Atomic Absorption Spectrometric Determination of Cd(II), Mn(II), Ni(II), Pb(II) and Zn(II) Ions in Water, Fertilizer and Tea Samples after Preconcentration on Amberlite XAD-1180 Resin Loaded with l-(2-Pyridylazo)-2-naphthol[1]

O. Hazer, Ş. Kartal, and Ş. Tokalıoğlu

Erciyes University, Faculty of Arts and Sciences, Department of Chemistry, Kayseri, 38039 Turkey
e-mail: serifet@erciyes.edu.tr
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Abstract—A new chelating resin, 1-(2-pyridylazo)-2-naphthol (PAN) coated Amberlite XAD-1180 (AXAD-1180), was prepared and used for the preconcentration of Cd(II), Mn(II), Ni(II), Pb(II) and Zn(II) ions prior to their determination by flame atomic absorption spectrometry (FAAS). The optimum pH for simultaneous retention of the elements and the best elution means for their simultaneous elution were pH 9.5 and 3 M HNO_3, respectively. The sorption capacity of the resin was found to be 5.3 mg/g for Cd and 3.7 mg/g for Ni. The detection limits for Cd(II), Mn(II), Ni(II), Pb(II) and Zn(II) were 0.7, 10, 3.1, 29 and 0.8 μg/L, respectively. The effects of interfering ions for quantitative sorption of the metal ions were investigated. The preconcentration factors of the method were in the range of 10–30. The recoveries obtained were quantitative (≥95%). The standard reference material (GBW07605 Tea sample) was analysed for accuracy of the described method. The proposed method was successfully applied to the analysis of various water, urea fertilizer and tea samples.

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As the number of ecological and health problems associated with environmental contamination continues to rise, the determination of heavy metal ions present at trace levels in environmental samples is gaining great importance [1]. Nickel is a moderately toxic element as compared with other transition metals. However, it is known that inhalation of nickel and its compounds can lead to serious health problems, including respiratory system cancer. Moreover, nickel can cause a skin disorder known as nickel-eczema [2]. Manganese is a necessity for the proper function of several enzymes and an essential micro-nutrient for the function of the brain, nervous system, and normal bone growth. It optimizes enzyme and membrane transport functions [3]. Cadmium is known to be highly toxic for animals, plants and humans even at low concentrations and can be accumulated in several organs. The most important anthropogenic sources of this element include emissions from industrial plants, such as zinc smelters, steel works, incinerators and power stations [4].

Zinc is an essential trace element of great importance for humans, plants and animals. Zinc deficiency slows growth and development of the neonate and also leads to cognitive defects and impairs the immune system. An excess of this metal can play an important role in the progression of several damages to human body,

including disturbances in energy metabolism or increasing in oxidative stress [5, 6].

Lead is one of the most widespread heavy metals in the environment, in view of its extensive use in storage batteries, solders, cable sheaths, pigments, anti-knock products and radiation shields and due to corrosion of household plumbing systems and erosion of natural deposits. The consumption of lead-contaminated drinking water causes delay in physical or mental development, slight deficit in learning abilities of children, high blood pressure and kidney problems in adults [7].

Despite the selectivity and sensitivity of analytical techniques such as atomic absorption spectrometry, there is a crucial need for the separation and preconcentration of trace elements before their analyses due to their low concentrations in numerous samples. In trace analysis, preconcentration and/or separation of trace elements from the matrix is frequently necessary to improve the detection limit and selectivity for their determinations by FAAS. For this purpose, several methods have been proposed and used for preconcentration and separation of trace elements according to the nature of the samples, the concentrations of the analytes and the measurement techniques [1, 8, 9]. These include ion exchange, solvent extraction, coprecipitation, cloud point extraction, electrodeposition and solid phase extraction (SPE).

