ANALYSIS OF TOXIC ELEMENT WITH ICP-OES AND LIBS METHODS IN MARINE SEDIMENTS AROUND THE SEA OF MARMARA IN KAPIDAĞ PENINSULA

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Abstract

In this work, the LIBS (Laser Induced Breakdown Spectroscopy) and ICP-OES technique has been applied to the determination of total contents of heavy metals (Fe, Zn, Al, Mn, Co, Cr, Cu, Ni, Na, Mg, K, Ca) in soil samples of Marmara Sea. In order to validate the technique, LIBS data were compared with data obtained on the same soil samples by application of conventional Inductively Coupled Plasma ICP spectroscopy. The partial agreement obtained between the two sets of data suggested the potential applicability of the LIBS technique to the measurement of heavy metals in soils.

According to the results, it was seen that the elements determined by ICP-OES analysis were also determined by LIBS method. The LIBS method is an important and practical technique for determining the elements that are enriched with anthropogenic factors as well as the elements resulting from natural processes.

Key words: LIBS, ICP-OES, Marmara Sea, Toxic Element

1. Introduction

Sediment is a chemically-complex matrix which contains almost all the elements. In marine environments, sediments have a very important role as they create a living and nutrient environment for many living things. In particular, living creatures that cannot move more or less on their own, live in sediment. The sea is a living environment that is a source of nutrition

and water for living things. But it has also been the receiving environment in which waste can be disposed within industries and cities. This process has been increasing uncontrollably with the rapid development of the industry. Due to the longtime application of sewage sludge, livestock manure and industrial wastewater irrigation in the agricultural land, heavy metal contamination in sea sediments has become more serious [1].

Biodegradable toxic pollutants such as heavy metals accumulate in the marine environment and accumulate in the sediment. Pollutants accumulated in the sediment poison both sediments and living things because they are not biodegradable. The determination of the concentrations of these toxic elements which are involved in marine environment is very important for the environment and living health. In recent years, the LIBS method has been used to analyze toxic elements rather than traditional methods such as ICP-OES ([2],[3],[4]). Conventional atomic spectroscopic techniques have excellent analytical performance, but their sample preparation method is difficult. As an atomic emission spectroscopy technique, LIBS is especially much good at metal analysis. LIBS, is an insitu method which can analyze solids, liquids and gases and provides versatile detection options with minimum sample preparation processes [5]. Therefore, studies about soil analysis were mainly focused on metals [6].

LIBS is a recent analytical technique that is based upon the measurement of emission lines generated by atomic species close to the surface of the sample, thus allowing their chemical identification ([6], [7], [8], [9]).

The main advantage of LIBS is to using the conventional methodology by avoiding laborious chemical steps, e.g., the preparation and dissolution of the soil sample. LIBS method has been used in many different studies (both qualitative and semi quantitative analysis, including environmental monitoring, industrial monitoring, biological, geological and agricultural materials) in previous years ([10],[11], [12], [13], [14], [15])

In this work, the LIBS technique has been applied to the determination of total contents of heavy metals (Fe, Zn, Al, Mn, Co, Cr, Cu, Ni, Na, Mg, K, Ca) in a number of reference soil samples. In order to validate the technique, LIBS data were compared with data obtained on the same soil samples by application of conventional Inductively Coupled Plasma ICP spectroscopy [16].

2. Materials and method

In this work, twelve core sediments samples have been examined. Samples were taken from Kapıdağ peninsula and Gulf of Erdek. 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.

Table 1. Sample coordinates of the work area

CORE SAMPLE NO	GPS NO	DEPTH (m)	GEOGRAPHIC POSITION (WGS-84)	
			Y	**X**
Core 1	GPS 116	30	058 14 59	447 46 77
Core 2	GPS 117	29	058 49 85	447 66 92
Core 3	GPS 119	30	058 81 05	448 16 39
Core 3	GPS 120	35	058 62 29	448 27 80
Core 4	GPS 121	30	058 23 93	448 35 51
Core 5	GPS 125	38	057 74 01	448 53 35
Core 6	GPS 126	40	056 68 40	448 63 34
Core 7	GPS 127	48	056 21 01	448 68 10
Core 8	GPS 128	39	055 81 97	448 48 62
Core 9	GPS 129	28	055 82 82	448 01 29
Core 10	GPS 138	19	055 62 81	446 36 87
Core 11	GPS 139	26	054 24 36	446 46 34
Core 12	GPS 140	11	053 19 59	447 10 35

