Research Article

Determination of As, Cd, and Pb in Tap Water and Bottled Water Samples by Using Optimized GFAAS System with Pd-Mg and Ni as Matrix Modifiers

Sezgin Bakırdere,[1] Tolga Yaroğlu,[2] Nihan Tırık,[3] Mehmet Demiröz,[4] A. Kemal Fidan,[5] Onur Maruldalı,[6] and Abdullah Karaca[7]

[1] *Department of Sciences Education, Yıldız Technical University, İstanbul, Turkey*

[2] *Faculty of Veterinary Medicine, Ankara University, Ankara, Turkey*

[3] *Department of Biology, Samsun 19 Mayıs University, Samsun, Turkey*

[4] *Karacabey MYO, Uludag University, Karacabey-Bursa, Turkey*

[5] *Department of Chemistry, Süleyman Demirel University, Isparta, Turkey*

[6] *Department of Biology, Çukurova University, Adana, Turkey*

[7] *Faculty of Veterinary Medicine, Fırat University, Elazig, Turkey*

Correspondence should be addressed to Sezgin Bakırdere; bsezgin23@yahoo.com

Arsenic, lead and cadmium were determined in tap and bottled water samples consumed in the west part of Turkey at trace levels. Graphite Furnace Atomic Absorption Spectrometry (GFAAS) was used in all detections. All of the system parameters for each element were optimized to increase sensitivity. Pd-Mg mixture was selected as the best matrix modifier for As while the highest signals were obtained for Pb and Cd in the case of Ni used as matrix modifier. Detection limits for As, Cd, and Pb were found to be 2.0, 0.036 and 0.25 ng/mL, respectively. 78 tap water and 17 different brands of bottled water samples were analyzed for their As, Cd and Pb contents under the optimized conditions. In all water samples, concentration of cadmium was found to be lower than detection limits. Lead concentration in the samples analyzed varied between N.D. and 12.66±0.68 ng/mL. The highest concentration of arsenic was determined as 11.54 ± 2.79 ng/mL. Accuracy of the methods was verified by using a certified reference material namely Trace Element in Water, 1643e. Results found for As, Cd, and Pb in reference materials were in satisfactory agreement with the certified values.

1. Introduction

Our green planet has been contaminated from day to day by different contaminants. One of the most serious contaminant groups is the heavy metals. Our ecosystem has been contaminated by high concentration of heavy metals released into the biosphere by human activity. Industrial activities, energy production, construction, urban waste treatment, and vehicle exhaust are some of the sources causing large quantities of heavy metal contamination in atmosphere, water, and soil [1].

Arsenic has been listed as one of the human carcinogens by the International Agency for Research on Cancer (IARC) since 1980. There have been many studies in the literature to show the positive association between arsenic exposure and cancer in different countries including the USA, Taiwan, Bangladesh, and India [2]. Blander cancer [3], skin cancer [4], and lung cancer [5] are some of the cancer types associated to arsenic exposure by many researchers. In addition to carcinogenic effects, there are some noncarcinogenic effects of chronic arsenic exposure [2]. According to Tsai et al., long-term accumulated arsenic in adolescence may cause neurobehavioral effects and exposure to high amount of arsenic may affect behavior later in life. In addition, in the case of lead, effects will be more severe by synergistic behavior of arsenic and lead [6]. There are many sources of arsenic exposure. One

of the big sources for human to inorganic arsenic exposure is groundwater. High concentration of arsenic in groundwater has been recognized as global concern [2].

