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The Quality of Yıldız River Water and Determining Trace Elements by Liquid-Liquid Micro-Extraction Analytical Method

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ABSTRACT

The present study was carried out between September 2019 and March 2020 in Yıldız River, which is located within the borders of the Yıldızeli district of Sivas province and used for agricultural irrigation purposes, to determine the chemical characteristics of river water and the trace elements. Water's alkalinity, chemical oxygen demand (COD), chloride (Cl^-), calcium (Ca^{2+}), total hardness, total phosphate (PO_4-P), dissolved reactive phosphate (SRP), ammonium nitrogen (NH_4-N), nitrate-nitrogen (NO_3-N), nitrite-nitrogen (NO_2-N), soluble reactive silica (SiO_2-Si) concentrations, as well as trace elements (ferrous, lead, cadmium). Moreover, during the sampling process, also the water temperature, dissolved oxygen, conductivity, pH, and total dissolved solids measurements were performed. Before using the flame atomic absorption spectrometer (FAAS) in determining the Fe, Pb, and Cd in water samples, a simple, environment-friendly, and new ultrasonic liquid-liquid micro-extraction method was suggested. Several parameters (pH, ionic fluid amount, dispersive solvent volume, and temperature) influencing the performance of micro-extraction were optimized. Under the optimized conditions, the detection thresholds for Fe (II), Pb (II), and Cd (II) were found to be 0.6, 0.15, and 1.5 µg L^{-1}, respectively.

Keywords: Yıldız River, Water chemistry, Ultrasonic supported sampling, Flame AAS.

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Introduction

Knowing the physical, chemical, and biological characteristics of the water, which is one of the necessities for our lives and activities (domestic use, industrial use, agricultural irrigation, recreational purposes, etc.), is very important [1]. Since the aquatic ecosystems and their near surroundings are important attraction centers for humans, as well as other organisms, they face the highest pollution pressure due to intensive settlement and use [2]. Water quality is affected by the wastes (canalization or toxic), intensive agriculture, and disposal of materials rich in phosphate or nitrogen [3]. It is important to identify the water quality by observing and determining the parameters (measurement locations, measurement times, and intervals) [4].

Clean water (containing no heavy metal, chemical materials, or pathogen microorganisms), which is a necessity for all vital activities, should be provided for humans. Heavy metals reaching risky levels especially due to technological advancements and increasing environmental pollution, accumulate within the bodies of plants, animals, and humans and pose a threat to human health [5,6]. It is also interesting that the number of studies examining water pollution and quality from this aspect has increased in the recent period.

Vegetables, which are widely consumed for their nutrient content and certain trace elements, have a significant contribution to human health [7]. Besides their benefits, these products also have harmful effects due to the metals they contain. The amount of trace elements depends on various factors such as the cultivation and harvest of vegetables, the use of chemicals such as fertilizers and pesticides/herbicides, and storage conditions [8]. The elements' concentrations exceeding a specific limit in the human body create a toxic effect and cause undesired health results. In order to prevent such problems, it is necessary to perform the quality controls of water being used and to determine the concentrations of heavy metals. Various analytical methods are used in analyzing heavy metals. These methods include various atomic spectrometric methods such as high-resolution continuum source flame atomic absorption spectrometer (HR-CS-FAAS) [9], inductive coupled plasma mass spectrometry (ICP-MS) [10], inductive coupled plasma optic emission spectrometry (ICP-OES) [11], hydride generation atomic absorption spectrometer [12], and hydride generation atomic fluorescence spectrometry (HG-AFS) [13]. These methods are used in determining the metals such as zinc (Zn), cobalt (Co), manganese (Mn), nickel (Ni), ferrous (Fe), cadmium (Cd), lead (Pb), selenium (Se), and arsenic (As).

Since these metals are present in water and plant samples at trace concentrations, a preliminary isolation and enrichment process should be performed. The analysis of the sample without preliminary processing is preferred because it would protect the sample from contamination. However, few instrumental methods can be used in procedures requiring very low concentrations. Since many instrumental methods have the same principle for technical concentration measurement, isolation-enrichment is used to increase the concentration to achieve the suitable analysis range during the measurements below the detection threshold of the analyte. Some of the methods frequently used in isolating and enriching the metals in real samples include cloud point extraction (CPE) [14], solid-phase extraction (SPE) [15], co-precipitation [16] , liquid-liquid extraction (LLE) [17] and dispersive liquid-liquid micro-extraction (DLLME) [18], solid-phase micro-extraction (SPME) [19], liquid-liquid micro-extraction (LLME) [20], stir bar sorptive extraction (SBSE) [21], coacervate micro-extraction (CME) [22], hollow fiber-based liquid-phase micro-extraction (HF-LPME) [23], electrochemical accumulation [24], and vortex-assisted liquid-liquid micro-extraction (VA-LLME) [25]. The enrichment methods used before the trace analysis offers various advantages such as enrichment of detection capacity of the method by increasing the concentration of analyte, minimizing the matrix intervention, decreasing the detection threshold of the method, and increasing the selectivity.

