DETERMINATION OF RADIOACTIVITY AND ELEMENT LEVELS OF SALINE WATERS FROM SIIRT REGION, TURKEY

İbrahim TEĞİN^a, Orhan ACAR^{b*}

^aChemistry Department, Faculty of Arts and Science, Siirt University, Siirt - Turkey ^bChemistry Department, Faculty of Science, Gazi University, 06500, Ankara – Turkey Corresponding Author: <u>oacar@gazi.edu.tr</u>

TÜRKİYE SİİRT BÖLGESİNDEKİ TUZLU SULARDA RADYOAKTİVİTE VE ELEMENT SEVİYELERİNİN TAYİNİ

Abstract:

In this study, gross α and gross β radioactivity concentrations and metal contents in saline waters collected from different areas of Siirt region were measured and evaluated by using PIC-MPC-9604 model α/β counting system and wavelength dispersive X-ray fluorescence spectrometry. The gross α activity concentrations (0.44 - 0.62 Bq L⁻¹) with minimum detectable concentrations (MDC) (0.11 - 0.20 Bq L⁻¹) and gross β activity concentrations (0.93 - 1.67 Bq L⁻¹) with MDC (0.10 - 0.17 Bq L⁻¹) in samples were determined. Comparison of radioactivity and element concentrations found in the saline waters were made with the reported values from World Health Organization (WHO), the United States Environmental Protection Agency (US-EPA), the Turkish Standards (TS) and values reported in previous studies. Principal component and cluster analyses were utilized to categorize the saline waters in terms of metal and activity concentrations. Three principal components found were nearly 90.4% of whole variance for the data.

Özet:

Bu çalışmada, Siirt bölgesinin farklı alanlarından toplanan tuzlu sularda toplam α ve toplam β seviyeleri ve metal içerikleri PIC-MPC-9604 model α/β sayım sistemi ve dalga boyu dağılımlı X-ışını floresans spektrometresi ile ölçüldü ve değerlendirildi. Örneklerde, minimum ölçülebilir derişimler (MÖD) (0,11 – 0,20 Bq L⁻¹) ile toplam α aktivite derişimleri (0,44 – 0,62 Bq L⁻¹) ve MÖD (0,10 – 0,17 Bq L⁻¹) ile toplam β aktivite derişimleri (0,93 – 1,67 Bq L⁻¹) olarak tayin edilmiştir. Tuzlu sularda bulunan radyoaktivite ve element konsantrasyonlarının karşılaştırılması Dünya Sağlık Örgütü (WHO), Birleşik Devletler Çevre Koruma Ajansı (US-EPA) ve Türk Standartları (TS) tarafından bildirilen değerleri ile daha önce yayınlanan çalışmalarda raporlanan değerler kullanılarak yapılmıştır. Tuzlu suları, metal derişimleri ve aktivite seviyeleri açısından kategorize etmek için ana bileşen ve küme analizleri kullanılmıştır. Bulunan üç ana bileşen, verilerdeki toplam değiskenin yaklasık % 90,4'ü olmuştur.

Keywords: Saline waters, gross alpha, gross beta, element, chemometric technique **Anahtar Kelimeler:** Tuzlu sular, toplam alfa, toplam beta, element, kemometrik teknik

1. Introduction

Water is one of the most important matters for human life and environmental science in the world because of its daily consumption by human, its ability to transport pollutants and radionuclides into environment. Saline waters contain dissolved salts such as NaCl and KCl, and salinity ratio varies from 0.1 to 3.5%. Total salt content of sea water is about 35.6 g L⁻¹ (Zapata-Garcia, Llaurado & Rauret, 2007). Natural radioactive elements found in saline waters may come from the environment, ground, air, human activities, etc. Natural and saline waters may contain both alpha (from decay of uranium, thorium and their daughters) and beta Makale Gönderim Tarihi : 11/11/2019

(from decay of 40 K) emitters in varying levels, and they may cause health hazards when they take into the body (Damla et al., 2009; Zorer, Ceylan & Doğru, 2009).

