REVIEW

By assoc. prof. Anton Tachev, PhD

Chief department "Food Composition and consumer products" at the "Analytical and laboratory activities" directorate of the National Center of Public Health and Analyses

on the dissertation topic **"Survey of total mercury content in various environments relevant to human health and the environment"**

written by doctoral student of independent training chief expert Daniela Stankova - Kostadinova, "Chemical Factors" Department at the "Analytical and Laboratory Activities", directorate at the National Center of Public Health and Analyses.

The work presented is relevant, especially since 2003, when mercury was declared a global pollutant by the Governing Council of the United Nations Environment Program (UNEP). Mercury is a highly cytotoxic, neurotoxic, immunotoxic, endocrine, inflammatory and reproductive toxin causing chronic neurological, immune and autoimmune, cardiovascular, hormonal, oral and reproductive diseases. Because of these adverse effects on human health and ecosystems, a process to achieve international cooperation to reduce its harmful impact has begun. The main human problem is related to the transboundary nature of mercury pollution, which calls for mandatory action at the local, regional, national and international levels.

The presented dissertation contains 119 pages, with 39 tables and 15 figures.

The literature review was developed precisely, focusing on the use of mercury in industry and technology. Due to its physical and chemical properties, mercury is used in: chloralkali production - chlorine and caustic soda; in the production of control and measuring instruments - barometers, thermometers, hydrometers, X-ray tubes, fluorescent lamps, in the mining and production of gold and silver, in agriculture - fungicides and bactericides, in dentistry as silver-mercury amalgams, and as a preservative in vaccines and cosmetic products - thiomersal and others. The subject of occupational and non-occupational exposure to mercury and its toxic effects as elemental, inorganic and organic mercury is also very comprehensively covered. The content of mercury in various environments (cosmetic products, food and nutritional supplements, soils and sediments and polymeric materials) has been discussed extensively. Normative documents on limiting mercury content in different environments and analytical methods (AAS, mass spectrometry with inductively coupled plasma ICP-MS, optical mass spectrometry with inductively coupled plasma ICP-OES, neutron activation analysis - NAA and direct mercury analyzer) for its analysis in different environments are described in detail.

Mercury is a naturally occurring chemical element in the earth's crust - 0.05 mg/kg. Since the beginning of the industrial period, its level in the environment has been increasing significantly.

The predominant form of mercury in the atmosphere is elemental mercury. It is extremely volatile, and the rate of evaporation is directly related to temperature, increasing the temperature increases the concentration of mercury in the surrounding air. After release into the environment, it undergoes complex transformations and cycles between the atmosphere, terrestrial and aquatic systems. Humans, plants and animals are exposed to mercury during this biochemical cycle, which can lead to various health effects.

Mercury is recognized as a toxic, persistent and mobile pollutant. Atmospheric mercury pollution continues to be one of the most important environmental problems in the modern world. It does not degrade in the environment and, because of its volatility, is very mobile. It has the ability to be

transported in air masses over very long. Mercury is released into the environment through human activities and through natural sources and processes, such as volcanoes and rock weathering. In the environment, mercury is involved in processes of biotransformation, migration and bioaccumulation, where it passes into various inorganic and organic chemical forms. After its release, it is transported between the major components of the environment - air, soil and water, and finally deposited in coastal and deep ocean sediments, lake sediments and subsurface soils.

It enters the human body through the respiratory system, the digestive tract and the skin. Its absorption depends primarily on the form in which it is found.

In the European Union and beyond, mercury is classified as a priority hazardous substance and is therefore included in almost all legislative documents relating to environments of importance to human health.There is no theoretical safe level for this highly toxic element - any concentration above the limit of quantification is unsafe.

The many environmental and health issues related to mercury are addressed by the international Minamata Convention, adopted in 2013 to reduce global anthropogenic mercury emissions. The Convention entered into force in 2017 and has so far been signed by 128 countries and ratified by 118 countries. Among the key objectives of the convention are the identification, quantification, control and reduction of mercury emissions to land and water and to achieve better awareness of the processes of transformation and distribution of mercury in the environment.Analytical methods with high sensitivity, selectivity, optimal technical and economic characteristics find application in the field of mercury content research in various environments.

Mercury content can be determined using different methods, with different detection limits: atomic absorption spectrometry (0.1 ng), atomic emission spectrometry (0.005 ng), mass spectrometry (0.005 ng), colorimetry (100 ng) , neutron activation assay (0.01 ng), X-ray fluorescence spectrometry (25 ng), etc. The high toxicity of mercury requires control of its contents in objects from the environment and foods at a very low concentration level. Particularly important/relevant is the information regarding the safety of various environments of importance to human health and the environment in terms of mercury content, which determines the main goals and tasks set in this dissertation work.

Everything said so far clearly shows the goals of the present development.

The aim of the dissertation work is to optimize methods for the determination of total mercury by direct analyzer of solid and liquid samples and to apply them to the assessment of the safety of various media of importance for human health and the environment.