Toxic effects of cadmium and lead are also well known [7]. Cadmium is not regarded as essential element for human being and known to be an element damaging organs such as the kidneys, liver, and lungs [8]. It is known that cadmium accumulates in both liver and kidneys and half-life of this element in human body is between one and four decades [9]. Exposure to high amount of cadmium can cause damages in central nervous and immune systems in addition to fertility disorders and occurrence of different cancer types [9, 10]. Toxic effect of lead is also studied. One of the molecular mechanisms for toxicity of lead is oxidative stress [11]. By the effect of lead, reactive oxygen species (ROS) levels increase via elevated intracellular Ca^{2+} [12]. There are different types of lead sources causing food, water contamination, and air pollution by industrial emission. According to Ahamed and Siddiqui, diet, lead-based paint in older housing, lead in soil and dust from contaminated leaded paint and gasoline, and mining and other industrial activities are the main sources of lead for children. By the displacement of leaded gasoline with unleaded one and lead water pipes and water tanks with nonlead alternatives, lead exposure from these sources has been reduced on a large scale [13]. It was also stated that anthropogenic contribution to cadmium and lead contamination is more important than natural input [14].

Due to the adverse health effects of arsenic, lead, and cadmium, detection of trace amount of these elements in any environmental samples related with human being is very important. Determination of these elements requires sufficiently sensitive techniques for detection at the μg/L or sublevels. In the literature, there are many techniques including atomic absorption spectrometry (AAS) [15, 16], graphite furnace atomic absorption spectrometry (GFAAS) [17, 18], inductively coupled plasma optical emission spectrometry (ICP-OES) [19, 20], and inductively coupled plasma mass spectrometry (ICP-MS) [21, 22] for the determination of As, Pb, and Cd in different matrices. Although AAS has been used for many elements in variety of matrices [23, 24], there is sensitivity problem for many elements in the case of using this instrument. Due to the high sensitivity, low cost, and easy operation, GFAAS has been popularly used in literature for As, Pb and Cd [25].

The main purpose of this study was to analyze tap water and bottled water samples for their As, Cd, and Pb contents by using optimized GFAAS system with Pd-Mg and Ni as matrix modifiers.

2. Experimental

2.1. Apparatus and Reagents. In order to determine As, Cd, and Pb in water samples, GFAAS instrument equipped with hollow cathode lamps (HCLS) was used. Instrumental parameters used throughout this study for the elements of interest can be seen in Table 1. Deuterium arc lamp background correction was applied for all the analytes.

Table 1: GF-AAS parameters used in the determination of As, Cd, and Pb.

	As	Cd	Pb
Lamp current, mA	10	4.0	5.0
Slit width, nm	0.5	0.5	0.5
Wavelength, nm	193.7	228.8	283.3
Background correction	D_2	D_2	D_2

All of the chemicals used throughout the experiments were in high-purity grade. In all dilutions and standard preparation, double distilled water was used. All of the containers were washed up with hot nitric acid and then rinsed with double distilled water before using in the experiments. All glass beakers and containers were kept and stored in 1.0 mol/L HNO_3 to eliminate any possible contamination. Nitric acid (65%, Merck) was used to eliminate the precipitation of analytes before measurement. In the preparation of working standards of analytes, proper dilutions were done by 1.0 mol/L nitric acid from the stock solutions of As, Cd, and Pb (1000 mg/L). 20 μL of samples and calibration solutions were pipetted into the graphite tube in the measurements. High purity N_2 was used as sheath gas. 500 mg/L of palladium and magnesium mixture for arsenic and 1010 mg/L of nickel for cadmium and lead were used as stock solutions of matrix modifiers. Standard reference material (Trace Element in Water, 1643e) bought from NIST was used for evaluating methods used in the determination of As, Cd, and Pb in water samples.

2.2. Sample Collection. Tap water samples were collected in three cities, namely, Kocaeli, Adapazarı, Düzce located in the west part of Turkey. 78 different sampling points were selected in these cities for homogenous representation of the region. Map of these cities is shown in Figure 1.

In the sample collection, bottles used for the samples were previously rinsed with double distilled water. One litter of tap water samples was collected for arsenic, cadmium, and lead determinations. Samples were brought to the laboratory and kept in the fridge prior to analysis. In addition, 17 different brands of bottled water samples were bought from the local markets of these cities. In the selection of these brands, consumption rates were considered. All the samples were analyzed within two days after sample collection to eliminate or minimize not only precipitation of analytes but also any possible contaminations.

