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Determination of Mercury, Cadmium, Lead, Zinc, Selenium and Iron by ICP-OES in Mushroom Samples from Around Thermal Power Plant in Muğla, Turkey

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Abstract *Scleroderma verrucosum*, *Stropharia coronilla*, *Lactarius deterrimus*, *Chroogomphus rutilus*, *Russula delica*, *Laccaria laccata*, *Clitocybe odora var. alba*, *Lyophyllum decastes*, *Coprinus comatus*, *Helvella leucomelaena*, *Melanoleuca cognata*, *Melanoleuca cognata*, *Paxina acetabulum*, *Clitocybe vermicularis*, *Sarcosphaera crassa*, *Rhizopogon roseolu* and *Thelephora caryophyllea* were collected from different localities in Muğla-Yatağan region of Turkey. Their trace metals concentrations were determined by ICPOES after microwave digestion. The results were 0.37 ± 0.01–5.28 ± 0.21 for cadmium, 467 ± 19–$3{,}280 \pm 131$ for iron, 0.69 ± 0.03–9.15 ± 0.37 for lead, 18.70 ± 0.75–67.10 ± 2.68 for selenium, 75 ± 3–213 ± 8 for zinc and 0.15 ± 0.01–0.55 ± 0.01 for mercury (as μg/g). The detection limits for ICPOES were found as 0.25 for Cadmium, 0.2 for iron, 0.1 for lead, 0.5 for selenium, 0.2 for zinc and 0.03 for mercury (as mg L^{-1}). The Relatively Standard Deviations (R.S.D.) were found below 4.0%. The accuracy of procedure was confirmed by certified reference material.

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Since mushrooms have low in calories, high in vegetable proteins, vitamins, and minerals, they are valuable health foods (Racz et al. 1996). In addition, mushrooms are the agents responsible for the breaking down of much of the organic matter and play an important part in the continual changes. To accumulate metals from environment, mushrooms have a very effective mechanism. Therefore, for the evaluation the level of environmental pollution, mushrooms are generally used (Sesli and Tüzen 1999). It has been reported that as mushrooms are therapeutic foods, it is taken into an account to prevent diseases such as hypertension, hypercholesterolemia and cancer owing to their chemical compositions (Manzi et al. 2001). In traditional Chinese medicine, they have been widely used (Mendil et al. 2004). On the consideration of dry weight basis, their fruiting bodies compose of about 39.9% carbohydrate, 17.5% protein, 2.9% fats and some other minerals (Mendil et al. 2005). In contrast to green plants, mushrooms consist of large concentrations of some metals, such as Pb, Cd, and Hg, and for the evaluation of possible danger to human health from the ingestion of mushrooms, a great effort should have been made (Kalac and Svaboda 2000). In order to find metal contents in the fruiting bodies of edible mushroom, many studies have been done using atomic absorption spectrometry (Işıldak et al. 2004). It is observed that although the degree of pollution in soil is low, the metal concentrations of some species of wild edible mushrooms may be high which depends on natural conditions (Falandysz et al. 2003). In some studies, high concentrations of metals in the fruiting bodies of

mushrooms collected from the areas adjacent to metal smelters have been observed (Kalac et al. 1996; Işiloglu et al. 2001).

As Turkey has a large edible mushroom potential, it becomes an important exporter of wild mushrooms (Demirbaş 2000). In literature, to find the metal contents of mushrooms in Turkey, some studies were carried out (Sesli and Tuzen 2006). Due to their importance role in biological systems, metals such as iron, copper, zinc and manganese are essential metals while lead and cadmium are non-essential metals since they are toxic even in trace levels (Soylak et al. 2005). In order to analyze the samples, the microwave digestion procedure was chosen due to more accuracy with respect to both time and recovery than wet digestion (Sesli et al. 2008).

In this study, mercury, cadmium, lead, zinc, selenium and iron were selected as representative metals whose levels in the environment represent a reliable index of environmental pollution. Mushroom samples collected from around thermal power plant in Muğla in Turkey and these metals were determined by inductively coupled plasma optical emission spectrometry (ICPOES) after microwave digestion. In this study, ICPOES technique was chosen instead of atomic absorption spectrometry because of its advantages over atomic absorption spectrometry which are multielement analysis capability, large dynamic range, reduction of matrix interferences, improved detection limits for refractory elements and enhancement of productivity. To the best of our knowledge, this is the first study to determine the some elements by ICPOES in mushroom samples from around thermal power plant in Turkey.

