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Determination of mercury in the urine by atomic absorption spectrometry - cold vapor technique

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Abstract: Urine is a liquid waste product of the body. Substances that are ingested and fail to be apsorbed are excreted, solid waste through the intestines, the urine through the kidney and ureter and another fluid from the body through perspiration. Determination of mercury content of urine is not included in routine examinations, but mercury can be present in urine at concentrations that could have serious effects on human health. Urine donors were selected in regard to their occupations, age, lifestyle habits, and different diet, with special reference to dental professionals, consumers of marine food and smokers, as a group of subjects that could have a higher concentration of this metal. To determine the mercury content in urine ,atomic absorption spectrometry – a tehnique of cold vapor method was used The total content of mercury in 76 analyzed urine samples was in the range of 0.12 to 12.24 ng/mL. There was a positive correlation between the number of teeth with amalgam fillings and urinary concentrations of mercury in some donors,. In contrast, the other analyzed factors that theoretically can affect the levels of mercury in urine,

INTRODUCTION

Determination of Hg in urine and blood is of a great importance and it was recommended as a method for biomonitoring of exposure to this type of xenobiotics both in nature and in the workplace (Gazewski et al., 2007). Mercury and its compounds are used in agriculture, pharmaceutical and chemical industry, in production of measuring instruments, etc. The most important sources of occupational exposure to mercury are factories for the production of chlorine, using mercury electrodes in production processes , and handling of amalgam fillings by dental staff in dental offices .. Exposure can occur through direct skin contact with mercury or mercury compounds or through inhalation of mercury vapor. The primary pathway of exposure is through the respiratory tract, ie. about 80 % of inhaled mercury is absorbed in the lungs (Trzcinka-Ochocka et al., 2007). For the assessment of occupational exposure to mercury, based on levels of mercury in urine, there are biological limits (BEI). In Poland, the current BEI value of exposure to inorganic or metal mercury is 35 mg/g creatinine (CIOP/PIP, 2003). In Germany, the biological tolerance value (BAT) to the Commission for investigating health hazards of chemical compounds for the urine workspace is 100 mg/L (DFG, 2004), while the value of 35 mg/g creatinine for BEI was adopted by American Conference of Governmental Industrial Hygienists (ACGIH) in 2004 (ACGiH, 2004). Apart from occupational exposure, mercury can get into the human body through the food chain, and by inhalation of toxic mercury vapor which get in the atmosphere by different sources. When it comes to the food chain, special case represent marine organisms, especially fish, which fall into the category of essential foods of human diet ,and in which mercury appears in one of more toxic states, in the form of methyl mercury (Taljaard and Staden, 1999). All forms of mercury have toxic effects on most human organs, especially kidneys. Mercury falls into the category of heavy metals and has an exceptional ability to bioaccumulate in the body. Therefore, mercury has a long-term stay in the body and causes specific effects on human health. The most important forms of mercury are elemental mercury, inorganic and organic mercury compounds. All three forms have different toxicity, their effects are manifested by various symptoms, and all three forms can be found in the atmosphere, the aquatic environment, soil and plant material. Mercury is

deposited in the kidneys, liver, small intestine wall, muscles, spleen, heart and lungs, penetrates less in the central nervous system and deposits in the cerebral gray mass. Therefore it is essential to gain a knowledge of "normal" levels of Hg in order to assess its concentration in body fluids and secretions (Gazewski et al., 2007). Research has shown that in healthy people who are not subject to any forms of mercury compounds, levels of mercury in blood and urine should not exceed the value of 5 mg L^{-1}, while values of 30 mg L^{-1} in blood and 50 mg L^{-1} in urine are shwowing long-term intoxication (Taljaard and Staden, 1999). Mercury who has entered the human body can be determined by analyzing the samples of hair, blood and urine and also indicates the period of exposure to mercury (Blaurock-Busch, 2009). As the mercury in these samples is present in trace amounts, well-sensitive measurement technique for its determination should be applied. For the determination of mercury in urine samples, which were analysied in this work, we used the method of atomic absorption spectrometry - cold vapor technique. In this method, long-term mineralization of urine samples is not required because the total Hg concentrations can be measured after the addition of saturated $KMnO_4$ and acid to the urine sample. The donors were selected in regard to their different occupations, ages, habits, and different diet with special emphasis on the dental staff, consumers of marine foods and smokers, as a target groups that could eventually have elevated concentrations of metals in the urine. The content of mercury in urine of all donors ranged from 0.12 to12.24 ng/mL. There was a positive correlation between the number of teeth with amalgam filling and urinary concentration of mercury in individual donors. That was not a case in other in other groups when other analyzed factors were taken into account.

