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Mercury

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Mercury

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MERCURY

Metal mercury is a wide-known pollutant of the environment. Mercury (molecular weight of 200.59) is a silvery liquid metal. Its boiling point is 356.58°C and the density equals 13.546. Its solubility in water is very low and it tends to increase in parallel with the oxygen content of water. The most frequent impurities are zinc, lead, silver and some rare metals. The Soviet Union is one of the world's top producers of mercury and satisfies its demands in this metal in full [1,2,3].

PRODUCTION PROCESS(ES)

Mercury is produced by processing mineral ores (cinnabar, metacinnabarite, livingstonite, etc.) by the so-called pyrometallurgical method that consists in roasting the ore in special furnaces in the presence of free oxygen at temperature of 800°C.

Substances polluting the atmosphere and the air of the working zone in mercury production are dust (with free silicon dioxide as the main constituent), sulfur dioxide, lime dust, arsenic and antimony sulfates, oxides and salts, as well as hydrogen sulfide and sodium hydroxide [4].

USE

The principal areas where mercury is used are: production of chlorine and caustic soda by the mercury method, various methods of amalgamation, extraction of precious metals from their ores, manufacture and use of metering devices and electrotechnical instrumentation, use of mercury rectifiers in A.C. electric locomotives, manufacture and use of diffusion vacuum pumps and special mercury vacuum apparatus, manufacture of incandescent electric lamps, mercury quartz and luminescent lamps, X-ray tubes and radio valves; production and use of mercurous and mercuric chloride, mercuric oxide, salicylate and cyanide, ethylmercurchloride, phenylmercuracetate and other inorganic and organic derivatives of mercury; production and use of high explosives with using mercury fulminate; use of mercury in electrolytic processes as the cathode; use of electrolytic alkali produced by the mercury method in the produc-

tion of viscose fibres, use of mercury as a catalyst in various chemical processes; use of mercury quartz lamps in electrophotography, use of copper and silver amalgams as tooth-filling materials; use of metal mercury for conducting experiments in teaching and research laboratories [1,2,3].

PATHWAYS INTO THE ENVIRONMENT

The main sources from which mercury gets to the environment can be divided into natural and anthropogenic ones. The natural sources, in their turn, are divided into global, regional and local ones.

The global sources are the upper mantle of the terrestrial surface, and namely, the products of rock decay, the World Ocean, the underground and all kinds of surface waters and biospheres.

The regional sources include territorially large mercury-containing mineral deposits such as ore belts and zones.

The local sources are individual ore-fields.

The principal anthropogenic sources of atmosphere pollution with mercury are production of mercury, chlorine and caustic soda, burning of all kinds of fuel, coke-chemical industry, non-ferrous metals production, use of mercury in shipbuilding and mechanical engineering industry.

Wood-processing, pulp-and-paper and pharmaceutical industries, the production of chlorine and caustic soda, the production of mercury salts and the iron-and-steel are the main sources of polluting waters, reservoirs with mercury.

The iron-and-steel as well as instrument-making and chemical industries are the principal sources of soil contamination with mercury-containing solid wastes [6,7].

The losses of mercury (mainly to the atmosphere) at mercury-producing plants reach 5 to 7% of the total metal produced [3]. In the production of one ton of black copper 2.09 tons of dust containing up to 4% of mercury are vented to the atmosphere [11].

Sewages, even treated by modern methods, contain up to 0.01 mg of mercury per ml.

Mercury gets to the atmosphere in the forms of vapours and aerosol particles on which the metal is adsorbed as well as in the forms of solutions and suspensions of salts and technological products (intermediates).

About 50% of mercury contained in sewage gets to the sediment in the sedimentation tanks of sewage treatment stations, or settle to the bottom of natural water reservoirs. Mercury gets to the soil by direct absorption or through water [7].

CONCENTRATIONS

The content of mercury in the lithosphere averages $7 \cdot 10^{-6}\%$; in sea water $3 \cdot 10^{-9}\%$; and in living matter $10^{-7}\%$ [11].