Although liquid-liquid extraction has proven to be a reliable and efficient technique, it is a time, reagent and

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labour consuming procedure, which can not be easily automated. SPE employs similar principles of metal partitioning between solid and liquid phases. It is one of the most effective procedures for trace metal analysis because it is an attractive technique that reduces consumption of reagents and exposure to solvents and disposal costs. The retention of trace elements on sorbents requires the addition of a ligand to the sample or ligand attachment to the sorbent by physical adsorption (impregnation) or chemical bonding (immobilization) [10, 11]. A number of reagents have been investigated for impregnation of sorbents as a means of increasing retention capacity and selectivity of the sorbent for trace elements [12–15]. Various adsorbents such as activated carbon [16], silica gel [17], chelating resins [18], polyurethane foam [19] and Amberlite XAD resins [20–22] have been used to preconcentrate trace metal ions. Amberlite XAD resins are good supports for developing chelating matrices. Their attractive features are easy regeneration for multiple sorption-desorption cycles, good mechanical stability and reproducible sorption characteristics. In comparison to silica gel and cellulose, the kinetics of sorption is faster [23].

l-(2-Pyridylazo)-2-naphthol forms stable complexes with many transition metals of interest; it is one of the most extensively used complexing agents for trace element analysis. Its solutions are stable. In acidic solutions the pyridine nitrogen is protonated and in basic solutions the proton of the OH group is ionized. The metal chelates of PAN have the metal atom bonded to O of the OH group, to pyridine N and to azo N [24].

In this paper, a new separation/preconcentration method is described for the determination of Cd(II), Mn(II), Ni(II), Pb(II) and Zn(II) ions in the water, fertilizer, tea and certified tea samples (GBW07605) by FAAS using Amberlite XAD-1180 resin loaded with PAN.

EXPERIMENTAL

Instruments. A Perkin Elmer 3110 model atomic absorption spectrometer equipped with single element hollow cathode lamps and air-acetylene burner, Shelton, USA was used for the determination of metals. The instrumental parameters were used according to the manufacturer's recommendations. The wavelenghts (nm) selected for the determination of the analytes were as follows: Cd 228.8, Mn 279.5, Ni 232.0, Pb 283.3 and Zn 213.9. A Jenco model 672 digital pH meter (San Diego, CA, USA) was used for the pH adjustments.

Reagents and solutions. All chemicals were of analytical reagent grade (Merck, Darmstadt, Germany). Distilled-deionized water was used in all experiments. Stock solutions (1000 mg/L) of the elements were prepared by dissolving appropriate amounts of their nitrate salts in 1.0 % (v/v) HNO_3 and further diluted daily prior to use. l-(2-Pyridylazo)-2-naphthol reagent was used as purchased. The following buffer solutions were used for the solid phase extraction procedures: CH_3COOH/CH_3COONa buffer for pH 4; Na_2HPO_4/NaH_2PO_4 buffer for pH 7; and NH_3/NH_4Cl buffer for pH 9–11. Non-ionic Amberlite XAD-1180 resin (Acros Organics, NJ, USA) is a polystyrene divinylbenzene copolymer (surface area 500 m^2/g, average pore size 400 Å and average particle diameter 530 μm). Prior to use it was washed with hydrochloric acid and ethanol and then rinsed with water until obtaining a neutral solution and then dried at 105°C in an oven.

20 mL of 0.1% (w/v) PAN solution were passed through a glass column (10 cm long, 1 cm i.d.) containing 0.5 g AXAD-1180 resin at a flow rate of 1 mL/min for the preparation of the AXAD-1180 resin loaded with PAN. The impregnated resin was rinsed with distilled water and conditioned with 10–15 mL of pH 9.5 buffer solution prior to passage of the sample solution.

Proposed preconcentration procedure. The method was tested with model solutions prior to the determination of the trace metals in the real samples. A 50 mL aliquot of the model solution containing 3.0 μg Cd(II), 7.5 μg Mn(II), 12.5 μg Ni(II), 30 μg Pb(II) and 1.5 μg Zn(II) ions was passed through the column at a flow rate of 1 mL/min after adjusting the pH to 9.5. The retained metal ions were eluted with 30 mL of 3 M HNO_3. The eluate was evaporated to 0.5–1 mL on a hot plate. The residue was dissolved and diluted to 5 mL with 3 M HNO_3 solution. The concentration of the metal ions in the final solution was determined by FAAS.

