Gazi University Journal of Science
GU J Sci
27(2):785-794 (2014)

Determination and Assessment of Metal Levels in Thermal Waters

Orhan ACAR[1]♠, O. Murat KALFA[2], Özcan YALÇINKAYA[1], A. Rehber TÜRKER[1]

[1] *Gazi University, Science Faculty, Department of Chemistry, 06500, Ankara, Turkey*
[2] *Dumlupınar University, Arts and Science Faculty, Chemistry Department, Kutahya, Turkey*

Received: 31.10.2013 Accepted: 23.01.2014

ABSTRACT

Concentration levels of metals (Cd, Pb, Fe, Zn, Ca, Mg, Na and K) in the thermal waters of Karakaya-Ayaş, İçmece-Ayaş, Beypazarı, Haymana and Kızılcahamam spas containing highly complex matrices and in water standard reference materials (SRMs: Spsww-1 and 1643e) were determined by electrothermal atomic absorption spectrometer (ETAAS), flame atomic absorption spectrometer (FAAS) and FAAS with atomic emission mode. Pyrolysis and atomization temperatures, atomization and background signals of Cd and Pb by ETAAS were investigated with Ni, Ni+Ru and Ni+Ru+CA modifier mixture and without. Concentrations of analytes found in the thermal waters were compared with water quality guidelines of the World Health Organization, European Legislation, Environment Protection Agency (US EPA) and the Turkish standards and regulations.

Key Words: *Ni+Ru+citric acid modifier mixture, ETAAS, FAAS, thermal waters, metals*

1. INTRODUCTION

Determinations of trace heavy metals (Cd, Pb Fe and Zn,) and major alkaline and alkaline earth elements (Na, K, Ca and Mg) in the thermal waters coming from underground by drilling at spas (sanus per aquams) have been important during the last few decades because of the public health and the environmental problems. Some of these waters are consumed by people as drinking or taking baths and others are used for heating the buildings and irrigating the local agricultural fields. The presence of Cd and Pb in the thermal waters are very important for the human life and the environment because of their toxicity [1], even if their concentrations are in low amounts. The excess of cadmium accumulated in the kidney causes the kidney dysfunction. Biological half-life of Cd in humans is ranged from 10 to 35 years and it is carcinogenic when taken by inhalation [2]. When lead is accumulated in the body for a long time, it may cause deficiencies in psychological functions such as learning ability and intelligence in humans [3]. Therefore, accurate determinations of Cd and Pb in the thermal waters are necessary to identify the concentration levels of water pollution. Iron and Zn may be essential elements in human body, but they can be toxic when taken in excess. As well known, the iron deficiency causes anemia disease. On the other hand, high levels of iron in the body may cause cancer risk, heart and liver diseases, diabetes and etc [4]. Maximum contamination level (MCL) of iron is limited to 2 mg L^{-1} by the World Health Organization (WHO) [5] and to 0.2 mg L^{-1} by European Legislation [6]. Zinc levels in ground waters generally do not exceed 0.05 mg L^{-1}, but concentration of it in the thermal water may be higher because of zinc dissolution from natural sources and pipes carrying thermal waters from underground. Maximum concentration levels of sodium,

---

♠Corresponding author, e-mail: oacar@gazi.edu.tr

potassium and calcium chlorides are restricted to 250 mg L^{-1} by the WHO and waters above this value give salty taste to waters [7]. Potassium is also an essential element in humans and its deficiency may cause muscular weakness and mental apathy.

Electrothermal and flame atomic absorption spectrometries (ETAAS and FAAS) are extensively used analytical techniques for the determinations of trace and major elements in water samples due to their operational facilities, simplicities, good selectivities, high sensitivities and low costs [8-10]. However, the direct determinations of Cd and Pb at low concentration levels by ETAAS are generally difficult because of high background absorption, possible matrix interferences and high salty contents in the thermal waters [11]. Using a platform technique and a suitable chemical modifier are preferable to reduce background absorption signals and interferences in real samples by ETAAS. Other advantages of the chemical modifiers are to increase thermal stability of analyte to the higher permissible pyrolysis temperature without loss of analyte mass, to volatilize the large amounts of sample matrix such as organic and inorganic compounds and to delay the vaporization of analyte [12, 13]. Different chemical modifiers such as Ni, Pd [14], tartaric acid [13] and Pd + Mg modifier mixture [15] were used for the thermal stabilization of analyte elements.

Aims of the presented study are to determine the concentration levels of Cd, Pb, Fe, Zn, Na, K, Ca and Mg in the thermal waters by ETAAS, FAAS and FAAS with atomic emission mode (AEM) and to compare the results of analytes found in samples with maximum permissible values given by the WHO, European Legislation, EPA and national standards and regulations. For this purpose, in order to determine Cd and Pb by ETAAS, various chemical modifiers such as Ni, Ni + Ru and Ni + Ru + CA were tested and the optimum one was selected. Other elements were determined by FAAS and FAAS with AEM.

2. EXPERIMENTAL

2.1. Instrumentation

Absorbance measurements of Cd and Pb were carried out by using Varian (Palo Alto, CA, USA) model SpectrAA 240Z electrothermal atomic absorption spectrometer with a Zeeman background correction system, equipped with a thermal graphite atomizer (TGA-120) and an autosampler (PSD-120). Varian center fixed platforms inserted into pyrolytically coated graphite tubes (P/N-63-100026-00) and integrated mode were used for the absorbance measurements by ETAAS throughout the studies. Varian model 240 FS FAAS was used for the determination of Fe, Zn, Ca and Mg with the integrated mode. Determinations of Na and K were carried out using Varian model 240 FS FAAS with AEM and the integrated mode. Varian model Cd, Pb, Fe, Zn, Ca and Mg single element hollow cathode lamps were used. Instrumental conditions of analytes recommended by the manufacturer are given in Table 1.

