Vol. 16, No. S2

2009

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# MERCURY CONTENT IN SMOKE AND TOBACCO FROM SELECTED CIGARETTE BRANDS

# ZAWARTOŚĆ RTĘCI W DYMIE I WYPEŁNIENIU WYBRANYCH MAREK PAPIEROSÓW

Abstract: The study aimed at evaluating the total mercury content in tobacco and smoke released from selected cigarette brands. "Mechanical lips" were applied for determining the mercury concentration in cigarette smoke, and its level was calculated by balancing it in tobacco, ash, and cigarette filter. Analyses were made using mercury analyser AMA-254. The study material consisted of selected-brands cigarettes grouped according to tar and nicotine substances contents declared by a producer: 3 brands (L1, L2, and L3) filled with low-tar and low-nicotine tobacco (4 and 0.3 mg/cigarette); 5 brands (M1, M2, M3, M4, and M5) characterized by medium tar and medium nicotine contents (6÷8 and 0.5÷0.6 mg/cigarette), and two remaining brands (S1, S2) with high-tar and high-nicotine levels (12 and 1.0 mg/cigarette). Mercury contents in tobacco from tested cigarette brands ranged from 2.95 to 10.2 ng Hg per a single cigarette. Almost all mercury contained was released to the smoke (from 86.7 to 100%). Cigarette filters made of cellulose acetate appeared to be insufficient barrier for volatile mercury. In some cases, release of mercury from the filter into the smoke was observed. The element content in the filter was higher after than before smoking the cigarette for most brands; however, these were similar values to the metal content before smoking out. Applied filter filled with activated charcoal (single cigarette brand) contained the same amount of mercury before and after smoking the cigarette. Considering 20 smoked cigarettes as daily mean value for an individual person, it can be stated that it is a serious mercury source which supplies the smoker with a dose of 60÷200 ng of the toxic element into his/her lungs every day.

Keywords: mercury, cigarette, smoke, tobacco, non-flame atomic spectrometry absorption

The results of a variety of studies on environmental contamination with heavy metals and their accumulation in human organism revealed an association between elevated mercury concentrations in people's hair and their smoking behaviour or staying in cigarette smoke atmosphere [1-3]. The influence of smoking on increase of daily mercury dose introduced into a smoker's organism was also observed about 30 years ago [4]. In consequence, a study aiming at evaluating the total mercury content in tobacco and fumes from some cigarettes was undertaken.

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# Materials and methods

### Cigarettes

The study material consisted of selected-brands cigarettes grouped according to tar and nicotine substances contents declared by a producer: 3 brands (L1, L2, and L3) filled with low-tar and low-nicotine tobacco (4 and 0.3 mg/cigarette, respectively); 5 brands (M1, M2, M3, M4, and M5) characterized by medium tar and medium nicotine contents ( $6\div8$  and  $0.5\div0.6$  mg/cigarette), and two remaining brands (S1, S2) with high-tar and high-nicotine levels (12 and 1.0 mg/cigarette). Every brand was represented by 5 packages (à 20 cigarettes) purchased at the same time.

### Preparation of material for mercury determination

Cigarettes of each brand were divided into two parts that were stored within a closed desiccator to prevent the material from drying. One part of each sample was subjected to determinations of total mercury content in tobacco, and the other was smoked in "mechanical lips" with subsequent determination of mercury content in ash and filter. Mercury amounts were calculated by means of balancing, taking into account that portion of the element that was released in the smoke. The "mechanical lips" device was made of water scrubber and a syringe pump 335 A (Unipan, Poland). The operating principle of the "mechanical lips" is presented in Figure 1.

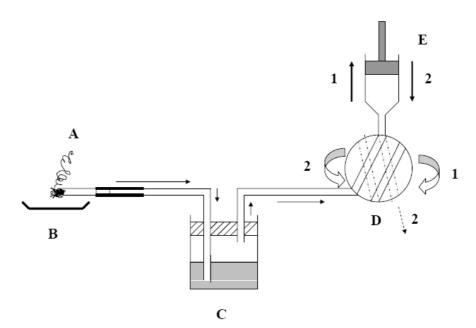


Fig. 1. Principles of operation of the ,,mechanical lips". Explanations: A - cigarette, B - sample boat for ash accumulation, C - water scrubber, D - balancing pump valve, E - pump syringe, 1 - movement of the valve and piston at air suction, 2 - movement of the valve and piston releasing sucked-in air

#### **Determination of mercury content**

Total mercury determination was carried out using mercury analyser AMA-254 (Altech, Czech Republic) [3], taking the 100 mg samples cut together with the paper using a scalpel. Achieved results were converted to the mercury content in a tobacco weight unit and to the filling of a single cigarette (taking into account its presence in the filter), and then the amount of the element released into the atmosphere in smoke was calculated. Drying, grinding, and averaging of tobacco samples were left out because any additional stage could contaminate vessels, drier or staff clothes with mercury, which could result in larger errors.