Collection and preparation of samples. Treated black Turkish tea sample was purchased from a local market. The urea fertilizer sample was purchased from Kayseri, Turkey. 3.0 g of the sample was dissolved in 1 M of nitric acid and diluted to 50 mL with water. The stream water and tap water samples were collected from Yozgat, Turkey. The water samples were filtered through a cellulose membrane filter (Millipore), 0.45 μm pore size, to remove particulate matter, and then acidified with cone. HNO_3 (5 mL per 1 liter of water sample).

To dissolve the certified reference material (GBW07605 Tea sample) and the tea sample, an aliquot of 0.5 g of each sample was taken into a 250 mL of PTFE beaker. 1 mL of 0.05 M nitric acid was added to the sample, following by 10 mL of concentrated nitric acid and then 1 mL of concentrated perchloric acid. The beaker was heated on a hot plate for 1 h. After cooling to room temperature, 4 mL of concentrated hydrofluoric acid was added and the contents of the beaker were evaporated near to dryness. The process was twice repeated by using 5 mL of concentrated nitric acid and 1 mL of concentrated hydrofluoric acid. The resulting solution was diluted to 50 mL with 0.05 M nitric acid.

RESULTS AND DISCUSSION

Effect of pH. The recovery values of each metal were investigated in the pH range 3–11 by use of relevant buffer solutions given above (Fig. 1). The recoveries of Cd(II), Mn(II), Ni(II), Pb(II) and Zn(II) ions were quantitative (≥95%) in the pH range of 9.5–11, except for Pb(II) ion that was 89% at pH 11, due to the formation of anionic lead hydroxides. From these results, pH 9.5 was selected as optimum pH and used in further experiments.

Effect of sample and eluent flow rates. One of the important parameters affecting recovery and preconcentration time is flow rate. There is a contradiction between recovery and preconcentration time changing with flow rates. So, the effect of flow rate of sample solution on the recovery of the analytes was examined under the optimum conditions (pH: 9.5, eluent type: 3 M HNO$_3$, sample volume: 50 mL, solid phase amount: 0.5 g). The sample solution was passed through the column with the flow rates varied from 0.5 to 10 mL/min. As can be seen in Fig. 2, the recoveries of metal ions were quantitative up to a flow rate of 1 mL/min for Cd(II), Ni(II) and Pb(II), 1.5 mL/min for Mn(II) and at all of the flow rates for Zn(II). At the flow rates greater than 1 mL/min there was a decrease in the recoveries for Cd(II), Ni(II) and Pb(II) due to insufficient equilibrium condition between the sorbent and the metal ions. Therefore, a flow rate of 1 mL/min was applied for subsequent experiments.

The effect of flow rate of eluent on the quantitative elution of the analytes was investigated by varying the flow rate from 0.5 to 3 mL/min. The recoveries of metal ions were quantitative up to a flow rate of 2 mL/min for Cd(II), Mn(II) and Zn(II), 1 mL/min for Pb(II) and at all of the flow rates for Ni(II) (Fig. 3). The eluent flow rate of 1 mL/min was chosen as optimum rate.

Effect of sample volume. In order to determine the maximum sample volume, 3.0 μg Cd(II), 7.5 μg Mn(II), 12.5 μg Ni(II), 30 μg Pb(II) and 1.5 μg Zn(II) were preconcentrated from volumes of 50, 100 and 150 mL of synthetic sample solutions under the optimum conditions by applying the procedure mentioned above. The recoveries of Cd(II), Ni(II) and Zn(II) were approximately quantitative up to 150 mL of the sample volume. The breakthrough volumes for Mn(II) and Pb(II) were found as 50 mL. Consequently, by considering the final solution volume of 5 mL and the breakthrough volumes of 50 and 150 mL, 10 and 30-fold enrichment factors could be obtained for the analyte ions, respectively.

