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ON THE CONTROL AND PROTECTION OF WORKERS HANDLING ORGANIC MERCURY COMPOUNDS

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In animal experiments it has been shown that mercury is excreted in the urine as soon as it has entered the blood stream, and that this excretion is continued as long as mercury can be demonstrated in the animal body. Accordingly, determination of mercury excretion is a fairly good method to demonstrate exposure to mercury compounds.

In practical work it is possible to follow the degree of exposure in the amount of mercury excreted in the urine of the workers, and by means of this control to determine if protective measures are satisfactory or if they must be improved. To make such a control possible, a new method for the determination of mercury in the urine is developed. However, the organic mercury compounds are not stable and the excretion of mercury in the urine of workers handling organic compounds may therefore be the result of the inhalation of vapour of metallic mercury. As metallic mercury is much less toxic than organic compounds, it was necessary to develop methods for rapid determination of both metallic mercury and organic mercury compounds in the air.

With these methods now available it is possible to control the risks associated with the handling of organic mercury compounds and to institute the necessary protection to eliminate undue risks.

Highly toxic organic mercury compounds are used nowadays more and more as fungicides in agriculture, paper pulp industry and textile industry. In Fig. 1 the results of an investigation of LD_{50} are summarized where the compounds in water solution are given to mice as a single injection intraperitoneally. LD_{50} is calculated for each day in an observation period of 7 days. The observation time was restricted to this period because no more deaths were registered during the second week. It appears from the figure that the toxicity is of the same order of magnitude for corrosive sublimate, phenyl mercuric acetate and different alkyl mercuric compounds administered in this way. If there is any difference the sublimate is the most toxic of the substances and the alkyl mercuric compounds the least toxic. Furthermore it is to be noticed that methyl and ethyl substances are equally toxic.

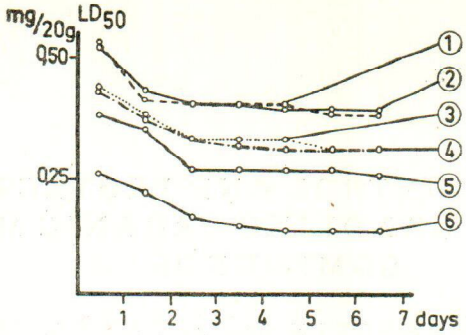


Fig. 1. LD_{50} for different mercury compounds. Single injection intraperitoneally. Mouse.

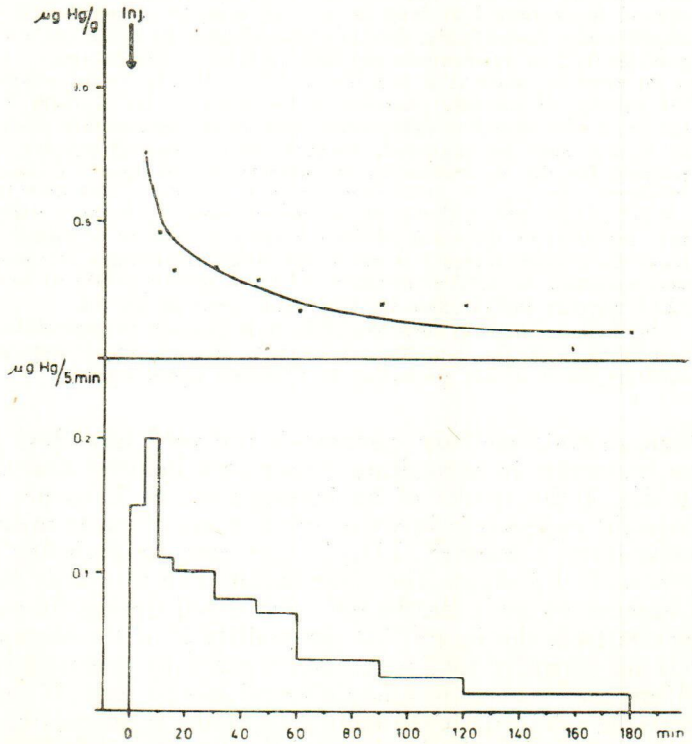


Fig. 2. Content of mercury in blood and excretion in the urine of a dog after intravenous injection of methyl mercury hydroxide, 0.1 mg Hg/kilogram of body weight.

Many alkyl mercuric compounds are very volatile as compared with the sublimate and phenyl mercuric acetate, and thus the alkyl compounds in practice may be more dangerous than the sublimate and the phenyl compound. Furthermore, when they are used as powder there may be quite a lot of dust that may be inhaled.