In the present study, it was aimed to determine the Fe, Pb, and Cd metals in the water samples by using the ionic liquid dispersive liquid-liquid micro-extraction (IL-DLLME) method, which is an environment-friendly and useful method, to determine the water quality of Yıldız River located in Yıldızeli district of Sivas province.

Materials and Methods

Research Area and Sampling Points

Yıldız River is located in the northeastern side of Central Anatolia region, 27 km away from Sivas, flowing from north to south, and merges with Kızılırmak [26]. Water samples were collected from 3 sampling stations with an interval of 2 months between September 2019 and March 2020. The sampling stations were limited to the region between Yeniyapan hamlet and the merge point of Yıldız River and Kızılırmak and, their coordinates are given below;

Station I (Yeniyapan Hamlet Bridge); 39°49'23.27"K / 36°47'10.45"D, Altitude 1275 m.

Station II (Historical Yıldız Bridge); 39°45'31.30"K / 36°45'55.99"D, Altitude 1256 m.

Station III (Historical Yıldız Bridge); 39°42'49.63"K / 36°46'41.48"D, Altitude 1250 m

Physicochemical Analyzes Related with Water Chemistry

The water samples obtained from the stations were taken into 1-liter brown bottles without an air gap. The samples were immediately taken to the laboratory and subjected to the preservation, storage, and filtration procedures. The chemical analyses were performed within 24 hours after the sampling. Water temperature, electrical conductivity, dissolved oxygen, total suspended solids (TDS), and pH were measured during sampling. Chemical analyses (total phosphate, dissolved reactive phosphate ammonium, nitrate, nitrite, silica, chloride, alkalinity, water hardness, calcium, and COD) were performed in the laboratory.

COD measurement was performed using the titration-based Closed Reflux Method. Chloride was measured using titration method that is based on the brick red color created by silver nitrate with chloride or chromate ions [27], whereas total phosphate and dissolved reactive phosphate were determined spectrophotometrically using Ascorbic Acid Method [28] and, total alkalinity was measured using the weak acid titration between pH 4.5 and pH 8.4 limits [29]. Nitrate analysis was performed by spectrophotometrically measuring the color originating from the reaction between sulfosalicylic acid, which forms because of the addition of sodium silicate and sulfuric acid, and nitrate in alkali medium. Nitrite analysis was performed by spectrophotometrically measuring the color arising from the reaction between nitrite ions and reactive-diluted phosphoric acid-containing sulfonamide and N-1 naphtylenediamine dihydrochloride, whereas ammonium was analyzed by spectrophotometrically measuring the indophenol blue originating from the reaction with phenol-alkali hypochlorite with the catalyzer pH 11.3-11.7 sodium nitroprusside [30]. Silica analysis was performed using Molybdosilicate Method [31], while calcium and total hardness analyses were performed EDTA titration method [32].

Chemicals

All the reactive materials were at analytical purity and obtained from Sigma (St. Louis, MO, USA) and Merck (Darmstadt, Germany) companies. Stıck solutions of Fe (II), Pb (II), and Cd(II) were obtained from their nitrate salts. Calibration and standard working solutions were prepared by gradually diluting the stock solutions. Metal ions' complexes were obtained using Patent Blue V (Sigma). Patent Blue V ($1x10^{-4}$ M) solutions were prepared using ultrapure water and stock solutions. pH 6.5 phosphate buffer solution (0.1 mol L^{-1}) was prepared to mix sodium dihydrogen phosphate monohydrate and sodium hydroxide at sufficient amounts. 1-butyl-3-methylimidazolium bis (trifluorosulfonyl) imid [C4mim] [Tf2N] was purchased from Sigma (St. Louis, MO, USA).

Instruments

The measurements in the research field were performed using the "Hanna HI9829" model multiparameter device, whereas COD analysis was performed using the "HACH DRB 200" model thermoreactor and spectrophotometric measurements were performed using Cecil CE5502 model spectrophotometer. The ferrous, lead, and cadmium concentrations of water samples were determined using a flame atomic absorption spectrometer (FAAS) (Shimadzu AAS-6300 model, Kyoto, Japan) device equipped with deuterium background correction. The measurement parameters of the device for each analyte are presented in Table 1. pH measurements of solutions were performed using a digital pH-meter (Sartorius Docu-model, North America). An ultrasonic bath (UCS-10 model, Seul, Korea) was used to ease the phase separation and to increase the micelle formation of extraction solvent. During the the extraction experiments, the separation of the ionic fluid phase from the liquid phase was performed with a centrifuge (Universal Hettich, London, England). Ultrapure water with a resistance of 18.2 MΩ cm was obtained using a Milli-Q water purifier device (Millipore Corp., USA).