The mercury concentration in non-polluted atmospheric air is 0.8 to 1.2 nanograms (ng) per m^3 . In the regions of large mercury-ore deposits this concentration reaches $240\text{ mg}/m^3$, and in the regions of natural gas fields up to $70.000\text{ mg}/m^3$. In the neighbourhood of mercury-producing or mercury-consuming plants (up to a distance of 2 km) the content of the metal in the air may exceed the maximum allowable concentration (which is $0.0003\text{ mg}/m^3$) by a factor of four, five and more [8].

In the Donets coal basin water seeping into mines contains $1 \cdot 10^{-6}\text{ g}$ of mercury per 1, this content being even higher in the water found in mines in the area of mercury-ore deposits [9,10].

Mercury was found to accumulate in the meta of farm animals receiving feeds contaminated with mercury-containing pesticides [12], as well as in fishes [13].

ENVIRONMENTAL FATE TESTS

Mercury is absorbed by the construction materials of factory buildings and dwelling houses, wooden parts of equipment and furniture, workers' overalls, etc. The amount of the adsorbed (absorbed) mercury depends on the duration of the exposure, the content of mercury in the air, the properties of the material and the environmental temperature. Use of special protective coatings (perchlorovinyl or other ones) diminishes the mercury sorption by the equipment parts and construction materials. Environmental objects contaminated with deposited mercury may become sources of "secondary" pollution of the air with mercury vapours.

The contamination of textiles with mercury depends on the nature of the component fibres, the thread structure, the fabric texture and the kind of its finishing [2,19,20,21,22].

Mercury is readily evaporable and yields vapours having a considerable (for metals) vapour tension at:

0°C - 0.000185 mm Hg ($2.02\text{ mg}/m^3$)

10°C - 0.000490 mm Hg ($5.45\text{ mg}/m^3$)

20°C - 0.001201 mm Hg ($13.1\text{ mg}/m^3$)

30°C - 0.00278 mm Hg ($30.4\text{ mg}/m^3$)

40°C - 0.006079 mm Hg

50°C - 0.01267 mm Hg

The diffusion coefficient for the mercury vapours is 0.1124 [1,2,23].

The mercury vapours that have got to the air are a) dispersed streams, b) adsorbed on aerosol particles contained in the air, c) washed out by atmospheric precipitation (rains, snow), d) absorbed by soil, plants, buildings. Mercury that has got to water or soil is included into the natural rotation of metals [2,7,11].

Mercury exhibits a marked capacity to bioconcentration, the property that explains cases of poisoning with organomercuric compounds on using them as food [13].

MAMMALIAN TOXICITY ARRAY

Mercury (metal) is present in the air in the form of monoatomic vapour and, therefore, the main route of its entrance to the body is the inhalation one. Swallowing of mercury particles from soiled hands (with food or during smoking) is also possible.

The range of the lethal concentrations is rather broad: a 6-hour exposure to a concentration of 0.04 to 3.0 mg/m^3 causes death of albino mice within 2 to 3 months; 10 to 16 mg/m^3 kills guinea pigs on daily 2- to 4-hour exposure within 3 days; 3 and 5 mg/m^3 kill the same animals on continuous exposure in 115 and 50 hours, respectively. A concentration of 15 to 20 mg/m^3 causes death of dogs on daily 8-hour exposure in 1 to 3 days; 12.5 mg/m^3 in 6 to 16 days. A concentration of 3 to 6 mg/m^3 causes in dogs a typical picture of mercury poisoning.

In chronic tests mercury concentrations of tenths and hundredths of mg per m^3 were found to cause the development of pronounced intoxication in rats and guinea pigs that manifested itself in body weight changes, disturbances of protein metabolism, impairment of thyroid functions, immunological shifts and disturbances of the conditioned-reflex activity. The maximal effective (threshold) concentration of mercury for albino rats, guinea pigs and cats on 6-hour exposure daily for 4 months were found to lie within the range of 0.03 to 0.01 mg/m^3 . The longer the exposure, the lower the threshold concentration. This points to an importance of cumulation in the development of the toxic effects of mercury. On longtime exposure of humans to concentrations of 0.01 to 0.03 mg/m^3 the mercury vapours cause a deterioration of the muscular working capacity, changes in the functions of analyzers, disturbances of the thyroid functions, development of the astheno-neurotic syndrome, an increase of morbidity with a temporary loss of the working capacity, disturbances of the ovarimenstrual cycle in women. The toxic effects of the mercury vapours are still greater at higher (over 28°C) air temperature [2,5,24,25,27].