Materials and Methods

All reagents were of analytical reagent grade. For the dilution of reagent solutions, double deionized water (Milli-Q Millipore 18.2 MΩ/cm) was used. HNO_3 and H_2O_2 were of suprapure quality (Merck). To clean all plastics and glasswares, they were soaked in dilute HNO_3 (10%) and were rinsed with distilled water prior to use. For calibration plot, the standard solutions were prepared by diluting stock solutions of 1,000 mg/L of each element (Sigma). In order to check accuracy of method, standard reference material (NIST-SRM 1547 peach Leaves) was used.

For elemental determination, Perkin Elmer Optima 2100 ICPOES was used. The operating parameters for working elements were set as recommended by the manufacturer given Table 1. Milestone Ethos D microwave closed system (maximum pressure 1,450 psi, maximum temperature 300°C) was used for the digestion of all samples. During the all digestion procedures, polytetrafluoroethylene (PTFE) reaction vessels were used.

Table 1 Instrumental analytical conditions of investigated elements for ICPOES

Wavelengths	Cd: 228.802; Fe: 238.204; Pb: 220.353 Se: 196.026; Zn: 206.200; Hg: 253.652
Plasma position	Axial
Frequency	27.12 MHz
Power	1.1 kW
Coolant gas	Ar, 14.01 L min^{-1}
Auxiliary gas	Ar, 0.5 L min^{-1}
Nebulizer gas	Ar, 1.0 L min^{-1}
Nebulizer pressure	2.4 bar
Sample flow rate	1.0 mL min^{-1}
Observation height	11 mm

The mushroom samples were collected from around thermal power plant in Muğla, in Turkey (Fig. 1). The all samples were dried at 105°C for 24 h and then these dried samples were homogenized using an agate homogenizer and stored in pre-cleaned polyethylene bottles until analysis.

To digest the mushroom samples, two different types of digestion procedures which were wet and microwave digestions were applied.

Wet Digestion: Using an oxi-acidic mixture of HNO_3:H_2SO_4:H_2O_2 (4:1:1), wet digestion of mushroom samples was performed. For this aim, 0.5 g of sample was used. This mixture was first heated until dryness at a temperature of 150°C for 4 h and brought into a value of 25 mL with deionized water. Blank digestions were also applied in the same procedure.

Microwave Digestion: For this purpose, 0.5 g of sample was digested with 6 mL of HNO_3 (Suprapure, merck), 2 mL of H_2O_2 (Suprapure, Merck) in a microwave digestion system for 23 min and finally diluted to 25 mL with deionized water. Blank digestion was also carried out at the same way. It was observed that all the sample solutions were clear. Operating conditions for mushroom samples in the microwave digestion system was shown in Table 2.

All analytical parameters for ICPOES which are frequency, power, coolant, auxilliary, nebulizer argon gases, and nebulizer pressure, sample flow rate, integration time and plasma position were optimized shown in Table 1 before analysis to obtain maximum signal to noise ratio. Detection limit (DL) is defined as the concentration corresponding to there times the standard deviation of blank signals (N = 11) (Tuzen et al. 2007). DL values of elements as mg L^{-1} in ICP-OES were found as 0.03, 0.25, 0.1, 0.2, 0.5 and 0.2 for Hg, Cd, Pb, Zn, Se and Fe, respectively.

In order the find accuracy of the method, standard reference material (NIST-SRM 1547 Peach leaves) was digested with microwave procedure. The results for this study are given in Table 3.

