



Determinations of Cadmium, Tin, Copper, Iron, and Zinc in Food Samples by Electrothermal and Flame Atomic Absorption Spectrometries

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Highlights

- Pyrolysis and atomization temperatures of Sn and Cd have been determined.
- Pyrolysis times of Sn and Cd have been determined.
- Cadmium, Sn, Fe, Cu, and Zn have been determined in food samples.
- The element results obtained have been compared with other literature values.

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Abstract

Cadmium, tin, iron, copper, and zinc in tea, rice, and liver samples, and standard reference materials (IRMM 804 Rice Flour, GBW 10010 Rice, Bovine Liver1577c and GBW 07605 Tea Leaves) were determined by using electrothermal and flame atomic absorption spectrometries. Cd and Sn in sample solutions were determined with electrothermal atomic absorption spectrometry by using palladium (Pd) as a matrix modifier. Pyrolysis and atomization temperatures and pyrolysis times of Cd and Sn in sample solutions were optimized in the absence or presence of Pd. Pyrolysis temperatures of Cd and Sn found in the presence of Pd were 800°C and 1200°C, respectively. Iron, Cu, and Zn in samples were determined by flame atomic absorption spectrometry. The accuracy and precision of the method were validated by determining elements in standard reference materials. Limits of detection for Sn, Cd, Fe, Cu, and Zn were found as 0.66, 0.26, 2.0, 1.9, and 1.2 µg/L, respectively. Concentrations of elements found in samples were compared with maximum values reported by World Health Organization (WHO) and other studies.

1. INTRODUCTION

Tea is the most popular beverage in the world and the Turkey. Most popular type of tea is black tea grown in Black Sea region of the Turkey and the second one is green tea, which is produced from fresh leaves [1]. Rice is second most consumed food in the world and in the Turkey. Different types of rice samples are grown in the Turkey and consumed mostly. Liver samples such as sheep, cow and chicken are mostly consumed in the Turkey. They may be polluted by toxic heavy metals from water, soil, environment or other samples. Therefore, presence of heavy metals in these samples and their products are more important for nutritional and toxicological point of view.

The living metabolism works like a factory with chemical events lined up respectively. This perfect balance works regularly with amounts of trace elements in the body or is disrupted. Therefore, amounts of trace elements in food samples mostly consumed should be determined from time to time and should be checked for compliance with standards [2]. Heavy metals are important pollutants in the environment due to their potentials to accumulate and to enter in food chains [3, 4]. Heavy metals may be categorized as toxic elements such as cadmium and necessary elements such as iron, copper and zinc [4, 5]. If toxic elements are taken over a long time, they can be very dangerous even at low concentrations. Essential metals can also be toxic when they are taken excessively [4, 5]. The determinations of both toxic and essential elements such as Cd, Sn, Fe, Cu and Zn are very important for human health.

