PRELIMINARY RESULTS OF SELENIUM STUDY IN SAPANCA LAKE'S WATER, SAKARYA-TURKEY

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Özet **– Organizmadaki yaşam için su kaynakları oldukça önemlidir. Sapanca gölü, Adapazarı şehri ve çevresindeki alanlar için endüstriyel ve içme suyu kaynağı olarak kullanılmaktadır. Göl ayrıca balıkçılık ve spor aktiviteleri için de uygundur. Elektrotermal Atomlaştırmalı Atomik Absorpsiyon Spektrometrik metot (ETA-AAS) ön atomlaştırma sırasında yüksek uçuculuğa ve tepkime vermeye yatkın selenyumun eser analizinde kullanılmaktadır. Bununla birlikte nikel, paladyum gibi matriks dönüştürücüler ön atomlaştırma basamağında kayıpları önlemek, sinyali iyileştirmek ve tekrarlanabilirliği artırmak için kullanılır. Selenyum, beslenme için su ve gıdalarda bulunabilen çok önemli bir elementtir. Fazlası alındığında ise toksik etki gösterebilir. Düşük derişimlerde eser element olarak tanınır. Bu çalışmada palladyum nitrat matriks dönüştürücü yardımıyla Sapanca gölünden örneklenen su numunelerinde selenyum elementinin ETA-AAS ile doğrudan tayini metodu uygulanmıştır. Araştırma sonunda elde edilen sonuçlara bakıldığında su örneklerinde selenyum düzeyinin 9.4-21.6 ng mL^{-1} aralığında olduğu sonucuna varılmıştır.**

Anahtar Kelimeler - Selenyum, Sapanca Gölü, ETA-AAS

Abstract **- Water sources are important for living organisms. Sapanca Lake which is used as the drinking and industrial water supply of the city of Adapazarı and its surrounding areas. The lake is also convenient for fisheries and sporting activities. Electrothermal atomization atomic absorption spectrometric method (ETA-AAS) is used for the trace analysis of selenium which has high volatility and reactivity during the preatomisation cycle. Consequently, matrix modifiers like nickel, palladium are always used to enhance the efficiency of pyrolysis step, improve reproducibility, etc[1,2].**

Selenium is very important for human diet as this element may be a toxic substance if excess amounts are found in food and water. However, it is recognised as a trace element at low concentrations. A method is described for the direct determination of selenium by ETA-AAS in water samples collected from Sapanca lake using palladium nitrate as chemical modifier. The results obtained that the selenium concentrations in samples were found to be in the range of 9.4-21.6 ng mL^{-1}.

Key Words - Selenium, Sapanca Lake, ETA-AAS

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I. INTRODUCTION

Sapanca Lake (figure 1) is situated in Marmara region and a multipurpose water source of surrounding towns (Adapazarı, Sapanca, Arifiye...) and industries. The lake is 30 m above the sea level and surface area is 40 km^2. Sapanca Lake is fed by rivers flowing through south and north sides of rivers and water coming up from the deep of the lake. Then the more water is drained by Çark river into the Sakarya river[3,4,5].

In recent years, there has been increasing interest in the trace determination of selenium. This element has been recognised as an essential nutrient for humans based on its presence in the enzyme glutahione peroxidase which affords cells protection againts oxidative damage. Se supplemented fertilization may impact to the concentration of selenium in lake ecosystem. The mean water Se concentration of lake surrounded by fields may significantly be higher than that of tap water.

II. EXPERIMENTAL

Electrothermal atomization atomic absorption spectroscopy (ETA-AAS) seems to be the appropriate technique to determine selenium because of its sensitivity and relative simplicity. The effectiveness of palladium nitrate as a chemical modifier for the determination of selenium in lake water samples by ETAAS was evaluated. Optimization of the temperature program,

modifier mass and pyrolysis temperature for the determination of selenium was carried out. The results indicate that the $Pd(NO_3)_2$ modifier allows the quantitative stabilization of Se in water samples at 900 °C during the pyrolysis step. The modifier further reduces the background absorbance caused by sample matrices and significantly enhances the sensitivity of Se determination.