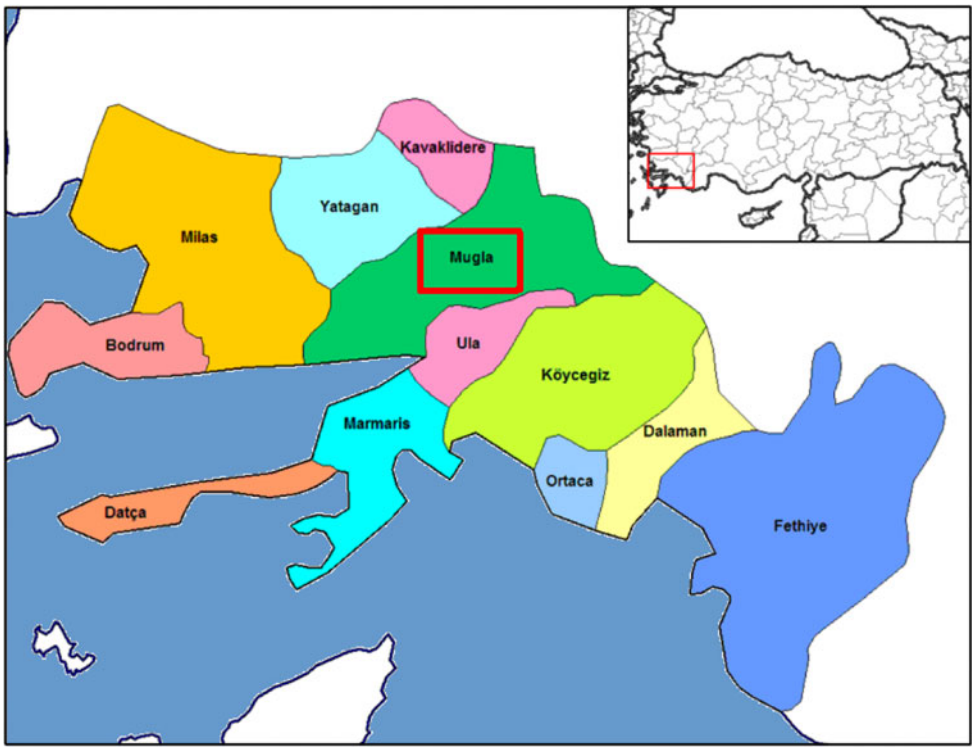

Fig. 1 Map of the study area in Turkey

Table 2 Operating conditions for mushroom samples in the microwave digestion system

Steps	Time (min)	Power (W)
1	2	250
2	2	0
3	6	250
4	5	400
5	8	550

Table 3 Experimental and certified values of trace metals in NIST-SRM 1547 peach Leaves (N = 5)

Element	Certified value (mg kg^{-1})	Experimental value (mg kg^{-1})
Cd	0.21	0.22 ± 0.12
Fe	218	216 ± 2.6
Pb	0.87	0.89 ± 0.38
Se	0.120	0.13 ± 0.25
Zn	12.5	11.2 ± 2.2
Hg	0.031	0.033 ± 0.09

Results and Discussion

In the preliminary of the study, the results of wet and microwave digestion methods were compared and found that there were no significant differences between both methods. In further studies, the microwave digestion procedure was chosen because it has more accuracy with respect to both time and recovery. The results of the analysis of the SRM revealed good agreement with the certified levels (Table 3).

The habitat, edibility and families of mushroom species are shown in Table 4. The results of the analysis of metal levels (mg kg^{-1}) are presented in Table 4 on a dry weight basis. In this study, the relative standard deviations (RSDs) were less than 4% for all elements. This is the one of most important advantages of ICPOES. The order of the levels of heavy metals in the mushroom samples was found as Fe > Zn > Cd > Pb > Se > Hg.

The trace metal contents in the mushrooms are affected by the function of acidic and organic matter content of their ecosystem and soil. Since the uptake of metal ions in mushrooms is in many respects different from plants, the concentration variations of metal contents depend on mushroom species and their ecosystem. In general, the amounts and contents of metals in mushroom samples depend on species of mushroom, collected sites of the sample, age of fruiting bodies and mycelium and also distance from the source of pollution (Sesli and Tüzen 1999).

Since cadmium inhibits many life processes, it is known as a principal toxic element. In particular, mushroom can include very high amount of cadmium. In literature, it has been demonstrated to cadmium accumulation (Svoboda et al. 2000). The lower and higher cadmium concentrations were found as 0.37 mg kg^{-1} in *C. rutilus* and 5.28 mg kg^{-1}

Table 4 Sample number, name, habitat and edibility of the mushrooms

Sample number	Name of mushrooms	Habitat	Edibility
1	*S. verrucosum* (Bull.) Pers.	On oak tree	Inedible
2	*S. coronilla* (Bull.) Fr.	Grass	Edible
3	*L. deterrimus* Gröger	On pine tree	Edible
4	*C. rutilus* (Fr.) O.K. Miller	On pine tree	Edible
5	*R. delica* Fr.	On pine tree	Edible
6	*L. laccata* (Scop.: Fr.) Berk. and Br.	On pine tree	Edible
7	*C. odora var. alba* J. E. Lange	On pine tree	Edible
8	*L. decastes* (Fr.) Singer	Grass	Edible
9	*H. leucomelaena* (Pers.) Nannf.	Grass	Inedible
10	*M. cognata* (Fr.) Konrad and Maubl.	Grass	Edible
11	*M. cognata* (Fr.) Konrad and Maubl.	Grass	Edible
12	*P. acetabulum* (L.: St. Amans) O. Kuntze	Grass	Inedible
13	*C. vermicularis* (Fr.) Quél.	On pine tree	Inedible
14	*R. roseolus* (Corda) Th. Fr.	Grass	Edible
15	*T. caryophyllea* (Schaeff.) Pers.	Grass	Inedible