3. Result and Discussion

All of the system parameters were optimized for each analyte to increase sensitivity. While optimizing, all the parameters were kept constant except one variable at a time.

3.1. Optimization of Temperature Program of GFAAS System for Analytes. Determination of arsenic in environmental matrices by using GFAAS has some difficulties. Many arsenic species are highly volatile, and possibility of losses of arsenic

TABLE 2: Temperature program used in the determination of As.

	Temperature, °C			Ramp, s (N$_2$, L/min)			Hold, s (N$_2$, L/min)		
	As	Cd	Pb	As	Cd	Pb	As	Cd	Pb
Drying	140	130	120	15 (0.2)	25 (0.2)	20 (0.2)	15 (0.2)	10 (0.2)	10 (0.2)
Ashing	600	280	380	10 (0.2)	10 (0.2)	10 (0.2)	10 (0.2), 1.5 (0)	5.0 (0.2), 1.0 (0)	10.0 (0.2), 1.0 (0)
Atomization	2300	1800	2000	0.9 (0)	0.8 (0)	0.9 (0)	1.0 (0)	—	—
Cleaning	2600	2500	2500	1.0 (1.0)	2.0 (1.0)	2.0 (1.0)	3.0 (1.0)	—	—
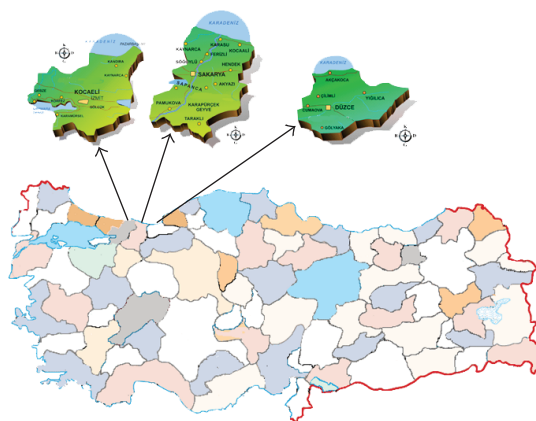
FIGURE 1: Map of sampling points (http://www.csb.gov.tr/, 21.12.2012).

during the ashing step is very high. Spectral interferences which appear in the presence of some anion and cations such as phosphate, iron, and aluminum are associated with the atomization step [26]. Hence, the optimization of temperature program of arsenic is very crucial to eliminate or minimize both analyte losses and possible interferences. Loss of arsenic was observed at the ashing temperature of 600°C. The highest signal was obtained when the temperature at the atomization step set to 2300°C. Optimum drying, ashing, and atomization temperatures were found to be 140, 600, and 2300°C, respectively. Cleaning of graphite tube was performed at a temperature of 2600°C. Optimum flow rate of sheath gas was found to be 0.2 L/min in drying and ashing steps, while this value was set to 1.0 L/min in the cleaning step.

It is known that Cd is one of the high volatile elements and it has less vaporization heat and low appearance temperature in the case of GFAAS measurements [27]. In this study, sensitivity of cadmium began to be lost at the ashing temperature which is higher than 280°C. The highest absorption was obtained at the atomization temperature of 1800°C. Optimum flow rates of N$_2$ were 0.2 L/min in drying and ashing steps, and 1.0 L/min in the cleaning step.

Lead is also known as a comparatively volatile element [27]. Temperature program for the analysis of lead is also optimized to provide maximum matrix decomposition without loss of lead in any step of GFAAS program. Absorption of lead started to decrease at the ashing temperature of 350°C. The highest lead signal was obtained at the atomization temperature of as high as 1800°C. The same flow rates of

N$_2$ with As and Cd were applied in the drying, ashing, and cleaning steps. Cleaning step was performed at a temperature of 1800°C in 2 seconds. Temperature programs for As, Cd, and Pb can be seen in Table 2.