II.1 Apparatus

A Shimadzu (Tokio, Japan) Model AA6701F graphite furnace atomic absorption spectrometer equipped with an autosampler was used. Background absorption was corrected by using a deuterium lamp in all experiments. A Koto brand aluminium hollow-cathode lamp operated at 12 mA and pyrolytically coated graphite tube were used. Atomic Absorption Spectrometer setting conditions are summarised in Table 1. Atomisation signals were obtained and processed using a computer and the results printed out using a laser printer (HP 6L). The temperature programs used are described in Table 2.

II.2 Reagents

All reagents used were of analytical-reagent grade (Merck, Darmstadt, Germany) and ultra high purity water (chemical resistivity; 18 $M\Omega$ cm^{-1}) was employed throughout. A 1000 mg l^{-1} spectroscopic grade Se stock standard solution was used for calibration purpose. Working standard solutions containing 5- 80 ng ml^{-1} of Se were prepared from the stock standard solution by serial dilution with 0.2 % v/v HNO_3 prior to use. Palladium nitrate solution was used as optimum matrix modifier because better signal response was obtained. Thus, palladium nitrate modifier was added to all solutions (standard and sample) to be analysed.

II.3 Cleaning and Storage Material

All glassware and polyethylene bottles were cleaned by soaking in 10 % HNO_3, rinsing five times with destilled deionised water prior to use. No glass vessels were used in order to minimise Selenium release and adsorption.

II.4 Calibration and Precision

A calibration graph was obtained using a series of selenium standard solutions containing matrix modifier at the optimum amounts. An acceptable linearity was obtained for selenium standards with $Pd(NO_3)_2$ matrix modifier (0.3 mg L^{-1}) in the range of 5-80 ng ml^{-1}. Furnace conditions as in table 2. The realtionship between the concentration and the absorption can be expressed by the following equation:

$$y = 0.0003x + 0.022 \qquad r = 0.9996$$

where is the correlation coefficient. The relative standard deviation calculated for the same conditions given above is % 4.8

Table 1. Setting conditions of Electrothermal Atomisation Atomic Absorption Spectrometer

Lamp Current (mA)	: 12
Wavelength (nm)	: 196.0
Slit Width (nm)	: 1.0
BG Correction	: Deuterium
Conc. unit	: ng mL^{-1}
Number of replication	: 3
Duplication	: 2
Injection volume (µL)	: 30

III. RESULTS

The results obtained are summarised in Tables 3 and 4.

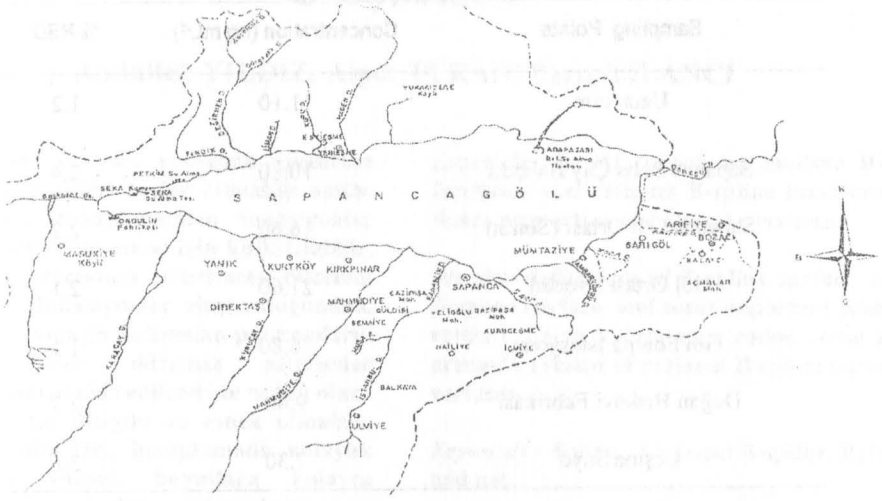

Figure 1: A map of Sapanca Lake and Surrounding Areas.