Table 1. Instrumental conditions of investigated analytes

Parameters	FAAS					
	Fe	Zn	Na	K	Ca	Mg
Acetylene, L min^{-1}	2.0	2.0	2.0	2.0	6.35	2.0
Air, L min^{-1}	13.5	13.5	13.5	13.5	11.0^{a}	13.5
Wavelength, nm	248.3	213.9	589.0	766.5	422.7	285.2
Lamp current, mA	5.0	5.0	0.0	0.0	10.0	4.0
Slit with, nm	0.2	1.0	0.2	0.2	0.5	0.5
	ETAAS					
	Cd	Pb				
Argon flow, mL min^{-1}	0.3	0.3				
Sample volume, µL	20	20				
Lamp current, mA	4	10				
Wavelength, nm	228.8	283.3				
Slit with, nm	0.5	0.5				
Heating program	Temperature (°C)		Ramp time (s)	Hold time (s)		
Dry-1	80		10	10		
Dry-2	130		15	10		
Pyrolysis	130-Variable^{b}		25	20		
Atomization	1800	2100	1	4		
Cleaning	2600		1	2		

^{a} 11.0 L min-1 for N_2O is used for Ca. b See Table 2.

2.2. Chemicals and Reagents

All chemicals were of analytical grade reagents unless specified otherwise and used without purification. Solutions of reagents, acids and samples were prepared by using ultra pure water (resistivity 18.3 MΩ cm) obtained from an ultra-pure water system (Human power I^{+}, Human Corporation, Korea) and diluted to suitable concentrations throughout. HNO_3 (65% m/m), H_2O_2 (35% m/m) and reagents used were purchased from Merck (Supra-pure grade acids and reagents, Darmstadt, Germany). All prepared solutions were kept in polypropylene bottles. Bottles, autosampler cups, pipettes and glassware were cleaned by soaking in HNO_3 (10%, v/v) for two days, rinsing three times with deionized water and dried before using. An autosampler solution of HNO_3 (0.1%, v/v) plus Triton X-100 (0.1%, v/v) mixture was used to improve dispersion of sample solution onto the platform and to avoid clogging of the sample into autosampler pipette [12, 16].

Nickel (II) stock solution (6.00 mg mL^{-1}) was prepared by dissolving 2.97 g of $Ni(NO_3)_2.6H_2O$ in HNO_3 (1%, v/v) and diluting to 100 mL. The Ru (III) solution (1.00 g L^{-1}) was prepared by dissolving 320 mg of $Ru(NO_3)_3$. $2H_2O$ in HNO_3 (5%, v/v) and diluting to 100 mL after evaporation of acids. Citric acid solution (4% m/v) was prepared daily before absorbance measurements.

Fresh working solutions of analytes were prepared by diluting the stock standard solutions of Cd, Pb, Fe, Zn, Na, K, Ca and Mg (1.00 g L^{-1} of each, Merck) to the suitable concentrations with nitric acid solution (0.1%, v/v).

Argon (99.98%, Oksan, Ankara) in ETAAS was used as carrier and protective gas during all stages (except atomization). An air-acetylene flame for Fe, Zn, Na, K and Mg determinations and an acetylene - nitrous oxide flame for Ca determination were used (Table 1).

Spsww-1 and 1643e water standard reference materials (SRMs) purchased from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) were used to check accuracy and precision for the analytes.

2.3. Collection and Preparation of Samples

The thermal waters were collected from underground waters at Karakaya - Ayaş, İçmece-Ayaş, Beypazarı (Dutluk - Tahtalı), Haymana and Kızılcahamam spas in Ankara province. Haymana, Beypazarı, Ayaş and Kızılcahamam are well-known recreation places with their spas. The distances of these regions from Ankara are about 45-70 km far. Temperatures of samples measured at the sampling sites are 31 °C, 52 °C, 50 °C, 44 °C and 75 °C for Karakaya - Ayaş, İçmece - Ayaş, Beypazarı, Haymana and Kızılcahamam, respectively. The pH values of all samples measured by a field pH-meter were from 5.0 to 8.0. The thermal waters were collected in 2-5 L new polyethylene bottles that were previously cleaned with HNO_3 solution (1%, v/v) and rinsed with the thermal water before filling. Stock solutions in bottles were acidified up to 1% (v/v) with concentrated HNO_3 prior to analysis.

Sample solutions were prepared according to Turkish Standard, TS 6290 [17]. 5 mL of concentrated HNO_3 and 5 mL of concentrated H_2O_2 were added to each polytetrafluroethylene (PTFE) beaker containing 100 mL of the thermal water sample. Samples were heated and vaporized on a hot-plate at 55 - 60 °C until volumes of them were approximately 20 mL to reduce carbonaceous residues [18] and organic compounds with wet digestion. After cooling, samples were poured into the 100-mL volumetric flask by cleaning interior surface of PTFE beaker three times with de-ionized water and diluted to 100 mL. One mL of 160 µg L^{-1} Cd and 2 mL of 1 mg L^{-1} Pb aqueous standard solutions were added to each thermal water solution and the procedure mentioned above was also repeated for spiked solutions. Blank solutions were prepared to observe interferences from chemical reagents for the determinations of analytes in sample solutions.