Table 1. FAAS operating parameters

Parameter	Ferrous	Lead	Cadmium
Wavelength (nm)	248.3	283.3	228.8
Lambda current (mA)	12	15	8
Spectral band width (nm)	0.2	0.2	0.7
Burning height (mm)	7.0	5	7
Acetylene and air flow rates (L min^{-1})	2.2/18	1.8/17	1.8/15

Suggested Method

For the micro-extraction of Fe, Pb, and Cd, 10ml water samples containing 2-500 µg L^{-1} Fe(II), 0.5-300 Pb(II) µg L^{-1}, and 5-600 µg L^{-1} Cd (II) were taken to 15 mL centrifuge tubes. The sample solution's pH was set to 6.5 by using phosphate-citrate buffer solution and 500 µL 1 x 10-3 mol L^{-1} Patent Blue V, 300 µL [C4mim] [Tf2N], and 500 µL ethanol (dispersive solvent) were added and the solution was diluted to 15 mL. Centrifuge tube was closed and sonication was performed using an ultrasonic bath at 40 °C for 10 minutes until IL droplets got completely dispersed and a cloudy solution was achieved. The triplet complexes containing Fe, Pb, and Cd were extracted into fine micro-droplets [C4mim] [Tf2N]. After centrifuging at 4000 rpm for 5 minutes, two phases including IL phase and liquid phase were obtained. The supernatant liquid phase was removed using a syringe. To increase the viscosity of IL phase and to ease the analysis process, IL phase was diluted to 2.0 mL using 0.1 mol L^{-1} HNO_3 to protect the stability of triplet complexes based on the formation of ion couple and to ease the atomization of analytes. Then, it was aspirated to FAAS to determine the Fe, Pb, and Cd. All the experiments were repeated three times and the mean values of results were calculated.

Results and Discussion

Water Quality

The parameters examined on the samples and the numerical data of these parameters were presented in Table 2.

Table 2. Physical and chemical analysis results of water samples taken from sampling stations on the Yıldız River

	09.30.2019			**11.30.2019**			**01.30.2020**			**03.24.2020**		
	STATIONS											
	I	II	III	I	II	III	I	II	III	I	II	III
Calcium (mg/L)	144	144	144	133	130	137	88	88	92	98	95	98
Hardness (Fr)	39.8	40.7	40.7	38.9	37.9	38.9	25.9	25.0	25.9	28.7	27.8	28.7
Alkalinity (mg $CaCO_3$/L)	320	320	325	300	295	310	205	200	210	215	225	220
Ammonium(mg/L)	0.08	0.04	0.03	0.03	0.01	0.003	0.04	0.02	0.02	0.02	0.04	0.02
Nitrate (mg/L)	0.43	0.48	0.56	0.84	0.79	0.86	0.78	0.77	1.04	0.74	0.81	0.88
Nitrite (mg/L)	0.001	0.001	0.0004	0.002	0.002	0.002	0.013	0.012	0.010	0.014	0.021	0.017
Total Phosphate (mg/L)	0.001	0.001	0.008	0.012	0.020	0.024	0.025	0.019	0.027	0.006	0.016	0.022
SRP (mg/L)	0.002	0.002	0.002	0.013	0.002	0.005	0.016	0.018	0.02	0.01	0.01	0.01
Chloride (mg/L)	9.4	18.9	18.9	14.2	16.5	18.9	9.4	9.4	9.4	9.4	9.4	9.4
COD (mg O_2/L)	16.0	48.1	32.1	32.1	3.2	16.0	32.1	32.1	16.0	32.1	32.1	16.0
Silica (mg/L)	9.8	9.9	10.4	9.4	8.3	9.0	9.6	9.8	9.2	9.9	9.8	9.8
Temperature (°C)	16.8	17.5	17.1	7.0	7.1	7.3	7.6	7.7	7.9	9.6	10	10
Dis. Oxygen (mg O_2/L)	9.8	9.6	8.9	11.4	11.3	11.3	8.5	7.9	8.1	7.0	7.0	7.1
pH	7.9	8.1	7.9	8.0	8.0	8.0	8.2	8.2	8.2	8.2	8.2	8.2
Conductivity (µs/cm)	568	581	625	480	507	562	327	331	347	349	367	378
TDS (mg/L)	304	309	331	259	273	302	172	180	182	187	196	202

The mean value and total values of measurements and analyses were presented in Table 3.