The determination of gross α and β activities in surface and underground waters may assist in the evaluation of the total natural environmental radiation dose for human health in the related fields (Damla et al., 2009; Zorer, Ceylan & Doğru, 2009; Atsor, Akpa & Akombor, 2015; Teğin, Yolbaş & Acar, 2017). Gross α and β activity concentrations in drinking (Damla et al., 2009), natural mineral (Teğin, Yolbaş & Acar, 2017; Taşkın et al., 2013; Gültekin & Dilek, 2005), river and lake (Zorer, Ceylan & Doğru, 2009) waters have been determined in various fields in the world for evaluation of the gross α and β activity contents. In many countries, water quality standards are regulated according to their economic, technical and political interests (Damla et al., 2009). When the gross α and β activity levels in drinking, saline or ground waters are below the recommended activity levels of the World Health Organization (WHO, 2011), the United States Environmental Protection Agency (USEPA, 2011) and Turkish standards (TS 266, 2005; TS 9130, 2010), these waters can be used for human consumption (Zorer, Ceylan & Doğru, 2009; WHO, 2011; Bonotto et al., 2009). If the activity concentrations in these saline waters are above the recommended values, they must be controlled by regularly measuring the activity concentrations in different seasons of the year (Damla et al., 2009; Damla et al., 2006). There has not been any information about gross α and β activities and metal contents reported in saline waters taken from Siirt region so far. These saline waters are consumed for domestic uses, local irrigations and salt production. The determinations of α and β activities and metal levels in these waters are, therefore, very important for protecting of human health and environment from harmful effects of radiation and toxic metals (Teğin, Yolbas & Acar, 2017; Taskin et al., 2013; Korkmaz Görür et al., 2011; Dueñas et al., 1998; Örgün et al., 2005; Ismail, Kullab & Saqan, 2009).

Chemometric analysis techniques such as principal component analysis (PCA), correlation analyses, linear discriminate analysis (LDA) and cluster analysis (CA) may improve upward explication and categorization among element, gross α and β activity levels in the environment for multivariate datum sets. PCA is especially, a useful statistical datum reduction technique to clarify most of the variances in the datum sets, by declining the number of variables to a few correlated components (Anderson, 2003). PCA has been used to evaluate whether or not there is a relationship between the element, gross α and β activity contents with the origins of sampling sites (Teğin, Yolbaş & Acar, 2017; Kara, 2009; Karadas & Kara, 2012; Fernandez-Caceres et al., 2001; Marcos et al., 1998; Moreda-Pineiro, Fisher & Hill, 2003). CA may be a practical technology to categorize likenesses or unlikeness of individuals or states because of their homogeneous gatherings or hereditary relations named as cluster. Individuals in every cluster may be inclined to be like their relations or attache and dissimilar to individuals in the other clusters. These two factors are important for the classification of similitudes or unlikeness for individuals or states due to their classifications (Teğin, Yolbaş & Acar, 2012; Tanasković, Golobocanin, & Miljević, 2012).

In this study, gross α and β activities along with the concentrations of the elements Na, Mg, Al, Si, S, Cl, K, Ca, Fe, Cr and Sr in saline waters from Gölgelikonak, Üzümlük, Akdoğmuş, Çöl, Tuzkuyusu, Çaykaya and Tuzcular regions in the Siirt Region were measured by PIC - MPC 9604 model α/β counting system and Wavelength Dispersive X-ray Fluorescence Spectrometry (WDXRF). WDXRF, being a non-destructive, fast and accurate method with minimum sample preparation, is the mostly used analytical technique (Söğüt et al., 2011). The determined gross α and β activity levels were compared and assessed with the recommended levels proposed by WHO, USEPA, the Turkish standards (TS) for drinking and mineral water and along with the values in literature. PCA and CA techniques for the classification of saline waters and elements were used for chemometric studies.

2. Material and method

2.1. Chemicals

A solution of nitric acid (1% v/v), prepared by diluting HNO₃ (65% m/m, Explanatory Grade, Merck, Darmstadt, Germany) with deionized water (resistivity 18.3 M Ω cm), was used to clean polypropylene bottles, Teflon beakers and glassware. Deionized water was prepared by Human power I+ (Human Corporation, Korea)