The first element analysis of (Fe, Zn, Al, Mn, Co, Cr, Cu, Ni, Na, Mg, K, Ca) the samples taken from the sediment samples obtained from the study area was carried out in the Scientific and Technological Research and Application Center of Namık Kemal University using the ICP-OES device [17]. Within the scope of these analyzes, firstly sediment samples have been dried and pounded using mortar. These samples have been separated as 0,5 gr. The collected samples are placed in incineration tubes and burned for 1 hour at 98^0C and 1.5 hours at 200^0C by adding 12 mL HNO_3 and 4 mL HCl. After the lids of the cooling tubes have been pulled out in the furnace, it has been completed to 50 mL with ultrapure water and filtered using filter papers. Geochemical analyses of these samples have been performed using ICP-OS device. The prepared samples have been placed in the measurement unit of the ICP-OS device and readings made ([18], [17], [19]).
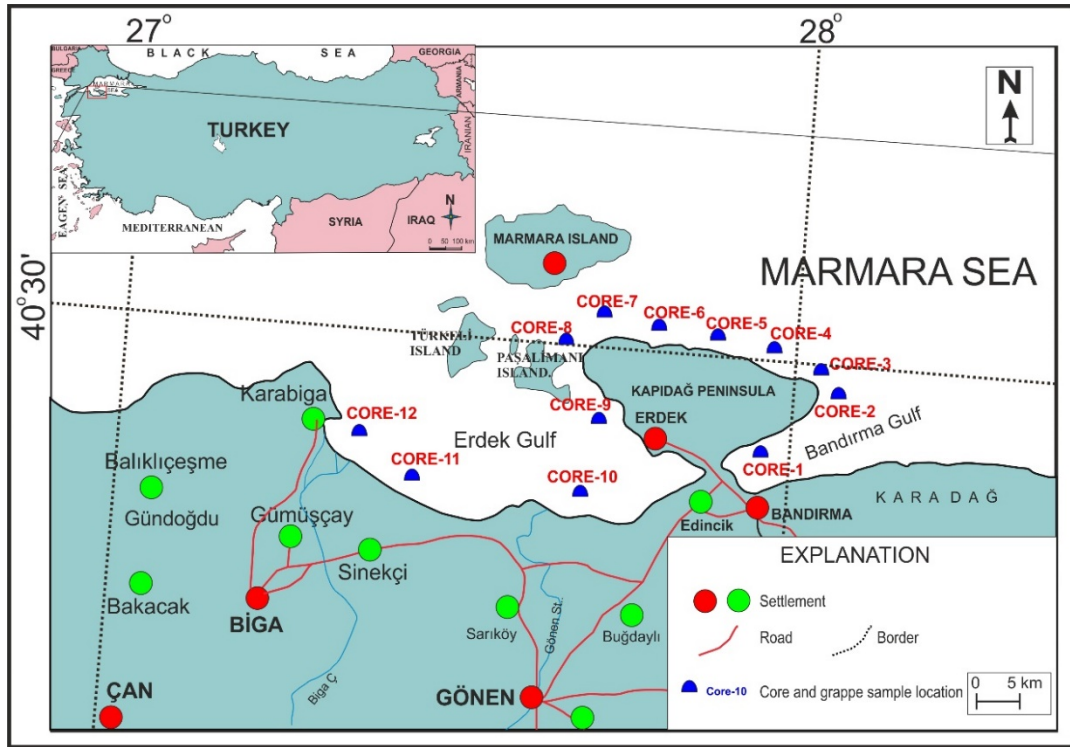
Figure 1. Location map of investigation area

The second method of analysis is LIBS. Laser Induced Plasma Spectroscopy (ICP-OES) is an optical emission spectroscopy method used for multi-elemental analysis of materials. In LIBS technique, a focused, high intensity pulsed laser beam is impinged on the target solid surface under investigation. As a result, a near-surface high-density plasma plume is formed, which expands into the ambient atmosphere [20]. 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 [21]. Samples taken from the same levels have been placed into the pellet container which is 20-25 gr and pressed for 5 seconds in the press machine under a pressure of approximately 100 bar. This form of samples is called the pellet. The pelletized samples have been placed in locked pouches and sent to the LİBS analysis [22].