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The major sources of heavy metal contaminants are industry, agriculture and mining activities [4]. Cadmium is widely used in industry and found in various mineral shoots, primarily zinc. It is mostly found in CdS form in zinc and other ores. It is obtained from zinc production and its compounds are very toxic. A person weighing 60 kg can get 0.113 mg Cd (maximum) in the body daily [6]. If it is accumulated excessively in the body, it may have disruptive effects such as cancer, lung failure, liver and kidney disorders [5, 7]. Commission Regulation (EC) No 1881/2006 gives maximum level of Cd (0.2 mg/kg wet weight) for rice samples [8]. Joint FAO/WHO food standard program codex committee on pollutions in foods (2011) also sets maximum level of Cd in leafy vegetables (0.2 mg/kg), legume vegetables (0.1 mg/kg) and rice polished (0.4 mg/kg) [9]. It is difficult to talk about the toxic effect of Sn because there is no Sn poisoning in history. Sn has been used in making bronze since the beginning of alloys. It takes values +2 and +4 in its compounds and interacts with organic compounds to form organic tin compounds. Organic tin compounds are used in many industries such as pesticides, plastics and paints. By forming an alloy with lead metal, a more robust product called soldering is obtained. It is widely used in automotive, aircraft and chemical industries. The effects of organic tin compounds on the body may vary. People can take tin ties with food, breathing and skin. Among of organic tins, triethyl tin is the most dangerous for human health. Copper can be found in many samples such as meat, seafood, nuts, raisins, legumes and cereals. Cu is an essential element for body and a certain amount of Cu can be taken into the body in every day. In normal nutrition, Cu deficiency is not observed much. Taking copper into the body with high exposure for a long time causes health problems such as nausea, vomiting, acute anemia and lung conditions. Amount of iron taken into the body is between 2.5 - 4.5 g in total. Easy oxidation of iron has made it an essential element for the body. It is required as a cofactor for synthesis of proteins and many enzyme systems such as catalase, cytochrome, peroxidase and oxygen transport [4, 5]. Iron plays an active role in the transport of oxygen in the body and it is involved in blood production. It is also essential for DNA synthesis, protection against free radicals and microbes [4]. Iron may be as a natural constituent of foods, plants and drinking waters. The most important sources of iron are meat, liver, eggs and green leafy plants. Fe occurs as iron oxides in foods and its deficiency is one of the most serious nutritional deficiencies such as anemia, resistance decreases and weakness in the body [4]. Daily intake of iron has been estimated as 17 mg/day for males and 9 - 12 mg/day for females. Excess intake of iron in the body may be deposited in liver, pancreas, adrenals, thyroid, pituitary and heart [9]. Zinc is used in metal coating, dye casting, construction of industry, alloys, dry cell batteries, medical, household applications and etc. Zn is an essential element for growth and development of living things, and very important for humans [5]. It may play a significant role as a cofactor in biochemical processes such as enzyme systems, proteins and nucleic acids synthesis. As a result of these reasons, daily intake of zinc is important. It is beneficial for immune system [5]. Seafood, milk and dairy products, legumes and cereals are good sources of Zn. In its deficiency, although growth and development disorders are observed in children, a chronic toxic effect of Zn has not been observed. The daily intake of zinc has been estimated as maximum 20 mg/day for adults [9].

There are various studies on determination of trace and essential elements in food samples. Concentrations of Cu, Pb and Sn in tomato sauce samples have been compared by solid and slurry sampling methods using graphite furnace atomic absorption spectrometry [10]. Results have been evaluated in 95% confidence interval for 10 different tomato sauce. Cd in sugar and chocolate products taken from markets in India has been determined [11]. 0.244 mg/L Cd in cocoa chocolates, 0.071 mg/L Cd in milk chocolate and 0.005 mg/L Cd in fruit chocolates have been determined. Cd by electrothermal atomic absorption spectrometry (ETAAS) and other elements by flame atomic absorption spectrometry (FAAS) have been determined. Cd in black tea samples has been found as $31.4 \pm 18.3 \mu\text{g/kg}$, while Cd in other tea samples have been found as $21.3 \pm 16.4 \mu\text{g/kg}$. Cd, Cu and Zn in black tea samples taken from the market have been determined by ETAAS. Results have been found as $44.6 \pm 12.9 \text{ mg/kg}$ Zn, $2.3 \pm 0.4 \mu\text{g/kg}$ Cd and $16.5 \pm 3.9 \text{ mg/kg}$ Cu, respectively [12].

Electrothermal and flame atomic absorption spectrometries are commonly used analytical techniques for determination of trace elements in foods such as rice, tea and environmental samples because their uses have been wider, faster and easier than other instrumental methods [1, 5, 13, 14]. Determinations of heavy and trace elements in biological, geological, environmental and food samples have made them ideal with high precision and accuracy. By using both instruments, determinations of trace and heavy metal

concentrations in food samples such as rice, tea and liver that consumed daily are necessary and important for human body.

Aim of this study was to determine Cd, Sn, Cu, Fe and Zn in tea, rice and liver samples and standard reference materials (SRMs) dissolved in presence of acidic medium. Optimization studies such as pyrolysis and atomization temperatures were performed for Cd and Sn determinations in samples. Bovine liver 1577c, Tea leaf GBW 07605, IRMM 804 Rice flour and GBW 10010 Rice SRMs were taken to investigate accuracy and precision of proposed method. While Cd and Sn in samples and SRMs were determined by ETAAS using Pd modifier, Cu, Fe and Zn in these samples were determined by FAAS.