EXPERIMENTAL

Sampling

Seventy six urine samples were collected from people of different age, place of residence, occupation, and with a different diet, health problems and lifestyle habits. All the participants of the study filled questionnaire designed to identify possible sources of mercury exposure. Information collected included demographics (e.g.,sex, age, address), information about potential sources of mercury (e.g., diet, type of employment, amalgam fillings, whether the respondent consumed cigarette or not and how much per day, health problems).

Determination of Hg in urine samples

The determination of mercury in urine, based on the method of Piotrowski et al. (Piotrowski et al., 1973; Gazewski et al., 2007), was carried out by cold vapor atomic absorption spectrometry (Spectraa-10, Varian). The method allows to determine the total Hg concentration after overnight mineralization of urine samples by potassium permanganate in sulphuric acid solution at room temperature. The excess of oxidants was reduced by hydroxylamine hydrochloride solution. Ionic mercury, Hg (II), from digested urine was converted into Hg^o by reaction with stannous (II) chloride and then vaporized. The vaporized Hg was determined by absorbance measurement at the absorption Hg wavelength of 253.7 nm.

In order to determine the mercury in urine: 10 % $SnCl_2$ and 10 % (v/v) HNO_3 solutions and 1 mg/mL solution of mercury were used. Using tehnique of cold vapor, the sample flow was set to 6.2 mL/min while the flow of reducer ($SnCl_2$) and 10 % HNO_3 was 0.90 mL/min. The instrument was previously calibrated with standard solutions. The value of relative standard deviation was 4 %. For the quantitative determination of mercury in samples calibration curve method was used.

Analytical quality control of results

In order to verify the analytical quality control of results, the urin spiking experiments were performed and recovery factors were calculated. The accuracy of the method was confirmed on the basis of satisfactory values of recovery factors (96-105 %). The limit of quantification for total mercury in urine, based on six standard deviations of the blank, was 0.2 μg/L (n = 10) (6 × SDb).

RESULTS AND DISCUSSION

The data shows the analysis results for mercury content in urine, depending on various factors that could affect the final content of mercury accumulated in the human body. The main parameters that could cause the elevated concentrations of this metal are: the number of teeth with amalgam filling, fish consumption, use of tobacco, the workplace and residence environment. The content of mercury in urine samples taken from 76 donors was compared with available literature data (Lie et al., 1982; Yamamura, 1990; Ulukapi et al., 1994; Khordi – Mood et al., 2001). All urine donors were residents of Sarajevo Canton.

Total mercury content in urine of all donors, aged 12 to 75 years, ranged from 0.12 to12.24 ng/mL. The maximum allowable concentration of mercury (that was not pathophysiological) during the eight-hour exposure was 0.1 mmol/L and 20.06 ng/mL (Đurić et al., 2008). Thus, in all of our analyzed samples mercury content did not exceed the quoted predefined value.

Out of 76 donors of urine, 32.89 % were male and 67.11 % female. The concentration of mercury in male donors ranged from 0.12 to 5.28 ng/mL, while the female population showed mercury content from 0.17 to 12.24 ng/mL.

The value of 60.52 % of donors had dental amalgam fillings. Concentrations of mercury ranged from 0.26 to 12.24 ng/mL. There was a positive correlation between the number of teeth with amalgam fillings and urinary concentration of mercury in individual donors (Table 1).

Table 1. The contents of mercury in individual urine donors with amalgam fillings.

Number of urine donors	Number of teeth with amalgam fillings	Interval of Hg concentrations in urine (ng/mL)
4	1	0.34 – 1.20
8	2	0.46 – 2.70
6	3	0.52 – 5.28
3	7	0.50 – 6.65
4	8	0.50 – 12.24

A study conducted in Iran (Khordi – Mood et al., 2001) also shows and explains the increase in concentration of mercury in urine after tested children received the amalgam fillings (value of Hg: 3.83 - 5.14 mg/L).

Research regarding the population of children with dental amalgam fillings shows the results of analysis of urinary concentration of mercury in children in Turkey after the amalgam restorations (Ulukapi et al., 1994). Mercury content ranged from 0.34 to 1.7 mg/L.

Twenty nine or 38.15 %, of urine donors were smokers. The content of mercury in urine ranged from 0.12 to 2.65 ng/mL. Some of the urine donors, also smokers, had a small number of teeth with amalgam fillings (from 1 to 3). Generally, one can say that in this population had low mercury content in urine. So, we did not found a significant correlation between the daily number of consumed cigarettes and the urinary concentration of mercury in individual donors (Table 2).

Table 2. The contents of mercury in individual urine donors (smokers).