3.2. Optimization of Type and Amount of Matrix Modifier. It is well known that matrix modifiers are used to both stabilize the analytes during the graphite furnace cycle and permit increases in the charring and atomization temperatures. Better separation of the element from interferences can be achieved by using proper matrix modifiers [28].

In order to stabilize arsenic at higher temperature of the ashing stage, different types of matrix modifiers, namely, palladium, magnesium, and mixture of palladium-magnesium were tried. In the optimization, 40 ng/mL of arsenic standard and 1.0 microgram of each modifier were used. Sensitivity was enhanced 2.23 times by using palladium-magnesium mixture, while this value was 1.91 in the presence of palladium. The highest signal was obtained in the case of palladium-magnesium mixture as matrix modifier, and arsenic signal was better in terms of sharpness and peak shape. Most probably palladium-magnesium mixture equalizes the thermal behavior of arsenic species in the water samples. The effect of the different masses of palladium-magnesium mixture as matrix modifier on arsenic signal was also investigated. 0.5, 1.0, 2.0, and 3.0 μg of palladium-magnesium were tried in this optimization. It was observed that arsenic signal was getting lower with higher amount of matrix modifier. Hence, 0.5 μg of each of palladium and magnesium as a mixture of modifier was selected as optimum modifier amount for the further real sample measurements.

Similar optimization studies were also performed for cadmium. Nickel, palladium, and palladium-magnesium mixture were tried to find relatively the best matrix modifier. In the optimization of matrix modifier type, 2.0 ng/mL of cadmium standard and 0.2 microgram of each modifier were used. There was no difference observed between the cadmium signals obtained from 2.0 ng/mL Cd solution with and without Pd-Mg mixture as matrix modifier. In the case of Pd, cadmium signal decreased about 3% while signal was enhanced 1.27 times by using nickel as a matrix modifier. Hence, nickel was selected as an effective matrix modifier for the determination of cadmium for real sample measurements. 0.25, 0.5, 1.0, 2.0, and 4.0 μg of nickel were tried in the optimization of the amount of matrix modifier.

It is clear in Figure 2 that cadmium signal decreased by using the nickel which is more or less than 1.0 μg. Therefore, 1.0 μg of nickel was found to be the best matrix modifier and

TABLE 3: Analytical figures of merit for As, Cd, and Pb.

	Arsenic	Cadmium	Lead
Limit of detection (LOD), ng/mL	2.0	0.036	0.25
Limit of quantitation (LOQ), ng/mL	6.6	0.12	0.83
Linear range, ng/mL	5.0–60	0.25–2.0	1.0–8.0
R^2	0.9991	0.9985	0.9981
Equation	$y = 0.0059x + 0.0028$	$y = 0.2414x + 0.0705$	$y = 0.0408x + 0.0176$

TABLE 4: Accuracy of the method used.

	CRM	Result certified (STD), ng/mL	Result found (STD), ng/mL
As	Trace Element in Water, 1643e	60.45 (0.72)	60.88 (1.99)
Cd	Trace Element in Water, 1643e	6.568 (0.073)	6.50 (0.33)
Pb	Trace Element in Water, 1643e	19.63 (0.21)	21.08 (1.69)
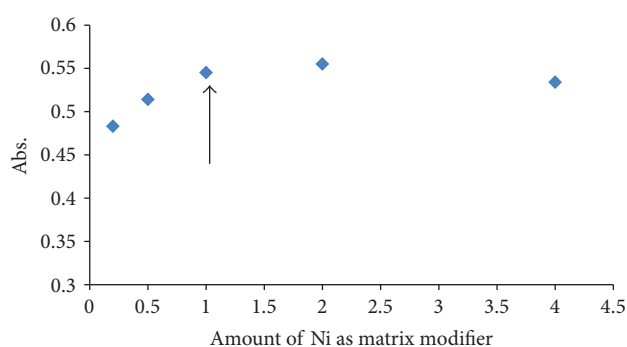
FIGURE 2: Optimization of the amount of matrix modifier (μg) by using 2.0 ng/mL of cadmium.

it is capable of not only the prevention of analyte losses during graphite furnace cycle but also the improvement of sensitivity.