2.2. Collection and preparation of waters

Saline waters from Gölgelikonak, Üzümlük, Akdoğmuş, Çöl, Tuzkuyusu, Çaykaya and Tuzcular regions were collected to determine the radioactivity and the element concentrations. Map of the sampling sites and their detailed descriptions are shown in Figure 1 and presented in Table 1, respectively. Polypropylene bottles (capacity about 2.5 L) were washed with prepared HNO₃ solution (1% v/v) to decrease contaminations from bottles and rinsed three times with the sample solution. Three original saline waters in three bottles were taken from each station and then, acidified with 5 mL concentrated HNO₃ per 2.5 L of sample solution in situ, to avoid the precipitation or adsorption of samples to the bottle walls, and diluted to the mark with sample solution. After getting into laboratory, water samples (20-100 mL portions in 100-mL Teflon beakers) were evaporated gradually down to about 5 mL volumes by IR lamps at 65 °C without boiling. Then, each water residue sample was transferred quantitatively into a stainless-steel planchette by cleaning inner surface of Teflon beaker with HNO₃ solution (1% v/v) and left to dry again under the IR lamp until complete precipitation was achieved. Precipitate in the planchette was put into a desiccator and allowed to reach the laboratory temperature. Each precipitate was weighed precisely (Jobbágy et al., 2011) and then immediately put into a PIC-MPC 9604 α/β counting system to measure gross α and β activity levels.

Determination of elemental concentrations of saline water was performed with WDXRF spectrometer. For this analysis, 400 mL of the water was put into 400 mL - glass beaker cleaned with 1% v/v of HNO₃ solution to prevent the adsorption of radionuclides and some metals to the surfaces of beaker. After evaporation of the sample under IR lamp, the precipitate was pressed with automatic press (40 tones) and weighed precisely. The prepared sample was measured directly with WDXRF spectrometer.

Location of	Geographic	cal Coordinates	Altitude	Sample Volume	
sample	Latitude N	Longitude E	- (III)	(IIIL)	
Akdoğmuş	37°51'38.27"	42° 3,06 '6.58"	622	25 ± 1	
Çöl	37°51'30.58"	42° 4'56.52"	695	40 ± 1	
Üzümlük	37°46' 69,90"	42°5' 44,3"	730	25 ± 1	
Gölgelikonak	37°46'21.46"	42° 6'53.96"	768	25 ± 1	
Tuzcular	37°53' 26,41"	42° 24' 10,41"	1334	25 ± 1	
Çaykaya	37°4'39,07"	41°45 '23,78"	598	25 ± 1	
Tuzkuyusu	38° 0'25.89"	41°50'36.23"	654	25 ± 1	

Table 1. Locations and parameters for saline waters sampled.



Figure 1. Map of the sampling sites.

2.3. Instrumentation

Gross α and β countings in saline waters were performed by a multi-detector α/β counting framework (Protean Instrument Corporation (PIC), USA) including one or more MPC-9604 units. Each PIC-MPC-9604 unit holds four sample detectors, guard detectors and a lid protecting attenuation of external radiation. A sample detector contains gas flow ultra-thin window-type counter (Zorer, Ceylan & Doğru, 2009; Teğin, Yolbaş & Acar, 2017; Acar et al., 2013). A gas mixture containing of 10% methane and 90% argon and stainless-steel planchette ~ 5 cm in diameter were used. An empty planchette was also used for background counting. The operating voltage for the detector was selected as 1515 V.

WDXRF spectrometer (A PAN - analytical Advanced Axios) equipped with an SST-mAX X-Ray tube, which has 4 kW power yield and 160 mA maximum emission current was used for elemental concentrations (Teğin, Yolbaş & Acar, 2017; Acar et al., 2013).

2.4. Gross α and β activity determinations in saline waters

Alpha and β energy and efficiency calibrations by α/β counting framework were carried out using concentrations of ²⁴¹Am (913 Bq) and ⁹⁰Sr (931 Bq) standard solutions, respectively. For each sample, counting time was set as 900 minutes because gross α and β activity contents in waters were very low. Decay factor was 1.00. The precipitates in planchettes prepared were counted. An empty planchette was also counted to determine the background for sample and detector. Background counting times, ranging from 7900 to 26500 min, efficiencies obtained for precipitates were presented in Table 2. Gross α and β activities (in Bq L⁻¹), lower limits of detection (LLD) (in dpm: disintegration per minute) and minimum detectable concentrations (MDC) in saline waters were determined by using the equations given as follows:

$$A (Bq L^{-1}) = \frac{A_f}{AD.\varepsilon\% AF.V.60}$$
(1)

$$LLD(dpm) = \frac{\frac{3}{T_s} + 3.29}{AD.\varepsilon\%AF} \sqrt{\frac{R_B}{T_s} + \frac{R_B}{T_B}}$$
(Brodsky method) (2)

$$MDC (Bq L^{-1}) = \frac{LLD}{V.60}$$
(Brodsky method) (3)