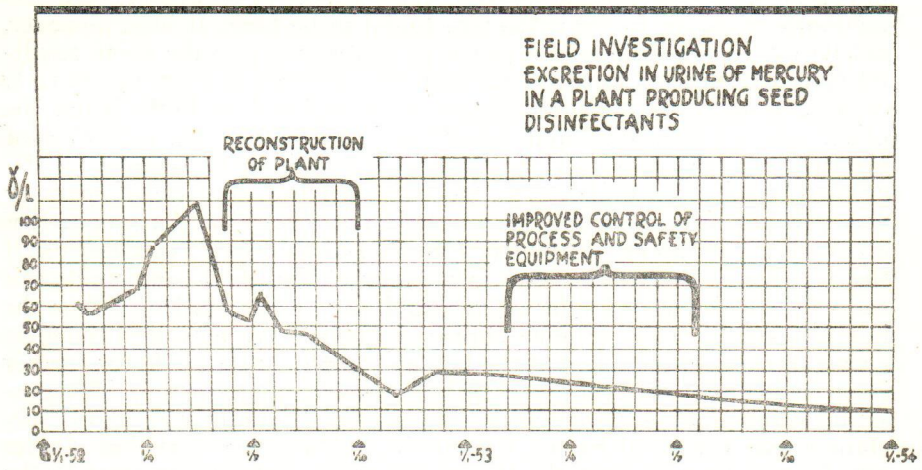


Fig. 3. Excretion of mercury in the urine of the groups of workers exposed to mercury compounds in a plant producing alkyl mercury compounds. The excretion used as a guide for the improvement of hygienic conditions.

For the above reasons and as there have been some cases of poisoning in Sweden in connection with the use of alkyl mercury compounds, we felt it necessary to introduce a thorough control of the working places where these substances were handled, and to undertake a rather extensive safety programme. In many working places the work varies from day to day and it is thus very difficult to obtain a true picture of the exposure and of the effect of hygienic improvements. This is possible only when one can use the worker as a sampling instrument and in one way or another determine to what extent he has been exposed.

As mercury is excreted in the urine we chose to study this excretion on groups of workers handling different organic mercury compounds. In animal experiments (Fig. 2) we have established that mercury appears in the urine immediately after its introduction into the blood stream of an animal, and that the amount excreted per time unit is roughly proportional to the concentration of mercury in the blood. In other experiments over a longer period of time we have shown that there is a continuous excretion in the urine and that the substances in question do not give any renal damage which could influence the excretion of mercury. The excretion of mercury in the urine continues as

long as there is any mercury in the organism. These results are in agreement with clinical observations.

We started our studies with the control of the employees of a factory producing alkyl mercuric compounds and using the conventional dithizone method for determination of mercury in the urine. The plant was old and hygienic conditions not very good. Accordingly, the excretion of mercury in the urine was found to be high. It was, however, not possible to determine how much of this mercury in the urine resulted from exposure to metallic mercury and how much from exposure to organic compounds. The employees were exposed to both. Then the plant was reconstructed and rebuilt and as a result the excretion of mercury in urine decreased, that is the exposure of the employees decreased, conf. Fig. 3. However, we felt that the excretion of mercury was still too high, especially as we could not determine the proportions of exposure to vapours of mercury metal and to organic compounds. If the workers were exposed only to vapours of the alkyl compounds this excretion of mercury in the urine could not be accepted and thus the hygienic conditions were to be improved further. We now used the mercury excretion in the urine of the human samplers as a guide for further improvements of different steps in the process of production. The process became highly mechanized; the workers' handling of toxic substances was protected by air line masks, rubber gloves, rubber clothes etc. As may be seen from the figure, there was a steady decrease in the excretion of mercury. During the last years the excretion has decreased still more.

A thorough clinical examination of these employees has not revealed any signs of damage.

Fig. 4. shows the result of a similar control of the workers of a seed dressing plant. Here, too, the results were used as a guide for the reconstruction of the plant and there has been quite a lot of improvement. When studying these results it is worth mentioning that the amount of seed treated during the period after the reconstruction has increased several times as compared with the earlier period.

As we have mentioned it is a serious drawback that it is impossible to determine if the mercury excreted in the urine is the result of exposure to vapours of metallic mercury or to vapours of organic compounds. However, this is a very important question as the vapours of the alkyl compounds are much more dangerous than the vapours of mercury metal. The alkyl compounds are excreted much more slowly and thus there may very easily be an accumulation in the body *(Swensson, Lundgren* and *Lindström,* 1959).