2. MATERIALS AND METHODS

2.1. Instrumentation

Varian ((Mulgrave Virginia, Australia) Spectra AA240Z model electrothermal atomic absorption spectrometry by using Zeeman background correction for Sn and Cd determinations and Varian 240FS model flame atomic absorption spectrometry with deuterium background correction for Cu, Fe and Zn determinations in samples were used. Varian Sn, Cd, Cu, Fe and Zn hollow cathode lamps were utilized as radiation sources. Wavelengths, slit widths and lamp currents of elements according to the recommendation of manufacturer were given as 228.8 nm, 0.5 nm and 4.0 mA for Cd, 286.3 nm, 0.7 nm and 4.0 mA for Sn, 324.8 nm, 0.5 nm and 10.0 mA for Cu, 213.9 nm, 0.5 nm and 7.0 mA for Zn and 248.3 nm, 0.2 nm and 12 mA for Fe, respectively. 20 μ L calibration standard solutions or sample solutions were injected into pyrolytically coated graphite tubes (Varian, P/N-63-100012-00) with a Varian SPD-20 auto-sampler. Ar gas (99.98% m/m, Oksan, Ankara, Turkey) was utilized in heating temperature program except for atomization step. Air/Acetylene flow rates for Cu, Zn and Fe were used as 13.5/2.0 L/min, respectively.

2.2. Reagents and Solutions

The reagents utilized in experiments were prepared from analytical grade purity metal salts by using ultrapure water (18.2 M Ω ·cm). The 1000 mg/L Cd, Sn, Cu, Fe and Zn atomic absorption standard stock solutions purchased from Merck (Darmstadt, Germany) were used. The 1000 mg/L Pd solution was prepared from 0.21g of PdCl₂·2H₂O (Merck) by dissolving in 20 mL of 15% (v/v) HCl and diluted to 100 mL with ultrapure water. HNO₃ (1%, v/v) solution was prepared from 5 mL of HNO₃ (65%, m/m, Merck) by diluting to 500 mL with ultrapure water. H₂O₂ solution (30 %, m/m, Merck) was used in experiments. All glass materials, Teflon flasks, beakers and tubes used in the experiments were wait in 5% HNO₃ (v/v) solution at one night in laboratory medium to remove impurities, cleaned with ultrapure water and used after drying.

2.3. Preparation of Samples

Four different rice samples were taken from supermarkets with sale packets (two packets for each sample) in Ankara, Turkey. About 0.31 - 0.36 g rice samples were weighed into four different Teflon beakers. 6 mL concentrated HNO₃ and 2 mL concentrated H₂O₂ solutions were poured into beakers and waited overnight in laboratory condition by closing with a cover. Afterwards, the samples were heated on hotplates for 3 - 4 h and evaporated until their volumes were about 3 mL. Solution was poured into 10 mL Teflon flask and diluted with ultrapure water to mark.

Liver samples (two packets for each sample) taken from four different local butchers in Ankara, Turkey were weighed in the range of 2 - 5 g in different packets. The samples were dried in drying device between 100 - 120 °C for about 4 h. The dried samples were homogenized by shrinking with the help of mortar. Samples were weighed in the range of 0.3 - 0.5 g and placed into different Teflon beakers. 8 mL concentrated HNO₃ and 3 mL concentrated H₂O₂ solutions were poured into each beaker and left overnight in laboratory by closing with a cover. The solution was continued to dissolve on a hotplate until volume was about 3 mL. Dissolved samples were taken into 10 mL flasks and diluted with ultrapure water to the marks.

Three different brands of dry black tea samples (two packets for each sample) were obtained from supermarkets in Ankara. The sample was homogenized and weighed about 0.5 g and placed into Teflon beaker. 6 mL concentrated HNO₃ and 2 mL concentrated H₂O₂ solutions were poured into each beaker. Sample was heated on a hotplate for about 4 h until volume was about 3 mL. Dissolved samples were poured into 50 mL flasks and diluted with ultrapure water to the marks. Two replicate study for dissolving samples from each packet was performed.