2.4. Optimization Studies

Pyrolysis temperatures of analytes in aqueous standards and sample solutions were obtained with and without modifiers studied while the atomization temperatures were fixed at 1800 °C for Cd and 2100 °C for Pb (Table 1). For this purpose, two different optimization studies were performed. Firstly, 1 mL of the thermal water solution was added into 1 mL of modifier solution (Ni (3.0 mg mL^{-1} Ni) or Ni+Ru (3.0 mg mL^{-1} Ni + 0.4 mg mL^{-1} Ru) or Ni+Ru+CA (3.0 mg mL^{-1} Ni + 0.4 mg mL^{-1} Ru + 20 mg mL^{-1} CA)). Secondly, 1 mL of 1.0 µg L^{-1} Cd or 1 mL of 10 µg L^{-1} Pb aqueous standard solution was added into 1 mL of modifier solution as given above. The prepared solutions were injected into the platform. Pyrolysis and atomization temperatures, ramp and hold times for Cd and Pb in samples and aqueous standard solutions were investigated with and without modifiers in Triton-X 100 (0.1%, v/v) plus nitric acid (0.1%, v/v) mixture by preliminary experiments. The optimized heating program for Cd and Pb obtained with Ni+Ru+CA modifier mixture is given in Table 1. Atomization temperatures of analytes were also obtained with and wihtout modifiers while the pyrolysis temperatures of analytes found were fixed. The integrated absorbance versus pyrolysis and atomization temperature curves of Cd and Pb obtained from standard and sample solutions in the absence and the presence of Ni+Ru+CA modifier mixture are given in Figure 1 as an example. The mean of three absorbance values of Cd and Pb with 2% relative standard deviation was plotted for all modifiers tested. The pyrolysis temperatures of Cd and Pb obtained from aqueous standard and sample solutions in the absence and the presence of modifiers studied are given in Table 2.

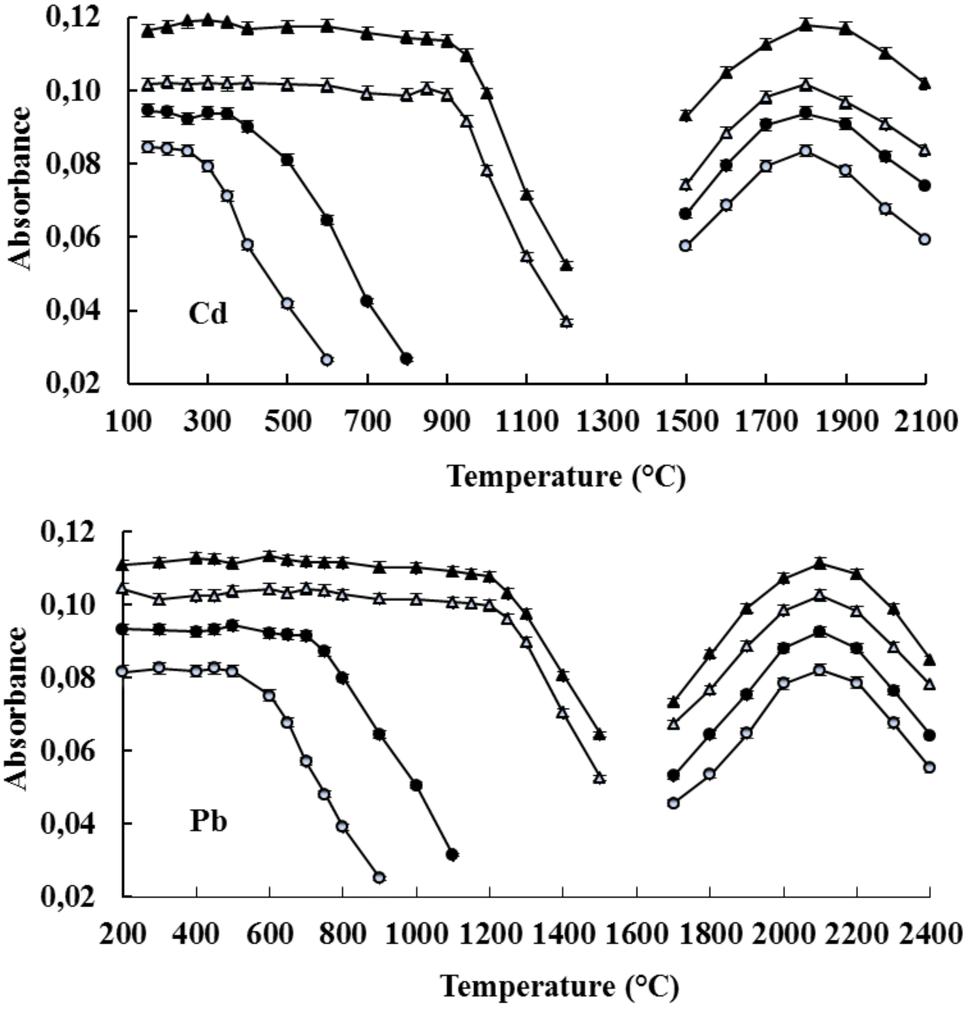

Figure 1. Pyrolysis and atomization temperature curves of Cd and Pb in aqueous standard solutions (1.0 µg L^{-1} Cd and 10 µg L^{-1} Pb) and İçmece-Ayaş thermal water: Without (-o- for aqueous standard solutions of Cd and Pb; -●- for Cd and Pb in the sample solution) and with Ni+Ru+CA modifier mixture (-Δ- for aqueous standard solutions of Cd and Pb; -▲- for Cd and Pb in sample solution).