Makale Gönderim Tarihi : 11/11/2019 Makale Kabul Tarihi :31/12/2019 where, A_f is the net counting obtained from gross α or gross β counting (in count min⁻¹) in sample by subtracting the background counting. *AD* is an activity divisor. For α and β activity divisors are denoted as AD_A and AD_B , respectively. If unused, they are used as 1.0. In general, these parameters change the efficiency value utilized in any equation. The ε is the % efficiency of detector used for gross α or gross β counting. *AF* is the efficiency decay factor of α or β or α - β for water samples removed from the calibration decay graphs (Teğin, Yolbaş, & Acar, 2017; Acar et al., 2013). *V* (in L) is sample volume. *Ts* and *TB* are counting times (in minutes) for sample and background, respectively. *RB* is counting rate (count min⁻¹) of background for gross α or gross β (Teğin, Yolbaş, & Acar, 2017; Acar et al., 2013; Ródenas et al., 2008). The $\varepsilon\%$, *AF*, *LLD* and *MDC* values achieved from the α/β counting system were given in Table 2. Activity concentrations (*A* in *Bq L*⁻¹), *LLD* (in disintegration per minute; dpm) and *MDC* (in *Bq L*⁻¹) values for water samples were calculated using the Equations (1) - (3), sample volumes given in Table 1 and instrumental parameters given in Table 2.

Table	e 2. Parameters	obtained	d from α/β cou	unting sy	rstem.	
Location of sample	Background	α/β	Efficiency ^a	AF	LLD	MDC
	time (min)		(8 %)		(dpm)	$(\operatorname{Bq} L^{-1})$
Akdoğmuş	7900	α	17.1 ± 0.2	0.82	0.24	0.16
		α-β	26.7 ± 0.6	1.02		
		β	40.9 ± 0.7	1.02	0.23	0.15
Çöl	7900	α	16.9 ± 0.2	0.83	0.27	0.11
		$A - \beta$	26.9 ± 0.6	1.03		
		β	42.3 ± 0.7	1.00	0.24	0.10
Üzümlük	26500	α	16.7 ± 0.2	0.66	0.29	0.19
		α-β	26.8 ± 0.6	1.07		
		β	40.1 ± 0.7	0.98	0.22	0.15
Gölgelikonak	25300	α	17.1 ± 0.2	0.71	0.27	0.18
		α-β	26.9 ± 0.6	1.06		
		β	41.2 ± 0.7	0.99	0.25	0.17
Tuzcular	16600	α	16.8 ± 0.2	0.60	0.28	0.19
		α-β	28.8 ± 0.6	1.08		
		β	40.6 ± 0.7	0.98	0.23	0.15
Çaykaya	16300	α	17.2 ± 0.2	0.60	0.30	0.20
		α-β	24.8 ± 0.6	1.08		
		β	41.5 ± 0.7	0.98	0.22	0.15
Tuzkuyusu	13600	α	16.9 ± 0.2	0.81	0.24	0.16
		α - β	27.8 ± 0.6	1.03		
		β	41.3 ± 0.7	0.98	0.23	0.16

^a Mean of three replicate efficiency measurements (N=3) with 95 % confidence level, $\overline{x} \pm \frac{ts}{\sqrt{N}}$.

3. Results and discussion

3.1. Checking activity levels in saline waters with regulations and literatures

Gross α and gross β activities found in saline waters from Siirt regions are given in Table 3. As seen in Table 3, the results were given as the means of gross α and β activity concentrations with statistical errors from three replicate measurements of three water samples taken from each station. Also, as seen in Table 3, the gross α contents are lower than gross β values for each water sample. The lowest gross α and β concentrations were found in water samples taken from Gölgelikonak and Tuzcular, while the highest gross α and β concentrations were found in water samples taken from Akdoğmuş and Cöl, respectively.