Table 5 Trace metal levels (mg kg^{-1}) in mushroom samples from around thermal power plant, Mugla

Sample number	Cd	Fe	Pb	Se	Zn	Hg
1	0.85 ± 0.03	1,320 ± 53	1.55 ± 0.06	67.10 ± 2.68	152 ± 6	0.18 ± 0.01
2	1.56 ± 0.06	1,440 ± 46	3.48 ± 0.14	39.70 ± 1.59	118 ± 5	0.34 ± 0.01
3	2.12 ± 0.09	831 ± 33	1.46 ± 0.06	55.70 ± 2.23	100 ± 4	0.29 ± 0.01
4	0.37 ± 0.01	1,460 ± 58	5.25 ± 0.21	43.90 ± 1.76	75 ± 3	0.55 ± 0.01
5	1.77 ± 0.07	704 ± 28	1.42 ± 0.05	42.60 ± 1.70	83 ± 3	0.54 ± 0.01
6	5.28 ± 0.21	710 ± 28	9.15 ± 0.37	52.70 ± 2.11	200 ± 8	0.21 ± 0.01
7	1.46 ± 0.06	1,460 ± 59	1.80 ± 0.07	54.20 ± 2.17	86 ± 4	0.18 ± 0.01
8	0.85 ± 0.03	467 ± 19	3.46 ± 0.14	27.70 ± 1.11	189 ± 8	0.30 ± 0.01
9	1.99 ± 0.08	2,340 ± 94	3.10 ± 0.12	18.70 ± 0.75	135 ± 5	0.26 ± 0.01
10	3.22 ± 0.13	1,740 ± 70	3.74 ± 0.15	47.70 ± 1.91	150 ± 6	0.42 ± 0.02
11	2.44 ± 0.09	914 ± 37	2.68 ± 0.11	34.00 ± 1.36	75 ± 3	0.19 ± 0.01
12	1.66 ± 0.06	734 ± 29	7.80 ± 0.31	32.10 ± 1.28	188 ± 8	0.17 ± 0.01
13	0.72 ± 0.03	3,280 ± 131	0.69 ± 0.03	54.70 ± 2.19	52 ± 2	0.39 ± 0.02
14	1.67 ± 0.07	1,320 ± 53	4.55 ± 0.18	39.80 ± 1.60	205 ± 8	0.30 ± 0.01
15	4.52 ± 0.18	683 ± 27	3.92 ± 0.16	49.70 ± 1.99	213 ± 8	0.15 ± 0.01

in *L. laccata*, respectively shown in Table 5. In literature cadmium contents in the mushroom samples have been reported as in the ranges from 0.81 to 7.50 mg kg^{-1} (Svoboda et al. 2000; Soylak et al. 2005), 0.10–0.71 mg kg^{-1} (Mendil et al. 2004), 0.28–1.6 mg kg^{-1} (Sesli et al. 2008) and 0.12–2.60 mg kg^{-1} (Malinowska et al. 2004). It reveals that the cadmium levels are in good agreement with the literature values (Cibulka et al. 1996).

In the mushroom samples, the highest iron content was 3,280 mg kg^{-1}, in *P. acetabulum*; on the other hand the lowest iron content found was 467 mg kg^{-1} in *L. decastes* shown in Table 5. Iron values in mushroom samples have been reported in the range of 31.3–1,190 mg kg^{-1} (Sesli and Tüzen 1999; Işıldak et al. 2004), 568–3,904 mg kg^{-1} (Turkekul et al. 2004), and 102–1,580 mg kg^{-1} (Soylak et al. 2005; Sesli et al. 2008). Our iron values are in agreement with literature values. In general, for an average adult (60 kg body weight), the tolerable daily intake (PTDI) for lead, iron and zinc should be 214 μg, 48 and 60 mg, respectively.