Table 3. Physical and chemical average analysis results of star river water

	Mean of Station I	**Mean of Station II**	**Mean of Station III**	**Total Mean**
Calcium (mg/L)	116	114	118	116
Hardness (Fr)	33	33	34	33
Hardness (mg $CaCO_3$/L)	326	323	328	326
Alkalinity	260	260	266	262
Ammonium (mg/L)	0.043	0.024	0.017	0.028
Nitrate (mg/L)	0.70	0.71	0.83	0.75
Nitrite (mg/L)	0.008	0.009	0.007	0.008
Total Phosphate (mg/L)	0.011	0.014	0.020	0.015
SRP (mg/L)	0.010	0.008	0.010	0.009
Chloride (mg/L)	10.6	13.6	14.2	12.8
COD (mg O_2/L)	28	29	20	26
Silica (mg/L)	9.8	9.4	9.6	9.6
Temperature (°C)	10.3	10.6	10.6	10.5
Dis. Oxygen (mg O_2/L)	9.2	9.0	8.9	9.0
pH	8.1	8.1	8.1	8.1
Conductivity (µS/cm)	431	447	478	452
TDS (mg/L)	231	240	254	241

Quality criteria of surface waters are presented in Table 4.

Table 4. Quality criteria according to the classes of surface water resources [32]

Water Quality Parameters	**Water Quality Classes**			
	I	**II**	**III**	**IV**
General Conditions				
Temperature (°C)	≤ 25	25	30	> 30
Dissolved Oxygen (mg O_2/L)	> 8	6	3	< 3
Chloride Ion (mg/L)	25	200	400	400
pH	6.5-8.5	6.5-8.5	6.0-9.0	< 6.0 or > 9.0
Conductivity (µS/cm)	< 400	1000	3000	> 3000
Chemical oxygen demand (COD) (mg/L)	< 25	50	70	> 70
Ammonium nitrogen (mg NH_4^+-N/L)	< 0.2	1	2	> 2
Nitrate nitrogen (mg NO_3^--N/L)	< 5	10	20	> 20
Nitrite nitrogen (mg NO_2^--N/L)	< 0.01	0.06	0.12	> 0.3
Total phosphor (mg P/L)	< 0.03	0.16	0.65	> 0.65

According to the quality classes given in Table 4, the purposes of waters are:

- •Class I – Very high-quality water (Very good water)
- •Class II – Less polluted water (Good water)
- •Class III – Polluted water (Moderate water)
- •Class IV – Very polluted water (Poor water; "Poor water")

Yıldız River's physical and chemical measurement/analysis results and the quality criteria set in SWQMR [33] are compared in Table 5.

When comparing the water of Yıldız River to SWQMR as in Table 5, it was determined that the river has Class I water quality, except for COD. Class I water refers to "very good" water quality and, the waters in this class can be used as drinking water, for recreational purposes including body contact such as swimming, trout farming, animal husbandry/farming, and agricultural irrigation.

Considering the aspect of water hardness, the river has very hard water.

Table 5. Water quality of Yıldız River

Parameters	Total Mean	Quality Class in SWQMR 2008
Temperature (°C)	10.5	Class I
Dissolved Oxygen (mg O_2/L)	9.0	Class I
Chloride (mg/L)	12.8	Class I
pH	8.1	Class I
Conductivity (µs/cm)	452	Class II
COD (Mg O_2/L)	26	Class I-II
Ammonium (mg/L)	0.028	Class I
Nitrate (mg/L)	0.75	Class I
Nitrite (mg/L)	0.008	Class I
Total Phosphate (mg/L)	0.015	Class II

The hardness values of waters and Yıldız River's hardness are presented in Table 6.

Table 6. Hardness classification of Yıldız River water

Hardness level (°F)	mg $CaCO_3$/L (ppm)	Water Class	Yıldız River
0-7	0-72	Very soft water	
7-14	72-145	Soft water	
14-22	145-215	Moderately hard water	
22-32	215-325	Hard water	
32-42	325-545	Very hard water	33 (°Fr) / 326 (mg $CaCO_3$/L)
> 42	> 545	Excessively hard water	

Optimization of Extraction Parameters

Effect of pH

Before the sample preparation, because of the effects on ionization status and analyte solubility, it is generally difficult to avoid the effect of sample pH. Since the pH of the medium affects the formation of the complex between metal ions and ligand and the enrichment procedure at the final step, pH optimization is important. Given the data presented in Figure 1, it can be seen that the best analytical signal for target analytes was achieved at pH 6.5.