Ranges of gross α (0.44 - 0.62 Bq L⁻¹) and gross β (0.93 - 1.67 Bq L⁻¹) activity contents found in saline waters (Table 3) were compared with guideline activity levels for drinking waters given by WHO (0.5 Bq L⁻¹ for α and 1.0 Bq L⁻¹ for β) (WHO, 2011), USEPA (0.55 Bq L⁻¹ for α and 1.85 Bq L⁻¹ for β) (USEPA, 2011), Turkish standard (0.1 Bq L⁻¹ for α and 1.0 Bq L⁻¹ for β) (TS 266, 2005) and recommended levels for natural mineral waters given by Turkish standard (1.5 Bq L⁻¹ for α and 2.0 Bq L⁻¹ for β) (TS 9130, 2010). It is clear that, gross α and β activity results in some water samples were smaller than the values reported by WHO, USEPA and Turkish standard (TS 266, 2005) for drinking waters. On the other hand, the gross α and β activities found in all samples were lower than the activity concentrations recommended for natural mineral waters given by Turkish standard (TS 9130, 2010).

Activity concentrations in saline waters (Table 3) were also compared with some previous literature results (gross α and gross β were described as α and β) such as thermal spring water from Batman (3.91 Bq L⁻¹ for α and 2.1 Bq L⁻¹ for β) (Damla et al., 2009), mineral water (0.01 – 3.04 Bq L⁻¹ for α and 0.02 – 4.85 Bq L⁻¹ for β) and thermal spa water (0.02 – 3.07 Bq L⁻¹ for α and 0.08 – 17.96 Bq L⁻¹ for β) (Taşkın et al., 2013), bottled mineral waters (average value of 0.541 Bq L⁻¹ for α and average value of 0.813 Bq L⁻¹ for β) (Şahin, Dirican & Yüksek, 2018), natural radioactivity concentrations in andalusian spas (0.02 – 2.42 Bq L⁻¹ for α and 0.05 – 5.80 Bq L⁻¹ for β) (Dueñas et al., 1998), Balatonfüred (1.75 Bq L⁻¹ for α and 2.02 Bq L⁻¹ for β) (Söğüt et al., 2011), Haymana (2.58 Bq L⁻¹ for α and 1.82 Bq L⁻¹ for β) and Kizilcahamam (1.85 Bq L⁻¹ for α and 2.61 Bq L⁻¹ for β) spa waters (Acar et al., 2013). As a result, the gross α and gross β concentrations in saline waters were either in agreement with or lower than the literature values.

The *LLD* and *MDC* values found in waters (Table 2) were 0.24 - 0.30 dpm and 0.11 - 0.20 Bq L⁻¹ for gross α , 0.22 - 0.25 dpm and 0.10 - 0.17 Bq L⁻¹ for gross β , respectively. The *MDC* values found in waters were in good agreement with the literature value (0.13 Bq L⁻¹ for α and 1.30 Bq L⁻¹ for β) reported for sea water (Zapata-Garcia, Llaurado & Rauret, 2007).

3.2. Element analysis in saline waters

The contents of elements in the precipitates of saline waters were determined using WDXRF. Mean and standard deviation of triplicate concentration measurements of an element found for each sampling site were given in Table 3. As seen in Table 3, Na, Mg, Al, Si, K, Ca, Fe, Sr, Cl, S and Cr levels were determined. However, U and Th concentrations in samples were not measured by WDXRF because their concentrations were lower than the detection limit of 2 mg kg⁻¹. Therefore, origin of gross α and β levels in these waters could not be studied. β activity maybe come from ⁴⁰K (Ismail, Kullab & Saqan, 2009; Blanchard et al., 1985) and/or ⁹⁰Sr, but there are no linear relations between the gross β activities and K and Sr contents in water samples (Table 3). Concentrations of Ca, K, Na and Mg found in samples (Table 3) were compared with the values set by Turkish standard (200 mg L⁻¹, 12 mg L⁻¹, 175 mg L⁻¹ and 50 mg L⁻¹ for Ca, K, Na and Mg,

respectively) (TS 266, 2005). Ca, K, Na and Mg contents in saline waters from Gölgelikonak, Üzümlük, Akdoğmuş, Çöl, Tuzkuyusu, Çaykaya and Tuzcular were higher than the values reported by the Turkish standard (TS 266, 2005).