### Calibration

The analyser was calibrated applying NIST-traceable Hg standard solution (Accu Trace Single Element Standard; AccuStandard Inc., New Haven, CT, USA). Determination uncertainty was estimated using about 10 g of cigarette tobacco previously dried and ground in a mortar to get a fine dust with subsequent averaging of sample; determination precision was evaluated by comparison with the analysis of certified referential materials (CRM): Mixture of Polish Herbs (INCT - MPH-2) and Tea Leaves (INCT - TL-1) prepared by Institute of Nuclear Chemistry and Technology, Warsaw (Table 1).

Table 1

Assessment of the accuracy and precision of the method using two standard reference materials: INCT-MPH-2 and INCT-TL-1, (Institute of Nuclear Chemistry and Technology, Warsaw, Poland)

INCT-MPH-2 [ng/g], n = 10		INCT-TL-1 [ng/g], n = 10		
certified value	determined value	certified value	determined value	
$17.60 \pm 1.60$	$16.70\pm0.50$	$4.92\pm0.74$	$5.27\pm0.43$	

#### Statistical analysis

The significance of differences in mercury contents in tobacco of particular cigarette brands was statistically assessed applying Duncan tests and SAS software (SAS Version 9.1, SAS Inst., Cary, N.C., USA).

## **Results and discussion**

Results for total mercury are presented in Table 2 and in Figures 2-4. Table 2 presents the total mercury content [ng/g] in cigarette filling (tobacco), in filters before and after smoking the cigarette, as well as in the ash. Figure 2 indicates results of absolute total mercury level [ng] for tobacco in a single cigarette of particular brands. Those results confirm numerical data in Table 2 referring to lower mercury content in L1 and M3 brands tobacco, and higher in M4 and S1 brands. Observed greater differences between mercury content per cigarette for L1, L2 and M3 brands result from the different weights of tobacco fillings. Figure 3 presents absolute mercury content in cigarette fumes [ng] calculated per a single cigarette. Results in Figure 3 are consistent with those from Figure 2, because in practice all mercury from the tobacco is released with the fumes during smoking. Figure 4 presents results [ng] for mercury determination in filters before and after cigarette smoking - for the tested brands.

#### Table 2

Mean content of total mercury in tested cigarettes tobacco, in the filter before smoking, as well as ash and filter after smoking out the cigarette. Explanations: \* charcoal filter, \*\* no filter. Values designated with the same letters (a, b, c) within column do not significantly differ at 5% error (Duncan's test). Values designated with the same letters (A<sub>1</sub>, B<sub>1</sub>, A<sub>2</sub>, B<sub>2</sub>) within line do not significantly differ at 5% error (Duncan's test)

Cigarette brand	Mean mercury content [ng/g]				
	Before smoking out		After smoking out		
	tobacco	filter	ash	filter	
L1	6.74±0.67cdA1	0.61±0.14dA2	0.02±0.00eB1	3.14±0.39aB <sub>2</sub>	
L2	9.89±1.84aA1	3.61±0.42aA2	0.19±0.02aB1	$0.32 \pm 0.08 dB_2$	
L3	$8.27 \pm 1.01 bA_1$	0.50±0.09dA2	$0.05 \pm 0.00 dB_1$	$0.54 \pm 0.08 dA_2$	
M1	9.46±1.29aA1	0.46±0.11dA <sub>2</sub>	$0.13 \pm 0.01 bB_1$	$0.54 \pm 0.08 dA_2$	
M2	$8.18 \pm 1.10 bA_1$	1.94±0.15bA2	$0.05 \pm 0.01 dB_1$	$0.44 \pm 0.07 dB_2$	
M3	6.48±1.29dA1	0.37±0.25dA2	$0.14 \pm 0.02 bB_1$	1.27±0.12cB <sub>2</sub>	
M4	10.35±0.76aA1	1.72±0.13bcA2	0.10±0.01cB1	1.76±0.14*cA2	
M5	$7.60 \pm 1.10 bA_1$	1.12±0.32cdA <sub>2</sub>	0.04±0.01deB1	$2.59 \pm 0.42 bB_2$	
S1	10.56±0.72aA1	**	$0.14 \pm 0.02 bB_1$	**	
S2	9.59±0.66aA1	0.39±0.08dA2	0.12±0.02bcB1	0.51±0.11dA <sub>2</sub>	