3. Findings

The results of ICP-OES analysis of the study area have been given in Table 2 and the results of LIBS method also in Table 3.

Tablo 2. ICP-OES analysis results of core samples

Num No	Zn, ppm	Mn, ppm	Co, ppm	Cr, ppm	Cu, ppm	Ni, ppm	Al, ppm	Fe, ppm	Na, ppm	Mg, ppm	K, ppm	Ca, ppm
Core-1	90.4	1974.4	84.12	89.60	25.47	222.83	24522	38779	2656.6	5104	3217.4	62476
Core-2	95.2	509.4	89.17	95.10	28.32	237.12	26694	39821	3465.4	5367	3913.4	22870
Core-3	104.9	510.5	91.44	98.60	28.14	244.31	27784	41544	3912.1	5691	4323.6	16987
Core-4	191.3	400.4	48.82	49.90	22.85	111.72	15697	28392	3041.8	3717	1892.2	93491
Core-5	226.1	442.7	54.69	60.60	21.16	133.84	19561	29171	3396.0	4115	2750.9	78906
Core-6	205.6	504.8	65.58	80.50	24.69	159.30	20416	35742	3891.1	4659	3627.1	90173
Core-7	99.4	386.4	62.96	48.70	15.57	78.49	26954	34743	7955.9	5753	7054.6	38647
Core-8	97.5	338.8	71.44	57.10	18.47	72.84	27589	36833	6213.6	5592	6898.5	44717
Core-9	62.9	293.9	44.58	28.50	11.58	45.02	19592	24426	6789.1	4395	4337.3	82890
Core-10	126.4	368.6	74.42	49.70	31.20	72.84	27511	41733	7556.6	4844	5029.5	14280
Core-11	200.3	339.2	80.19	67.70	31.35	93.72	29107	45093	10660	5846	6045.5	13938
Core-12	321.2	689.9	109.36	116.00	52.53	170.88	31749	58647	10227	7802	6719	15254

Tablo 3. LIBS analysis results of core samples

Num No	Zn (%)	Mn (%)	Co (%)	Cr (%)	Cu (%)	Ni (%)	Al (%)	Fe (%)	Na (%)	Mg (%)	K (%)	Ca (%)
Core-1	10	25	15	20	10	3	75	95	80	90	95	75
Core-2	8	27	18	21	11	4	73	96	70	90	95	76
Core-3	8	20	16	31	11	3	69	94	75	89	86	79
Core-4	5	16	18	38	6	3	71	95	78	73	90	74
Core-5	15	25	16	19	10	2	72	95	79	84	95	75
Core-6	33	19	15	23	1	3	68	95	91	79	89	74
Core-7	15	19	12	20	5	1	70	95	90	78	85	72
Core-8	12	15	10	15	5	1	75	95	90	75	84	72
Core-9	16	24	17	8	2	1	75	95	80	91	93	75
Core-10	6	31	18	17	5	1	72	96	71	89	93	75
Core-11	10	28	18	13	18	1	79	95	73	91	90	66
Core-12	9	19	15	15	17	1	70	93	69	89	87	60