Effect of patent blue V volume

The rapid and stable complex structure of Fe(II), Pb(II), and Cd(II) ions were achieved using Patent Blue V. Together with pH, for metal ions in medium to establish a complex, the amount of complexing material should be sufficient. Patent Blue V solution (1x 10^{-3} mol L^{-1}) was added to the analyte solutions, pH of which was set to 6.5 by making use of a phosphate-citrate buffer, and the signals obtained after the enrichment process are presented in Figure 2. At 900 µL final volume of Patent Blue V, the highest signal among the absorbance values was achieved with 500 mL Patent Blue V. Thus, this amount was used as an optimal value in the next studies.

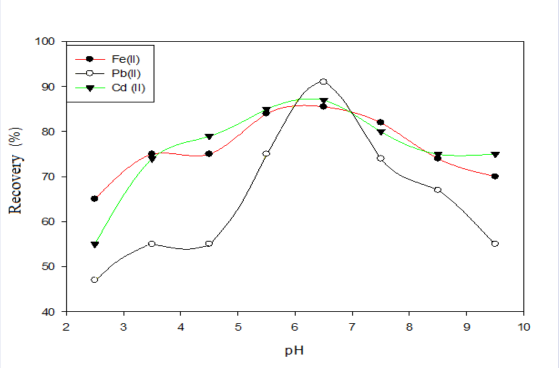

Figure 1. Effect of pH, amount on recovery of ions Fe (II), Pb (II), and Cd (II)

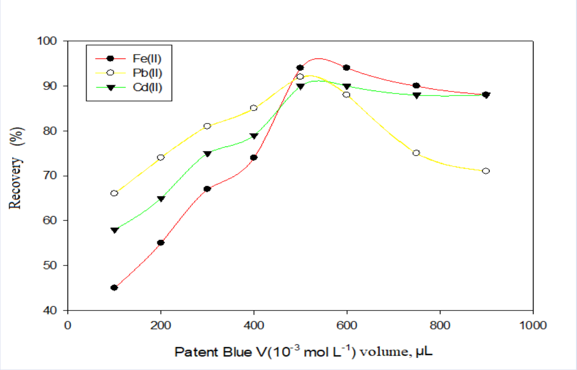

Figure 2. Effect of Patent Blue V volume on amount on recovery of ions Fe (II), Pb (II) and Cd (II)

The effect of the amount of ionic liquid

In maximizing the extraction and increasing the selectivity of target analytes, the selection of an appropriate ionic liquid is a very important parameter for the micro-extraction process. To achieve these targets, an ionic liquid meeting the following criteria should be chosen; (i) high capacity for target analytes; (ii) low water-solubility; (iii) capacity of mixing with a solvent more dispersive and viscose than water; (iv) being present in liquid form; and (v) affordable. In conclusion, 1-butyl-3-methylimidazolium chloride [C4mim] [Tf2N] was used in the present study. After selecting the [C4mim] [Tf2N], its amount's effect on the analytical signal was analyzed between 100 and 700 µL and in presence of ethanol (disperser solvent). According to Figure 3, the analytical signal for Fe, Pb, and Cd was increased between 100-300 µL by increasing the amount of [C4mim] [Tf2N]. Thus, 300µL [C4mim] [Tf2N] was chosen for the next studies.

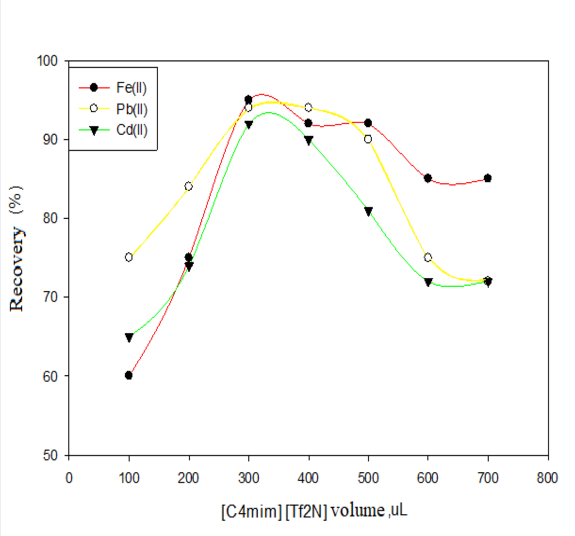

Figure 3. Effect of ionic liquid, [C6mim] [Tf2N], amount on recovery of ions Fe (II), Pb (II) and Cd (II).