To fulfill this goal, the author sets herself the following tasks:

1. Optimization and verification of methods for the determination of total mercury with a direct mercury analyzer DMA-80 in cosmetic products, foods and nutritional supplements, waters, soils and sediments, polymeric materials.

2. Study of total mercury content in various environments of importance for human health and the environment:

2.1. Mercury content in cosmetic products.

2.2. Mercury content in foods and food supplements.

2.3. Mercury content in water.

2.4. Mercury content in soils.

2.5. Mercury content in sewage sludge.

2.6. Mercury content in products made of polymeric materials.

3. Summarizing, systematizing and evaluating the data obtained regarding the level of total mercury contamination of the various environments and evaluating their safety in terms of human health and the environment.

A direct analyzer of solid, liquid and gas samples DMA 80, Milestone, was used to determine mercury concentrations in various environments. Milestone's direct mercury analyzer DMA-80 is an integrated system based on the principle of atomic absorption spectrometry.

For the study of mercury content in various environments of importance for human health and the environment, chief. expert Daniela Stankova-Kostadinova has examined a large number of samples from different environments: Cosmetic products – 1051 samples; foods and food supplements – 227 samples; water – 998 samples; soils – 90 samples; sediments – 109 samples and products from polymeric materials – 94 samples.

The author optimized and verified the EPA 7473 method for the determination of total mercury in various media with a direct mercury analyzer DMA-80, which is a huge research and scientific-practical task. Undisputed personal contribution of chief expert Daniela Stankova – Kostadinova is the optimization of the analytical conditions of DMA-80 for the determination of total mercury in different media with adaptation and modification according to the characteristics of the tested samples, including the analytical procedure for the quantitative determination of mercury by DMA-80 with drying stages, pyrolysis, amalgamation, desorption and measurement of Hg concentration at a wavelength of 253.7 nm.

The verification of the methods for determining total mercury in different environments with a direct mercury analyzer DMA-80 was carried out in accordance with BDS EN ISO/IEC 17025 according to the following parameters: LOD and LOQ; measurement interval; linearity; analytical yield; coefficient of variation in repeatability conditions; coefficient of variation under reproducibility conditions; displacement; uncertainty.

Along with the variety of tested samples from different environments, special attention should be paid to the large number of analyzed samples of cosmetic products, such as face creams, decorative color cosmetics, cosmetics used around the eyes, etc., which are widely used in modernity, which is also a great contribution to the development. The presence of mercury and its compounds in cosmetic products is prohibited by Regulation (EC) 1223/2009, with the exception of special cases included in Annex 5 - thiomersal and phenylmercury salts, which are preservatives in cosmetic eye products, authorized for use at concentrations in the finished product, equal to or less than 0.007 % (as mercury), which corresponds to 70 mg Hg/kg. These mercury compounds provide the microbial protection of eye care products to avoid serious eye infections and only in cases where no other preservatives with equivalent effect exist. The exempt mercury preservatives are particularly effective against Pseudomonas aeruginosa bacteria, which can cause serious eye problems and damage, including blindness.

6 conclusions and 6 contributions are presented from the development.

1. For the first time in Bulgaria, comprehensive studies have been carried out on mercury content in various environments of importance for human health and the environment: cosmetic products, water, food and nutritional supplements, soils, sediments for use in agriculture, products made of

polymer materials by applying a validated and optimized EPA 7473 "Method for Direct Determination of Mercury in Solid and Liquid Samples".

2. Compliance with the requirements of European and national legislation regarding mercury content in the studied environments was evaluated.

3. A large number of data were obtained and evaluated to establish the levels of mercury contamination of cosmetic products, water, food and nutritional supplements, soils, sediments for use in agriculture, products made of polymer materials.

4. The summarized and systematized information on the presence of mercury in the studied environments can be used in fulfilling Bulgaria's commitments in implementing the Minamata Convention on mercury and Regulation (EU) 2017/852 on mercury (in relation to research activities, in accordance with Article 19, paragraph 1, letter b) of the Convention).

5. Collected data on mercury content in environments important to human health and the environment can serve to accumulate a database on mercury content in the studied environments and take preventive actions.

6. The resulting data on mercury content provide quantitative information on the actual mercury exposure of the population and can be used to estimate the mercury exposure for the population from the analyzed environments.

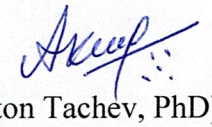
On the subject, there are 5 publications and participation in 8 scientific forums (congresses, conferences, seminars, etc.).

Not as a remark, but the large volume of proposed work for the educational and scientific degree "Doctor" should be indicated.

Conclusion:

The presented work has undeniable theoretical, scientific and practical contributions, for which I give my high positive assessment. I propose to the honorable members of the Scientific Jury to award chief expert Daniela Stankova-Kostadinova, doctoral student of independent training, the educational and scientific degree "doctor" in the Higher Education Department 7. Health and Sports, Professional Direction 7.1. Medicine, Scientific specialty "Hygiene" with the topic of the dissertation work " Survey of total mercury content in various environments relevant to human health and the environment" with supervisor assoc. prof. Rositsa Georgieva, PhD.

Sofia, 14.02.2024

Gave the review: 

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