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Determination of Ni, Pb and Cd in drinking fountain water in Kırklareli/Turkey by FAAS after preconcentration on quercetin modified using granular activated carbon

Cemile Ozcan[a,*], Serpil Akozcan[b]

[a]*Department of Chemistry, Science and Art Faculty, Kırklareli University, Kırklareli, Turkey, Tel. +90 288 2461734; email: cemilebal.ozcan@klu.edu.tr (C. Ozcan)*
[b]*Department of Physics, Science and Art Faculty, Kırklareli University, Kırklareli, Turkey*

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ABSTRACT

The purpose of this study was to determine the level after preconcentration of trace heavy metals ions using drinking fountain water (20 points) in Kırklareli province by flame atomic absorption spectrophotometer. The method is based on the adsorption of nickel(Ni), lead(Pb) and cadmium(Cd) on quercetin loaded on granular activated carbon. In this study, the effectiveness of variabilities including solution pH, the amount of the ligand and solid phase, the condition of eluting solutions and sample volume on the recoveries of metals were optimized. Under the optimal experimental conditions, the preconcentration factor, detection limit, linear range and relative standard deviation (RSD%) of Ni, Pb, and Cd were investigated. RSDs were found below 5%. Further, the accuracy of the proposed method was also checked by the analysis of certified reference material NIST-SRM-1643e. Eventually, the recommended method was successfully implemented for the analysis of the Ni, Pb, and Cd in environmental water samples. The concentrations of Pb, Ni, and Cd in the waters ranged from 11.0 to 187 $\mu g\ L^{-1}$ for Pb, 14.3 to 56.8 $\mu g\ L^{-1}$ for Ni and 1.21 to 8.90 $\mu g\ L^{-1}$ for Cd.

Keywords: Flame atomic absorption spectrophotometer (FAAS); Enrichment; Activated carbon; Quercetin; Solid phase extraction

1. Introduction

Contamination of the water environment by heavy metals is becoming prevalent across the globe. The usability and quality of freshwater are two of the enormous objection for humanity since the twenty century, with contamination of surface waters with pollutants such as heavy metals, pesticides and permanent organic compounds being of Mondial concern [1]. Heavy metal pollution in drinking water is a serious concern for the environment even at low concentrations [2]. Industrial products that are used in homes, and which have been produced with heavy metals are origins of human exposure to like heavy metals. The investigations of heavy metals have been receiving much attention because of ecological funerals and public health studies. Water resources in the world have been extremely impressed in recent years by human activities, by which the world is recently facing critical water supply and drinking water problems.

However, some others have been reported to have no known bio-importance in human biochemistry, physiology, and consumption, nevertheless at very low concentrations can be toxic [2,3]. For example, chronic oral references doses of 0.4 and 1.0 $\mu g\ kg^{-1}\ d^{-1}$ according to the United States Environmental Protection Agency (USEPA) have been established for cadmium exposure via drinking water and food, respectively [3]. Therefore, according to the World

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* Corresponding author.

Health Organization (WHO) is 3.0 μg L^{-1} the maximum acceptable concentration of Cd [4–6]. Lead is a broadly subsided environmental toxicant for neurological, immune system, hepatic and renal [7]. Nickel is widely used in the contemporary industry and Its over-exposure of humanity can set on substantial effects, including lung, cardiovascular and kidney diseases [8,9].

Kırklareli which in the northwestern Thrace region of Turkey is one of the Black Sea provinces. Among the main activities are industrial facilities and agriculture. Trace-level residues of metals situated in water samples have happened a matter of many studies which have attained international attention. For example, Cd and Pb are biopersistent and once absorbed by an organism, remain resident for many years although it is in the end excreted. Because these metals emerge naturally within the raw ore, cadmium is manufactured as an indispensable by-product of zinc (or infrequently lead) refining. At the same time, once gathered the cadmium is passably easy to recycle. Since rechargeable or secondary power sources exhibiting high output, long life, low maintenance and high tolerance to physical and electrical stress, the most prominent use of cadmium is in nickel/cadmium batteries. Cd coatings supply good corrosion resistance, exceptionally in high-stress environments like marine and aerospace applications where upper safety or trustworthiness is needed, but the coating is liefer corroded if harmed. Cd which with the inclusion of phosphate fertilizers, detergents and refined petroleum products are also available as an impurity in several products. In the widespread, major exposure pathway of Cd in non-smoking inhabitants is thro food, which upon the receipt of the addition of cadmium to agricultural soil from diverse sources (atmospheric deposition and fertilizer application) and uptake with food/fodder crops. Supplementary, exposure to humans is originated because of cadmium in ecological air and drinking water.

