard deviation of the response and S is the slope of the calibration curve). The ICP-MS method provided LOD values ranging between 0.009 μg/L and 2.36 μg/L, while the LOQ values ranged between 0.027 μg/L and 7.16 μg/L (see Table IV). The limit of linearity (LOL) is the concentration at which the calibration curve departs from linearity and was found to be in the range of 1.0 μg/L–100.0 μg/L resulting in correlation coefficients between 0.9911 and 1.000.

**Evaluation of Toxic, Essential, and Other Metal Levels in the Lake Water Samples**

Natural and anthropogenic events are considered the main source for introducing metals into the aquatic systems (23). In this

## TABLE IV
### List of LOD and LOQ Values of the Metals Analyzed

|     | r      | LOD (µg/L) | LOQ (µg/L) |
|-----|--------|------------|------------|
| Cr  | 1.0000 | 0.1320     | 0.40       |
| Mn  | 1.0000 | 0.083      | 0.25       |
| Co  | 1.0000 | 0.03       | 0.091      |
| Ni  | 0.9999 | 0.152      | 0.46       |
| Cu  | 0.9988 | 0.174      | 0.527      |
| As  | 0.9995 | 0.115      | 0.348      |
| Fe  | 0.9962 | 2.36       | 7.16       |
| Zn  | 0.9911 | 0.121      | 0.360      |
| Al  | 0.9988 | 1.983      | 6.00       |
| Se  | 0.9993 | 0.123      | 0.372      |
| Cd  | 0.9999 | 0.009      | 0.027      |
| Sb  | 1.0000 | 0.0027     | 0.008      |
| Hg  | 0.9999 | 0.019      | 0.058      |
| Ti  | 0.9998 | 0.084      | 0.025      |
| Pb  | 0.9999 | 0.060      | 0.181      |

r: correlation coefficient.
LOD: limit of detection.
LOQ: limit of quantification.

## TABLE V
### Mean Metal Levels Measured in Lake Mogan and Lake Eymir vs. Permissible Limit for Drinking Water by WHO (24), EU (25), US EPA (26), and the Turkish Ministry of Health Standards (27)

| Metals    | Lake Mogan   | Lake Eymir   | WHO  | EU   | US EPA | Turkish Ministry of Health |
|-----------|--------------|--------------|------|------|--------|----------------------------|
| Al (µg/L) | 50.38±0.39   | 50.80±0.62   | –    | 200  | 200    | 200                        |
| Sb (µg/L) | 1.13±0.09    | 1.08±0.08    | 5    | 5    | 6      | 5                          |
| As (µg/L) | 12.15±0.41   | 11.49±0.66   | 10   | 10   | 10     | 10                         |
| Cu (µg/L) | 2.59±0.38    | 2.75±0.21    | 2000 | 2000 | 1300   | 2000                       |
| Hg (µg/L) | 0.30±0.11    | 0.21±0.02    | 6    | 1    | 2      | 1                          |
| Zn (µg/L) | 6.04±0.41    | 6.20±0.46    | –    | –    | 5000   | –                          |
| Fe (µg/L) | 60.20±0.72   | 63.50±0.88   | –    | 200  | 300    | 200                        |
| Cd (µg/L) | 0.10±0.03    | 0.11±0.03    | 3    | 5    | 5      | 5                          |
| Cr (µg/L) | 0.91±0.09    | 1.03±0.25    | 50   | 50   | 100    | 50                         |
| Co (µg/L) | 0.15±0.01    | 0.27±0.013   | –    | –    | –      | –                          |
| Pb (µg/L) | 1.78±0.24    | 2.17±0.67    | 10   | 10   | 15     | 10                         |
| Mn (µg/L) | 1.59±0.27    | 24.7±1.54    | 50   | 50   | 50     | 50                         |
| Ni (µg/L) | 3.82±0.26    | 3.79±0.19    | 20   | 20   | –      | 20                         |
| Se (µg/L) | 0.59±0.04    | 0.56±0.04    | 10   | 10   | 50     | 10                         |
| Ti (µg/L) | 0.082±0.03   | 0.068±0.007  | –    | –    | –      | –                          |

WHO: World Health Organization.
EU: European Union.
US EPA: United States Environmental Protection Agency.

study, the levels of some toxic metals (Al, As, Hg, Pb, Cd, Ni, Cr, and Sb) along with some essential and other elements (Fe, Cu, Zn, Mn, Se, Co, and Ti) in water samples collected from 20 sites of Lake Eymir and Lake Mogan in Ankara, Turkey, were determined by ICP-MS. The mean concentrations of the metals in the water samples of Lake Mogan can be seen in Table V, the mean metal levels measured in Lake Mogan and Lake Eymir were compared to standards of World Health Organization (WHO) (24), European Union (EU) (25), United States Environmental Protection Agency (US EPA) (26) and Turkish Ministry of Health (27). The As level both in Lake Mogan and Lake Eymir water was found to be higher than the permissible limit recommended for drinking water. Although all other measured metal concentrations are at safe levels, it should however not be assumed that lake waters are acceptable for human consumption.

## CONCLUSION

Water pollution of heavy metals is one of the most important environmental problems due to their toxicity and bio-accumulation in aquatic organisms. The results of the proposed ICP-MS method in the analysis of heavy metals (Al, As, Hg, Pb, Cd, Ni, Cr, and Sb), along with essential and other elements (Fe, Cu, Zn, Mn, Se, Co, and Ti), showed good linearity with a correlation coefficient between 0.9911 and 1.000. Imprecision was measured as the coefficient of variation, which ranged between 1.16% and 4.79%. The recoveries ranged from 97.3% to 103.6%, which proved the method to be accurate. The procedure described is relatively simple, precise, and applicable for routine environmental metals analysis in natural water samples. The mean concentrations of most metals were found at safe levels, except for As in Lake Mogan (12.15±0.41 µg/L) and in Lake Eymir (11.49±0.66 µg/L) which were higher than the permissible limits (10.0 µg L$^{-1}$ As),

and thus the water is not safe for human consumption. The findings obtained from this study will be a good reference for future assessment of metal levels in environmental water samples from other parts of the world.

## ACKNOWLEDGMENT

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