The IRMM 804 Rice Flour, GBW 10010 Rice, Bovine Liver1577c and GBW 07605 Tea Leaves taken from National Institute of Standards and Technology (NIST) and China National Analysis Center (Beijing, China) were utilized to control accuracy and precision of the method and evaluate results found. Nearly 0.5 g of each SRM sample was taken into each Teflon beaker, 6 mL concentrated HNO₃ and 2 mL concentrated H₂O₂ solutions were poured into each Teflon beaker. The 1.0 mL of 4.0 µg/mL Sn atomic absorption standard solution was spiked into each SRM sample because they do not contain Sn. Teflon beaker was closed with a cover. The solutions were kept one night in the laboratory and heated on a hotplate until their volumes were remained about 3 mL. Three SRM solutions were poured into 25 mL flasks and diluted with ultrapure water to the marks. 1.0 mL of 5.0 µg/mL Sn standard working solution was also spiked to GBW 07605 Tea Leaves solution. It was also poured into a 50 mL - flask and diluted with ultrapure water to mark.

Blank solution containing 6 mL concentrated HNO₃ + 2 mL concentrated H₂O₂ + ultrapure water was placed into a Teflon beaker and evaporated on a hotplate until approximately 3 mL volume was remained. The Blank solution was poured into a 25 mL volumetric flask and diluted with ultrapure water to mark.

3. RESULTS AND DISCUSSIONS

3.1. Optimization Studies for Tin and Cadmium Determinations

Pyrolysis and atomization temperatures, and pyrolysis times of Sn and Cd in sample solutions by using ETAAS were optimized. One mL sample solution and 1 mL of 1% HNO₃ solution were poured into the first 2 mL sample cup. One mL same sample solution, 0.5 mL of 800 µg/mL Pd solution and 0.5 mL of 1% HNO₃ solution were added into second 2 mL sample cup. The solutions were injected into a pyrolytic coated graphite tube with an auto-sampler set at 20 µL, separately. In the graphite furnace heating temperature program, pyrolysis temperatures of Sn and Cd were studied while other parameters were kept constant by keeping values given in catalogue of instrument. In the absence or presence of Pd modifier, absorbance values of Cd and Sn versus pyrolysis temperatures were studied. The absorbances of analytes versus atomization temperatures were studied by keeping pyrolysis temperatures optimized and other parameters given in the catalogue. The means of absorbance values of elements from three replicate measurements obtained by standard deviation (about 3%) versus pyrolysis and atomization temperatures were depicted in Figure 1. As seen in Figure 1, pyrolysis temperatures of Sn and Cd were found as 800°C and 700°C in the absence of modifier and 1200 °C and 800°C in the presence of Pd modifier, respectively. The atomization temperatures of Sn and Cd were found as 2200°C for Sn and 1800°C for Cd in absence or presence of Pd modifier. Absorbance values of elements obtained with Pd modifier were higher than absorbance values obtained without using modifier at the same concentrations of elements in sample solutions. Thus, signal / noise ratio obtained for the same concentration of element in the presence of Pd modifier was higher than the signal / noise ratio obtained in absence of Pd. Background absorbance values of elements also reduced in the presence of the Pd.

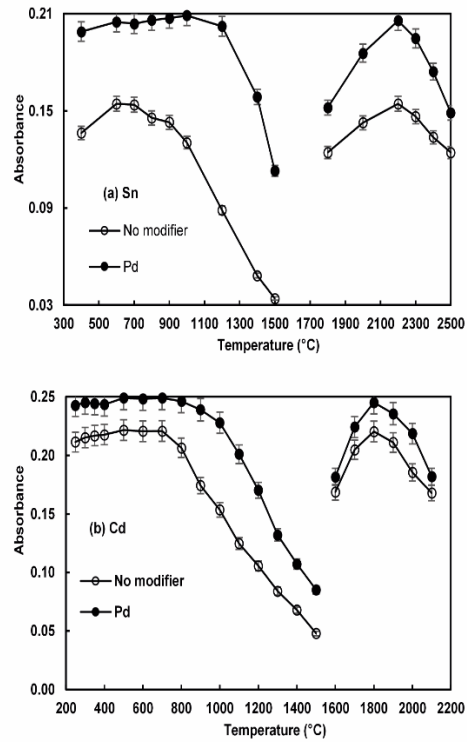


Figure 1. Absorbance values of (a) Sn and (b) Cd versus pyrolysis and atomization temperatures with and without of Pd modifier