Small amounts of Ni are needed by the human body to create red blood cells, but, in immoderate amounts, can become light-weight toxic [9]. Short-lived overexposure to nickel is unknown to engender any health problems, even though long-term exposure can bring about lessened body weight, heart and liver vitiation, and skin irritation. Ni levels in drinking water do not currently regulate by Environmental Protection Agency. Although Ni's presence is not increased throughout food chains, it can amass in aquatic life.

The extensively, in the analysis of heavy metals used techniques as electrothermal atomic absorption spectrometry, inductively coupled plasma-atomic emission spectrometry, and inductively coupled plasma-mass spectrometry. Trace metals quantification by flame atomic absorption spectrophotometer (FAAS) necessitates pre-concentration rung to augment the sensitivity and particularity grades by pre-concentrating the analytes using an intelligible matrix for the samples as detailed [10–12]. Since, the FAAS can be taken as consideration the preferred method because it is faster, cheaper, and does not require skillful operators yet its responsiveness is adequate [13–18]. The separation and pre-concentration techniques for heavy metals are solid-phase extraction (SPE) [19], liquid–liquid extraction [20–23], sonication [24,25] and cloud point extraction [26], which are used to solve these problems of trace metal analysis. The chelating agents used for SPE ought to have high dispersal coefficients and pH dependence. Diversified supports and adsorbents, with the inclusion of activated carbon (AC), chelating resin (Amberlite XAD, Merck, Germany), Chelex-100, silica gel, Chemisorb 108, Dowex® 50WX4, (Merck, Germany), surfactant coated alumina and chromosorb [27–41] can be exercised in the chelate extraction practice.

This study aimed to determine with SPE using quercetin and granular activated carbon for heavy metals pre-concentration in a drinkable water fountain from Kırklareli (Turkey) by FAAS. On account of its intensive industry and agriculture, Kırklareli was chosen as the study field. The developed method was applied for the determination of the Pb, Ni, and Cd in water samples of different points collected.

2. Experimental setup

2.1. Instrumentation

The Pb, Ni, and Cd concentrations were detected by an Agilent-240 Duo FAAS (ABD). Samples were made ready with microwave digestion (MW) (Mars 6 CEM Corporation). The practical tool provisos are given in Table 1. pH was measured with an inoLab® pH 7310 WTW D-82362 Weilheim pH meter. For the enrichment procedure, a thermal-magnetic stirrer, a Hettich centrifuge, a JeioTechoven, (Korea), and a Shimadzu, (Korea) analytical balance were used.

2.2. Standards and reagents

The Pb, Ni and Cd solutions (1,000 mg L^{-1}, stocks) were made ready (Darmstadt, Germany). Subsequently, calibration standards of each metal were made ready by proper dilution (in 2.5% HNO_3) of the present solution. On account of the digestion of the samples, nitric acid and hydrogen peroxide were utilized. Whole chemicals utilized were of high purity analytical reagent grade unless otherwise stated. For all preparations were used to double-distilled water acquired with a water purification system, and whole glassware and Teflon vessels were kept for always fulfill of 2.5% HNO_3. All the vessels utilized in the digestion were bumped off by soaking them in 15% HNO_3 bath for 24 h, followed by three times churning using Milli-Q Reference Water Purification System.

Buffer solutions in the pH range of 1.0–12.0 ± 0.2 were prepared by using 0.2 M KCl, 0.1 M potassium hydrogen phthalate, 0.1 M KH_2PO_4, $Na_2B_4O_7{\cdot}10H_2O$, 0.1 M Na_2HPO_4 solutions. The pH adaptation was fulfilled by suffixing 0.01–1.0 M HCl and/or NaOH until the wished-for pH was attained.