3. RESULTS AND DISCUSSION

3.1. Thermal Stabilizations of Cd and Pb by Modifiers

Zeeman background correction, platform inserted into a tube and a chemical modifier were used to decrease background and interferences from sample matrix. Thermal stabilization studies of Cd and Pb in the thermal waters with Ni, Ni+Ru and Ni+Ru+CA modifier mixture and without were performed because high contents of ions such as Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} were present in such samples. Optimum masses of modifiers found as 30 µg Ni and 4 µg Ru in our previous works [13, 19] were used and 200 µg CA was added as a reducing agent. Maximum pyrolysis temperatures for Cd and Pb in aqueous standard solutions and sample solutions such as Beypazarı (Dutluk - Tahtalı) and Haymana obtained with Ni, Ni+Ru and Ni+Ru+CA modifier mixture and without are given in Table 2. As seen in Table 2, pyrolysis temperatures of analytes in samples and aqueous standard solutions obtained with Ni+Ru+CA are sufficient to remove large amounts of sample matrix without the risk of analyte loss. The use of both platform and modifier mixture delays the vaporization of analytes in the sample solution until the maximum pyrolysis temperatures, thus reducing interferences [20]. Maximum pyrolysis temperatures of analytes obtained with Ni+Ru+CA modifier mixture were compared with the previous studies [19, 21-25] and the results found were similar. The small differences in pyrolysis temperatures are ascribed to the instrumental conditions and different batch of tubes and platforms used, and the reactivity of analytes with the modifier mixture used. As seen in Table 2, without a modifier, Cd and Pb mass are lost at temperatures higher than 250 ºC for Cd and 500 ºC for Pb, but with the Ni+Ru+CA modifier mixture, analytes are lost at temperatures higher than 900 ºC for Cd and 1200 ºC for Pb. Pyrolysis temperatures of analytes found by Ni+Ru+CA are enough to eliminate interferences and to reduce background in sample solutions in the presence of alkaline and alkaline earth metal ions such as Na^{+}, K^{+}, Ca^{2+} and Mg^{2+} [26]. In general, addition of CA as a reducing agent together with Triton X-100 to the sample solution as Ni+Ru+CA modifier mixture reduces the modifiers and analytes effectively into their reactive metallic forms [27, 28].

Table 2. Pyrolysis temperatures, limit of detection (LOD), limit of quantification (LOQ) and characteristic masses (mo) of Cd and Pb obtained with ETAAS using various modifiers.

	Temperature (°C)									
	Cd		Pb		LOD (µg L^{-1})		LOQ (µg L^{-1})		m_o (pg)	
Modifier	Sample	Standard[a]	Sample	Standard[a]	Cd	Pb	Cd	Pb	Cd	Pb
Without	350	250	700	500	0.86	2.14	2.84	7.06	2.4	45
Ni	700	600	900	750	0.34	1.82	1.12	6.00	1.7	33
Ni+Ru	850	800	1150	1100	0.15	1.28	0.50	4.22	1.1	22
Ni+Ru+CA	900	900	1200	1200	0.06	0.81	0.20	2.67	0.7	16

[a] Maximum pyrolysis temperatures of Cd and Pb found by using aqueous standard solutions (1.0 µg L^{-1} Cd and 10.0 µg L^{-1} Pb).

Atomization and background profiles of Cd and Pb in sample solutions with Ni, Ni+Ru and Ni+Ru+CA and without were studied comparatively to show how the modifiers affect the atomization / background signals of analytes [24, 29-31]. Figure 2 shows the Cd and Pb atomization and background signals obtained with Ni+Ru+CA and without in Kızılcahamam thermal waters as an example. As seen in Figure 2, in the presence of Ni+Ru+CA, maximum peak and appearance times of atomization signals of Cd and Pb obtained in samples were higher than in the absence of a modifier and there was no reduction in atomization signal [19, 31, 32]. High background absorption signals of analytes were obtained in the absence of a modifier. By using Ni+Ru+CA modifier mixture, the lowest background signals of analytes were obtained and matrix effects in the sample solutions were reduced. The signal / noise ratios of analytes obtained with the Ni+Ru+CA were higher than those obtained without a modifier [19]. As a result of this high signal / noise ratio, the lowest detection limits and characteristic masses of analytes were obtained with Ni+Ru+CA modifier mixture.

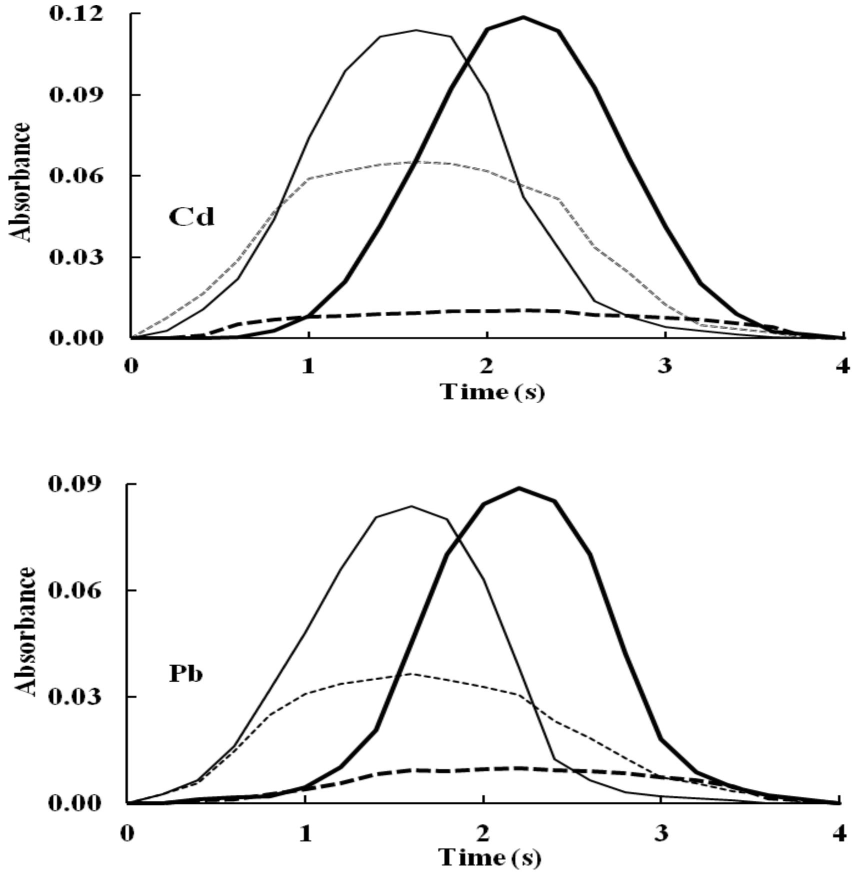

Figure 2. Atomization and background profiles of Cd and Pb in Kızılcahamam thermal water without (Atomization,—; Background,----) and with the Ni+Ru+CA modifier mixture (Atomization,▬; Background,▪▪▪▪▪).