Element /	Unit	Akdoğmuş	Çöl	Üzümlük	Gölgelikonak	Tuzcular	Çaykaya	Tuzkuyusu
Radioactivity								
Na	g kg ⁻¹	396 ± 14	319 ± 13	371 ± 15	371 ± 16	384 ± 16	397 ± 16	466 ± 19
Κ	g kg ⁻¹	2.1 ± 0.1	9.0 ± 0.4	1.2 ± 0.1	1.2 ± 0.1	0.6 ± 0.1	0.9 ± 0.1	3.0 ± 0.1
Mg	g kg ⁻¹	8.0 ± 0.3	75 ± 3	3.3 ± 0.1	3.3 ± 0.1	0.5 ± 0.1	4.7 ± 0.2	43 ± 2
Al	g kg ⁻¹	n.d. ^b	n.d. ^b	3.1 ± 0.2	3.1 ± 0.2	3.3 ± 0.2	1.2 ± 0.1	n.d. ^b
Si	g kg-1	1.2 ± 0.1	1.2 ± 0.1	9.1 ± 0.4	9.1 ± 0.5	9.7 ± 0.5	2.5 ± 0.1	1.4 ± 0.1
S	g kg ⁻¹	14.3 ± 0.6	27.8 ± 1.2	10.3 ± 0.4	10.3 ± 0.4	2.2 ± 0.1	2.2 ± 0.1	11.5 ± 0.5
Cl	g kg-1	542 ± 22	510 ± 21	524 ± 21	525 ± 22	548 ± 23	578 ± 24	501 ± 21
Ca	g kg ⁻¹	10.9 ± 0.5	11.8 ± 0.5	33.1 ± 1.4	33.1 ± 1.3	18.5 ± 0.8	3.8 ± 0.2	6.8 ± 0.3
Fe	g kg ⁻¹	0.12 ± 0.01	0.14 ± 0.01	1.46 ± 0.06	1.43 ± 0.07	1.64 ± 0.07	0.66 ± 0.03	0.34 ± 0.02
Cr	mg kg ⁻¹	8.7 ± 0.3	5.2 ± 0.2	12.0 ± 0.5	21.3 ± 1.0	23.5 ± 1.1	8.8 ± 0.4	1.7 ± 0.1
Sr	mg kg ⁻¹	48 ± 2	78 ± 3	75 ± 3	44 ± 2	24.4 ± 1.0	15.4 ± 0.6	60 ± 2
Gross α	Bq L ⁻¹	0.62 ± 0.03	0.58 ± 0.19	0.52 ± 0.02	0.44 ± 0.01	0.54 ± 0.02	0.48 ± 0.02	0.58 ± 0.02
Gross β	Bq L ⁻¹	1.04 ± 0.04	1.67 ± 0.05	1.19 ± 0.04	1.05 ± 0.04	0.93 ± 0.04	1.11 ± 0.05	1.42 ± 0.05

Table 3. Element concentrations and activity levels determined in saline water samples^a.

^a Mean of three replicate measurements from samples (N= 3) at 95 % confidence level. ^b n.d.: Not determined.

3.3. Correlation analysis

Correlation analysis of metal concentrations and activity concentrations in saline waters is important to describe the parameters such as geological composition of the water source and its mineral level (Teğin, Yolbaş & Acar, 2017; Söğüt et al., 2011). The correlation coefficients of elements and activity contents determined in saline waters were calculated from correlation matrix and illustrated in Table 4. From the Table 4, the correlations were pointed out that the relations among the concentrations of elements were complex and difficult to clarify individually. The linear correlation coefficients of elements at 95% and 99% confidence level were examined. Pairs of Mg – K (0.950), S - K (0.919), gross β – K (0.898), gross β – Mg (0.957), Si - Al (0.994), Fe - Al (0.962) and Fe - Si (0.984) were showed very high and significant correlations at 99% confidence level. Pairs of S - Mg (0.829), Ca - Al (0.871), Cr -Al (0.860), Ca - Si (0.841), Cr - Si (0.871), Sr - S (0.799), gross β – S (0.804), Fe - Ca (0.755), Cr - Fe (0.853) and gross β – Sr (0.716) were showed high correlations at 95% confidence level. In addition, the pairs of Cr - Ca (0.636), Sr - K (0.3635) and Sr - Mg (0.616) were showed moderate correlations at 95% confidence level.