The effect of volume of dispersive solvent

In this micro-extraction process, the selection of dispersion solvent is very important for solubility in both IL and liquid phases because it acts as a bridge in dispersing the extraction solvent to achieve fine droplets. In presence of [C4mim] [Tf2N], a cloudy phase system was achieved using ethanol dispersion solvent. As seen in Figure 4, the best analytical signal was achieved when using 500 µL ethanol as disperser solvent. In literature, the reasons for a decrease in analytical signal were reported to be related to (i) the increase in solubility of the complex in high volumes of water and (ii) the absence of complete cloudy phases at low volumes. In conclusion, 500 µL ethanol volume was found to be suitable for use as a dispersive solvent in future studies.

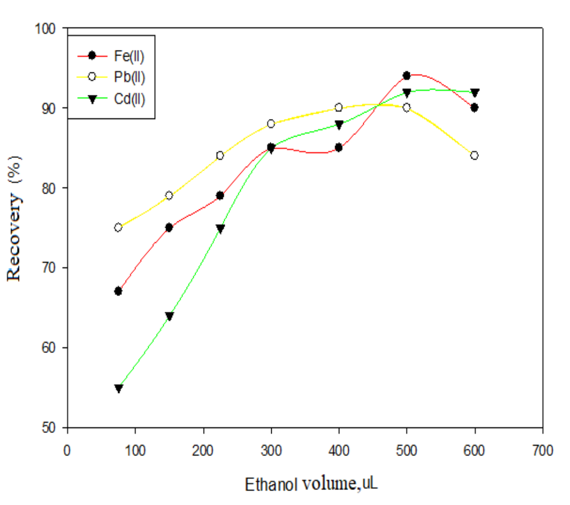

Figure 4. The effect of volume of dispersive solvent on recovery of ions Fe (II), Pb (II) and Cd (II).

Effect of temperature

After the optimization of reactive materials influencing the extraction process, the balance temperature was optimized for the efficient separation of phases. The effect of balanced temperature on the recovery of trace elements was examined using ultrasonic force between 25 and 55 °C. It was found that the recovery of Fe (II), Pb(II), and Cd (II) increased with the increase in temperature between 25 and 40 °C and reached the maximum at 40 °C. The recovery of ions decreased after 40 °C. Since the complex including the analytes reversibly disperses into the aqueous solution depending on the increase in temperature, the recovery of analytes decreased at temperatures higher than 40 °C. Thus, the balance temperature of 40°C was chosen as the optimum temperature for the extraction experiments.

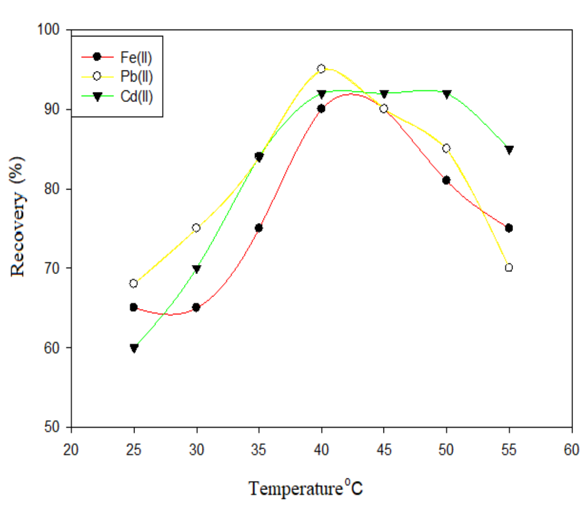

Figure 5. Effect of temperature on recovery of ions Fe (II), Pb (II) and Cd (II).

Effect of ultrasonication time

One of the important parameters for obtaining the best analyte signal is the sample solutions' time in an ultrasonic bath. For this reason, the effect of sonication was investigated between 0 and 20 minutes. The results showed that the recovery of Fe (II), Pb(II), and Cd (II) increased with prolonging sonication time until 10 minutes but partially decreased with longer durations. Excessive length of ultrasonication time causes a decrease in absorbance [34]. For this reason, 10 minutes of sonication time was chosen to be the optimum value for extraction experiments.

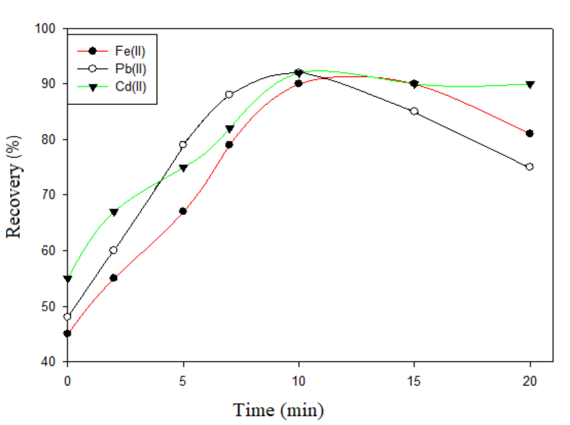

Figure 6. Effect of ultrasonication time on recovery of ions Fe (II), Pb (II) and Cd (II).