Effect of concentration, type and volume of eluent. The HCl and HNO$_3$ solutions prepared at various concentrations between 1–3 M were tested to elute the metal ions retained on the impregnated resin. While quantitative recovery values for all of Cd(II), Mn(II), Ni(II), Pb(II) and Zn(II) ions were obtained with only 3 M HNO$_3$ and the recoveries for the elements were not quantitative for all the HCl concentrations.
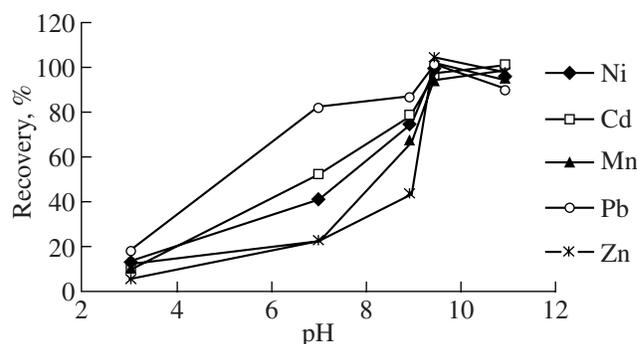
Fig. 1. Effect of pH on the recovery of Cd(II), Ni(II), Mn(II), Pb(II) and Zn(II) ions (sample volume: 50 mL, eluent: 30 mL of 3 M HNO$_3$, amount of the ions: 3.0 μg Cd(II), 12.5 μg Ni(II), 7.5 μg Mn(II), 30 μg Pb(II) and 1.5 μg Zn(II)).
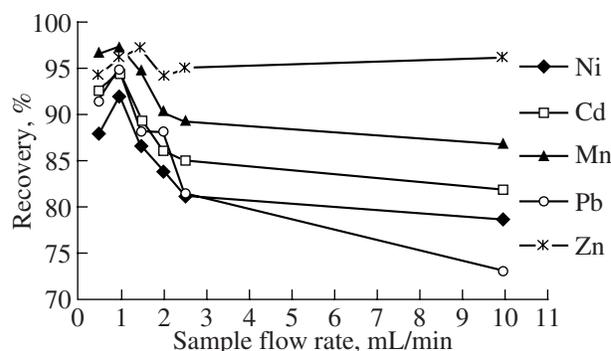
Fig. 2. Effect of the sample flow rate on the recovery of analytes ($n = 3$).
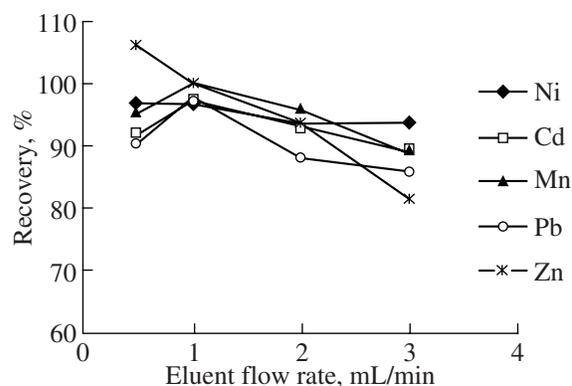
Fig. 3. Effect of the eluent flow rate on the recovery of analytes (pH: 9.5, amount of solid phase: 0.5 g, eluent: 30 mL of 3 M HNO$_3$).