In addition, pyrolysis times of Sn and Cd in sample solutions were studied in absence or presence of Pd modifier by keeping optimized pyrolysis and atomization temperatures and other parameters given in the catalogue of the instrument. Absorbance values of elements in sample solutions versus pyrolysis times of Cd and Sn in absence or presence of Pd were depicted in Figure 2. As seen in Figure 2, total pyrolysis times (ramp + hold times) for both Sn and Cd with the absence or presence of Pd obtained were about 30 s. The optimized heating temperature program for Sn and Cd in sample solutions with presence and absence of Pd was given in Table 1. Optimized conditions obtained were used in the determinations of Sn and Cd in SRMs and sample solutions.

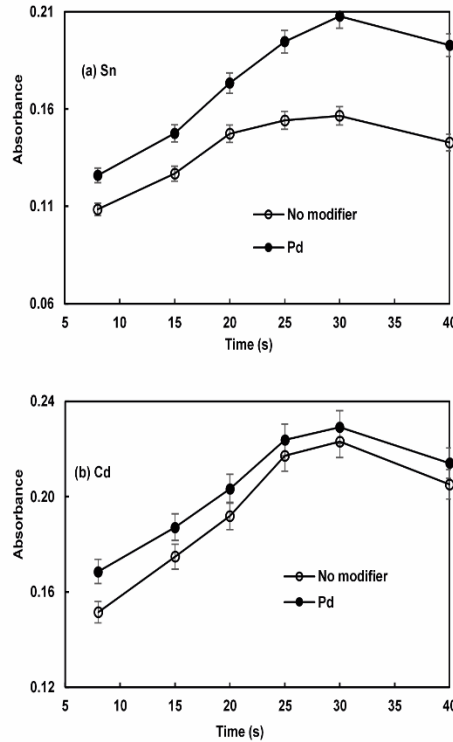


Figure 2. Pyrolysis times of (a) Sn and (b) Cd obtained in the presence or absence of Pd

Table 1. Optimum heating temperature program obtained for Sn and Cd in samples

Step	Temperature (°C)		Time (s)		Gas flow rate (mL/min)
	Cd	Sn	Ramp	Hold	
Dry I	50	50	5	5	0.3
Dry II	120	120	10	10	0.3
Pyrolysis	700 ^a /800 ^b	800 ^a /1200 ^b	10	20	0.3
Atomization	1300	2200	1	2	0.0
Cleaning	2200	2400	-	3	0.3

^a Pyrolysis temperatures in the absence of modifier

^b Pyrolysis temperatures in the presence of the Pd modifier

By using 2 mL sample cups containing 200 µg/mL of Pd, 25, 50, 100, 150 and 200 µg/L working standard solutions of Sn were prepared from 1000 mg/L Sn standard stock solution (Merck). Absorbance values of Sn were measured with ETAAS, calibration curve was obtained and equation was $A(\text{Sn}) = 0.0003 \cdot C - 0.0016$ ($R^2 = 0.9953$, where A is absorbance and C is concentration). Likewise, by using 2 mL sample cups containing 200 µg/mL of Pd, and 1.0, 2.0, 4.0 and 8.0 µg/L standard solutions of Cd were prepared from 1000 mg/L Cd standard stock solution (Merck). Absorbance values of Cd were measured with ETAAS. Calibration curve was obtained and equation was $A(\text{Cd}) = 0.0099 \cdot C - 0.0006$ ($R^2 = 0.9998$). After obtaining calibration curves immediately, Sn and Cd concentrations in Bovine Liver1877c, GBW 07605 Tea Leaver, IRMM 804 Rice Flour and GBW10010 Rice certified SRMs and sample solutions were determined by using optimized heating temperature program in presence of Pd modifier. Absorbance values of elements in SRMs and sample solutions were measured again by making necessary dilutions within the calibration curves. Three replicate absorbance measurements from each sample were performed. These measurements were repeated 4 times for each sample solution. Average concentrations and confidence intervals of Sn and Cd in SRMs and food samples at 95% confidence level were determined and the results found were given in Tables 2 and 3.

