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Research Article

Determination of Heavy Metal Distribution of Yenikapı (Istanbul) Sea Sediments Using Libs Method

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Abstract

In this study, the toxic element concentrations of the marine sediments of the Yenikapı (Istanbul) coast were determined by LIBS (Laser Induced Plasma Spectroscopy) technique. Six samples of core sediment were taken from the region for analysis. The samples were brought to the laboratory and made ready for analysis. The area is open to pollution from boat waste, fishing waste and domestic waste water. The LIBS method has advantages such as faster results than all other conventional methods, being portable, low analysis costs, not being damaged of sediments, reused after analysis, and short preparation process, and it is an important and practical technique for determining elements of natural and anthropogenic origin. The method is used in many fields such as environment, geology, forensic medicine, food, health and it has been found to give accurate and fast results.The analysis results obtained with the LIBS method give the probability of the elements in that sample as a% value. Analysis does not provide the amount of elements in the sample. Although this is seen as a disadvantage, this method gives very useful results for practical and preliminary research. In this study, ECCO®2 branded LIBS machine was used. The heavy metal distribution of six sediment samples taken from the Yenikapı region is shown by graphs. According to LIBS analysis results, it was seen that the distribution of elements such as Fe, K, Li, Sr, Zn and Mg was higher in percentage. All elemental data obtained were examined by the basic component analysis (PCA) method in the literature. Thanks to this analysis, the contribution of each variable to the content of the sediment has been tried to be revealed. Analyzes showed 83.39% discrimination for six samples taken from the region. It has been determined that Fe, Al, Mn, Ca, K, Na and Zn elements contribute more in the composition of sediment samples. The contents of six samples taken from the region were found to be similar. Elemental compositions of marine sediments were revealed in the study area. As a result of the analysis, it was seen that LIBS method can be used on sediment samples.

Keywords: LIBS, Sediment, Marmara Sea, Yenikapı, PCA.

Yenikapı (İstanbul) Deniz Sedimalarinin Ağır Metal Dağılımının Libs Yöntemi İle Belirlenmesi

Öz

Bu çalışmada, Marmara Denizi Yenikapı (İstanbul) kıyısındaki denizel sedimanların toksik element konsantrasyonları LIBS (Laser Induced Plasma Spectroscopy) tekniği ile belirlenmiştir. Analiz için bölgeden altı adet yüzeysel sediman numunesi alınmıştır. Numuneler laboratuvar ortamına getirilerek analiz için hazır hale getirilmiştir. Bölge tekne atıklarından, balıkçılardan ve evsel atık sulardan kirlenmeye açıktır. LIBS yöntemi, diğer tüm geleneksel yöntemlerden daha hızlı sonuç alma, taşınabilir olması, düşük analiz maliyetleri, numunenin analiz sırasında hasar görmemesi ve tekrar kullanılması ve kısa hazırlık süreci gibi avantajlara sahiptir. Doğal jeolojik yapının ve antropojenik kaynakların bileşiminin belirlenmesi için önemli ve pratik bir tekniktir. Yöntem çevre, jeoloji, adli tıp, gıda, sağlık vb. birçok alanda kullanılmaktadır ve doğru ve hızlı sonuçlar verdiği tespit edilmiştir. LIBS yöntemi ile elde edilen analiz sonuçları o numunedeki elementlerin olasılığını % değer olarak verir. Analiz, numunedeki elementlerin miktarını sağlamaz. Bu bir dezavantaj olarak görülse de bu yöntem pratik ve ön araştırmalar için oldukça faydalı sonuçlar vermektedir. Bu çalışmada ECCO®2 markalı LIBS cihazı kullanılmıştır. Yenikapı bölgesinden alınan altı sediman örneğinin ağır metal dağılımı grafiklerle gösterilmiştir. LIBS analiz sonuçlarına göre Fe, K, Li, Sr, Zn ve Mg gibi elementlerin dağılımının yüzde olarak daha yüksek olduğu görülmüştür. Elde edilen tüm veriler, temel bileşen analizi (PCA) yöntemi ile incelenmiştir. Bu analiz sayesinde her değişkenin sedimanın içeriğine katkısı ortaya çıkarılmaya çalışılmıştır. Analizler, bölgeden alınan altı numune için % 83.39 ayrım göstermiştir.