Table 1
Instrumental operating conditions for FAAS

Parameter	Pb	Ni	Cd
Wavelength (nm)	217.0	352.5	228.8
HCL current (mA)	4.0	4.0	4.0
Acetylene flow rate (L min^{-1})	2.00	2.00	2.00
Air flow rate (L min^{-1})	13.5	13.5	13.5
Slit width (nm)	0.7	0.2	0.5

AC used as an adsorbent, passed through a 250 g (Merck 2514, Germany), was treated with concentrated HCl for 3 h, washing with ultrapure water, drying at 100°C, then, one night waited in the king water. After, the white band was filtered through filter paper and washing with ultrapure water of active carbon by using the vacuum pump was carried out, until the turbidity was exhausted. After washing, the AC was dried at 100°C and passed through a 200 mesh sieve. It has been made available for experimental procedures [16]. Since AC is a type of hydrophobic adsorbent that adsorbs non-polar or few polar substances in aqueous solution, metal ions to be pre-concentrated need to be converted corresponding metal chelates. For this reason, the groups on AC can be activated using the quercetin ligand (Fig. 1).

2.3. Collection of water samples

The water of twenty different fountains in Kırklareli City Center was used as samples in this study (Fig. 2). Approximately 1,000 mL of water from fountains were gathered. All samples were put into a dry plastic bottle (cleaned down 2.5% HNO_3 and distilled water).

For the MW of water samples, 40 mL of sample was digested with 5 mL of concentrated HNO_3 and 5 mL of concentrated H_2O_2 in the MW system, which the probable organic content in the water samples was oxidized. In the blank samples were made ready in the similar via, and the put forward pre-concentration separation process was enforced.

2.4. Optimization study for preconcentration

In the optimization studies, 100 mL of 80 ng mL^{-1} nickel, 100 ng mL^{-1} Pb and 50 ng L^{-1} Cd solutions including the matrix components: Na 1,000 mg L^{-1}, Ca 100 mg L^{-1}, Mg 25 mg L^{-1}, Fe, Mn, Zn and Al 0.5 mg L^{-1}, were used as model solutions that represent the natural water example.

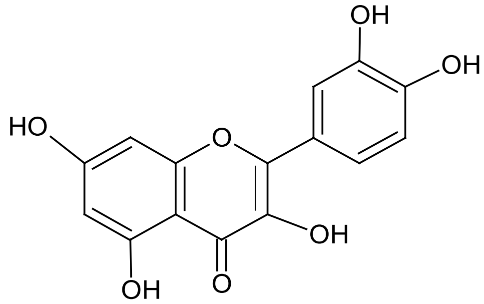

Fig. 1. Structure of the ligand.

Fig. 2. Sampling points of water taken from the fountains in the city center of Kırklareli.

2.4.1. Effect of pH

The model solutions of Pb, Ni, and Cd were preconcentrated using pH values ranging from 1.0–12.0 and the recoveries obtained are shown in Fig. 3. On the AC (0.2 g) and quercetin ligand (0.2 mol L^{-1} in methanol) used to determine the optimum pH range, 5 mL of 100 ppb Pb, 80 ppb Ni and 50 ppb Cd model solutions were added.

2.4.2. Effect of stirring time

The pre-concentration procedure was implemented to the model Pb, Ni, and Cd solutions by using dissimilar stirring times at the optimum conditions illustrated in Fig. 4.

2.4.3. Effect of the amount of quercetin

The amount of ligand used in the quantitative recovery of metal ions is very important (Fig. 5).

2.4.4. Effect of the amount of AC

To investigate the effect of active carbon utilization and recovery as an adsorbent in the SPE process, the amount of active carbon in the value range shown in Fig. 6 was studied.

2.4.5. Effect of the sample volume

The influences of the sample volume on the recoveries of analytes (Pb, Ni, and Cd) were investigated in the sample volume range from 5–1,000 mL by using model solutions (Fig. 7).

2.4.6. Effect of interference

The influences of potential various ions on the efficiency of analytes were inspected by adding of dissimilar ions in the known concentrations. The results were summed up in Table 2.