SPECIAL TOXICITY STUDIES

Neurotoxicity/Behaviour. Mercury vapours possess a pronounced neurotoxicity and produce an effect on the endocrinal system [2,27,28,29,30].

Reproduction. A gonadotropic effect of mercury vapours at concentrations of about 0.01 mg/m^3 was revealed experimentally. The gonadotropic effect was also observed on single exposure of male rats to mercury at concentrations of 20 to 40 mg/m^3 [31].

The prolonged round-the clock exposure to mercury vapours in concentrations of 1 and 6 mg/m^3 causes a gonadotropic effect in experimental animals (albino rats) which remains active in the first generation of animals. In the course of these experiments it was shown that the viability of the first and second generations of animals declines in spite of the relatively favourable indicators of their physical development [32].

EFFECTS ON ORGANISMS IN THE ENVIRONMENT

Aquatic toxicity. In a concentration of 0.008 - 0.2 mg/l mercury (in the form of ions) produces toxic and lethal effects on many aquatic microorganisms. In a concentration of 0.05 mg/l it inhibits photosynthesis, and in a concentration of some thousandth of mg per l it lowers the reproductive capacity of daphnias [3].

SAMPLING/PREPARATION/ ANALYSIS

For determining mercury use is made of chemical colorimetric (the coloration of copper tetraiodomercuroate versus that of copper iodine, dithizone and nephelometric in the form of mercuric sulfide precipitate); physical (atomic absorption, neutron activation analysis, spectrometry) and physico-chemical (gas-liquid chromatography) methods.

Mercury vapours contained in the air can be determined directly or after their absorption by the solution of iodine in potassium iodine (or by a solution of potassium permanganate acidified with a solution of permanganate). In the first case mercury is determined from the colour reaction of copper tetraiodomercuroate, in the second the dithizone method or atomic absorption are used.

In water, soil and sediment samples mercury is determined after preliminary sample treatment (concentration, extraction) by one of the above-indicated methods.

In biological materials mercury is determined after their digestion with the mixture of nitric and sulfuric acids on heating by one of the methods indicated above [14,15,16,17,18].

SPILLS

Solid wastes (dismantled parts of furnaces, the contaminated mercury absorbents, broken gas-discharge lamps, parts of mercury instruments) are to be processed for recuperating mercury (by thermal regeneration right on the spot or transportation to a mercury-producing plant for using them as secondary raw materials).

Liquid wastes (mercury spills or condensed sediment from sedimentation tanks, etc.) are either to be processed for mercury recuperation (use as secondary raw material), or to be buried.

Wastes of the mercury production from ores also include the ore residues (after roasting), which are to be dumped in special sites.

The mercury-producing plants, particularly those using the pyrometallurgical technology, discharge relatively large volumes of vent-gases. The average volume of those gases per one ton of processed ore can be estimated at 850 m³ of technological, and up to 170 m³ of ventilation gases. In the process of roas-

ting one ton of the ore up to 40 g of mercury may get to the atmosphere. Even if the sanitary scrubbing is effective by more than 90%, the total loss of mercury per ton of the ore comprises about 4 g, or approximately 4 mg per m³ of the vent gases. The gases are vented through a chimney to a height providing their sufficient dilution with air. Mandatory for scrubbing the vent gases is the use of wet scrubbers mounted after the condensers. The sanitary scrubbing of the vent gases provides, that the latter should be treated by contacting with chemicals with which mercury forms stable compounds. These compounds are to be processed for utilizing the mercury [3,4,23].