The effect of volume of 3 M HNO$_3$ for the quantitative elution of all the metal ions was also examined. When it was used 10 mL and 20 mL of 3 M HNO$_3$, the recoveries of analytes were not quantitative, except for Mn(II), Ni(II) and Pb(II) for 20 mL of 3 M HNO$_3$. It

Table 1. Effect of some ions on the recovery of Ni(II), Cd(II), Mn(II), Pb(II) and Zn(II) (pH 9.5, eluent: 30 mL of 3 M HNO_3, sample volume: 50 mL, $n = 4$)

Ion	Concentration (µg/mL)	Recovery (%)				
		Ni	Cd	Mn	Pb	Zn
Na^+	1000	98	98	100	100	100
	2500	97	98	100	100	105
	5000	97	98	100	100	105
K^+	1000	100	100	98	100	98
	2500	100	100	99	100	100
	5000	100	100	99	99	100
NO_3^-	1000	99	100	98	100	98
	2500	99	99	99	100	100
	5000	99	99	99	99	100
Cl^-	1000	100	96	98	98	100
	2500	100	96	98	97	105
	5000	99	96	98	97	105
Ca^{2+}	1000	100	100	97	99	99
	2500	100	100	96	99	97
	5000	100	99	96	99	97
Mg^{2+}	1000	100	100	99	95	100
	2500	99	100	99	95	96
	5000	99	98	99	95	96
SO_4^{2-}	1000	100	99	97	97	97
	2500	100	98	96	95	97
	5000	100	98	96	95	100
Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, Cl^-, SO_4^{2-}	1000	99	98	97	95	96

was found that quantitative recoveries for all the analyte ions could be obtained with 30 mL of 3 M HNO_3.

Effect of matrix ions. The preconcentration procedures for trace metals can be strongly affected by other constituents of samples. For this reason, the reliability of the proposed niethod was examined in the presence of possible interfering ions. The alkali and alkaline-earth elements were added to the model solution including the analytes as their nitrate, chloride and sulphate salts. The concentration of analytes was fixed and the concentration of interfering metal ions was adjusted in the range of 1000–5000 µg/mL. Table 1 shows that the effect of interfering ions present individually up to 5000 µg/mL are negligible on the determination of the analytes. There are no observed any interfering effect on the determination of the analytes when Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, Cl^- and SO_4^{2-} ions are present together with a concentration of 1000 µg/mL from each one ($R \geq 95\%$). Therefore, Cd(II), Mn(II), Ni(II), Pb(II) and Zn(II) in the water, fertilizer and tea samples can be recovered quantitatively and determined accurately by using the proposed method.

Analytical performance of the method. In order to assign the detection limit (DL, $n = 20$) of the proposed method, a 50 mL portion of blank solution was passed through the column under optimal experimental conditions and the retained metal ions were eluted. The DLs obtained as three times the standard deviation of the blank solution by dividing to the slope of the calibration curve were 0.7 for Cd(II), 10 for Mn(II), 3.1 for Ni(II), 29 for Pb(II), and 0.8 µg/L for Zn(II). The precision of the method was determined by performing successive seven retention and elution cycles followed by FAAS. It was found that the recoveries ($R\% \pm s$) of Cd(II), Mn(II), Ni(II), Pb(II) and Zn(II) were 97.1 ± 0.6, 96.5 ± 1.4, 100 ± 2, 98.3 ± 0.8 and 98.3 ± 2.8, respectively.

