CONTENT OF MANGANESE IN SERUM, ERYTHROCYTES, AND HAIR OF MEN – AIRPORT EMPLOYEES

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Abstract

Manganese is a component and cofactor for many important enzymes. In blood Mn is complexed to transferrin, and it quickly passes through the body to be extracted mainly in the bile and urine. Almost all Mn pool in blood is located in erythrocytes. Content of manganese in serum, erythrocytes, and hair of 26 men, workers of an airport, was determined. The control group consisted of administrative workers and the test group was composed of airplane servicemen. Hair samples of 0.5 g and 3–4 cm in length measured from the scalp were taken from some places on a head, washed with a detergent solution, rinsed with deionized water, acetone, and dried. Samples of blood were spun. All the samples were mineralized in a mixture of spectrally clean acids HNO_3 and $HClO_4$. Concentration of Mn was analyzed by electrothermal atomic absorption spectrometry GFAAS. The concentrations of Mn in the samples of erythrocytes were statistical significantly higher in the test group. In samples of hair, Mn concentrations were comparable between both groups of men. The coefficients of correlation between Mn concentrations in serum and hair, erythrocytes and hair, and between serum and erythrocytes did not imply significant correlations between Mn concentration in the analyzed clinical samples. In contrast, in the erythrocytes of men exposed on aviation fuel the content of Mn was significantly higher.

K e y   w o r d s: manganese, serum, erythrocytes, hair, atomic absorption spectroscopy.

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ZAWARTOŚĆ MANGANU W SUROWICY, ERYTROCYTACH I WŁOSACH MĘŻCZYZN – PRACOWNIKÓW LOTNISKA

Abstrakt

Mangan jest kofaktorem i składnikiem wielu enzymów. We krwi jest związany głównie z transferyną, szybko ulega dystrybucji i szybko jest wydalany z organizmu, przede wszystkim z żółcią. Niewielkie ilości tego pierwiastka są wydalane w moczu. Prawie cała pula Mn we krwi jest zlokalizowana w erytrocytach. W pracy oznaczono zawartość manganu w surowicy, erytrocytach i włosach 26 mężczyzn będących pracownikami lotniska. Grupę kontrolną stanowili pracownicy administracyjni, natomiast grupę badaną – mężczyźni obsługujący samoloty. Włosy pobrano z kilku punktów głowy, w ilości ok. 0.5 g i długości 3–4 cm, licząc od skóry. Próbki włosów umyto w roztworze detergentu, wodzie dejonizowanej i acetonie, a następnie wysuszono. Próbki krwi odwirowano i oddzielono masę erytrocytarną od surowicy. Tak przygotowane próbki mineralizowano w mieszaninie spektralnie czystych kwasów HNO_3 i $HClO_4$. Zawartość manganu oznaczono metodą spektrometrii absorpcji atomowej z atomizacją w piecu grafitowym GFAAS. Oznaczona zawartość Mn w badanych próbkach erytrocytów była statystycznie istotnie wyższa w grupie kontrolnej. W próbkach włosów zawartość Mn była porównywalna w obu grupach mężczyzn. Wyznaczone współczynniki korelacji między zawartością Mn w surowicy i we włosach, erytrocytach i we włosach oraz w surowicy i erytrocytach nie wskazują na występowanie istotnych zależności między zawartością Mn w badanych próbkach klinicznych. W badaniach, zarówno w surowicy, erytrocytach i włosach mężczyzn z grupy kontrolnej, jak i w badanej, nie stwierdzono, aby w znaczący sposób kumulował się mangan. Jednak w erytrocytach pracowników obsługujących lotnisko ilość Mn była znamiennie wyższa.

S ł o w a   k l u c z o w e: mangan, surowica, erytrocyty, włosy, spektrometria absorpcji atomowej.