Copper, Zn and Fe in SRMs and sample solutions were determined by FAAS using calibration graph method. 0.1, 0.2, 0.4 and 0.8 mg/L standard solutions of zinc and copper were prepared from atomic

absorption standard stock solutions (1000 mg/L of Zn and Cu respectively, Merck). Calibration curves and equations were obtained by measuring absorbance values of elements versus concentrations of working standard solutions. Calibration equations of elements obtained from calibration curves were $A = 0.1919 \cdot C - 0.0036$ ($R^2 = 0.9984$) for Zn and $A = 0.1241 \cdot C + 0.0028$ ($R^2 = 0.9963$) for Cu, respectively. The 0.1, 0.2, 0.4 and 0.8 mg/L standard solutions of Fe were prepared from atomic absorption standard stock solution (1000 mg/L) (Merck). Calibration equation was obtained by measuring absorbance values of Fe versus concentrations and it was $A = 0.0977 \cdot C + 0.0004$ ($R^2 = 0.9998$). By using calibration graphs and equations, Zn, Cu and Fe concentrations in certified Bovine Liver1877c, GBW 07605, IRMM 804 and GBW10010, tea, rice and liver sample solutions were determined by FAAS. The measurements were repeated 4 times. Average values and confidence intervals of elements in SRMs and sample solutions at 95% confidence level were determined. Concentrations of Cu, Fe and Zn found in samples were multiplied by dilution factors and divided by amount of sample to determine amounts of elements in samples. The Cu, Fe and Zn results found in SRMs and food samples were given in Tables 2 and 3.

3.2. Analytical Features

Accuracy and precision of the method were explained as percent relative error and percent relative standard deviation (% RSD), respectively. As seen in Table 2, concentrations of elements found in SRM samples were compared with the certificated values (spiked values for Sn) and they were good agreement with certificate values. Percent relative errors for elements obtained were lower than 5% and % RSDs of elements found were lower than 4% with four replicate determinations. The method proposed was good accuracy and precision for analysis of Cd, Sn, Zn, Cu and Fe in SRM samples. Therefore, determinations of elements in SRMs and food samples were satisfactory.

Limits of detection and quantification (LOD and LOQ) of Cd and Sn in blank solutions were determined by ETAAS with and without Pd modifier. The LOD and LOQ values for Cu, Zn and Fe were determined by FAAS. Absorbance values of each element from blank solution were measured 22 times and standard deviation (Sb) of the measured absorbance values was calculated. The LOD can be expressed as ratio of three times of the standard deviation calculated to the slope of calibration curve ($LOD = 3 \cdot Sb/m$). Similarly, LOQ can be expressed as $10 \cdot Sb/m$. LOD and LOQ values of elements obtained from blank solutions were given in Table 4.

Table 2. Cd, Sn, Cu, Fe and Zn determinations in Standard Reference Materials (SRMs)

SRM	Parameter	Cd ($\mu\text{g/kg}$)	Sn ^b ($\mu\text{g/kg}$)	Cu (mg/kg)	Fe (mg/kg)	Zn (mg/kg)
Bovine Liver 1577c	Certified value	97 ± 1.4	8.0	275.2 ± 4.6	197.9 ± 0.7	181.1 ± 1.0
	Found value ^a	95 ± 3	8.3 ± 0.4	267 ± 10	195 ± 6	183 ± 5
	Relative error (%)	-2.06	+3.75	-2.98	-1.47	+1.05
	RSD (%)	1.99	3.03	2.36	1.94	1.72
GBW 07605 Tea Leaves	Certified value	57 ± 8	10.0	17.3 ± 1	264 ± 10	26.3 ± 0.9
	Found value ^a	59 ± 3	9.7 ± 0.5	18.0 ± 1.0	257 ± 8	25.0 ± 1.0
	Relative error (%)	+3.51	-3.00	+4.00	-2.65	-4.94
	RSD (%)	3.25	3.24	3.49	1.96	2.52
IRMM 804 Rice Flour	Certified value	1610 ± 70	8.0	2.74 ± 0.24	-	23.1 ± 0.3
	Found value ^a	1570 ± 40	8.2 ± 0.3	2.67 ± 0.12	3.1 ± 0.2	24 ± 1
	Relative error (%)	-2.48	+2.50	-2.55	-	+3.90
	RSD (%)	1.60	2.30	2.83	-	2.62
GBW10010 Rice flour	Certified value	87 ± 5	8.0	4.9 ± 0.3	7.6 ± 1.9	23 ± 2