Selection of suitable matrix modifier for electrothermal atomization of lead was also performed. For this purpose, Pd, Ni, Mg, and Pd-Mg mixture were tried. 10.0 ng/mL of lead standard and 1.0 microgram of each modifier were used throughout the optimization. The highest lead signal was obtained in the case of Ni as chemical modifier. No difference was observed in the lead signals obtained with and without Pd as matrix modifier. In the optimization of Ni amount, 0.2, 0.5, 1.0, 2.0, 4.0, 5.0, and 6.0 μg were tested. The highest lead signal was obtained in the case of 5.0 μg Ni used. Hence, 5.0 μg of nickel was selected as the optimal matrix modifier for the further studies.

3.3. Analytical Figures of Merit. Analytical characteristics of the optimized GFAAS system including the linear range, limit of detection, limit of quantification, and best line equation are summarized in Table 3. In the calculation of limit of detection (LOD) and limit of quantification (LOQ), 3 s/m where s is standard deviation of lowest concentration of linear range and 10 s/m were used, respectively.

It is clear in Table 3 that detection limit for Cd using the nickel as matrix modifier and optimum temperature program is better than the values found for As and Pb. Linear ranges

for As, Cd, and Pb were in the range of 5.0–60, 0.25–2.0, and 1.0–8.0 ng/mL, respectively. R^2 values for each analyte were found to be at least 0.998.

3.4. Accuracy Check. Evaluation of accuracy was performed using standard reference material (Trace Element in Water, 1643e). Results are given in Table 4.

Concentrations of As, Cd, and Pb were found as 60.88 ± 1.99, 6.50 ± 0.33, 21.08 ± 1.69 ng/mL, respectively. The certified values of the analytes were reported as 60.45 ± 0.72 for As, 6.568 ± 0.073 for Cd, and 19.63 ± 0.21 ng/mL for Pb. According to Students t-test at 95% confidence level calculated and reported values are the same. It is clear that high level accuracy of the GFAAS method is demonstrated by the good agreement of the results found in the analysis of standard reference material with the values certified.

3.5. Analysis of Water Samples for Their As, Cd, and Pb Contents. Many elements are present in water samples playing important functions in the human body. Their levels remain within the specified ranges which are recommended by the World Health Organization [29]. Trace levels of metals which are normally not harmful to human health are common in water. Exposure to lead, cadmium, and arsenic is the main trouble to human health from heavy metals [30]. Guideline values for As, Cd, and Pb which are of health significance in drinking water is 10, 3.0, and 10 μg/L, respectively [29]. For the region interested in this study, there have been no studies in the literature for the quantitative determination of As, Cd, and Pb in drinking and bottled water samples; however, there are some literature where heavy metals have been determined in water samples taken from different regions of Turkey [31–33]. In this study, 78 tap water samples and 17 different brands of bottled water samples consumed in Kocaeli, Adapazarı, and Düzce cities located in the west part of Turkey were analyzed for their As, Cd, and Pb contents under the optimum conditions. Standard addition method was also applied to make sure whether there is any interferences coming from matrix or not. There is no difference observed in the slopes of both direct calibration and standard addition method. Hence, direct calibration

TABLE 5: As, Cd, and Pb results of the samples analyzed.