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Sediman numunelerinin bileşiminde Fe, Al, Mn, Ca, K, Na ve Zn elementlerinin katkısının daha fazla olduğu tespit edilmiştir. Bölgeden alınan altı numunenin içeriği birbirine benzer bulunmuştur. Çalışma alanında denizel sedimanların elementel kompozisyonları ortaya konmuştur. Analiz sonucunda, LIBS yönteminin sediman örneklerinde kullanılabileceği görülmüştür.

Anahtar Kelimeler: LIBS, Sediman, Marmara Denizi, Yenikapı, PCA.

1. Introduction

Investigation of marine sediments in marine pollution studies has been one of the most important issues in recent years. Marine sediments form a habitat for living creatures that live in the sea connected to sediments and at the bottom. Therefore, it is very important to identify and monitor the pollution in the sediment. Heavy metals are one of the most important pollutant parameters in marine sediments. Heavy metals accumulate in the environment in which they are found because they cannot be physically, chemically and biologically degraded in nature. Surface waters, industrial wastewater, solid waste seepage waters, atmospheric transport, ship traffic and Natural Resources (geological structure, thermal waters, mineral deposits, etc.) heavy metal is mixed into the marine environment. Heavy metals that cannot be broken down either form new compounds with different elements or ionize. While these processes continue, the water column circulates between the sediment and the living body and accumulates in the area where it collapses [1, 2, 3, 4]. Traditional methods (ICP-OES, ICP-MS, XRF, etc.) has been used in many studies for many years in the determination of heavy metals [5, 6, 7, 8, 9].

Although these methods have many advantages, disadvantages such as long preliminary processes, damage to the sample, inability to be portable, practical methods have been investigated. The LIBS method has been a preferred method in many areas in recent years, as it is portable and does not require pre-processing. LIBS method is used in many different fields such as environment, geology, food, medicine, forensic medicine [10, 11, 12, 13, 14, 15, 16]. Although the LIBS method is used in many areas, its use in marine sediment analysis is quite new. In this study, the elemental analysis of the marine sediment samples taken from the Yenikapı (Istanbul) coast was done by LIBS method and the distribution of heavy metals was investigated. Thanks to this distribution, the pollution potential of the region has been investigated. In addition, the LIBS method for determining toxic elements in the field of study was used for the first time in this study. And LIBS analysis has been shown to be usable in toxic element analysis. By applying PCA analysis to the results of LIBS analysis, the interpretation of the results has been made easier. PCA accepts the original data as a set of linear variables and tries to reveal the contribution of each variable to the basic component.

2. Material and Method

2.1. Sample Collection

In this work, six core sediments samples have been examined. Samples were taken from Yenikapı (İstanbul) coast. Samples were collected by core box method. The soil samples were selected on the basis of their representativity of investigation area. The coordinates of the samples are given in Table 1 and the location map are shown in Figure 1.

Figure 1. Investigation location map

2.2. LIBS Analysis

Laser Induced Plasma Spectroscopy (LIBS) is a method of optical emission spectroscopy used for multiple analysis of elements. This method is able to make elemental analysis of all conductive and nonconductive substances [17, 18, 19]. In the analysis, the laser beam emanating from a high energy laser source is focused on the sample surface with various optics. The high-energy laser beam creates a spark where it is focused and evaporates the parts in the sample, causing it to decompose into neutral, ions and atoms and form plasma. The plasma formed on the surface is transmitted to the spectrometer by a collector lens. Atomic lines in the spectrum are analyzed by correlating with elements, and the intensity of atomic lines is correlated with elemental concentration. Approximately 0.1 microseconds after plasma formation, first ionic diffusion and then atomic diffusion can be detected from the elements. Calibration curves are usually drawn when determining the concentration of any element in the sample. The slope of this curve gives information about the sensitivity of the method [20, 21, 22]. The optimum instrumental parameters for soil analysis have been obtained when repetition rate, td, and tw equaled 10 Hz, 1 µs, and 10 µs, respectively. Standard reference material (SRM-2586) has been used to prepare pellets for the parameter analysis [23, 24].

