Bull. Environ. Contam. Toxicol. (2005) 74:968–972

DOI: 10.1007/s00128-005-0674-3

Bulletin of Environmental Contamination and Toxicology

Mercury Contamination in Mushroom Samples from Tokat, Turkey

M. Tuzen,[1] M. Soylak[2]

[1] Gaziosmanpasa University, Faculty of Science and Arts, Chemistry Department, 60250 Tokat, Turkey
[2] Erciyes University, Faculty of Art and Science, Department of Chemistry, 38039 Kayseri, Turkey

Received: 25 September 2004/Accepted: 23 February 2005

Mercury is a toxic element in small quantitaties. The main source of mercury for humans is food. If the total amount of food consumed is 10 kg/week, the recommended maximal mercury intake for an adult is 0.03 mg/kg of food according to WHO standard (Vetter and Berta, 1997). The mercury content of mushrooms plays an important practical and toxicological role. Mercury poisoning results in severe nausea, vomiting, abdominal pain, kidney damage is also reported (Falandysz and Chwir 1997; Vetter and Berta, 1997; Nixon *et al.*, 1999; Dadfarnia *et al.*, 2002). Consumption of wild-growing edible mushrooms has been high in many countries, exceeding 10 kg per year in some individuals. Mushrooms have been used as bioindicators by various researchers to determine the heavy metal pollutions in the environments (Tuzen *et al.*, 1998; Garcia *et al.*, 1998; Tuzen *et al.*, 2003). Many mushroom species accumulate mercury at high levels (Stijve and Besson, 1976; Svoboda *et al.*, 2000). Studies on the mercury content of mushroom samples were performed (Svoboda *et al.*, 2000; Falandysz and Chwir 1997; Rincon-Leon and Zurera-Cosano, 1986). Some authors have suggested that the accumulation of mercury in mushrooms could depend on the content of sulfhydryl, disulfide and methionine groups of the proteins (Stijve and Besson, 1976; Falandysz and Chwir 1997). Cold vapour atomic absorption spectrometry is one of the important techniques for mercury determination in mushroom samples. Because mercury is a volatile element even low temperature, closed vessel microwave systems are preferred for the digestion of samples prior to vapour atomic absorption spectrometry (CV-AAS) determination.

In the present study, the total mercury content of mushroom samples collected from Tokat, Turkey were determined by cold vapour atomic absorption spectrometry (CV-AAS) after microwave digestion.

MATERIALS AND METHODS

A Perkin Elmer AAnalyst 700 atomic absorption spectrometer with MHS-15 Mercury/Hydride System was used in this study. All measurements were carried out using high purity argon. Mercury hollow cathode lamp was used. The wavelength and slit width for mercury were 253.6 nm and 0.7 nm. Peak height was used for quantitation.

Correspondence to: M. Soylak

All reagents were of analytical reagent grade unless otherwise stated. Double deionised water (Milli-Q Millipore 18.2 $M\Omega cm^{-1}$ resistivity) was used for all dilutions. HNO_3 and H_2O_2 were of suprapur quality (E. Merck). All the plastic and glassware were cleaned by soaking in dilute HNO_3 (1+9) and were rinsed with distilled water prior to use. Standard solutions for calibration were produced by diluting a stock solution of 1000 mg/L of mercury supplied by E. Merck. All dilutions were made in 1.5 % HNO_3. 3 % Sodium borohydride in 1 % NaOH was used as reducing solution.

Fifteen different mushroom samples were collected from uncontaminated agricultural lands from Tokat-Turkey during 2003. The mushroom samples were dried at 80 °C for 24 h. The dried mushroom samples were homogenized using an agate homogenizer and stored in pre-cleaned polyethylene bottles until mercury determinations.

Milestone Ethos D closed vessel microwave system was used in this study. 0.25 G of sample was digested with 6 mL of HNO_3 (65 %) and 1 mL of H_2O_2 (30 %) in microwave digestion system for 23 min and diluted to 25 mL with deionized water. A blank digest was carried out in the same way. Digestion conditions are given in Table 1.