3.2. Analytical Performance of the Method

Limit of detection (LOD), limit of quantification (LOQ) and characteristic masses (m_o) [33] of analytes in ETAAS are related to the sensitivity of the method proposed. The LOD ($3\sigma_b$/m; the concentration of an analyte related to the three times of the standard deviation of absorbance values from a blank solution divided by slope of calibration curve), LOQ ($10\sigma_b$/m) and the m_o (the mass of analyte related to the 0.0044 absorbance unit) values for Cd and Pb were obtained from 20 replicate measurements of blank solutions by calibration graph method using aqueous standard solutions with and without modifiers [33, 34] and results are given in Table 2. As seen in Table 2, the lowest LOD, LOQ and m_o values of analytes were obtained by using Ni+Ru+CA modifier mixture and it was preferred for the accurate and reliable determinations of Cd and Pb in the thermal waters by ETAAS. Detection limits of Fe, Zn, Na, K, Ca and Mg obtained by FAAS and FAAS with AEM were 5.2, 4.9, 5.6, 7.1, 11.2 and 5.4 µg L^{-1}, respectively.

Determinations of Cd and Pb by ETAAS using Ni+Ru+CA modifier mixture and metals (Fe, Zn, Na, K, Ca and Mg) by FAAS and FAAS with AEM in SRMs and sample solutions were performed by using calibration graph method. Linear dynamic ranges of analytes obtained by using aqueous standard solutions were 0.2 - 1.5 µg l^{-1} for Cd, 2.7 - 40 µg l^{-1} for Pb, 0.02 - 3.2 mg L^{-1} for Fe, 0.02 - 0.6 mg L^{-1} for Zn, 0.02 - 1.5 mg L^{-1} for Na and K, 0.04 - 1.2 mg L^{-1} for Ca and 0.02 - 0.4 mg L^{-1} for Mg, respectively. Calibration graphs for analytes were linear and correlation coefficients (R^2) were higher than 0.99.

Cd, Pb, Fe, Zn, K, Na, Ca and Mg in SRMs (Spsww-1 and 1643e water) and sample solutions spiked with aqueous standard solutions of Cd and Pb were analyzed by ETAAS using Ni+Ru+CA mixture, FAAS and FAAS with AEM to carry out the recovery tests and to evaluate the accuracy and precision of the method proposed. The satisfactory results of analytes found in SRMs are given in Table 3. As seen in Table 3, the percent recovery ranges of analytes obtained are from 96% to 105% and they are in good agreement with the certified values. Percent relative standard deviation (RSD %) of analytes obtained is less than 5%. The aqueous standard solutions of Cd and Pb were added into the thermal waters to control the mass of analyte during measurements, effects of sample matrix interferences on analyte atomization and differences such as viscosity of sample and standard. The recoveries of Cd and Pb found in spiked samples are also given in Table 4. As seen in Table 4, the percent recoveries of analytes are in the range from 95% to 105% and RSD (%) is less than 5%. These results show that the accuracy of the procedure is satisfactory.

Table 3. Recovery studies of analytes in SRMs (1643e and Sps-ww-1) by ETAAS using Ni+Ru+CA modifier mixture, by FAAS and by FAES.

		Concentration[a] (µg L^{-1})			
Sample	Element	Certified value	Found[a]	RSD %	Recovery %
1643e	Cd	6.57 ± 0.07	6.32 ± 0.20	3.02	96
	Pb	19.6 ± 0.2	19.2 ± 0.6	2.98	98
	Fe	98.1 ± 1.4	97.2 ± 1.9	1.86	99
	Zn	78.5 ± 2.2	79.4 ± 2.1	2.52	101
	Na	20740 ± 260	20430 ± 340	1.59	99
	K	2034 ± 29	2041± 31	1.45	100
	Ca	32300 ± 1100	32100 ± 655	1.94	99
	Mg	8037 ± 98	7981 ± 139	1.66	99
Spsww-1	Cd	20 ± 1	21 ± 1	4.54	105
	Pb	100 ± 5	97 ± 4	3.93	97
	Fe	1000 ± 5	992 ± 14	1.35	99
	Zn	600 ± 6	608 ± 10	1.57	101

[a] Mean of 6 replicate measurements with 95 % confidence level, $\bar{x} \pm \frac{t \cdot s}{\sqrt{N}}$.

Table 4. Recovery tests for Cd and Pb spiked in samples by ETAAS using Ni+Ru+CA matrix modifier mixture (Dilution factors of analytes were 1/4 for Cd and 1/2 for Pb, respectively).

		Concentration[a] (μg L^{-1})			
Sample	Element	Spiked	Found[a]	RSD %	Recovery %
Karakaya - Ayaş	Cd	0.0	0.81 ± 0.03	3.53	-
		0.4	1.19 ± 0.05	4.00	98
	Pb	0.0	3.26 ± 0.12	3.51	-
		10	12.9 ± 0.58	4.29	97
İçmece - Ayaş	Cd	0.0	0.93 ± 0.03	3.07	-
		0.4	1.29 ± 0.05	3.69	97
	Pb	0.0	4.18 ± 0.15	3.42	-
		10	13.6 ± 0.58	4.06	96
Beypazarı	Cd	0.0	1.07 ± 0.04	3.56	-
		0.4	1.41 ± 0.06	4.06	96
	Pb	0.0	3.96 ± 0.16	3.85	-
		10	13.7 ± 0.61	4.24	98
Haymana	Cd	0.0	0.69 ± 0.03	4.14	-
		0.4	1.04 ± 0.04	3.67	95
	Pb	0.0	3.89 ± 0.13	3.19	-
		10	14.1 ± 0.52	3.52	102
Kızılcahamam	Cd	0.0	1.08 ± 0.04	3.53	-
		0.4	1.42 ± 0.06	4.03	96
	Pb	0.0	3.04 ± 0.11	3.45	-
		10	12.8 ± 0.58	4.32	98

[a] Mean of 6 replicate measurements with 95 % confidence level, $\bar{x} \pm \frac{t \cdot s}{\sqrt{N}}$.