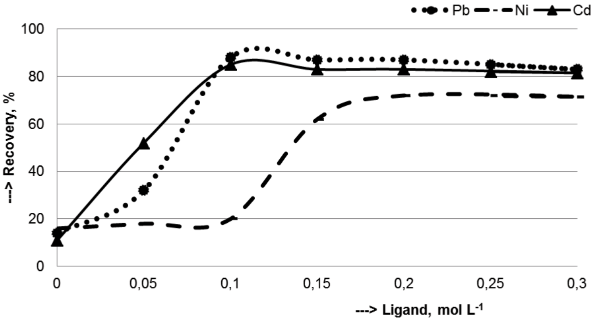

Fig. 5. Effect of the amount of quercetin ligand on the recovery of analyte ions.

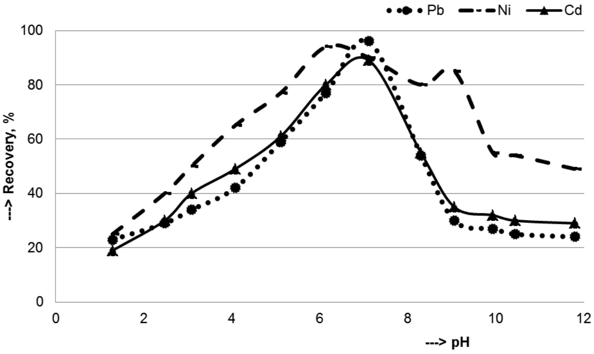

Fig. 3. Effect of pH on the recovery of analyte ions.

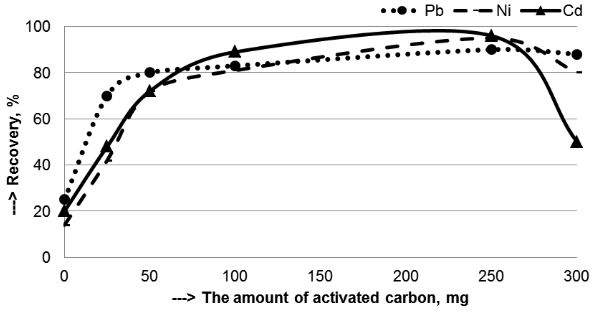

Fig. 6. Determination of the optimum amount of activated carbon using quercetin.

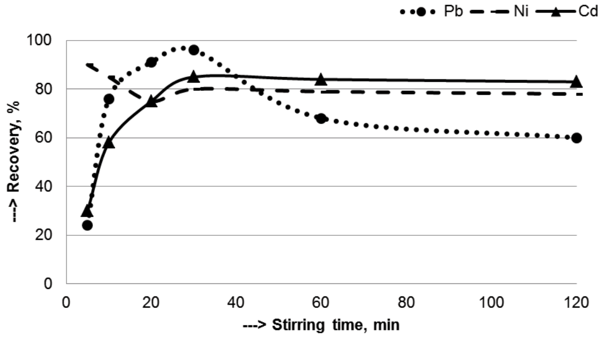

Fig. 4. Effect of stirring time on recovery of analyte ions.

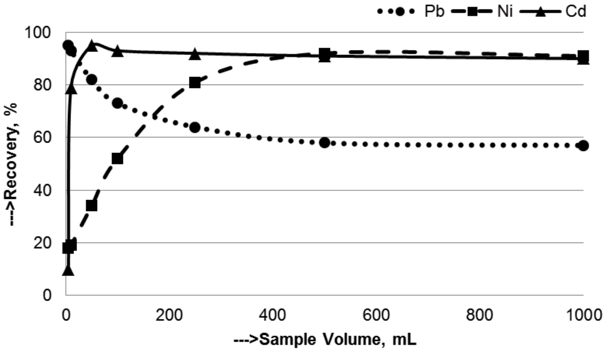

Fig. 7. Effects of sample volume on the recoveries.

The optimum conditions for Pb, Ni, and Cd in the SPE pre-concentration method are shown in Table 3. Moreover, linearity, accuracy, precision, the limit of detection, the limit of quantitation and relative standard deviation (RSD%) parameters were found for Pb, Ni, and Cd (Table 3).

To test the accuracy of the developed method was applied to standard reference material (SRM), NIST-SRM-1643e. The results of the analysis of ultra-pure water samples with added 50 μg L^{-1} Pb, Ni, and Cd standard are shown in Table 4.

SPE-preconcentration parameters were applied to the collected tap water samples collected in Kırklareli province. Also, the standard addition and recovery studies have been made. The results for Pb, Ni, Cd, are shown in Tables 5–7, respectively.