Sample Number	As, ng/mL	Cd, ng/mL	Pb, ng/mL
TW1	N.D.	N.D.	3.50 ± 0.23
TW2	N.D.	N.D.	3.15 ± 0.21
TW3	N.D.	N.D.	N.D.
TW4	N.D.	N.D.	N.D.
TW5	N.D.	N.D.	2.03 ± 0.13
TW6	N.D.	N.D.	3.42 ± 0.22
TW7	N.D.	N.D.	2.86 ± 0.19
TW8	N.D.	N.D.	N.D.
TW9	N.D.	N.D.	N.D.
TW10	N.D.	N.D.	3.15 ± 0.21
TW11	N.D.	N.D.	2.86 ± 0.19
TW12	N.D.	N.D.	2.33 ± 0.15
TW13	N.D.	N.D.	3.98 ± 0.26
TW14	N.D.	N.D.	2.59 ± 0.17
TW15	N.D.	N.D.	3.15 ± 0.21
TW16	9.14 ± 0.75	N.D.	2.33 ± 0.15
TW17	9.20 ± 0.68	N.D.	2.33 ± 0.15
TW18	N.D.	N.D.	N.D.
TW19	N.D.	N.D.	2.59 ± 0.17
TW20	8.51 ± 1.20	N.D.	2.33 ± 0.15
TW21	8.72 ± 1.35	N.D.	2.33 ± 0.15
TW22	9.04 ± 1.80	N.D.	2.33 ± 0.15
TW23	N.D.	N.D.	2.86 ± 0.19
TW24	N.D.	N.D.	2.10 ± 0.11
TW25	N.D.	N.D.	2.40 ± 0.13
TW26	N.D.	N.D.	2.59 ± 0.14
TW27	N.D.	N.D.	3.77 ± 0.20
TW28	N.D.	N.D.	1.61 ± 0.09
TW29	N.D.	N.D.	12.66 ± 0.68
TW30	N.D.	N.D.	2.59 ± 0.14
TW31	N.D.	N.D.	2.99 ± 0.16
TW32	N.D.	N.D.	2.20 ± 0.12
TW33	N.D.	N.D.	2.79 ± 0.15
TW34	N.D.	N.D.	N.D.
TW35	N.D.	N.D.	N.D.
TW36	N.D.	N.D.	1.42 ± 0.08
TW37	N.D.	N.D.	2.01 ± 0.11
TW38	N.D.	N.D.	2.59 ± 0.14
TW39	N.D.	N.D.	1.42 ± 0.08
TW40	10.06 ± 0.82	N.D.	N.D.
TW41	11.54 ± 2.79	N.D.	1.42 ± 0.08
TW42	9.13 ± 0.99	N.D.	N.D.
TW43	9.11 ± 1.03	N.D.	1.42 ± 0.08
TW44	N.D.	N.D.	2.40 ± 0.13
TW45	N.D.	N.D.	3.18 ± 0.17
TW46	N.D.	N.D.	N.D.
TW47	N.D.	N.D.	N.D.
TW48	N.D.	N.D.	N.D.
TW49	N.D.	N.D.	N.D.
TW50	N.D.	N.D.	N.D.
TW51	N.D.	N.D.	1.00 ± 0.09

TABLE 5: Continued.