The lead content ranged from 0.7 mg kg^{-1} in *C. vermicularis* to 9.2 mg kg^{-1} in *L. laccata* shown in Table 5. In literature, lead contents of mushroom samples have been reported in the range from 0.40 to 2.80 mg kg^{-1} (Svoboda et al. 2000; Sesli et al. 2008), and 0.75–1.99 mg kg^{-1} (Soylak et al. 2005). The fact that toxic metals are present

in high concentrations in mushrooms is of particular importance in relation to the standards for lead and cadmium as toxic metals. (Bakirdere and Yaman 2008). Furthermore, the lead concentrations of previous studies were between 0.1 and 40 mg kg^{-1} (Işıldak et al. 2004) has been known that lead increases blood pressure and cardiovascular disease in adults (Sesli et al. 2008).

The lower and higher selenium concentrations were found to be 18.7 mg kg^{-1} in *C. comatus* and 67.1 mg kg^{-1} in Scleroderma verrucosum, in turn shown in Table 5. In the literature, selenium contents of mushroom samples have been reported in the range of 0.05–37 mg kg^{-1} (Tuzen et al. 2007), 1.30–21.5 and 1–367 mg kg^{-1} (Kalac and Svaboda 2000; Tuzen et al. 2007). It is shown from the results that our results are in agreement with reported results in the literature. In general, the total content of selenium and its chemical form are also important because of the differences in bioavailability and toxicity of the different forms (Tuzen et al. 2007). These days, it is recognized as an essential micronutrient in animal and humans so it plays a important biological roles as antioxidant. If mushrooms are grown in soils with high selenium contents, they can accumulate selenium (Tuzen et al. 2007).

The highest zinc content was 213 mg kg^{-1} in *T. caryophyllea*. However, the lowest zinc level in our mushroom sample is 75 mg kg^{-1} in *M. cognate* shown in Table 5. Since zinc has biological significance, it is widespread among living organisms. Furthermore, mushrooms are known as zinc accumulators and sporophores: Substrate ratio for zinc changed from 1 to 10 mg kg^{-1} and our zinc values are in good agreement with other values (Işiloglu et al. 2001).

The mercury content ranged from 0.15 mg kg^{-1} in *T. caryophyllea* to 0.55 mg kg^{-1} in *C. rutilus* shown in Table 5. In literature, lead contents in mushroom samples have been reported in the range from 0.40 to 2.80 mg kg^{-1} (Svoboda et al. 2000; Sesli et al. 2008), and 0.75–1.99 mg kg^{-1} (Soylak et al. 2005; Sesli et al. 2008). It is known that mercury is a toxic element to humans and wildlife, and alkyl mercury compounds such as methylmercury and ethyl mercury are extremely toxic. In the case of mercury, it is known that some species of mushrooms (*genera Calocybe*, *Agaricus*, *Lepista*, *Macrolepiota*, *Boletus*, and *Lycoperdon*) can accumulate great concentrations even when grown in less polluted area (Flandysz et al. 2001). In literature, mercury concentrations in the fruiting bodies of fungi which were collected near a mercury plant in Idrija and Bela were up to 45 mg kg^{-1} of dry matter whereas in King Bolete mushroom (*B. edulis*) from an area adjacent to a mercury plant in Czech Republic, Hg concentrations were up to 32 mg kg^{-1} of dry matter (Kalac et al. 1996). In another study, the greatest concentrations of mercury found in the flesh of Sweating mushroom (*C. rivulosa*) of up to 5.2 ± 1.5 mg kg^{-1} of dry matter in the caps and 1.9 ± 0.9 mg kg^{-1} of dry matter in the stalks, followed by King Bolete (*B. edilus*) with 3 ± 1.6 mg kg^{-1} and 1.8 ± 0.9 mg kg^{-1} and Common Puffball (*L. perlatum*) with 2.8 ± 0.5 mg kg^{-1}. The Common Earth Ball (*S. citrinum*) had the lowest level of mercury with 9.3 ± 3.0 ng g^{-1} of dry matter (Falandysz et al. 2003).

Metal levels of 15 mushrooms collected from around thermal power plant in Muğla in Turkey were investigated. The highest Pb and Cd are in *L. laccata*, the highest Fe level is in *P. acetabulum*, the highest Hg level is in *C. rutilus*, and the highest Zn level is in *T. caryophyllea*. It is observed from the results that there is no significant pollution coming from the thermal power plant compared to samples collected from the other places in literature. Relative standard deviations (RSD) were found below 4.0%. This is the one of the most important advantages of ICPOES technique.

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