It became necessary for us to study this problem more closely when we found very high contents of mercury in the urine, 600–700 μg/l, in some workers of a plant producing phenyl mercury compounds. This excretion was so high that the workers would have been seriously ill if it had been the result of absorption of phenyl mercuric compound. How-

ever, they were quite healthy. Examination of the plant revealed the exposure to mercury metal vapours in this case. The same question arose in a paper pulp plant using organic mercury compounds as fungicides. We felt it thus necessary to work out methods for both the determination of mercury metal vapour and the determination of vapours of organic compounds. For the determination of the mercury vapours we used a Kruger ultraviolet photometer. In the inlet we put a furnace,

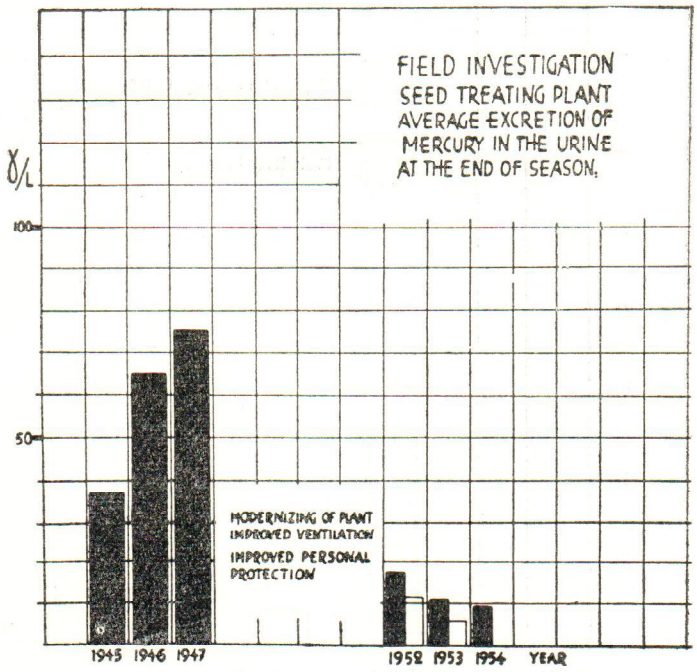
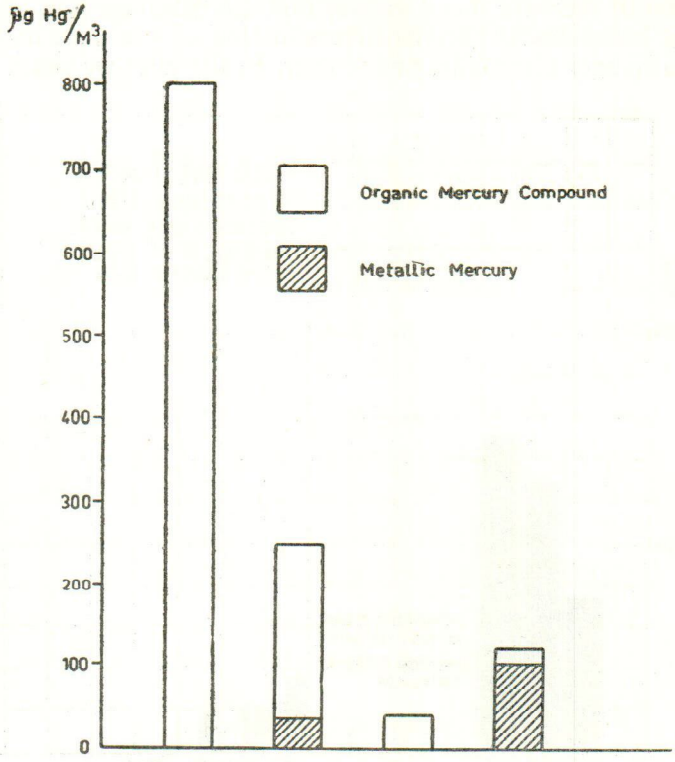


Fig. 4.

in which the air is heated. The air stream then passes a cooler and a filter before it reaches the instrument. When the furnace is used the organic mercuric compound vapours are decomposed and we can determine the total amount of mercury in the air. When the furnace is not used, we can determine the amount of vapour of mercury metal. The difference between the two readings gives the amount of organic compounds. The instrument is easily handled and makes the study of different mercury compounds in the air possible. It should be pointed out that high concentrations of different solvents in the air may give too high readings when the furnace is not used. Therefore it is necessary to determine the amount of solvents in the air. The instrument has been constructed by Lindström.