When the LIBS analysis results were examined, it was observed that the elements such as Fe, Al, Ca, K, Mg and Na which are in the natural structure of the soil, had a higher percentage. The LIBS results of the same elements have been compared with the ICP-OES results, it has been observed that the elements with high percentage in the LIBS analysis are high concentration values in the ICP-OES results (Figure 2 and 3).
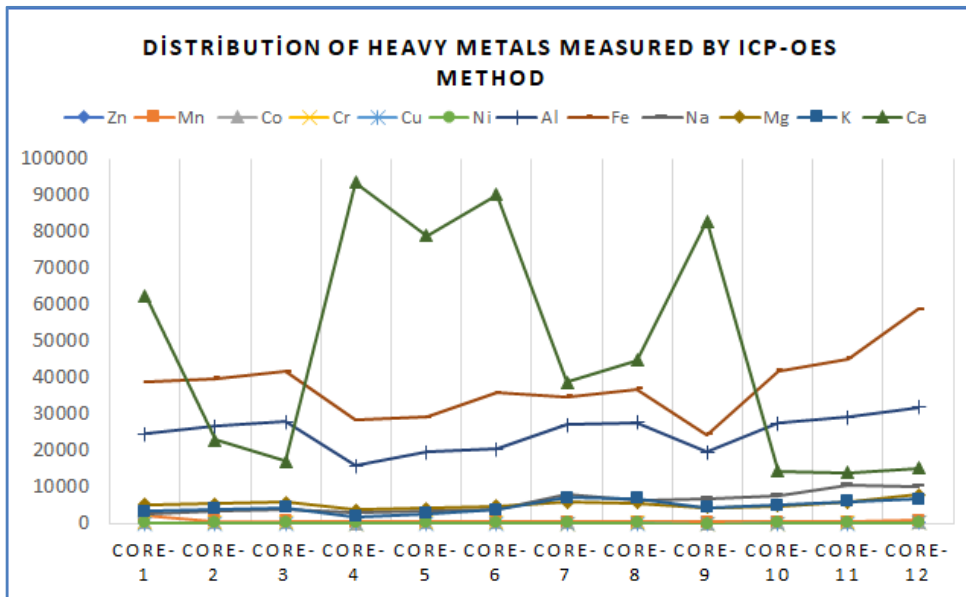
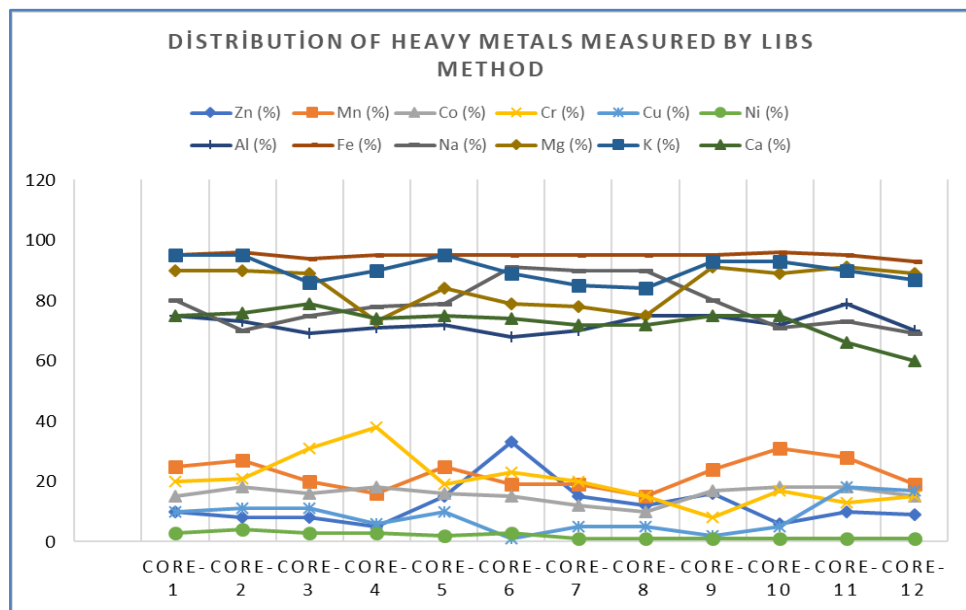**Figure 2.** ICP-OES analysis results of core samples

Figure 3. LIBS analysis results of core samples

In addition, the LIBS method; It has also shown important results in the determination of toxic elements such as Cr, Co and Cu which increased in sea sediment with anthropogenic factors (Figure 3).

4. Conclusions

Results obtained in this work show that the LIBS technique applied to the determination of several heavy metals in soils is successful for the qualitative recognition of metal species but is still to be considered semiquantitative when the metal concentration values have to be

measured. As a result of this study, it was revealed that LIBS method is a new method according to ICP-OES method. Despite its some drawbacks, LIBS can be considered a promising analytical technique for its intrinsic advantages. The presence of the elements present in the sample by the LIBS method is determined by a probability defined by%. In contrast, the analysis does not provide the amounts of elements in the sample. Although this is seen as a disadvantage, this method gives very useful results for practical and preliminary investigations.

In this study, when the analysis results were examined, it has been seen that the elements (Fe, Zn, Al, Mn, Co, Cr, Cu, Ni, Na, Mg, K, Ca) determined by ICP-OES analysis were also determined by LIBS method. In the analyzes made by ICP-OES method, the amounts of the elements in ppm are determined, while the results of LIBS analysis show the presence of the element only in%. If analyzes are carried out to determine the origins of the elements present in the environment, the LIBS method is an important technique for determining the elements that are enriched with anthropogenic factors as well as the elements resulting from natural processes.

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