TREATMENT OF POISONING

At present a number of pathogenetic means of treating the intoxications with mercury and its compounds has been suggested. As means of the pathogenetic therapy a broad use is made of various thiol compounds the most efficacious of which are dithiols, i.e. organic compounds having two free thiol groups located close to each other. Such compounds, as BAL and unithiol, bind mercury with formation of stable water-soluble complexes. The bound mercury loses its toxic properties and is excreted from the body by the kidneys.

In cases of initial, mild forms of the mercurialism the therapy comes to some symptomatic measures, such as intravenous infusions of glucose with ascorbic acid, intramuscular injections of calcium gluconate, diathermy to the hepatic area, iontophoretic calcium collar according to Shcherbak, vitamin therapy, administration of lipoic acid amide (lipamide) and food pectin. In some cases (when indicated) oral intake of unithiol (does 0.5 g twice a day for three days; these cycles can be repeated at 2- to 3-week intervals) is recommended. These therapeutic measures are usually taken in outpatient clinics.

If the mercury intoxication is more marked, and the treatment is given in hospital conditions unithiol is injected intramuscularly in the form of 5 per cent solution in a dose of 5 ml for 10 days running or in 5-day courses at a 3- to 4-day interval. Efficacious in the treatment of mercurialism is also the application of unithiol in the form of a highly disperse aerosol. It is recommended to use a 5 percent solution of the drug in a dose of 5 ml twice a day for a period of 10 days [34,35].

In the USSR a new mercury antidote - mesodimercaptosuccinic acid or succimer - has been synthesized. The mechanism of its action in the treatment of mercury intoxications is based (like that of other thiol compounds) on the competitive relations with tissue and enzyme proteins for mercury. The drug owes its physiological activity to two free SH-groups which have a high reaction capacity. Succimer is manufactured in tablets of 0.5 g for oral use and in vials of 0.3 g for intramuscular injections. The drug is dissolved *ex tempore* in 6 ml of sterile 5 per-cent solution of sodium bicarbonate. The succimer therapy of patients with the initial, advanced and far-advanced stages of mercurialism is accompanied in all cases with a considerable increase of mercury excretion with the urine, an improvement of the patients' general condition, a diminution of the tremor and a pronounced relief of the vegetovascular dis-

turbances. Worthy of a particular note is the fact that in the course of the treatment with the drug no excretion of trace elements, such as, copper and iron, was observed. The drug is well tolerated by patients [36].

The schedule of the succimer use is the following:

1. Intramuscular injections: 1st day: 0.3 g 4 times a day at 6-hour intervals; 2nd day: 0.3 g 3 times a day at 8-hour intervals; 3rd to 7th day: 0.3 g twice a day at 12-hour intervals. The total dose of the drug per treatment course is 5.1 g.

2. Oral use: 1st to 3rd day: 0.5 g 4 times a day at 6-hour intervals; 4th to 7th day: 0.5 g 3 times a day at 8-hour intervals. The drug should be taken after meals or washed down with alkaline mineral waters. The total dose of the drug per treatment course is 12.0 g.

When the intoxication is severe the succimer dose can be increased both by giving a higher (1.5 to 2 times) single dose, and by prolonging (if indicated) the treatment course.

The mercury intoxications can be also treated with such a chelate agent as D-penicillamine. This drug was tested in the treatment of patients with initial and moderate forms of mercury intoxication. The drug was given once a day in a single dose of 0.6-0.9 -1.2 g. It was found that the excretion of mercury from the body with the urine increased to a lesser degree than after taking unithiol and succimer [34]. There are also data pointing to an expedience of using lipoic (thioctic) acid for the therapy of mercury intoxications [37].

There is an experimental substantiation of using unithiol, succimer and lipamide not only for the therapy, but also for individual prophylaxis of mercurialism.

The most preferable and promising within the scope of the pathogenetic means of individual prophylaxis is the use of some substances contained in food products. Among such substances that produce no side-effects on the body there are, in particular, pectin substances which are polysaccharides contained in various fruits and root crops.