Na	Na 1.000	K	Mg	Al	Si	S	Cl	Ca	Fe	Cr	Sr	Gross a	Gross β
K	-0.482	1.000											
Mg	-0.212	0.950**	1.000										
Al	-0.229	-0.501	-0.570	1.000									
Si	-0.211	-0.551	-0.615	0.994**	1.000								
S	-0.488	0.919**	0.829*	-0.404	-0.478	1.000							
Cl	-0.030	-0.539	-0.634	0.003	0.087	-0.661	1.000						
Ca	-0.367	-0.283	-0.396	0.871^{*}	0.841*	-0.051	-0.244	1.000					
Fe	-0.125	-0.620	-0.654	0.962**	0.984**	-0.598	0.185	0.755*	1.000				
Cr	-0.281	-0.537	-0.654	0.860*	0.871^{*}	-0.499	0.326	0.636	0.853*	1.000			
Sr	-0.273	0.635	0.616	-0.077	-0.154	0.799*	-0.839*	0.285	-0.268	-0.458	1.000		
Gross a	0.149	0.452	0.474	-0.542	-0.604	0.484	-0.329	-0.498	-0.665	-0.558	0.394	1.000	
<u>Gross</u> β	-0.200	0 .898 **	0.957**	-0.535	-0.571	0.804*	-0.651	-0.297	-0.600	-0.732	0.716	0.366	1.000

Table 4. Correlation matrix for the element concentrations in saline water samples (Listwise, N=7)

** Correlation is significant at the 0.01 level (2-tailed).

* Correlation is significant at the 0.05 level (2-tailed).

3.4. Principal component analysis

The more explications among the metals, gross α and β activity concentrations and the source of the saline waters could be provided by utilizing chemometric methods such as PCA. The PCA was planned to decrease a set of real factors such as saline water chemical composition into a small number of signals for analyzing the similarities and distinctions available among sighted factors that were not easily marked from basic correlation analysis (Teğin, Yolbaş & Acar, 2017; Söğüt et al., 2011). PCA was performed by correlation matrix using PCA subroutine of IBM SPSS statistic V22 package to define the fundamental design from elements and to assist the explication of datum sets (Teğin, Yolbaş & Acar, 2017). PCA was applied to the matrix of the whole metal concentrations and to the gross α and β activities $(13 \times 7 \text{ cases})$ in the saline waters. The three factor loadings obtained after executing the maximum turning and cumulatives were presented in Table 5. The results in Table 5 were showed that two eigenvalues >1 were described about 90.39% of the whole variety, the third eigenvalue was described about 9.38% of variety. Principal component loading for saline waters was taken out and three components were described about 90.39% of the whole variety with the addition of each factor being 56.23%, 24.78% and 9.38%, respectively. Factor 1 showed high loadings for Al, Si, Ca, Fe and Cr, and described about 56.23% of the whole variety. Factor 2 was loaded by gross α and β , Sr, S and Mg, and described nearly 24.78% of whole variety. Factor 3 was loaded by Cl and Na and was described 9.38% of whole variety.

The two way-loadings and score plots of elements, gross α and β activities and locations were shown in Figure 2. Every fundamental component was plotted against PC1 to indicate high percentage of whole variety (56.23 – 24.78%). A 3-D plot of the PCA charging was shown in Figure 3. In this figure, the relations among the elements, activity concentrations and locations were readily shown.

Classification of the species from the view point of metal concentrations, gross α and β activity contents were accomplished by utilizing the three-way PC score graphs. The highest percentage of whole variety around 81.01% was detected with PC 1–2, while PC 1–3 score graph was indicated to be around 65.61% of whole variety. It is clear from PC 1–2 and PC 1–3 graphs of Figure 2, and Figure 3 along with Table 5, saline waters can be clustered into four

groups considering the element contents, gross α and β activity concentrations and the geological features of saline waters. According to the results of PCA, these groups were classified as follows:

Group 1: Akdoğmuş, Çaykaya and Tuzcular

Group 2: Gölgelikonak and Üzümlük

Group 3: Tuzkuyusu

Group 4: Çöl

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Element /	The loading The score							
Activity	PC 1	PC 2	PC 3	Vocational	PC 1	PC 2	PC 3	
Al	0.985 ^a	-0.065	-0.049	Akdoğmuş	-0.79949	-0.2659	-0.29735	
Si	0.977	-0.148	-0.053	Çöl	-0.71124	1.08196	1.80312	
Ca	0.935	0.230	0.064	Üzümlük	1.11436	0.68121	-0.2855	
Fe	0.932	-0.251	-0.106	Gölgelikonak	1.24795	-0.05294	0.23735	
Cr	0.822	-0.433	0.107	Tuzcular	0.81573	-0.78923	-0.10586	
Gross a	-0.597	0.403	-0.121	Çaykaya	-0.81903	-1.64177	0.2179	
Cl	-0.054	-0.967	0.096	Tuzkuyusu	-0.84827	0.98667	-1.56966	
Sr	0.007	0.946	0.154					
S	-0.321	0.747	0.531					
Gross β	-0.477	0.731	0.340					
Mg	-0.537	0.675	0.387					
Na	-0.282	-0.084	-0.934					
Κ	-0.454	0.618	0.620					
Eigenvalue	7.31	3.22	1.22					
Variance (%)	56.23	24.78	9.38					
Cumulative (%)	56.23	81.01	90.39					

^a The bold values are the highest values obtained in the loadings.



Figure 2. The score and loading plots (a and c are the score plots and b and d, the loading plots).



Figure 3. The classification of saline waters

3.5. Cluster analysis

This technique is a sorting process that involves the measurement of likeness among the objects to be clustered (Teğin, Yolbaş & Acar, 2017; Karadas & Kara, 2012). Saline waters can be grouped into clusters due to their similarities. The estimation of similarity is based on the Euclidean span. The clustering technique utilized was the Ward's technique and it was performed by utilizing the statistical package (IBM SPSS Statistics 22) (Teğin, Yolbaş & Acar, 2017). The results found in cluster examination were illustrated eventually by dendrograms provided in Figures 4 and 5. As seen in Figure 4, fundamentally four groups were located. These groups were exemplified the similarity on the foundations from claiming metals, gross α and β contents in saline waters. After the implementation of PCA and CA, similar metals and gross α/β activity contents acquired from distinct saline waters were gathered. The same results obtained with PCA and they were shown in the followings:

Group 1: Akdoğmuş, Çaykaya and Tuzcular

Group 2: Gölgelikonak and Üzümlük

Group 3: Tuzkuyusu

Group 4: Çöl

As seen in Figure 5, mainly three cluster analysis for concentrations of elements, gross α and β activity levels were observed. Group 1 owned Na and Cl; Group 2 owned Si, Fe, Cr and Ca; and Group 3 owned K, S, Mg, gross α and β .



Dendrogram Ward Linkage, Squared Euclidean Distance

Figure 4. Dendrogram of cluster analysis for saline water places

Dendrogram Ward Linkage, Correlation Coefficient Distance



Figure 5. Dendrogram of cluster analysis for element concentrations and radioactivity levels

4. Conclusions

In this study, gross α and gross β activities and metal contents were measured in saline waters collected from Gölgelikonak, Üzümlük, Akdoğmuş, Çöl, Tuzkuyusu, Çaykaya and Tuzcular regions of the Siirt Region. Gross α and β concentrations in saline waters were compared with the recommended values given by WHO, USEPA and Turkish standards and they were usually in agreement with reported values and literature results.

Chemometric assessment was demonstrated that there was a relationship between saline waters from Na, Si, Fe, Cr, Ca, K, Mg etc. metal concentrations. There is no any relationship between gross α / β activities and element concentrations of saline waters taken from different regions of Siirt. Types of saline waters were categorized into four groups by PCA and CA through chemometric evaluations of element concentrations, gross α and β activities with very similar groupings. The first group contains Akdoğmuş, Çaykaya and Tuzcular, the second group Gölgelikonak and Üzümlük, the third group Tuzkuyusu, and the fourth group contains Çöl, respectively. Whole group members determined by PCA and CA were in the predicted class that 100.0% of main grouped conditions were categorized correctly.

Gross α and β activities and element concentrations in saline waters from different regions of Siirt may be used for the evaluation of possible changes in radioactivity and element levels in the future as database for investigations.

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7. Conflict of interest

İbrahim Teğin and Orhan Acar have reported that they have no conflict of interests in the study done.

8. Human and animal rights and informed consent

This study is not interested with human or animal subjects.

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