	Number of urine donors	Interval of Hg concentrations (ng/mL)	Mean concentrations of Hg (ng/mL)
Consumers of 5 to 20 cigarettes per day	16	0.33 – 1.91	0.79
Consumers of 20 to 40 cigarettes per day	12	0.12 – 2.65	0.65
Consumers of 40 to 60 cigarettes per day	1	1.20	1.20

High percent, (80.26 %) of all donors were consumers of marine products, especially fish. Comparing the content of mercury in urine in freshwater fish consumers, as well as people who do not consume marine products, with a content of mercury in urine of marine products consumers we concluded that no correlation between a level of mercury in urine and consumption of marine products could be derived.

One of the target groups of tests was one where donors are occupationally exposed to mercury The dental staff of School of Dentistry at University of Sarajevo, that include dentists and dental nurses was tested. Dental staff in their practice works with dental amalgam fillings on a daily base. The results of analysis of mercury content, with a total of 15 urine donors from this group were compared with the results of mercury with other donors and significant variation in the content of mercury in urine were not observed. Concentrations of mercury ranged from 0.50 to 1.55 ng/mL in doctors' samples, while the mercury content in the urine provided by dental nurses was even lower and ranged from 0.50 to 0.78 ng/mL. For future studies more comprehensive studies with a higher number of donors from dental offices would certainly give better picture of levels of mercury exposure.

Research done in Norway (Lie et al., 1982), where the respondent populations living in highly industrialized areas and one living in an industrially undeveloped area were tested, reveals significantly higher urinary mercury concentrations especially in donors living in more industrial region (mean Hg 7.4 μg/L). A similar level of mercury as in our samples (mean Hg 2.8 μg/L) was noted in the study population which was not occupationally exposed to mercury in Japan (Yamamura, 1990).

CONCLUSIONS

Total mercury content in urine of all 76 donors was determined by atomic absorption spectrometric method - cold vapor technique.

The content of mercury in the urine of all donors aged 12 to 75 years ranged from 0.12 to 12.24 ng/mL. The maximum allowable concentrations of mercury in eight-hour exposure was 0.1 mmol/L or 20.06 ng/mL. Thus, in either our sample analyzed mercury content did not exceed the said defined value.

Higher values of total mercury concentrations in urine were noted in the female donors (0.17 to 12.24 ng/mL), while in male donors those values were comparing it with the total concentration of mercury in urine (0.12 to 5.28 ng/mL) for all donors.

The precent of 60.52 of all donors had dental amalgam fillings. Concentrations of mercury ranged from 0:26 to 12:24 ng/mL. There was a positive correlation between the number of teeth with amalgam fillings and urinary concentration of mercury in individual donors.

Twenty nine (38.15 %). urine donors were smokers. Mercury content ranged from 0.12 to 2.65 ng/mL. Some of urine donors (also smokers) had a small number of teeth with amalgam fillings (from 1 to 3). There was no significant correlation between the daily number of cigarettes consumed and the urinary concentration of mercury in individual donors.

With 80.26 % of donors who consume marine products, especially fish, elevated concentrations of mercury in urine were not detected in relation to the donors who consume freshwater fish.

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Summary/Sažetak

Urin je produkt otpada iz čovječijeg organizma. Tvari koje su unesene u organizam i ne uspiju se apsorbovati izlučuju se, čvrsti otpad putem crijeva, tekući preko bubrega i mokraćovoda, a jedan dio tečnosti iz organizma izađe kroz znoj. Određivanje sadržaja žive u urinu ne spada u rutinske analize, ali živa može da bude prisutna u urinu u koncentracijama koje mogu da indiciraju prisustvo ovog teškog metala u čovječijem organizmu što za posljedicu može imati ozbiljne efekte na ljudsko zdravlje. Odabrani su donatori urina različitih zanimanja, starosne dobi, životnih navika, te različite prehrane, sa posebnim osvrtom na stomatološko osoblje, konzumente morskih namirnica i pušače, kao ciljane grupe ispitanika koje bi eventualno mogle da imaju povišenu koncentraciju ovog metala u urinu. Za određivanje sadržaja žive u uzorcima urina korištena je metoda atomske apsorpcione spektrometrije – tehnika hladnih para. Sadržaj žive u urinu, kod svih donatora urina, se kretao u rasponu od 0,12 do 12,24 ng/mL. Uočena je pozitivna korelacija između broja amalgamiranih zuba i urinarne koncentracije žive kod pojedinih donatora, za razliku od ostalih analiziranih faktora, koji mogu uticati na povišen sadržaj žive u urinu, gdje to nije bio slučaj.