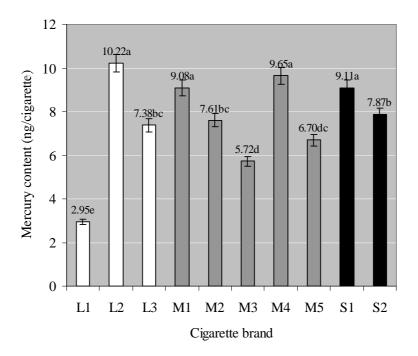


Fig. 2. Absolute mercury content in tobacco of single cigarettes [ng]. Explanations: Values designated with the same letters (a, b, c...) do not significantly differ at 5% error (Duncan's test)

Analysis of achieved results revealed lower mercury levels in only one tested cigarette brand containing low-tar and low-nicotine tobacco (L1) and a single brand (M3) containing medium levels of tarry substances and nicotine (6.74 and 6.48 ng/g, respectively). However, the highest mercury content was found in a brand with medium amounts of tar and nicotine (M4) and one with higher contents of these substances (S1) (10.3 and 10.6 ng/g). In the other cigarette brands - regardless of the content of tar and nicotine - mercury level did not significantly differ ranging from 7.60 to 9.89 ng/g of the filling. Such results seem to indicate the lack of any dependence between tar substances and nicotine contents in cigarette tobacco vs mercury levels determined in them. Eight of the tested brands had filters made of cellulose acetate, one (S1) had no filter, and another one (M4) was equipped with charcoal filter. Analysis of these filters (9 cigarette brands) - before their burning - revealed that they contained mercury at levels from 0.03 to 0.72 ng, ie about 1-2 orders lower than in tobacco. Most of the filters did not retain mercury during smoking. The charcoal filter had the same property. Only in the case of 4 brands (L1, L3, M3, and M5) mean retention of 0.30, 0.23, 0.18, and 0.35 ng of mercury was recorded (vs 2.95, 7.38, 5.72, and 6.70 ng before smoking), which was 10.2, 3.12, 3.15, and 5.22% of released mercury, respectively.

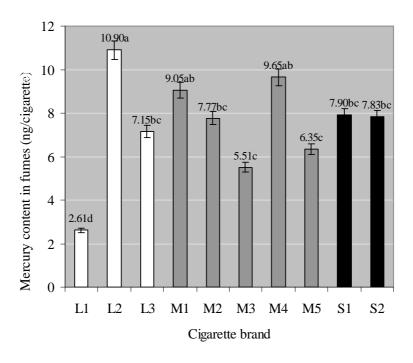
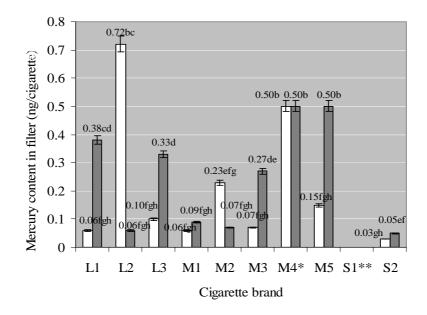


Fig. 3. Absolute mercury content in smokes of single cigarettes [ng]. Explanations: Values designated with the same letters (a, b, c...) do not significantly differ at 5% error (Duncan's test)

Worldwide literature is not abundant in works on mercury occurrence in tobacco. Only few publications [4-9] describe issues attributed to methodology of mercury determination in tobacco and cigarette smokes. Those researches mention such techniques as: atomic absorption spectroscopy using - after sample digestion - cold vapours technique (CV-AAS) [5, 9], photodiode detection and high-performance liquid chromatography with separation of heavy metal chelates with tetra-(4-aminophenyl)-porphyrin on reversed phase RP-HPLC [7], as well as inflammable technique GF-AAS [10]. Similarly small number of studies give results of mercury content determinations in tobacco products and cigarette smoke [4, 5, 11-13]. Results referring to mercury amounts in cigarette smoke found by Chang et al [5] ranged from 5.0 to  $7.4\pm0.4$  ng/cigarette, and for smoke of referential cigarettes: from  $1.7\pm0.2$  ng to  $7.4\pm0.4$  ng/cigarette, while results published for cigarette smoke by Canadian Report [11] mention values from 11.5 to 16.6 ng/cigarette.