3.3. Determinations of Analytes in the Thermal Waters

Cd and Pb by ETAAS using the Ni+Ru+CA modifier mixture, Fe, Zn, Ca and Mg by FAAS, and Na and K by FAAS with AEM in the thermal waters were determined. The concentrations of analytes expressed as the average ± confidence interval at 95% confidence level are given in Table 5. As seen in Table 5, the results of analytes found in the thermal waters were compared with maximum permissible levels (MPLs) of analytes for water quality criteria given by the WHO [5, 7], European Community Directive [6], US EPA [35, 36], the Turkish standards and regulations [37-40] and a previous study [41]. Unfortunately, a water quality guideline or a standard for the thermal waters was not found. Metal contents of these waters can be changed in different regions of the world and the results of analytes found may be higher than the maximum permissible values for drinking water given by the WHO or EPA.

Table 5. Results of analytes found in thermal waters and comparison with maximum admissible concentrations of analytes given in guidelines, regulations, standards and previous study.

		Concentration[a]					
Element	Unit	Karakaya-Ayaş	İçmece - Ayaş	Beypazarı	Haymana	Kızılcahamam	MPL for drinking waters [Ref. No.]
Cd	μg L^{-1}	3.2 ± 0.2	3.7 ± 0.2	4.3 ± 0.2	2.8 ± 0.2	4.3 ± 0.2	3 [7,37,38,41], 5 [6,35,36,40]
Pb	μg L^{-1}	6.5 ± 0.1	8.4 ± 0.4	7.9 ± 0.3	7.8 ± 0.1	6.1 ± 0.2	10 [6,7,37-40], 15 [35]
Fe	μg L^{-1}	361 ± 17	391 ± 22	373 ± 18	146 ± 21	323 ± 15	200 [6,39,40], 300 [7,35-37], 1000 [38], 2000 [5]
Zn	μg L^{-1}	67 ± 3	49 ± 2	13 ± 1	84 ± 3	98 ± 4	3000 [7], 5000 [35-37], 980 [41]
Na	mg L^{-1}	147 ± 5	121 ± 4	524 ± 23	71 ± 3	583 ± 28	200 [6], 250 [7], 175 [37]
K	mg L^{-1}	47 ± 2	41 ± 3	9.3 ± 0.6	11 ± 2	45 ± 2	250 [7], 12 [37]
Ca	mg L^{-1}	536 ± 21	548 ± 25	528 ± 22	93 ± 4	22 ± 1	100 [7,37], 421 [41]
Mg	mg L^{-1}	76 ± 3	82 ± 4	11 ± 1	27 ± 1	34 ± 2	36.5 [7], 50 [37], 447 [41]

[a] Mean of 6 replicate measurements with 95% confidence level, $\bar{x} \pm \frac{t \cdot s}{\sqrt{N}}$.

It was observed that average values of Cd found in water samples are lower than the MPLs of Cd given by European Community, Directive 98/83/EC [6], the WHO [7], US-EPA [35, 36], the Turkish standards and regulations [37 - 40] and also previous study [41] (Table 5). From the guidelines for drinking water quality given by the WHO [7], the level of Cd in drinking water should be less than 1 µg L^{-1} and provisional tolerable monthly intake (PTMI) of Cd is 25 µg kg^{-1} of body weight for 60 kg adult. Concentrations of Pb found in sample solutions are also lower than the MPLs of Pb for water quality given by European Community, Directive 98/83/EC [6], the WHO [7] and the Turkish standards and legislations [37 - 40] and given by US-EPA [35] (Table 5). The level of Pb in drinking-water is generally below 5 µg L^{-1} and established provisional tolerable weekly intake (PTWI) of Pb is 25 µg kg^{-1} body weights for 60 kg adult.

Iron concentrations in Karakaya - Ayaş, İçmece - Ayaş, Beypazarı and Kızılcahamam thermal waters are higher than maximum permissible values given by European Community, Directive 98/83/EC [6], the WHO [7], EPA [35, 36] Turkish standard [39] and legislations [37, 40], but they are lower than MPL given by the Turkish standard [38]. Concentration ranges of Fe in natural fresh waters are from 0.5 to 50 mg L^{-1} and provisional maximum tolerable daily intake (PMTDI) of Fe is 0.8 mg kg^{-1} body weight. Zn concentrations in water samples are also lower than the MPLs given by the WHO, EPA, Turkish legislation and previous study [7, 35 - 37, 41] (Table 5). The PMTDI of Zn proposed is 1 mg kg^{-1} body weight, but Zn level above 3 mg L^{-1} in drinking water may not be acceptable to consumers. Concentrations of Na found in thermal waters of Karakaya-Ayaş, İçmece-Ayaş and Haymana (Table 5) are lower than the MPLs given in the WHO [7], European Community, Directive 98/83/EC [6] and the Turkish legislation [37], but Na results in Beypazarı and Kızılcahamam are higher than those values given by the WHO and the Turkish legislation. The range of K concentrations found in samples is from 9.3 to 47 mg L^{-1}. Some of the results are higher than the MPL given in the Turkish Legislation [37], but all results found in samples are lower than the MPL given in the WHO [7] (Table 5). Concentrations of Ca found in Karakaya-Ayaş, İçmece-Ayaş and Beypazarı thermal waters are higher than the MPLs given in the WHO [7] and the Turkish Legislation [37] and they may be depend on the geological features of rocks through which the water passes. Concentrations of Mg found in the thermal waters of Karakaya - Ayaş and İçmece - Ayaş are higher than the MPLs given in the WHO [7] and Turkish Legislation [37], but they are lower than the provious study [41] (Table 5).