Effect of foreign ions

To test the stability and selectivity of the suggested chemical method for Fe, Pb, and Cd ions, an interventional process was used. The results presented in Table 7 showed that the best tolerance limits and high recovery achievements were obtained in presence of various analyte ions. These results suggest that the suggested method has good selectivity for the analyte ions under the selected conditions.

Table 7. Selectivity of the method in the presence of foreign ions (n= 3)

Foreign ions	Ferrous		Lead		Cadmium	
	Tolerance limit	Recovery (%)	Tolerance limit	Recovery (%)	Tolerance limit	Recovery (%)
Ca^{2+}	1500	97.5	1500	97.8	1000	97.5
K^{+}	1500	96.1	1500	98.5	1000	97.2
Ba^{2+}	1500	97.5	1000	97.3	1500	98.6
Mg^{+}	1000	97.8	750	96.4	1500	98.5
F^{-}	1000	96.2	750	96.1	500	96.2
Mn^{2+}	750	96.0	750	97.5	500	96.9
Al^{3+}	750	98.5	1000	96.2	100	95.5
Pb^{4+}	750	97.8	100	95.4	250	96.4
CO_3^{2-}	750	96.3	500	96.8	250	96.8
Zn^{2+}	500	95.4	500	97.2	1500	98.8
Fe^{3+}	500	97.5	250	97.7	100	97.1
Cu^{2+}	250	96.1	250	96.1	50	95.2
Co^{2+}	250	95.2	50	95.0	750	96.7
Cr^{3+}	100	95.0	100	96.4	750	97.6
As^{3+}	100	96.7	250	97.6	750	97.1
VO^{2+}	50	96.3	100	96.2	250	96.3

Analytical performance

The analytical parameters of the suggested analyte method under the optimum conditions are listed in Table 8. The linear operational range of methods for Fe, Pb, and Cd are 2-500, 0.5-300, and 5-600 µg L^{-1}, respectively.

Table 8. Analytical characteristics of the method

Analytical characteristics	Fe(II)	Pb(II)	Cd(II)
Calibration equation	A=0.0052[Fe(II)]+0.00085	A=0.00127[Pb(II)]+0.00103	A=0.00376[Cd(II)]+0.00053
Correlation coefficient (r^2)	0.9913	0.9972	0.9953
Operational range (µgL^{-1})	2-500	0.5-300	5-600
Detection limit($3S_{empty}/m$, µgL^{-1})	0.6	0.15	1.5
Detection limit($10S_{empty}/m$, µgL^{-1})	2.0	0.5	5.0
%BSS (accuracy for day, n:5)	1.4	1.7	2.0
%BSS(accuracy for day, n:3x5)	2.3	2.6	3.2
% Recovery	95.8	97.8	96.3
Preliminary concentration factor	75	75	75
Sensitivity factor	94	105	87

3.2.8. Validation studies

To test the accuracy and validity of the suggested method, the analysis of the certified reference sample was performed using the suggested method and the results and reference values were compared. The results are presented in Table 9. It can be stated that the results obtained from the suggested method were in good harmony with the certified values at the confidence level of 95%.

After the reliability test of the suggested method, the applicability of the suggested method for detecting the ferrous, lead, and cadmium in the water samples of Yıldız River was invested. The accuracy of suggested methods was tested by adding the samples with different concentrations of standard analyte solutions and analyzing the recovery values. The results are presented in Table 10. As seen in the results, the recovery values are at acceptable levels.

Table 9. Results of the method validation study

CRM	Fe			Pb			Cd		
	Result	%BSS, %Recovery	t_{exp}	Result	%BSS, %Recovery	t_{exp}	Result	%BSS, %Recovery	t_{exp}
INCT-TL-1 (Tea leaves)	42.7±1.7	3.9 (98.8)	0.75	17.2±0.7	4.0 (96.6)	1.38	29.6±1.4	4.7 (98.6)	0.96

Certified values were found to be 43.2±1.3 $\mu g\ kg^{-1}$ for ferrous, 17.8±2.4 $\mu g\ kg^{-1}$ for lead, and 30±4.0 $\mu g\ kg^{-1}$ for cadmium. For the confidence level of 95% and SD 4, $t_{crit.}$ = 2.78

Table 10. Analysis results of water samples by method (n: 3)