Table 2. Graphite Furnace program optimised for Sapanca lake's water samples.

Step	Procedure	Temp/ °C	Heat Time/s	Heat Mode	Sensitivity	Ar Flow Rate/ L min^{-1}
1	Drying I	95	15	Ramp	Regular	1.0
2	Drying II	120	5	Step	Regular	1.0
3	Ashing I	900	5	Ramp	Regular	1.0
4	Ashing II	900	1	Step	Regular	1.0
5	Atomisation	2100	2	Step	High	0.0
6	Cleaning	2700	1	Ramp	Regular	1.0

Table 3. Recovery test for Selenium in deionised and sample water. Results are averages of three replicates[6].

	Selenium added ($\mu g\ L^{-1}$)	Selenium found ($\mu g\ L^{-1}$)	% Recovery	% RSD
Deionised Water	5.0	4.51	90.2	5.0
Sample Water (Polis Çay Bahçesi)	5.0	4.10	82.0	3.8

Table 4. Selenium levels measured in Sapanca Lake's water samples.

Sampling Points	Concentration (ng mL^{-1})	% RSD
Uzunkum	11.10	1.2
Sapanca Polis Çay Bahçesi	10.80	2.4
Sapanca Göl Ortası (South)	16.60	2.2
Göl Ortası (North)	21.60	2.1
Göl Pompa İstasyonu	16.80	1.1
Doğan Bisküvi Fabrikası	9.40	2.7
Çeşme Suyu	7.30	3.8

IV. DISCUSSION

A method was applied for the direct determination of trace selenium in Lake Sapanca. This method uses electrothermal atomic absorption spectrometry with platform atomization and a chemical modifier of palladium nitrate. The optimal temperature program and modifier mass allowed quantitative stabilization of selenium in water solution up to 900 degrees C. The selenium concentrations in these samples were found to be in the range of 9.4-21.6 ng mL^{-1} when sample volumes of 30 µL were used. Because of the low detection limit and the tolerance to interference, the proposed method offers a low-cost solution to the determination of trace selenium in drinking and natural waters. The total selenium levels of lake water samples were determined and the results are in aggrement with the literature data. The results of the selenium study are shown in tables 3 and 4. It is indicated that the mean water Se concentration of lake surrounded by fields was significantly higher than that of tap water. The values of selenium concentrations were found to increase as the distance of the sampling points from the coast are increased. The highest level was measured in the middle of the lake Sapanca (table 4).

V. CONCLUSIONS

It is indicated that the mean water Se concentration of lake surrounded by fields was significantly higher than that of tap water. Because of the low detection limit and the tolerance to interference, the proposed method offers a low-cost solution to the determination of trace selenium in drinking and natural waters. It can be concluded that this high consumption product is a reasonable source of selenium in the human diet.

REFERENCES

[1]. Verlinden, M., Deelstra, H.A., Adriaenssens, E., Talanta, 28, 637, 1981

[2]. Küçükbay, F.Z., Demir, M., Turk J. Chem., 25, (2001), 341.

[3].Anonymous, T.C. Başbakanlık ve Çevre Müsteşarlığı, Sapanca 83 Sempozyumu Bildiriler Kitabı, Ankara, 1984.

[4]. Anonymous, "APHA, AWWA, WPCF, For The Examination of Water and Wastewater" 16 th Edition, 1985.

[5]. Yalçın. N., Sevinç. V., Tr. J. Engineering and Environmental Sciences, 17, (1993), 151.

[6]. TS 8088, Suyun Analiz Metotları – Selenyum Tayini, Mart 1990.