Adsorption isotherm and adsorption capacity. The adsorption capacity of PAN impregnated AXAD-1180 resin was determined for Cd(II) and Ni(II) by using the column technique. Therefore, 50 mL of model solutions containing 1–400 mg/L Cd(II) and Ni(II) from each one at pH 9.5 were passed through the column filled with 0.5 g of the impregnated resin at a flow rate of 1 mL/min. The retained metal ions were eluted from the resin with 3 M HNO_3. The concentra-
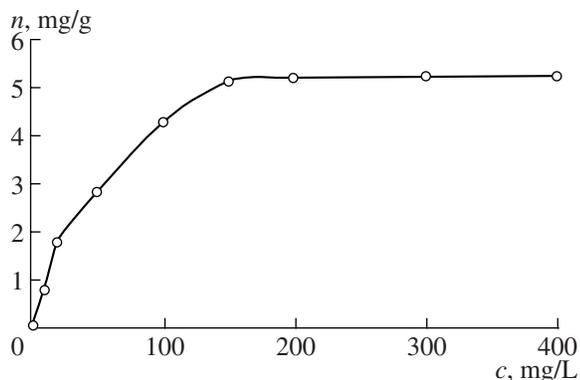
Fig. 4. Adsorption isotherm of the chelating resin for cadmium.
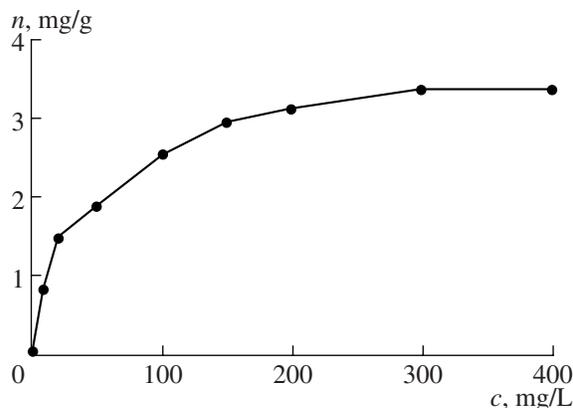
Fig. 5. Adsorption isotherm of the chelating resin for nickel.

tions Cd(ll) and Ni(II) in the eluate were determined by FAAS. The concentration of adsorbed metal ion (n) in mg/g was studied as a function of the metal ion concentration (c, mg/L) in the initial solution. Fig. 4 for Cd(II) and Fig. 5 for Ni(II) show the adsorption isotherms which conform to the Langmuir equation [20], as c/n is proportional to c. The adsorption capacities (n_m) of the resin for cadmium and nickel were calculated from the Langmuir equation. This equation can be given as the following form:

$$\frac{c}{n} = \frac{1}{n_m K} + \left(\frac{1}{n_m}\right)c.$$

The adsorption capacity (n_m) and the binding equilibrium constant (K) were calculated from the slope and the intercept of the regression plot obtained by the least squares method, respectively. The adsorption capacities of the chelating resin for cadmium and nickel were 5.30 mg/g (0.047 mmol/g) and 3.67 mg/g (0.062 mmol/g) and the binding equilibrium constants were 0.24 L/mg (2.66×10^4 L/mol) and 0.029 L/mg (1.70×10^3 L/mol), respectively. The adsorption capacity of this chelating resin is higher than that for the adsorbents reported in literature [22, 25, 26].

Validation and application of the proposed method. The proposed method was applied to the water, fertilizer and tea samples. For the validation of the method, the certified reference material (GBW07605) was analysed and recovery studies were performed in which analytes were added at the known concentrations to the water and fertilizer samples. The obtained results by analysing of the CRM for Cd(II), Mn(II), Ni(II), Pb(II) and Zn(II) ions are given in Table 2. It was found that there is no significant difference between the results obtained by the proposed method and the certified values. The results of analysis the tea sample are also shown in Table 2. Cadmium in the CRM and the tea sample could not be determined because of its low concentrations.

The recovery results found by adding trace metal ions at the different concentrations to the tap water,

stream water and fertilizer samples are shown in Table 3. A good agreement was obtained between the added and found analyte contents. While the recovery values for the analyte ions are in the range of 94–114%, the standard deviation values for the spiked samples are ≤11%.

The proposed SPE procedure based on the loaded of PAN on the Amberlite XAD-1180 resin is a simple, accurate, selective, reproducible, and cheap technique for the enrichment of Cd(II), Mn(II), Ni(II), Pb(II) and Zn(II) ions. The AXAD-1180-PAN resin seems to be stable up to at least 15 runs. It was found that the recoveries of the elements were ≥94%. The results obtained from the proposed method were in a good agreement with the certified values for Cd(II), Mn(II), Ni(II), Pb(II) and Zn(II) ions. The resin exhibits higher sorption capacities in comparison to other adsorbents. The method can be satisfactorily applied to the determina-

Table 2. Determination of Cd(II), Mn(II), Ni(II), Pb(II) and Zn(II) ions in the certified reference material (GBW07605) and the tea sample ($n = 3$)