□ before smoking out the cigarette ■ after smoking out the cigarette

Fig. 4. Absolute mercury content in filter before and after smoking the cigarette [ng]. Explanations: \* charcoal filter, \*\* no filter, Values designated with the same letters (a, b, c...) do not significantly differ at 5% error (Duncan's test)

The results obtained in this study for smoke of tested cigarette brands are almost in the middle of those ranges, amounting to 2.61 ng (in the case of only one brand), whereas for other ones the range of values is  $5.51 \div 10.9$  ng/cigarette. According to Suzuki et al [4], mercury contents in tobacco of Japanese and foreign cigarettes oscillate around 60 and 30 ng/cigarette, respectively. Cigarettes tested in the present study are characterized by mercury amounts at the level of  $2.95\pm0.2$  ng (L1), the other brands within range of  $5.72\pm0.31$  ng to  $10.2\pm0.70$  ng per single cigarette.

Considering 20 smoked cigarettes as daily mean value for an individual person, it can be declered that it is a serious mercury source which supplies a smoker with the dose of  $60\div200$  ng of the toxic element into his/her lungs every day.

They are not high levels for human organism that is able to secrete such doses even at complete metal absorption in the course of intoxication. However, the mercury is absorbed by an organism via the respiratory tract. Mercury introduced in this way is retained in the organism in 80%. Diffusion absorption of the element into the semi-liquid layer of the respiratory tract, namely lungs, occurs with subsequent dissolution in ependyma and enters into the blood where it is oxidized in red cells. This process is not complete and some amounts of elemental mercury that remains in blood penetrate through brain-cortex and placenta barrier, which causes mercury deposition in embryo brain and other tissues. The ratio of mercury contained in red cells to that in blood plasma is about 2 [10, 14].

According to the American Environmental Protection Agency [15], for mediumweight adult human organism, daily dose of mercury that does not invoke apparent health disturbances may reach up to 21  $\mu$ g. However, it is well known that cigarettes are not the only source of the element, toxic for human organism, and may be crucial for the reduction of the organism abilities to secrete absorbed mercury rates.

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# ZAWARTOŚĆ RTĘCI W DYMIE I WYPEŁNIENIU WYBRANYCH MAREK PAPIEROSÓW

Abstrakt: Podjęto badania mające na celu określenie zawartości rtęci całkowitej w wypełnieniu papierosów (tytoniu), a następnie w dymie uwalnianym z papierosów. Przy oznaczeniu pierwiastka w dymie zastosowano "sztuczne usta" (wykonane z pompy strzykawkowej 335A (Unipan), a zawartość rtęci obliczano przez zbilansowanie jej poziomu w tytoniu, popiele i filtrze papierosa. Oznaczanie prowadzono z użyciem analizatora rtęci AMA-254. Materiał badawczy stanowiły papierosy wybranych marek pogrupowane według zawartości substancji smolistych i nikotyny podawanych przez producenta. Grupę pierwszą reprezentowały 3 marki (L1, L2 i L3) wypełnione tytoniem o małej zawartości substancji smolistych i nikotyny w porównaniu z pozostałymi (odpowiednio: 4 i 0,3 mg/papieros). Grupa druga obejmowała 5 marek papierosów (M1, M2, M3, M4 i M5) charakteryzujących się średnią zawartością substancji smolistych i nikotyny (odpowiednio: 6÷8 i 0,5÷0,6 mg/papieros). Grupę trzecią stanowiły papierosy dwu marek (S1, S2) o największej zawartości substancji smolistych i nikotyny (odpowiednio: 12 i 1,0 mg/papieros). Zawartość rtęci całkowitej w tytoniu przebadanych papierosów wahała się w granicach od 2,95 do 10,2 ng Hg na pojedynczy papieros. Prawie cała zawarta w nim rtęć przechodziła do dymu papierosa (od 86,7 do 100%). Zastosowane w papierosach filtry z octanu celulozy okazały się być niewystarczającą barierą dla par tego pierwiastka. W niektórych przypadkach zauważono nawet uwalnianie się do dymu rtęci zawartej w filtrze papierosa. W większości badanych papierosów zawartość tego pierwiastka w filtrach po spaleniu tytoniu była większa niż przed, ale były to wartości zbliżone do zawartości metalu w filtrze przed spaleniem. Zastosowany filtr z węglem aktywnym (jeden gatunek papierosów) zawierał przed i po spaleniu tę samą ilość rtęci. Przyjmując 20 szt. jako średnią dobową ilość wypalanych papierosów przez osobnika, można stwierdzić, że stanowią one dość znaczne źródło rtęci, dostarczające dzienną dawkę palaczowi do płuc w przedziale 60÷200 ng tego toksycznego metalu.

Słowa kluczowe: rtęć, papierosy, dym papierosowy, tytoń, bezpłomieniowa absorpcyjna spektrometria atomowa