Table 1. Operating conditions for mushroom samples in microwave digestion system

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

Vent: 8 min

Total mercury content of mushrooms was performed by cold-vapour atomic absorption spectroscopy (CV-AAS). A few drops of 5 % $KMnO_4$ were added to 5 ml of the digested solution which was transferred to the reduction vessel then the 3 % $NaBH_4$ in 1 % NaOH was added and the mercury vapour generated was directed to the optical cell. The absorbance reading was recorded at the maximum value reached. Aliquots of the calibration standard solutions and blanks were analysed in the same way as the samples. The volume of calibration and sample solutions was 10 mL. Calibration curve was linear in the range of 0-50 µg/L (r=0.999).

RESULTS AND DISCUSSION

In order to validate accuracy and precision of the method, hay powder certified standard reference material (IAEA-V 10) was analyzed for mercury contents. Mercury concentration was found to be 12.8 µg/kg in the certified reference material. The certified value for mercury was 13 µg/kg. The student's t-test was

applied at the 95% confidence level and no difference was found between these two results. Recovery values for mercury were nearly quantitative ($\geq$95 %). Detection limit is defined as the concentration corresponding to three times the standard deviation of ten blanks. Detection limit value of mercury was found 0.65 μg/L. Characteristic mass for 0.0044 absorbance was found to be 5.20 ng for Hg. The relative standard deviations for all measured mercury concentrations were lower than 10 %.

The mercury concentrations for microwave digested mushroom samples from Tokat-Turkey are given in Table 2. Mercury concentration was determined on a dry weight basis. According to the results, mercury contents in the samples studied depend on the analyzed species.

Table 2. Mercury concentrations of mushroom species from Tokat-Turkey (Mean±SD)

Mushroom Species	Number of Samples (n)	Edibility	Concentration (μg/g)
Rhizopogon luteolus	7	Not edible	1.51±0.08
Polyporus squamosus	5	Edible	2.61±0.12
Armillaria mellea	10	Edible	1.48±0.11
Amanita soliteria	6	Poisonous	3.39±0.20
Agaricus macrosporus	9	Edible	0.28±0.01
Morchella esculenta	12	Edible	0.35±0.02
Boletus sp.	8	Poisonous	4.01±0.25
Lactarius acerrimus	5	Edible	0.56±0.02
Pholiota adipose	7	Edible	0.24±0.01
Lycogola epidendron	9	Poisonous	3.94±0.10
Helvella leptopodra	6	Poisonous	4.67±0.32
Lentinus tigrinus	10	Not edible	2.17±0.07
Lepista nuda	6	Edible	2.50±0.14
Pleurotus ostreatus	8	Edible	1.42±0.05
Laccaria laccata	5	Edible	0.12±0.01

The lowest and highest values of mercury were found in *Laccaria laccata* (edible) (0.12 μg/g) and *Helvella leptopodra* (poisonous) (4.67 μg/g) species, respectively. Generally, mercury content in poisonous mushrooms was found to be higher than those of edible mushrooms. Mercury concentrations in mushroom samples analyzed in this study were found to be higher than those reported in earlier studies in Turkey (Sesli and Tuzen, 1999; Demirbas, 2001). The chemical form of mercury is important. Methyl mercury is more dangerous than the inorganic mercury. Methyl mercury is a minor (0.6-28 %) chemical species of total mercury detected in mushroom (Falandysz and Chwir, 1997).

Compared to green plants, mushrooms can accumulate large concentrations of some heavy metals such as lead, nickel, cadmium, mercury, and a great effort has been made to evaluate the possible danger to human health from the ingestion of mushrooms (Gast *et al.*, 1988). The trace heavy metals content of the mushroom

samples are related to species of mushroom, collecting site of the sample, age of fruiting bodies and mycelium, and distance from the source of pollution (Kalac *et al.*, 1991; Stoica *et al.*, 2004). High concentrations of trace heavy metals have been observed in heavily polluted areas, such as in close proximity to highways with heavy traffic levels or industrial areas (Garcia *et al.*, 1998; Kalac and Svoboda, 2000; Tuzen *et al.*, 2003; Záray *et al.*, 2005). The mercury content of mushroom samples collected from near the roadside was not affected by the traffic. This situation is in agreement with that reported in the literature (Alonso *et al.*, 2000).

The trace metal content including mercury of mushroom is hardly affected by pH and organic matter content of the soil (Gast *et al.*, 1988; Sesli and Tuzen, 1999). Total mercury content of some edible mushrooms can be high, even when the degree of pollution in soil is low (Falandysz *et al.*, 2002). It has been reported that some mushroom species collected from polluted area should not be consumed at all (Svoboda *et al.*, 2000).