Element	(GBW07605, Tea sample)		Tea sample
	Concentration ($\bar{x} \pm s$), µg/g		
	Certified	Found	Found
Ni	4.6 ± 0.5	4.3 ± 0.2	2.7 ± 0.2
Mn	1240 ± 70	1233 ± 30	1559 ± 3
Pb	4.4 ± 0.3	5.0 ± 0	14.2 ± 0.7
Zn	26.3 ± 2.0	23.0 ± 0.6	32.4 ± 0.2
Cd	0.057 ± 0.010	nd*	nd*

Note: * Not detected.

Table 3. Determination of Cd(II), Mn(II), Ni(II), Pb(II) and Zn(II) in various water and fertilizer samples (sample volume: 50 mL, $n = 5$)

	Added, µg/L	Stream water (1)		Stream water (2)		Tap water (1)		Tap water (2)		Tap water (3)		Urea fertilizer	
		Found*, µg/L	R, %	Found, µg/L	R, %	Found, µg/L	R, %	Found, µg/L	R, %	Found, µg/L	R, %	Found, µg/L	R, %
Ni	0	23.2 ± 2.6		10.1 ± 2.6		12.7 ± 2.6		4.8 ± 2.6		7.5 ± 2.6		0.82 ± 0.04	
	100	121 ± 3	97.8	107 ± 3	96.9	112 ± 3.0	99.3	105 ± 3	100	105 ± 3	97.5	2.48 ± 0.05	99.4
	250	273 ± 3	99.9	252 ± 3	96.8	254 ± 3.0	96.5	247 ± 3	96.9	259 ± 8	101	4.93 ± 0.05	98.6
Mn	0	189 ± 4		519 ± 7		21.8 ± 2.2		<DL		<DL		0.18 ± 0.04	
	50	238 ± 3	98.0	566 ± 3	94.0	72 ± 2.5	100	54.3 ±2.5	109	57.2 ± 2.5	114	1.03 ± 0.04	102
	150	333 ± 3	96.0	663 ± 3	96.0	167 ± 3	96.8	149 ± 3	99.3	159 ± 3	106	2.61 ± 0	97.2
Cd	0	<DL		2.2 ± 0.5		2.2 ±0.5		2.2 ± 0.5		<DL		0.08 ± 0	
	40	38.5 ± 0.6	96.2	40.5 ± 0.6	95.8	41.2 ±0.6	97.5	40.5 ± 0.6	95.8	38.1 ± 0.6	95.2	0.73 ± 0	97.4
	60	57.3 ± 0.0	95.5	59.3 ± 0.0	95.2	59.3 ± 0.0	95.2	61.0 ± 0.6	98.0	58.6 ± 0.6	97.7	1.06 ± 0	98.0
Zn	0	31.3 ± 0.3		33.4 ± 1.2		45 ± 1.8		161 ± 3		36.9 ± 1.0		0.69 ± 0.01	
	20	50.2 ± 0.0	94.5	52.2 ± 0.0	94.0	64.3 ± 0.8	96.5	181 ± 3	100	56.1 ± 0.3	96.0	1.03 ± 0.01	102
	30	60.2 ± 1.0	96.3	62.3 ± 0.3	96.3	74.3 ± 0.9	97.7	192 ± 1	103	66.2 ± 0.8	97.7	1.16 ± 0.01	94.0
Pb	0	<DL		<DL		<DL		<DL		<DL		1.46 ± 0.16	
	400	397 ± 0	99.2	397 ± 0	99.2	384 ± 11	96.0	397 ± 0	99.2	397 ± 0	99.2	8.10 ± 0.18	99.6
	600	581 ± 11	96.8	606 ± 0	101	581 ±11	96.8	606 ± 0	101	581 ± 11	96.8	11.3 ± 0.18	98.4

Note: * $\bar{x} \pm s$.

tion of the elements in various water, fertilizer and tea samples.

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