Sample Number	As, ng/mL	Cd, ng/mL	Pb, ng/mL
TW52	N.D.	N.D.	1.04 ± 0.08
TW53	N.D.	N.D.	N.D.
TW54	N.D.	N.D.	N.D.
TW55	N.D.	N.D.	N.D.
TW56	N.D.	N.D.	N.D.
TW57	N.D.	N.D.	N.D.
TW58	N.D.	N.D.	N.D.
TW59	N.D.	N.D.	N.D.
TW60	N.D.	N.D.	N.D.
TW61	N.D.	N.D.	N.D.
TW62	N.D.	N.D.	1.50 ± 0.07
TW63	N.D.	N.D.	N.D.
TW64	N.D.	N.D.	N.D.
TW65	N.D.	N.D.	N.D.
TW66	N.D.	N.D.	N.D.
TW67	N.D.	N.D.	N.D.
TW68	N.D.	N.D.	N.D.
TW69	N.D.	N.D.	N.D.
TW70	N.D.	N.D.	N.D.
TW71	N.D.	N.D.	1.51 ± 0.06
TW72	N.D.	N.D.	N.D.
TW73	N.D.	N.D.	N.D.
TW74	N.D.	N.D.	N.D.
TW75	N.D.	N.D.	N.D.
TW76	N.D.	N.D.	N.D.
TW77	N.D.	N.D.	2.40 ± 0.15
TW78	N.D.	N.D.	N.D.
BW1	N.D.	N.D.	2.99 ± 0.16
BW2	N.D.	N.D.	4.13 ± 0.22
BW3	N.D.	N.D.	1.78 ± 0.10
BW4	N.D.	N.D.	2.46 ± 0.13
BW5	N.D.	N.D.	2.79 ± 0.15
BW6	N.D.	N.D.	2.46 ± 0.13
BW7	N.D.	N.D.	2.10 ± 0.11
BW8	N.D.	N.D.	N.D.
BW9	N.D.	N.D.	2.46 ± 0.13
BW10	N.D.	N.D.	N.D.
BW11	N.D.	N.D.	4.82 ± 0.26
BW12	N.D.	N.D.	2.10 ± 0.11
BW13	N.D.	N.D.	1.78 ± 0.10
BW14	N.D.	N.D.	1.78 ± 0.10
BW15	N.D.	N.D.	2.79 ± 0.15
BW16	N.D.	N.D.	3.12 ± 0.17
BW17	N.D.	N.D.	2.10 ± 0.11

method was applied throughout the analysis of all samples. Concentrations of analytes found in the samples of interest in this study are presented in Table 5.

It is clear that concentration of arsenic in bottled water samples was found to be below detection limits while nine water samples contained detectable levels of arsenic in the

range of 8.51–11.54 μg/L. Two tap water samples exceeded the safe limit of 10 mg/L given in WHO. It is clear that bottled water samples do not fall under toxic and alert categories with respect to arsenic.

Based on the safe limit set by WHO for cadmium at 3.0 μg/L, none of the tap water and bottled water samples exceeded the specifications. Cd concentration for all samples was found to be lower than detection limit. This is good news for the people who live in this area because there are some indications that cadmium is carcinogenic by the inhalation route. In addition, according to IARC, cadmium and cadmium compounds accumulating primarily in the kidneys and having long biological half-life in humans of 10–35 years are classified in Group 2A [29].

Lead was found in 37 (47.4%) tap water samples in which one of the samples (12.66 ± 0.68 μg/L) does not obey the regulations on safe limit of lead in water by WHO. Detectable lead concentration in tap water samples was found to be in the range of 1.00 ± 0.09–12.66 ± 0.68 μg/L. For bottled water samples, although detectable levels of lead were found in 88.2% of the samples interested (1.78±0.10–4.82±0.26 μg/L), none of the samples exceeded the WHO safe limit of 10 μg/L.

4. Conclusion

Determination of trace amounts of arsenic, cadmium, and lead in tap water and bottled water samples consumed in Kocaeli, Adapazarı, and Düzce cities of Turkey was performed by graphite furnace atomic absorption spectrometry. All of the system parameters were optimized to obtain lower detection limits. Direct calibration method was applied throughout the sample analysis. Nickel was selected as effective matrix modifier for the determination of both cadmium and lead, while the highest arsenic signal was obtained in the case of palladium-magnesium mixture as matrix modifier. In order to verify the accuracy of the GFAAS method with the optimum matrix modifiers selected, certified reference of Trace Element in Water, 1643e was analyzed and the results obtained were in good agreement with the certified values for all analytes. In the real sample analysis, detectable levels of arsenic were found in the range of 8.51–11.54 μg/L in tap water samples while this element was not detected in bottled water samples. There is no analytical signal observed for cadmium for all the samples analyzed. Analysis of lead in 78 tap water and 17 bottled water samples showed that concentration of this element in all of the samples with the exception of TW29 with 12.66 ± 0.68 μg/L was below safe limit of 10.0 μg/L accepted by WHO. From all the experiment results obtained, it could be concluded that there is no extensive nature of metal contamination (As, Cd, and Pb) of tap water and bottled water samples consumed in the area interested.

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