The use of microwave digestion system in mushroom samples provides a better, safer and cleaner method of sample preparation prior to mercury determination by CV-AAS. The precision and accuracy, expressed as relative standard deviation and relative error, respectively, were lower than 10 % in all cases; recoveries for mercury were nearly quantitative for all elements studied ($\geq$95 %). The accuracy of the procedure was checked and confirmed by a standard reference material (Hay powder IAEA-V 10).

REFERENCES

Alonso J, Salgado MJ, Garcia MA, Melgar MJ (2000) Accumulation of mercury in edible macrofungi: Influence of some factors. Arc Environ Contam Toxicol 38: 158-162

Byrne AR, Ravnik V, Kosta L (1976) Trace element concentrations in higher fungi. Sci Total Environ 6: 65-78

Dadfarnia S, Salmanzadeh AM, Haji Shabani AM (2002) Preconcentration and determination of mercury(II) and methylmercury in waters by immobilized 1,5-diphenylcarbazone and cold vapor atomic absorption spectrometry. Bull Korean Chem Soc 23: 1719-1723

Demirbas A (2001) Concentrations of 21 metals in 18 species of mushrooms growing in the East Black Sea region. Food Chem 75: 453-457

Falandysz J, Chwir A (1997) The concentrations and bioconcentration factors of mercury in mushrooms from the Mierzeja Wislana Sand-Bar, Northern Poland. Sci Total Environ 203: 221-228

Falandysz J, Gucia M, Skwarzec B, Frankowska A, Klawikowska K (2002) Total mercury in mushrooms and underlying soil substrate from the Borecka Forest, North-eastern Poland. Arc Environ Contam Toxicol 42: 145-154

Garcia MA, Alonso J, Fernandez MI, Melgar MJ (1998) Lead content in edible wild mushrooms in northwest Spain as indicator of environmental contamination. Arc Environ Contam Toxicol 34: 330-335

Gast CH, Jansen E, Bierling J, Haanstra L (1988) Heavy metals in mushrooms and their relationship with soil characteristics. Chemosphere 17: 789-799

Kalac P, Burda J, Staskova, I (1991) Concentrations of lead, cadmium, mercury and copper in mushrooms in the vicinity of a lead smelter. Sci Total Environ 105: 109-119

Kalac P, Svoboda L (2000) A review of trace element concentrations in edible mushrooms. Food Chem 69: 273-281

Nixon DE, Burritt MF, Moyer TP (1999) The determination of mercury in whole blood and urine by inductively coupled plasma mass spectrometry. Spectrochim. Acta B 54: 1141-1153

Rincon-Leon F, Zurera-Cosano G (1986) Flameless atomic absorption spectrophotometric determination of mercury in mushroom samples, using a mercury/hydride system. Atom Spectr 7: 82-84

Sesli E, Tuzen M (1999) Levels of trace elements in the fruiting bodies of macrofungi growing in the East Black Sea region of Turkey. Food Chem 65: 453-460

Stijve T, Besson R (1976) Mercury, cadmium, lead and selenium content of mushroom species belonging to the genus Agaricus. Chemosphere 2: 151-158

Stoica AI, Peltea M, Baiulescu GE, Ionica M (2004) Determination of cobalt in pharmaceutical products. J Pharmaceut Biomed 36: 653-656

Svoboda L, Zimmermannova K, Kalac P (2000) Concentrations of mercury, cadmium, lead and copper in fruiting bodies of edible mushrooms in an emission area of a copper smelter and a mercury smelter. Sci Total Environ 246: 61-67

Tuzen M, Ozdemir M, Demirbas A (1998) Heavy metal bioaccumulation by cultivated Agaricus bisporus from artificially enriched substrates. Z Lebensm Unters Forsch 206: 417-419

Tuzen M, Turkekul I, Hasdemir E, Mendil D, Sari, H (2003) Atomic absorption spectrometric determination of trace metal contents of mushroom samples from Tokat, Turkey. Anal Lett 36: 1401-1410

Vetter J, Berta E (1997) Mercury content of some wild edible mushrooms. Z Lebensm Unters Forsch 205: 316-320

Záray G, Kröpfl K, Szabó K, Taba G, Ács E, Berlinger B, Dogan M, Salih B, Akbulut A (2005) Comparison of freshwater biofilms grown on polycarbonate substrata in Lake Velence (Hungary) and Lake Mogan (Turkey). Microchem J 79: 145-148