INTRODUCTION

Manganese is a cofactor for many important enzymes such as kinases, hydrolases, and trasferases. Mn is also a component of superoxide dismutase (SOD), arginase, pyruvate carboxylase, glutamine synthetase, and katalase. This element participates in carbohydrate and lipid metabolism, synthesis of proteins, hormones (e.g. thyroxine), and also nucleic acids, steroids, hemoglobin, erythrocytes, neurotransmitters, cartilaginous and bone tissue. In blood Mn is complexed to transferrin, and quickly passes through the body to be extracted mainly in bile and urine. Across the cell membrane Mn is transported by transferrin, carrying DMT1 protein, and via Ca^{2+} gated channels. DMT1 is responsible for the cellular uptake of divalents cations (Fe^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Pb^{2+}). Almost all Mn pool in blood is located in erythrocytes. Chronic Mn deficiency can be linked to lipid metabolism disturbances, skeletal mineralization, dermatitis, and teratogenic effect. Depressed serum Mn levels have been reported in osteoporosis, epilepsy, and diabetes (ROTH, GARRICK 2003). Mn overexposure (mainly by the respiratory tract) results in damage of Fe absorption and metabolism, generation of reactive oxygen species (ROS) and oxidative stress, slow growth, respiratory

and neurological disorders. Neurological symptoms of Mn overload are similar to those observed in Parkinson's disease. Elevated Mn levels in many tissues were observed in many patients suffering from this disease. Deficiency of Fe promotes manganese accumulation in the body, specially in the brain and liver. In a biological medium manganese exists mainly as Mn(II) and Mn(III) cations (ROTH, GARRICK 2003, ZHANG et. al 2003, HUSSAIN, SYED 1999). Up to now, inverse relationships between manganese and magnesium, calcium, iron, mercury, and cadmium (Mn-SOD inhibition) were reported (ROTH, GARRICK 2003, CASALINO et. al 2002).

Simultaneous exposure to As, Pb, and Mn can produce synergistic interactions, which result in elevated level of those elements, mainly in the brain. They also cause depressed brain dopamine level, and intellectual and neurological dysfunctions (WRIGHT et. al 2006). Both lead and manganese are gasoline additives used as anti-knocking agents and they are components of many fuels (DAVYDOWA 2005).

The aim of the work was to evaluate Mn contents in serum, erythrocytes, and hair of men aging 30-45 years, occupationally exposed to aviation fuel.

MATERIAL AND METHODS

Samples of hair and blood were taken from 26 men aged 30–45. Sixteen men were airplane servicemen exposed to aviation fuel. The control group was made of men working in the administration section of the airport. Hair samples weighing 0.5 g and 3–4 cm in length measured from the scalp were taken from few places on the head. Samples of hair were washed with a detergent solution, rinsed with deionized water, acetone and dried.

Blood was collected by venipuncture into plastic tubes. Next, blood samples were centrifuged at 3000 rpm for 10 minutes; erythrocytes and plasma were separated and kept at – 20ºC until analyses. About 1 g of the prepared samples was mineralized in a mixture of spectrally clean acids HNO_3 (65%) and $HClO_4$ (65%) (3 + 1).

Concentration of Mn was analyzed by electrothermal atomic absorption spectrometry (GFAAS) using a spectrometer AVANTA Σ (GBC) equipped with a graphite furnace GF3000 fitted with a deuterium lamp for background correction and an autosampler PAL3000. The wavelength applied was λ=279.5 nm, the temperature program was 700/2400ºC, and the intensity of lamp current was 5.0 mA with a slit width 0.2 nm.

RESULTS AND DISCUSSION

Analytical characterization of the method and results of certificated material analysis (human hair NCS ZC 81002) is presented in Table 1.