Sample preparation and Measurement: For elemental analysis, 25 g of samples were taken from each core from sediment samples. The sediment samples taken were placed in a specially made pellet container with 20-25 gr and compressed in the press machine under a pressure of about 100 bar for 5 seconds. This shape of the samples is called “pellet”. Standard reference material (SRM-2586) was used to prepare pellets for the parameter analysis. The pelleted samples were placed in sealed bags and sent for LIBS analysis [16].

3. Results and Discussion

3.1. Evaluation of LIBS Analysis Results

Analysis of sediment samples was carried out by LIBS technique. There are approximately 18 elements determined by LIBS technique in sediment samples. Looking at the results of the LIBS analysis, the distribution of elements such as Fe, K, Li, Sr and Mg was found to be higher in percentage terms. When the comparison is made, the observed differences are due to random and systematic errors in the measurements made, and since these differences are very small, it can be said that the results are in harmony.

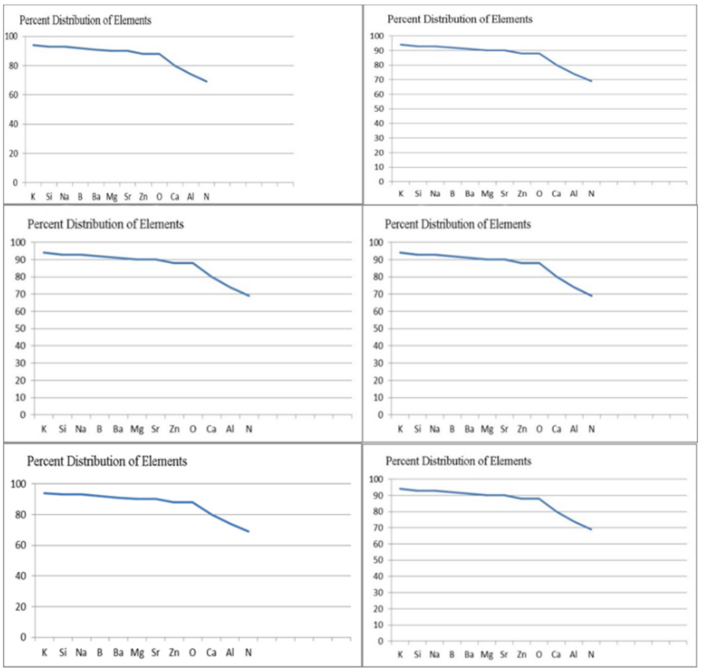

Figure 2. Percentage distributions of the elements of the first, second, third, fourth, fifht and sixth samples

The results obtained in this study show that the LIBS technique applied in determining the heavy metal in sediments is successful. Elemental distributions of LIBS analysis results of six samples are shown in Figures 2, 3 and 4.