3. Results and discussion

The preconcentration procedures (the effect of pH, stirring time, the amount of quercetin and AC, etc.) were applied for the determination of Pb, Ni and Cd in water samples and the results obtained are given in Figs. 3–7.

The optimal pH for the maximal, quantitative recoveries of the examined metal ions by quercetin (0.2 mol L^{-1} in methanol) with AC (0.2 g) was found to be 7.0 ± 0.2 for Pb, Ni, and Cd, respectively (Fig. 3). At less high pH amounts, owing to the protonation of the hydroxyl part and the nitrogen atom of the recommended ligand and the rivalry both protons and metal ions from binding with the chelating agent, the recoveries declined notably [42]. This indicates that the positively charged adsorbent regions at low pH

Table 2
Recovery effect of matrix ions for Pb, Ni, and Cd ($n = 5$)

Interferences		Added (μg mL^{-1})	Recovery%		
			Pb(II)	Ni(II)	Cd(II)
Na^+	NaCl	1,000	99 ± 1	91 ± 2	90 ± 1
Ca^{2+}	$CaCl_2$	100	100 ± 2	93 ± 4	99 ± 3
Mg^{2+}	$Mg(NO_3)_2$	25	98 ± 3	92 ± 1	95 ± 2
Al^{3+}	$Al(NO_3)_3·9H_2O$	0.5	96 ± 2	98 ± 2	94 ± 1
Fe^{3+}	$Fe(NO_3)_3·9H_2O$	0.5	100 ± 2	99 ± 2	99 ± 2
Mn^{2+}	$MnSO_4·H_2O$	0.5	100 ± 2	100 ± 4	103 ± 1
Zn^{2+}	$Zn(NO_3)_2·6H_2O$	0.5	95 ± 1	94 ± 4	98 ± 2

Table 3
Optimum conditions for Pb, Ni, and Cd

Optimized parameters	Pb	Ni	Cd
pH	7.0	7.0	7.0
Extraction time, min	30	5	30
Amount of quercetin, mol L^{-1}	0.1	0.2	0.1
Amount of activated carbon, g	0.25	0.25	0.25
Sample volume, mL	5	500	50
Enrichment factor, fold	1	100	10
Linear regression ($y = ax + b$)	$0.2339x + 0.0063$	$0.0964x + 0.0018$	$1.9628x + 0.0507$
Correlation coefficients (R^2)	0.9998	0.9995	0.9991
RSDs, %	0.1–2.8	0.1–2.6	0.3–1.8
Limit of detection, μg L^{-1}	7.26	8.13	0.78
Limit of quantitation, μg L^{-1}	24.1	27.6	2.6

Table 4
Application to the presented method of standard reference material (SRM), (μg L^{-1})

	Pb	Ni	Cd
Certified value, (NIST-SRM-1643e), μg L^{-1}	19.15 ± 0.20	60.89 ± 0.67	6.408 ± 0.071
Found, μg L^{-1}	18.9 ± 0.21	59.8 ± 0.21	6.26 ± 0.21
Absolute error	–0.25	–1.09	–0.148
Recovery, %	98.7	98.2	97.7

Table 5
Application of standard addition/recovery for Pb of the presented procedure for fountain water ($n = 5$)