This instrument has proved very useful. For instance, it can be used for the determination of the nature of the vapours above a container with a mercurial seed dressing in it (Fig. 5), and the conditions in a barn where treated seed is stored (Fig. 6).

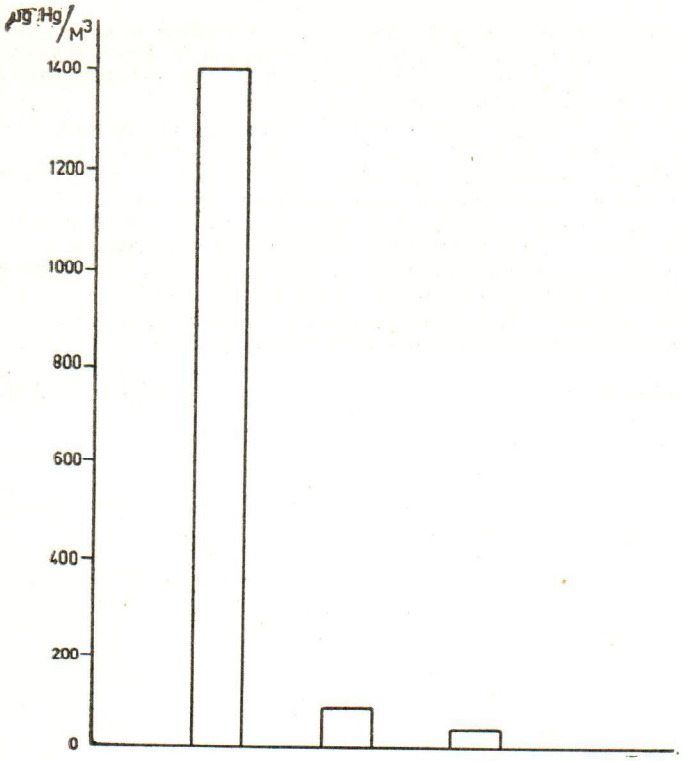


Mercury concentration in the air above different liquid seed dressings containing Organic Mercury Compounds.

Fig. 5.

Now, for the regular control of the employees the determination of mercury in the urine is the best method. In order to make the control of a great number of employees posible it was necessary to develop a less tedious method for the determination of mercury than the ordinary dithizone method. For this purpose Lindström has developed a method based on the Kruger ultraviolet photometer (Fig. 6). The urine is passed through a burner-atomizer. The gases are then passed through condensors and filters to remove a. o. salt mist, moisture etc. The content of mercury vapour is then determined by the ultraviolet photometer. By this method, which has been extensively checked against the dithi-

zone method, it is possible to determine the mercury content of the urine in small samples, 10 cub. cm. in 1–2 minutes with a sensivity of 2 μg/l. In routine work it is possible to examine 10–15 samples per hour



Mercury content in the air of a closed chamber containing a standard amount of treated seed. Different preparations.

Fig. 6.

In this way we can use the worker as a sampling device during his whole working day and check his exposure by the amount of mercury excreted in his urine. When an unexpected amount of mercury is excreted, it is possible to study the atmosphere of the working place and determine whether the worker is exposed to organic mercury compound vapours or to vapours of metallic mercury, and thus we can suggest the necessary improvements of the process.

Sadržaj

ZAŠTITA RADNIKA PRI RUKOVANJU ORGANSKIM SPOJEVIMA ŽIVE

U pokusima na životinjama se pokazalo, da se živa izlučuje iz urina čim uđe u krv i da se to izlučivanje nastavlja sve dotle, dok se živa može demonstrirati u tijelu životinje. Prema tome je određivanje izlučivanja žive prilično dobra metoda za određivanje stepena ekspozicije živinim spojevima.

U praksi je stepen ekspozicije radnika moguće kontrolirati na temelju količine žive izlučene u urinu i na taj način utvrditi, da li zaštitne mjere zadovoljavaju ili se moraju popraviti. Da se omogući takva kontrola, prikazana je nova, vrlo brza metoda za određivanje žive u urinu. Međutim, organski spojevi žive nisu stabilni i prema tome izlučivanje žive u urinu radnika, koji rukuju organskim spojevima žive, može biti rezultat udisavanja para metalne žive. Budući da su pare metalne žive manje toksične nego pare organskih živinih spojeva, bilo je potrebno razviti metodu za brzo određivanje i metalne žive i organskih živinih spojeva u zraku.

Tom metodom omogućena je kontrola opasnosti pri radu s organskim živinim spojevima i uvođenje potrebnih zaštitnih mjera za uklanjanje nepotrebnih opasnosti.

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