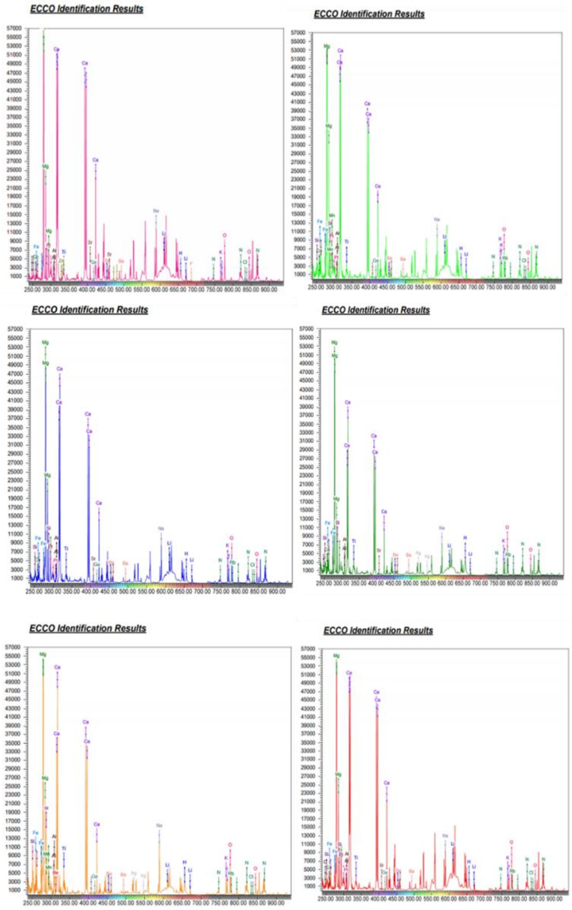

Figure 3. Spectra of the first, second, third, fourth, fifht and sixth samples

According to LIBS analysis results, the distribution of elements such as Fe, K, Li, Sr and Mg was found to be higher in percentage. The differences observed in comparison are due to random and systematic errors in the measurements made, and since these differences are very small, we can say that the results are in harmony.

Table 1. Comparison of the elements obtained in LIBS analysis

Rate	Sample 1	Sample 2	Sample 3
Mg (279.55) / Ca (317.93)	1.114	1.044	1.12
Mg (285.21) / Si (263.13)	13.194	6.003	6.736
Mg (285.21) / Fe (259.94)	6.986	3.729	3.947
Ca (534.95) / Pb (405.78)	6.026	2.65	5.483
Fe (438.35) / Mn (403.31)	7.177	5.392	5.632
Si (413.09) / Sr (407.77)	.02	.348	.155
Na (589) / Ca (558.88)	.793	1.005	1.093
Na (589) / Li (610.37)	2.318	2.493	2.907
Li (670.79) / F (685.6)	71.019	126.34	124.568
K (766.49) / N (862.92)	2.446	5.763	4.573
N (821.63) / O (777.42)	.38	.39	.389
Rate	**Sample 4**	**Sample 5**	**Sample 6**
Mg (279.55) / Ca (317.93)	1.399	1.078	1.115
Mg (285.21) / Si (263.13)	3.127	3.574	6.814
Mg (285.21) / Fe (259.94)	1.873	2.242	3.751
Ca (534.95) / Pb (405.78)	2.97	2.73	5.426
Fe (438.35) / Mn (403.31)	9.799	8.437	5.013
Si (413.09) / Sr (407.77)	.361	.556	.142
Na (589) / Ca (558.88)	1.504	2.239	.613
Na (589) / Li (610.37)	4.102	6.785	1.797
Li (670.79) / F (685.6)	57.987	77.268	72.722
K (766.49) / N (862.92)	4.629	5.451	4.359
N (821.63) / O (777.42)	.387	.383	.378

3.2. PCA Analysis and Results

Basic Component Analysis (PCA); It is one of the multivariate data analysis techniques used to reduce the size of data. In this technique, the total variation in the data set is explained through new 'principal components' that allow the original variables to be restated in several linear combinations and have no correlation between them. The best result is obtained with PCA when the variables that make up the data set have the highest negative or positive correlation with each other [25].

Table 2: PCA analysis results

PC	Eigen value	%Variance
1	5.00339	83.39
2	0.698365	11.639
3	0.206004	3.4334
4	0.0644832	1.0747
5	0.0218634	0.36439
6	0.005896	0.098267

In this study, basic Component Analysis (PCA) was used as a separation layer in order to reduce the number of variables and separate samples into groups. When the PCA analysis is performed, the contribution of the matching values of the elements that should be selected as components is 0%, that is, if it is not detected on the sample, it weakens the discrimination power of the PCA analysis. This is because the role of selected components in PCA analysis is quite large. Analysis results were carried out with PCA analysis techniques and the discrimination power of 83.39% was achieved.