Points	Name of the fountain	pH	Added standard, $\mu g\ L^{-1}$	Pb, $\mu g\ L^{-1}$	Recovery, %	RSD, %
1	Yayla Neighborhood, Yayla Mosque Fountain	7.9	0	12.5		2.3
			100	113	101	0.5
2	Demirtas Neighborhood, Timurtas Pasha Mosque Fountain	8.2	0	11		2.1
			100	110	100	1.1
3	Kurtuluş Street, Karakol Street Kurtuluş Fountain	7.5	0	43.8		3.3
			100	144	100	1.2
4	Karacaibrahim Neighborhood, Kurtuluş Street, Saltukbey Street Kayyumoglu Fountain	7.9	0	37.9		3.0
			100	137	99.5	0.5
5	Yayla Neighborhood, Veterans Street Clock Tower Fountain	8.4	0	46.6		2.4
			100	150	103	0.6
6	Karakas Neighborhood, Prison Fountain	7.8	0	22.8		3.2
			100	120	97.2	1.1
7	İstasyonaltı Neighborhood, Sungurbey Street, Sungurbey Fountain	8.5	0	96.7		2.4
			100	195	98.3	1.7
8	Karakas Neighborhood, Ahmet Cevdet Pasha Mosque Fountain	8.0	0	73.3		2.0
			100	175	102	0.1
9	Kocahidir Neighborhood, Kuru Pasha Çeşme Street, Pasha Mosque Fountain	7.3	0	58.6		2.6
			100	160	101	1.3
10	Eastern Neighborhood, Balkan Street, Gerdanlı Fountain	7.7	0	117		2.5
			100	220	103	0.5
11	Tırnova Street, Akcihan Street, Kemal Canlı Mosque Fountain	8.0	0	86.9		2.4
			100	185	98.1	1.4
12	Karacaibrahim Neighborhood, Kapan Mosque Fountain	7.6	0	73.3		2.6
			100	175	102	1.8
13	Demirtaş Neighborhood, Karaumur Street, Hızırbey Mosque Fountain	7.5	0	80.1		0.8
			100	180	99.9	1.7
14	Bademlik Neighborhood, Bademlik Street, Bademlik Street Fountain	8.0	0	187		2.8
			100	285	98.0	1.9
15	İstasyon Neighborhood, School Street, Gifts and Tevfik Hayratı Fountain	8.1	0	113		3.9
			100	215	102	2.7
16	Karakas Neighborhood, Karakasbey Street, Karakas Mosque Fountain	8.2	0	167		2.2
			100	265	98.0	2.6
17	Karakas Neighborhood, Hasanpasa Street, Nüshediye Street Fountain	9.0	0	127		2.9
			100	225	98.0	1.6
18	Karacaibrahim Neighborhood, Melek Street Fountain	8.1	0	60.0		2.6
			100	160	100	0.3
19	Karacaibrahim Neighborhood, Kurtuluş Street, Provincial Special Administration Service Building Fountain	7.6	0	90.3		1.1
			100	190	99.7	0.9
20	Nüshet Sonay Street, Rıfat and Memnune Karpuzcu Hayratı Fountain	8.0	0	33.4		2.2
			100	130	96.6	1.2
21	Mosque Gate Street, Kırklar Mosque Fountain	7.9	0	50.1		3.7
			100	150	99.1	2.7
22	East Neighborhood, Balkan Street, Kadı Ali Fountain	7.7	0	33.3		1.8
			100	132	98.7	1.5

Table 6
Application of standard addition/recovery for Ni of the presented procedure for fountain water ($n = 5$)

Points	Name of the fountain	pH	Added standard, µg L^{-1}	Ni, µg L^{-1}	Recovery, %	RSD, %
1	Yayla Neighborhood, Yayla Mosque Fountain	7.9	0	37.3		5.3
			100	140	103	2.2
2	Demirtas Neighborhood, Timurtas Pasha Mosque Fountain	8.2	0	28.8		4.0
			100	130	101	3.2
3	Kurtuluş Street, Karakol Street Kurtuluş Fountain	7.5	0	18.3		3.8
			100	120	102	2.3
4	Karacaibrahim Neighborhood, Kurtuluş Street, Saltukbey Street Kayyumoglu Fountain	7.9	0	23.3		2.9
			100	125	102	1.5
5	Yayla Neighborhood, Veterans Street Clock Tower Fountain	8.4	0	13.0		4.7
			100	115	102	1.1
6	Karakas Neighborhood, Prison Fountain	7.8	0	56.8		3.1
			100	155	98.2	1.7
7	İstasyonaltı Neighborhood, Sungurbey Street, Sungurbey Fountain	8.5	0	17.3		1.9
			100	117	102	0.1
8	Karakas Neighborhood, Ahmet Cevdet Pasha Mosque Fountain	8.0	0	19.6		2.5
			100	120	100	1.8
9	Kocahidir Neighborhood, Kuru Pasha Çeşme Street, Pasha Mosque Fountain	7.3	0	14.3		3.2
			100	115	101	2.6
10	Eastern Neighborhood, Balkan Street, Gerdanlı Fountain	7.7	0	29.4		4.3
			100	130	101	1.6
11	Tırnova Street, Akcihan Street, Kemal Canlı Mosque Fountain	8.0	0	15.8		3.3
			100	115	99.2	1.4
12	Karacaibrahim Neighborhood, Kapan Mosque Fountain	7.6	0	17.5		2.7
			100	120	103	2.6
13	Demirtaş Neighborhood, Karaumur Street, Hızırbey Mosque Fountain	7.5	0	23.8		3.8
			100	125	101	2.7
14	Bademlik Neighborhood, Bademlik Street, Bademlik Street Fountain	8.0	0	25.4		2.7
			100	125	99.6	0.3
15	İstasyon Neighborhood, School Street, Gifts and Tevfik Hayratı Fountain	8.1	0	28.8		3.7
			100	125	96.2	0.2
16	Karakas Neighborhood, Karakasbey Street, Karakas Mosque Fountain	8.2	0	17.0		2.1
			100	120	103	1.1
17	Karakas Neighborhood, Hasanpasa Street, Nüshediye Street Fountain	9.0	0	14.8		2.9
			100	115	100	0.7
18	Karacaibrahim Neighborhood, Melek Street Fountain	8.1	0	18.3		3.6
			100	115	96.7	1.6
19	Karacaibrahim Neighborhood, Kurtuluş Street, Provincial Special Administration Service Building Fountain	7.6	0	26.7		2.9
			100	130	103	1.6
20	Nüshet Sonay Street, Rıfat and Memnune Karpuzcu Hayratı Fountain	8.0	0	18.3		4.6
			100	120	102	3.4
21	Mosque Gate Street, Kırklar Mosque Fountain	7.9	0	20.4		2.8
			100	120	99.6	2.8
22	East Neighborhood, Balkan Street, Kadı Ali Fountain	7.7	0	16.3		4.6
			100	115	98.7	1.2