Samples	Months	Additive ($\mu g\ L^{-1}$)	Result ($\mu g\ L^{-1}$)			Recovery (%)			BSS (%)		
		Fe(II)/Pb(II)/Cd(II)	Fe	Pb	Cd	Cu	Pb	Cd	Cu	Pb	Cd
Station -1	09.30.2019	-	45.7	14.3	6.8	-	-	-	2.4	1.8	2.4
		100	140.4	111.4	102.3	94.7	97.1	95.5	2.2	1.7	2.2
Station -2		-	67.9	21.6	12.4	-	-	-	2.5	1.5	2.5
		100	164.1	115.4	108.5	96.2	94.4	96.1	2.4	1.4	2.3
Station -3		-	24.3	7.5	16.2	-	-	-	2.3	1.7	2.3
		100	121.8	101.1	113.8	97.5	93.6	97.6	2.1	1.6	2.0
Station -1	11.30.2019	-	62.1	33.4	19.9	-	-	-	1.9	1.4	2.6
		100	158.7	130.6	118.7	96.6	97.2	98.8	1.7	1.2	2.5
Station -2		-	100.2	21.9	26.7	-	-	-	1.8	1.6	2.4
		100	195.1	120.4	119.2	94.9	98.5	92.5	1.5	1.4	2.4
Station -3		-	44.8	11.6	8.1	-	-	-	2.3	1.5	2.5
		100	142.1	109.4	105.0	97.3	97.8	96.9	2.1	1.4	2.3
Station -1	01.30.2020	-	65.8	33.6	9.5	-	-	-	2.1	1.5	1.9
		100	160.5	131.7	102.5	94.7	98.1	93.0	2.0	1.3	1.7
Station -2		-	36.1	15.9	21.8	-	-	-	1.8	2.6	2.2
		100	132.6	112.3	117.6	96.5	96.4	95.8	1.6	2.4	2.0
Station -3		-	89.3	64.1	17.3	-	-	-	2.3	1.9	1.8
		100	187.5	157.8	114.6	98.2	93.7	97.3	2.0	1.7	1.5
Station -1	03.24.2020	-	32.4	14.1	10.6	-	-	-	2.7	1.8	2.6
		100	130.6	107.4	105.6	98.2	93.4	95.0	2.4	1.6	2.4
Station -2		-	76.5	26.8	31.7	-	-	-	2.4	1.9	2.5
		100	173.6	122.8	128.9	97.1	96.5	97.2	2.3	1.7	2.3
Station -3		-	65.8	42.9	17.3	-	-	-	2.4	1.7	2.1
		100	162.5	137.8	110.9	96.7	94.9	93.6	2.5	1.6	2.0

Conclusions

As a result of the analyses of water samples taken from Yıldız River, the lowest calcium concentration in the river was found to be 88 mg/L, and the highest one was found to be 144 mg/L. Water hardness ranged between 250 and 400 mg/L. River water has an alkali character, and the maximum alkalinity was found to be 325 mg $CaCO_3$ /L. The highest values of ammonium, nitrate and nitrite parameters in the water were found to be 0.0846 mg/L, 0.857 mg/L, and 0.0004 mg/L, respectively. The highest total phosphate concentration in the present study was found to be 0.0268 mg/L and the lowest one to be 0.0011 mg/L. During the sampling period, the water temperature ranged between 7 and 17.5 °C. The chloride concentration was found to range between 9.43 and 18.87 mg/L. pH values ranged between 7.94 and 8.18. The highest electrical conductivity in river water was found to be 625 µS/cm and the lowest one to be 327 µS/cm. Oxygen concentration, which is important for the water quality, did not fall below 7.03 mg/L during the sampling period, and the highest value was found to be 11.35 mg O_2/L. The silica concentration in the river water was found to be very high. The highest silica concentration was 10.39 mg O_2/L and the lowest one was 8.33 mg O_2/L. Moreover, even though the sulfate analysis was performed for the water samples, no sulfate could be detected. The water of Yıldız River was found to be Class I water quality, and the hardness class was found to be very hard water.

In the present study, a new, rapid, and simple method for preliminary concentration and isolation of ferrous, lead, and cadmium was optimized and then applied for measurements with FAAS. Fe (II), Pb (II), and Cd (II) ions become complex with [C4mim][Tf2N] at pH 6.5 and all the optimization procedures for the suggested method were completed. As a result of the experiment, it is predicted that, since the suggested method is simple, rapid, selective, highly sensitive, and suitable for the use at low concentrations, it would ease the observation, measurement, and identification of Fe (II), Pb(II), and Cd (II) heavy metals in water samples.

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Conflicts of interest

The authors state that did not have conflict of interests.

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