4. CONCLUSION

In this study, Ni+Ru+CA modifier mixture was proposed for the determination of Cd and Pb in the thermal waters having complex matrices by ETAAS. Major elements (Fe, Zn, Na, K, Ca and Mg) in these waters have also been determined by FAAS and FAAS with AEM. The highest signal/noise ratios, better detection and quantification limits, and characteristic masses of Cd and Pb have been obtained by using Ni+Ru+CA. The accuracy, the precision and the sensitivity of analytes found are highly good for the determinations of Cd and Pb in the thermal waters. It can be concluded that Ni+Ru+CA modifier mixture may be used for the direct determinations of Cd and Pb in such thermal water samples in the future. Although the samples have highly complex matrices and interferences, chemical pre-treatment procedures such as solvent extraction and solid phase extraction for the sample solutions are not necessary for the determination of analytes. In this work, results of some metals such as Fe, Na, Ca and Mg found in sample solutions have exceeded the MPLs for drinking waters given by the WHO and the Turkish Legislation criteria. Concentrations of these elements may be determined to control the metal contamination levels of thermal water samples or to research the origin of elements from underground in the future.

ACKNOWLEDGMENTS

The supports of Gazi University Research Fund (BAP No: 41/2008 - 03) are gratefully acknowledged.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

[1] Citak, D., Tuzen, M. and Soylak, M., "Simultaneous coprecipitation of lead, cobalt, copper, cadmium, iron and nickel in food samples with zirconium(IV) hydroxide prior to their flame atomic absorption spectrometric determination", *Food Chem. Toxicol.,* 47: 2302 – 2307 (2009).

[2] Wang, F. Y., Wang, H. and Ma, J. W., "Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent- bamboo charcoal", *J. Hazard. Mate.,* 177: 300 – 306 (2010).

[3] Júnior, D. S., Júnior, F. B., De Souza, S. S. and Krug, F. J., "Cryogenic sample grinding for copper, lead and manganese determination in human teeth by slurry sampling GFAAS", *J. Anal. Atom. Spectrom.,* 18: 939 - 945 (2003).

[4] Niederau, C., Fischer, R., Purschel, A., Stremmel, W. and Haussinger, D., "Long-term survival in patients with hereditary hemochromatosis", *Gastroenterology,* 110: 1107 – 1119 (1996).

[5] WHO, Rolling revision of the WHO guidelines for drinking water quality, Nutrient minerals in drinking-water and the potential health consequences of long-term consumption of demineralized and remineralized and altered mineral content drinking-waters, World Health Organization, Geneva, Switzerland, (2003).

[6] European Community, Directive 98/83/EC on the quality of water intended for human consumption (1998).

[7] WHO, Guidelines for Drinking-water Quality- 4th ed. 1. Potable water - standards. 2. Water-standards. 3. Water quality-standards. 4. Guidelines. I. World Health Organization. Geneva 27, Switzerland, (2011).

[8] Luu, T. T. G., Sthiannopkao, S. and Kim, K.-W., "Arsenic and other elements contamination in groundwater and a risk assessment study for the residents in the Kandal Province of Cambodia" *Environ. Int.*, 35: 455 – 460 (2009).

[9] Meeravali, N. N. and Kumar, S. J., "Determination of Cd, Pb, Cu, Ni and Mn in effluents and natural waters by a novel salt induced mixed-micelle cloud point extraction using ETAAS", *Anal. Methods*, 4: 2435 – 2440 (2012).

[10] Lelis, K. L. A., Magalhães, C. G., Rocha, C. A. and Silva, J. B. B., "Direct determination of Cr and Cu in urine samples by electrothermal atomic absorption spectrometry using ruthenium as permanent modifier (R1)", *Anal. Bioanal. Chem.,* 374: 1301 – 1305 (2002).

[11] Souza, J. M. O. and Tarley, C. R. T., "Sorbent separation and enrichment method for cobalt ions determination by graphite furnace atomic absorption spectrometry in water and urine samples using multiwall carbon nanotubes", *Int. J. Environ. Anal. Chem.,* 89: 489 – 502 (2009).

[12] Lima, E. C., Barbosa, R. V., Brasil, J. L. and Santos, A. H. D. P., "Evaluation of different permanent modifiers for the determination of arsenic, cadmium and lead in environmental samples by electrothermal atomic absorption spectrometry", *J. Anal. Atom. Spectrom.,* 17: 1523 – 1529 (2002).

[13] Acar, O., Kılıç, Z. and Türker, A. R., "Determination of bismuth, indium and lead in geological and sea water samples by Electrothermal atomic absorption spectrometry with nickel containing chemical modifiers", *Anal. Chim. Acta,* 382: 329 – 338 (1999).

[14] Hagarová, I., Matúš, P., Bujdoš, M. and Kubová, J., "Analytical Application of Nano-Sized Titanium Dioxide for the Determination of Trace Inorganic Antimony in Natural Waters", *Acta Chim. Slov.*, 59: 102 – 108 (2012).

[15] Caldas, N. M., Raposo, Jr J. I., Neto, J. A. G. and Barbosa, Jr F., "Effect of modifiers for As, Cu and Pb determinations in sugar-cane spirits by GFAAS", *Food Chem.,* 113: 1266 – 1271 (2009).

[16] Lima, E. C., Barbosa Jr, F., Krug, F. J. and Taravers, A., "Copper determination in biological materials by ETAAS using W–Rh permanent modifier", *Talanta,* 57: 177 – 186 (2002).

[17] TS 6290, "Water quality-Determination of cobalt, nickel, copper, zinc, cadmium and lead - Flame atomic absorption spectrometric method", Turkish Standard, (1989).