Table 1

Analytical characterization of used method

Characteristic mass (pg)	Limit of detection (ng ml^{-1})	Precision (%)	Recovery (%)	Certificated Mn concentration $x \pm s$ (µg g^{-1})	Found Mn concentration $x \pm s$ (µg g^{-1})
0.32	0.17	1.4	102.3	2.94 ± 0.2	2.84 ± 0.17

Concentration of Mn in serum of both groups exceeded 2 g/kg. Smaller contents of Mn were received by other authors: 11 nmol l^{-1} by KUCERA et. al (1995) and 0.5 g l^{-1} by CORNELIS et. al. (1995). The Mn concentration obtained from the analyzed samples of erythrocytes is statistically significantly higher in the test group – 11.8 µg kg^{-1}. According to IUPAC (CORNELIS et. al 1995) a typical content of Mn in erythrocytes is about 15 µg kg^{-1}. In samples of hair Mn concentrations were comparable between both groups of men: 0.07–0.42 µg kg^{-1}. Similar quantities of this element were received by other authors (Table 2). The coefficients of correlation between Mn concentration in serum and hair ($r = -0.10871$), erythrocytes and hair ($r = -0.1393$) and between serum and erythrocytes ($r = 0.1764$) did not suggest any significant relationships between Mn concentrations in the analyzed clinical samples.

Interactions between Pb and Mn in blood of children form Sydney were analyzed by GULSON et. al (2006) after enriching fuel with an admixture of Mn compound instead of Pb as an anti-knocker. In these children the content of Pb was much lower, but the content of Mn was the same. Similarly, the Mn concentration in blood of mothers living in Paris, where Pb is added to fuel, was identical as that in blood of mothers living in Montreal, where Mn is used (about 23 µg L^{-1}). Somewhat larger contents of Mn were in samples of umbilical cord blood of mothers living in Canada, but without statistical significance. However, differences were observed in the case of Pb. Lower contents were found in blood of women living in Canada and in umbilical cord blood (AUDREY et. al 2002). One statistically proven significant reverse correlation was found between neuropsychological functions as well as intelligence quotient between children whose hair had higher quantities of Mn and As in comparison to the control group (WRIGHT et. al 2006).

Table 2

Concentration of Mn in serum, erythrocytes and hair, $x \pm s$ (µg kg^{-1})

	Serum	Erythrocytes	Hair	Authors
Tested group (n = 16)	2.5 ± 0.9 (1.0 − 4.7)	11.8 ± 1.7 (4.3 − 13.5)	201 ± 110 (120 − 420)	own research
Control group (n = 10)	2.2 ± 0.9 (1.1 − 3.7)	7.4 ± 2.8, p <0.05 (8.5 − 14.0)	231 ± 90 (70 − 370)	own research
		165 ± 51* nmol l^{-1}		KRISTIANSEN et al. 1997
	11 ± 3 nmol l^{-1}			KUCERA et al. 1995
		7.40 (1.5 − 22.0)*µg l^{-1}		WHITE, SABBIONI 1998
	0.5 µg l^{-1}	15 µg kg^{-1}		CORNELIS et al. 1995
		2 − 27* µg l^{-1}		APOSTOLI 2002
			0.03 − 1.2 µg g^{-1}	BERMEJO--BARRERA et al. 1998
		5.0 −12.8* µg l^{-1} 0.63 − 2.26** µg l^{-1}	0.016 − 0.57 µg g^{-1}	GOULLE et al. 2005
		0.0037 − 0.0140 µg ml^{-1}	0.10 − 2.4 µg g^{-1}	TERESA et al. 1997
		1.8 − 45.0* µg l^{-1}		GULSON et al. 2006
		6.3 − 151.2* µg l^{-1} (mother) 14.9 - 92.9 *µg l^{-1} (child)	0.1 − 3.24 µg g^{-1} 0.05 − 13.33 µg g^{-1}	TAKSER et al. 2003
			0.383 µg g^{-1}	VIOLANTE et al. 2000
			0.02 − 35.48 µg g^{-1}	PEREIRA et al. 2004
			89.1 − 2145.3 ng g^{-1}	WRIGHT et al. 2006
		1.2 - 4.0* µg l^{-1}		AUDREY et al. 2002

* blood
**plasma

CONCLUSIONS

In the analyses presented here serum and hair of men from the test and the control groups were not found to accumulate essential amounts of Mn. In contrast, in the erythrocytes of men exposed on aviation fuel the content of Mn was significantly higher. With regard to increasing environmental exposition of human to Mn, there is a justified need to continue research on interactions between Mn and other elements in biological media.

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