Table 7
Application of standard addition/recovery for Cd of the presented procedure for fountain water ($n = 5$)

Points	Name of the fountain	pH	Added standard, $\mu g\ L^{-1}$	Cd, $\mu g\ L^{-1}$	Recovery, %	RSD, %
1	Yayla Neighborhood, Yayla Mosque Fountain	7.9	0	3.11		1.5
			100	103	99.9	0.7
2	Demirtas Neighborhood, Timurtas Pasha Mosque Fountain	8.2	0	3.98		2.8
			100	104	100	0.2
3	Kurtuluş Street, Karakol Street Kurtuluş Fountain	7.5	0	5.18		2.2
			100	105	99.8	0.7
4	Karacaibrahim Neighborhood, Kurtuluş Street, Saltukbey Street Kayyumoglu Fountain	7.9	0	5.53		1.7
			100	105	99.5	0.2
5	Yayla Neighborhood, Veterans Street Clock Tower Fountain	8.4	0	3.11		1.4
			100	104	101	1.2
6	Karakas Neighborhood, Prison Fountain	7.8	0	4.73		2.6
			100	105	95.3	0.6
7	İstasyonaltı Neighborhood, Sungurbey Street, Sungurbey Fountain	8.5	0	3.37		3.2
			100	104	101	0.3
8	Karakas Neighborhood, Ahmet Cevdet Pasha Mosque Fountain	8.0	0	8.90		1.4
			100	109	1000	1.1
9	Kocahidir Neighborhood, Kuru Pasha Çeşme Street, Pasha Mosque Fountain	7.3	0	1.21		1.2
			100	121	100	0.8
10	Eastern Neighborhood, Balkan Street, Gerdanlı Fountain	7.7	0	2.16		1.6
			100	102	99.8	1.9
11	Tırnova Street, Akcihan Street, Kemal Canlı Mosque Fountain	8.0	0	4.28		2.5
			100	104	99.7	1.4
12	Karacaibrahim Neighborhood, Kapan Mosque Fountain	7.6	0	4.49		1.9
			100	104	99.5	1.1
13	Demirtaş Neighborhood, Karaumur Street, Hızırbey Mosque Fountain	7.5	0	4.93		1.8
			100	105	100	0.1
14	Bademlik Neighborhood, Bademlik Street, Bademlik Street Fountain	8.0	0	7.01		1.0
			100	106	99.0	0.6
15	İstasyon Neighborhood, School Street, Gifts and Tevfik Hayratı Fountain	8.1	0	5.96		2.4
			100	106	100	0.7
16	Karakas Neighborhood, Karakasbey Street, Karakas Mosque Fountain	8.2	0	2.33		2.8
			100	102	99.7	2.1
17	Karakas Neighborhood, Hasanpasa Street, Nüshediye Street Fountain	9.0	0	2.20		4.2
			100	102	99.8	1.9
18	Karacaibrahim Neighborhood, Melek Street Fountain	8.1	0	3.63		2.4
			100	104	100	0.9
19	Karacaibrahim Neighborhood, Kurtuluş Street, Provincial Special Administration Service Building Fountain	7.6	0	3.11		1.4
			100	103	99.9	0.6
20	Nüshet Sonay Street, Rıfat and Memnune Karpuzcu Hayratı Fountain	8.0	0	7.35		2.5
			100	107	99.7	0.9
21	Mosque Gate Street, Kırklar Mosque Fountain	7.9	0	2.16		1.6
			100	102	99.8	0.9
22	East Neighborhood, Balkan Street, Kadı Ali Fountain	7.7	0	4.41		2.2
			100	104	99.6	1.6