Found value ^a	85 ± 5	7.8 ± 0.4	5.0 ± 0.2	7.4 ± 0.4	24.0 ± 1.0
Relative error (%)	-2.30	-2.50	+2.04	-2.63	+4.35
RSD (%)	3.70	3.22	2.52	3.40	2.62

^a Results were means of 4 replicate measurements at 95% confidence level, $\bar{x} \pm 3.18 \cdot s / \sqrt{N}$

^b Sn was spiked into SRM samples

Table 3. Cd, Sn, Cu, Fe and Zn amounts in food samples, mg/kg^a

Sample	Cd	Sn	Cu	Fe	Zn
Tea 1	0.273 ± 0.012	0.016 ± 0.001	4.7 ± 0.1	90.5 ± 1.8	58.6 ± 4.5
Tea 2	0.071 ± 0.003	0.018 ± 0.001	-	76 ± 1	46.3 ± 1.6
Tea 3	0.042 ± 0.001	-	4.7 ± 0.3	95.8 ± 1.2	39.3 ± 1.2
Rice 1	0.290 ± 0.013	0.043 ± 0.002	-	4.5 ± 0.2	12.3 ± 0.6
Rice 2	0.231 ± 0.008	0.036 ± 0.003	-	9.4 ± 0.7	20.8 ± 1.4
Rice 3	0.180 ± 0.006	0.094 ± 0.005	0.500 ± 0.005	2.75 ± 0.21	10.7 ± 0.4
Rice 4	0.130 ± 0.006	0.026 ± 0.002	0.67 ± 0.05	1.42 ± 0.11	13.5 ± 0.7
Liver 1	0.350 ± 0.013	0.042 ± 0.003	52.6 ± 1.1	59.8 ± 1.5	37.7 ± 1.4
Liver 2	0.210 ± 0.010	0.028 ± 0.002	77.8 ± 0.5	61.6 ± 1.3	24.7 ± 1.5
Liver 3	0.300 ± 0.005	0.034 ± 0.002	41.5 ± 1.3	87.3 ± 1.4	76.1 ± 2.2
Liver 4	0.240 ± 0.011	0.021 ± 0.001	83.3 ± 1.6	72.4 ± 1.2	52.6 ± 1.7

^a Results were means of 4 replicate measurements at 95% confidence level, $\bar{x} \pm 3.18 \cdot s / \sqrt{N}$

Table 4. Limits of detection and quantification for elements measured by ETAAS and FAAS

Analytical Parameter	ETAAS			FAAS			
	Cd		Sn	Pd	Cu	Zn	Fe
	No modifier	Pd	No modifier				
LOD, µg/L	0.34	0.26	0.78	0.66	1.9	1.2	2.0
LOQ, µg/L	1.13	0.87	2.60	2.20	6.3	4.0	6.7

3.3. Comparison of Elements Found in Samples with other Literature Studies

Cadmium concentrations found in black tea samples were varied from 0.042 ± 0.001 to 0.273 ± 0.012 mg/kg. The Cd results found in Tea 2 and Tea 3 samples were similar to the results reported by Podwika et al. [1] (49 ± 36 µg/kg). The Cd concentrations found in Tea samples are much lower than results reported by Ashraf and Mian [15] (1.1 ± 0.5 mg/kg), Narin et al. [12] (2.3 ± 0.4 mg/kg), Srividhya et al. [16] (0.89 ± 0.10 mg/kg) and Gajewska et al. [17] (with an average Cd concentration of black teas was 426 ± 506 µg/kg) in their studies published, respectively. The Cd concentrations found in rice samples were varied from 0.130 ± 0.006 to 0.290 ± 0.013 mg/kg with an average content of 0.208 ± 0.005 mg/kg. The Cd concentrations in rice samples reported by Da Silva et al. [18] were changed from 11.6 to 44.9 µg/kg with an average content of 30.1 µg/kg. The range of Cd values detected in rice grain samples were 0.67 - 0.8 mg/kg [19]. The Cd results found in samples were higher than the results reported by Da Silva et al. [18], but lower than the results reported by Abd Rashid et al. [19].