Of a substantial importance within the scope of the therapeutic and prophylactic measures aimed at controlling occupational mercurialism are (in addition to the above-mentioned physiotherapeutic measures) also the use of sulfide baths, four-cell galvanic baths filled with sodium thiosulfate or sulfur; ultraviolet irradiation in combination with warm pine baths and galvanic collar. Also desirable is treatment at health resorts (Matsesta, Pyatigorsk, Sernovodsk) with sulfur or sulfide waters. People working with mercury or its compounds should receive adequate therapeutic and prophylactic food rations. It is suggested that those rations should include lipotropic agents, vitamin B₁₂ and folic acid [38].

REMOVAL

For removing mercury (ionic or its dissolved salts) from sewages a number of sufficiently effective and extensively tested methods have been offered. These are: precipitation in the form of the sulfide, adsorption on activated

charcoal, lime treatment, ion exchange [23,33].

For extracting mercury vapours from vent gases various adsorbents, such as, activated charcoal, activated manganese dioxide, silica gel - iodine - copper absorbent, as well as treatment of the vent gases in special apparatus with solutions of mercury-binding or precipitating agents (sulfides, polysulfides, oxidants plus sulfides) have been offered. The mercury-saturated absorbents are used as a secondary raw material. The solids formed in the processes of the sewage treatment and the wet scrubbing of the vent gases are processed for mercury recuperation or are buried.

In industrial conditions mercury is washed off the walls, floors and equipment with water (the premises must have the necessary facilities). In laboratories mercury drops are removed by vacuum aspiration, using amalgamated plates or wetted sawdust with subsequent washing of the contaminated places with chemical demercurizers, such as, solutions of ferric chloride, sodium polysulfide, HNO_3 -acidified solution of potassium permanganate, etc. [2,5].

For removing adsorbed mercury from construction materials and elements thermal demercurization is recommended (39). Also recommended are special construction operations the scope of which is determined by the mercury content and the depth of the contamination of the construction element in question [40].

Workers' overalls are decontaminated by thermal treatment, use of chemicals (iodine/potassium iodide solution with subsequent bleaching) and washing, as required by a special instruction.

RECOMMENDATIONS/ LEGAL MECHANISMS

The principal measures to be taken for preventing mercury intoxications are:

1. Limination of possible sources of mercury intoxication (proper storage of mercury and its compounds, exclusion and replacement of mercury in industrial production with less toxic compounds);
2. Implementation of measures aimed at localization and, wherever possible, elimination of sources of mercury vapours contaminating the air of the working zone and other premises;
3. Protection of construction elements, equipment and working furniture;
4. Observation of established safety measures while working with mercury, as well as measures of personal prophylaxis;
5. Regular demercurization of premises where there are sources of mercury contamination;
6. Efficient cleaning of mercury-contaminated working garments;
7. Preliminary and current briefing of workers dealing directly with mercury on safety measures.

Preliminary when hiring new workers and regular periodic medical examinations of workers employed in industries where there are sources

of mercury vapours are necessary. These examinations should be carried out by a team of doctors including a therapist, neuropathologist, dentist, and, on indications, psychiatrist and gynecologist. The main task of the medical examinations consists in revealing initial signs of occupational intoxication and disease. Should signs of the mercurialism be detected in the persons contacting mercury, the medical commission decides on suspending the contact and instituting clinical or ambulatory treatment to those persons [2,3,5,21,23,41].

In the USSR the following hygienic standards for the permissible content of mercury and its compounds in the air of the working zone of production premises, in the atmospheric air and in the water reservoirs used as sources of drinking water or as recreational areas [42].

Substance standardized	Maximum allowable concentrations in:			
	Working zone air (mg/m ³)	Atmospheric air (mg/m ³)	Water reservoir (mg/l)	Soil (mg/kg)
Metal mercury	0.01 (maximum single) 0.005 (mean per shift)	0.0003 (mean daily)	0.005*	2.1***
Mercuric chloride	0.1 (maximum single)			
Mercury diethide	0.005 (maximum single)		0.0001**	
Ethylmercurchloride (as Hg)	0.005** (maximum single)			
Ethylmercurphosphate (as Hg)	0.005** (maximum single)			

* for inorganic mercury compounds determined as the mercury ion.

** determined as the mercury ion.

*** for mercury containing compounds determined as the mercury ion.

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