values reduce the adsorption efficiency of metals. High pH (after 8) suggests that it is transformed into a soluble form by complexion. The pH of the samples was measured before and after the FAAS.

The results of the effect of stirring time in Fig. 4 show that 30 min was sufficient for maximum recovery (96%–80%), and the recovery did not change up to 120 min. A stirring time of 30 min was utilized for all further studies (Fig. 4).

Fig. 5 shows that the recoveries enhanced up to 85% by adding 0.15 mol L^{-1} quercetin and did not change up to a 0.3 mol L^{-1}. It is more convenient to take 0.2 mol L^{-1} for each of the three analytes, although maximum yields of 0.1 mol L^{-1} quercetin are obtained for Pb and Cd (Fig. 5). The maximum yield (90% for Pb, 95% for Cd and 96% for Ni) was obtained when 0.25 g of AC was used (Fig. 6).

The results of the sample volume are shown in Fig. 7. Recovery in volumes above 500 mL was found to be fixed. The analytes were quantitatively (ratio of 92%–95% for Pb, Ni, and Cd) recovered in the sample volume range of 5–500 mL. The enrichment factor of 1, 10, and 100 times for Pb, Cd, and Ni the analytes, respectively can be attained when the ultimate volume was 5.0 mL.

The permitted amounts of each ion were the concentration values tried which created less than 5% the absorbance amendment (Table 2). These ions do not interfere under the experimental situations utilized.

As a result, the application of the developed SPE method to the fountain waters has used the determination of Pb, Ni, and Cd concentrations by the FAAS method. A high enrichment factor in repeated measures was defined as 1–100-fold and a low (%RSD) < 5.

From the results obtained, it was found that the heavy metal concentrations in the studied waters ranged from 11.0 to 187 μg L^{-1} for Pb, 14.3 to 56.8 μg L^{-1} for Ni and 1.21 to 8.90 μg L^{-1} for Cd. From these values, except for Pb; sampling points 2–5, 7–9, 11–13, 16–18, 20 and 21 for Ni; sampling points 1–7, 9–13, 16–19 and 21–22 for Cd, were found to be below the limit values allowed by the WHO and the Ministry of Health. The permissible limit values for Pb, Cd, and Ni are 10, 3 and 70 μg L^{-1} respectively [4–6]. The absolute error between –0.73, –2.61, and –0.31 was determined for Pb, Ni and Cd measurements in the SRM water to determine the accuracy of the FAAS measurements. This shows that the measurements made are true-acceptable.

4. Conclusion

The developed and presented methods are simple, decrease the time spent and economical procedure which does not require a complex purification processing. Furthermore, the held metal ions might be expeditiously-efficiently eluted by 5 mL of 1 M HNO_3 and analyzed by FAAS. The suggested procedure demonstrates good detection limits and precision with a practicable little eluent volume (5 mL) and an enrichment factor (500/5 for Ni, 50/5 for Cd and 5/5 for Pb) higher than that of other SPE preconcentration methods.

Because most heavy metals are toxic-toxic substances, they can harm human and animal health and natural balance and create environmental pollution problems. This method can be applied to the determination of concentrations of Pb, Cd, Ni and Cu elements at ppb level in other environmental and food samples such as soil and plants.

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