The chart of the Eigen values is given in Figure 8. Using Eigen values, there are factors to be interpreted in PCA analysis. This factors greater than 1 are considered significant, and factors less than 1 are not considered.

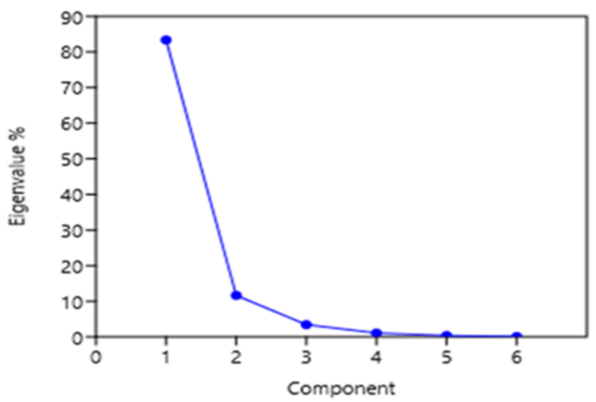

Figure 4. Scree Plot Chart

The total variance associated with each factor is shown in the Scree Plot chart. Break occurred after the 2nd point in the graph. And a certain decrease has been observed. Hence, the factor number was determined as one. No significant downward trend is seen after three and other factors. In other words, the contributions of the three and the following factors to the variance are close to each other.

Table 3. Relationships between element data detected in samples obtained from the study area

Element	1. Sample	2. Sample	3. Sample
Fe	0,748772	1,26141	0,9895
K	1,013045	1,1926	0,93084
Li	0,748772	1,055	0,75484
Sr	1,079113	0,77978	0,87217
O	0,616636	0,71097	0,57884
Si	0,682704	0,57337	0,63751
Mg	0,616636	0,29815	0,57884
Ca	-0,11011	0,22935	0,34417
Ba	0,418431	-0,11467	0,28551
Na	0,4845	-0,25228	-0,3598
Al	-0,969	-0,5275	-0,4185
N	-0,969	-0,5963	-0,2425
Cl	-0,90293	-1,21554	-2,2958
H	-2,15823	-2,10999	-1,7678
Ti	-1,29934	-1,28434	-0,8878
Element	**4. Sample**	**5. Sample**	**6. Sample**
Fe	0,82752	0,87319	0,8849
K	0,78709	0,83174	0,8849
Li	0,70622	0,74884	0,76275
Sr	0,58493	0,66595	0,59988
O	0,50406	0,5416	0,6406
Si	0,46363	0,6245	0,6406
Mg	0,62536	0,3758	0,47774
Ca	0,26146	0,29291	0,11129
Ba	0,4232	-0,2045	0,11129
Na	-0,02156	-0,0801	-0,0109
Al	-0,18329	-0,1216	-0,133
N	-0,30459	-0,2874	-0,2144
Cl	-3,01358	-3,0645	-0,7437
H	-1,11325	-1,0335	-1,0695
Ti	-0,54719	-0,163	-2,9424

According to the PCA results, the fact that these elements are in the same factor (F1) indicates that they enter the system from the same source. As is known, the high correlations observed between specific heavy metals are an indication that they are being discharged into the system from the same sources [26, 27, 28].

4. Conclusions and Recommendations

In the study, emission lines of Al, Ca, Fe, K, Mg, Mn, Na, Zn and Si were determined in all samples. Principal component analysis (PCA) was applied to LIBS spectra of the samples. Thanks to the principal component analysis, data that do not affect the composition are reduced. All variances for all items are included in the analysis. According to analysis result most of the examples showed a similar emission pattern. Looking at the analysis of sediments, the impact of external factors on the ecosystem is the possible cause of the observed anomalies. The combination of LIBS with multivariate data analysis has been suitable for the rapid detection of abnormal metal compositions in marine sediments.

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