Means of Cu concentrations found in black tea samples were about 4.7 ± 0.16 mg/kg. They were smaller than Cu concentrations in black tea samples reported by Podwika et al. [1] (varied from 9.1 ± 0.2 to 32.7 ± 0.4 mg/kg with an average value of 31.3 ± 11.2 mg/kg), by Narin et al. [12] (16.5 ± 3.9 mg/kg), by Srividhya et al. [16] (14.34 ± 0.49 mg/kg for black teas), by Gajewska et al. [17] (31.3 ± 11.2 mg/kg), by Binh et al. [20] ($10.84 - 18.05$ mg/kg) and by Antakli et al. [21] (Content of Cu in tea samples varied from 10.6 to 54.4 mg/kg), respectively. The Cu concentrations in liver samples were varied from 41.5 ± 1.3 to 83.3 ± 1.6 mg/kg (Mean value equaled to 63.8 ± 20 mg/kg). The Cu results found in liver samples were similar to the results reported by Yayayürük. [4] (Concentration range of Cu in liver samples were as 26.4 - 676 mg/kg). The Cu concentrations found in rice samples were in the range of 0.50 - 0.67 mg/kg and they were

smaller than range of Cu values detected in rice grain samples reported by Abd Rashid et al. [19] (2.14 - 7.0 mg/kg).

Zinc concentrations in black tea samples were varied between 39.3 ± 1.2 and 58.6 ± 4.5 mg/kg (Mean value equaled to 48.1 ± 9.8 mg/kg). They were similar to the results reported by Podwika et al. [1] (Zn concentration in all tea samples varied from 12.6 ± 0.2 to 45.5 ± 0.1 mg/kg), results reported by Srividhya et al. [16] (25.39 ± 0.59 mg/kg for black teas), reported by Rene et al. [22] (21.5–75.2 mg/kg), reported by Ashraf and Mian [15] (65.7 ± 31.3 mg/kg) and reported by Srividhya et al. [16] The Zn contents in tea samples ranged from 23.47 mg/kg to 52.32 mg/kg with an average value of 39.55 mg/kg were reported by Binh et al. [20]. In the study of Antakli et al. [21], Zn contents in tea samples were ranged from 18.76 mg/kg to 44.2 mg/kg.

Iron concentrations in tea samples were varied between 76 ± 1 and 95.8 ± 1.2 mg/kg (Mean value equaled to 87.4 ± 10.3 mg/kg). They were similar to the results reported by Antakli et al. [21] (74.8 - 854.9 mg/kg), by Binh et al. [20] (Fe levels ranged from 48.65 mg/kg to 86.55 mg/kg and averaged at 74.79 mg/kg). The Fe contents found in samples were lower than the result reported by Street et al. [22] (233 mg/kg). The total Fe content analyzed in black tea varied from 21.3 mg/kg to 37.6 mg/kg was reported by Mandal et al. [23]. The Fe concentrations in liver samples were varied from 59.8 ± 1.5 to 87.3 ± 1.4 mg/kg (Mean value equaled to 70.3 ± 12.6 mg/kg) and they were lower than Fe contents in liver samples reported by Yayayürük et al. [4] (129 – 411 mg/kg).

4. CONCLUSIONS

Determinations of trace and heavy metals in tea, rice and liver consumed mostly in the Turkey are very important in terms of human health because some heavy metals accumulate in the body and their toxic effects are caused severe damage. For this reason, it is very important to keep trace elements in food, water, tissue and environmental samples such as living things directly. Optimization processes such as pyrolysis times, pyrolysis and atomization temperatures for Sn and Cd were carried out by using ETAAS before analyzing the samples, separately. ETAAS and FAAS spectrophotometric methods used are simple and sensitive for determination of Cd, Sn, Cu, Fe and Zn in various samples. Decomposition of food samples are also simple. The results of elements found in food samples such as tea, rice and liver are different. It has been indicated that metal contents of plants may have been found different depending on the growing in environmental conditions and water used. It is thought that the results and evaluations will shed light and help for future studies.

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CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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