[18] Vinas, P., Martinez, M. P. and Cordoba, M. H., "Rapid determination of selenium, lead and cadmium in baby food samples using electrothermal atomic absorption spectrometry and slurry atomization", *Anal. Chim. Acta*, 412: 121 – 130 (2000).

[19] Acar O., "Determination of cadmium and lead in biological samples by Zeeman ETAAS using various chemical modifiers", *Talanta*, 55: 613 – 622 (2001).

[20] De Castro Maciel, C. J., Miranda, G. M., De Oliveira, D. P., De Siqueira, M. E. P. B., Silveira, J.N., Leite, E. M. A. and De Silva J. B. B., "Determination of cadmium in human urine by electrothermal atomic absorption spectrometry", *Anal. Chim. Acta,* 491: 231 – 237 (2003).

[21] Tsalev, D. L. and Slaveykova, V. I., "Chemical modification in electrothermal atomic absorption spectrometry. Organization and classification of data by multivariate methods, Invited lecture", *J. Anal. Atom. Spectrom.,* 7: 147 – 153 (1992).

[22] Tsalev, D. L. and Slaveykova, V. I., "Comparative study of ruthenium, rhodium and palladium as chemical modifiers in graphite furnace atomic absorption spectrometry", *Spectrosc. Lett.,* 25: 221-238 (1992).

[23] Mandjukov, P. B. and Tsalev, D. L., "Study of cerium (IV) and cerium (VI)- palladium (II) as chemical modifiers in electrothermal atomization

atomic absorption spectrometry", *Microchem. J.*, 42: 339 – 348 (1990).

[24] Tsalev, D. L., Dimitrov, T. A. and Mandjukov, P. B., "Study of vanadium (V) as a chemical modifier in electrothermal atomisation atomic absorption spectometry", *J. Anal. Atom. Spectrom.,* 5: 189 – 194 (1990).

[25] Slaveykova, V. I. and Tsalev, D. L., "Stuy of some tungsten- containing chemical modifiers in graphite furnace atomic absorption spectrometry", *Anal. Lett.,* 23: 1921 – 1937 (1990).

[26] Tsalev, D. L., Lampugnani, L., Georgieva, R., Chakarova, K. K. and Petrov Jr, I. I., "Electrothermal atomic absorption spectrometric determination of cadmium and lead with stabilized phosphate deposited on permanently modified platforms", *Talanta,* 58: 331 – 340 (2002).

[27] Imai, S., Hasegawa, N., Nishiyama, Y., Hayashi, Y. and Saito, K., "Effect of ascorbic acid and sucrose on electrothermal atomic absorption signals of indium", *J. Anal. Atom. Spectrom.*, 11: 601 – 606 (1996).

[28] Byrne, J. P., Chakrabarti, C. L., Gilchrist, G. F. R., Lamoureux, M. M. and Bertels, P., Chemical modification by ascorbic acid and oxalic acid in graphite furnace atomic absorption spectrometry, *Anal. Chem.*, 65: 1267 – 1272 (1993).

[29] Havezov, I., Detcheva, A. and Rendl, J., "Study of some palladium-containing chemical modifiers in graphite furnace atomic absorption spectrometry", *Mikrochim. Acta*, 119: 147 – 155 (1995).

[30] Russeva, E., Havezov, I. and Detcheva, A., "Arsenic Speciation in Waste Waters by Extraction Chromatography Followed by Atomic Absorption Spectromety", *Fresenius J. Anal. Chem.,* 347: 320 – 323 (1993).

[31] Shan, X.-Q. and Wen, B., "Is palladium or palladium–ascorbic acid or palladium–magnesium nitrate a more universal chemical modifier for electrothermal atomic absorption spectrometry? " *J. Anal. Atom. Spectrom.,* 10: 791 – 799 (1995).

[32] Welz, B., Schlemmer, G. and Mudakavi, J. R., "Palladium nitrate–magnesium nitrate modifier for electrothermal atomic absorption spectrometry. Part 5. Performance for the determination of 21 elements", *J. Anal. Atom. Spectrom.,* 7: 1257 – 1271 (1992).

[33] Bermejo-Barrera, P., Aboel-Somoza, M., Soto-Ferreiro, R.M. and Dominguez-Gonzalez, R., "Palladium -magnesium nitrate as a chemical modifier for the determination of lead in mussel slurries by electrothermal atomic absorption spectrometry", *Analyst,* 118: 665 – 668 (1993).

[34] Commission on Spectrochemical and Other Optical Procedures for Analysis, *Spectrochim. Acta B*, 33: 241 - (1978).

[35] US EPA, Environmental Protection Agency, Drinking Water Contaminants, List of Contaminants and their Maximum Contaminant Level (MCLs), http://www.epa.gov /safewater/ contaminants/index. html, Last updated on June 5th (2008).

[36] US EPA, US Environmental Protection Agency, Edition of the Drinking Water Standards and Health Advisories EPA, *820-R-11-002*: 1 – 80 (2011).

[37] Turkish Legislation, İçilebilir nitelikteki suların istihsali, ambalajlanması, satısı ve denetlenmesi hakkında yönetmelik. R.G. no. 23144, Resmi Gazete (Official Newspaper of the Turkish Government) (in Turkish), (1997).

[38] TS 9130, Natural mineral water, Turkish Standard, (in Turkish), (2010).

[39] TS 266, Water intended for human consumption, Turkish Standard (in Turkish), (2005).

[40] İnsani Tüketim Amaçlı Sular Hakkında Yönetmelik, 25730 sayılı Resmi Gazete (in Turkish), 17 February (2005).

[41] Guler, C., "Evaluation of maximum contaminant levels in Turkish bottled drinking waters utilizing parameters reported on manufacturer’s labeling and government-issued production licenses", *J. Food Compos. Anal.,* 20: 262 – 272 (2007).