A semi-quantitative test for mercury in air

KNUD DREYER JØRGENSEN

Department of Technology, Royal Dental College, Copenhagen, Denmark

Dreyer Jørgensen, K. A semi-quantitative test for mercury in air. *Acta Odont. Scand.* 32, 305—308, 1974.

A simple method for semi-quantitative detection of mercury vapour in air is described. The method is based on the well-known reaction between the yellowish-brown $PdCl_2$ and mercury vapour resulting in the formation of gray colloidal palladium. Discs of filter paper are impregnated with a 1% $PdCl_2$ solution, dried, and suspended in the air whose mean mercury vapour concentration during a given period of time is to be analyzed. For the low mercury vapour concentrations to be expected in a dental office or laboratory, an exposure time of the test paper of 1—4 weeks is probably indicated. The mean mercury vapour concentration during the exposure time can be estimated colorimetrically by means of a gray-color scale. The sensitivity of the method is better than 0.01 mg Hg/m^3 air at an exposure time of 4 weeks. The accepted maximum concentration of mercury vapour in air for prolonged exposure of human beings (the so-called threshold limit value) is different in different countries; for Denmark it is 0.05 mg/m^3.

Carbon monoxide also reacts with $PdCl_2$ in forming a gray or black color. It is not very probable, however, that this reaction in a dental environment should result in fallacies as regards the mercury vapour analysis.

Key-words: Air pollution; mercury; dental amalgam

Knud Dreyer Jørgensen, Department of Technology, Royal Dental College, Jagtvej 160, 2100 Copenhagen Ø, Denmark

It is well known from the spot test chemistry that small concentrations of mercury vapour in the atmospheric air can be shown by means of filter paper impregnated with palladium chloride (*Feigl*, 1960). The yellowish brown palladium chloride reacts with the mercury vapour according to the formula

$$PdCl_2 + Hg^\circ \rightarrow Pd^\circ + HgCl_2$$

The colloidal palladium is black, and the reaction on the filter paper can be observed as a deepening gray coloring. At weak reactions the gray coloring is made better visible if the paper after the test is kept over concentrated ammonia water for a few seconds. The palladium ammonium chloride $Pd(NH_3)_4Cl_2$ thus formed is almost colorless.

For the reaction between $PdCl_2$ and Hg the following formula applies

$$c \cdot t = k$$

where c is the concentration of mercury vapour in mg per m^3 air, t is the time in hours needed to reach a certain degree of coloring on the test paper, and k a constant. The inverse proportionality between c and t means that a certain degree of coloring is reached in the shorter time, the higher the concentration of mercury vapour is.

Received for publication, March 18, 1974.

MATERIAL AND METHODS

1. Test paper and impregnation. Since visual evaluation of color reactions on paper may depend on the paper type, ash-free filter paper of the type Frisenette 644—24 (Frisenette A/S, Egsmark, Denmark) cut in circular discs with a diameter of 24 mm was used throughout the study.

The discs were impregnated with a 1% filtered aqueous solution of $PdCl_2$ (Fluka AG, Buchs, Switzerland).

The impregnation was made by dipping the discs in the solution; excess of solution was removed by placing the discs between two larger pieces of filter paper from just after the impregnation till the paper had dried.

2. Establishment of an atmosphere with known and constant concentration of mercury vapour. For this purpose a 20 l clear glass bottle was used the bottom of which was covered with abt. 500 cm^2 mercury complying with the requirements of the FDI standard specification No. 2; the neck of the bottle was closed with a 45/53 mm rubber stopper. At various times after closure of the bottle $PdCl_2$ impregnated filter paper was suspended at different heights in the bottle; at the suspension the rubber stopper was loosened only partly from the bottle neck and at most for five seconds. The filter paper was removed from the bottle after one hour's exposure. Remaining $PdCl_2$ in the test paper was hereafter bleached 10 to 15 seconds over 30 % ammonium water and inspected in diffuse daylight on a uniform white background. During the inspection the test paper was placed on a clear glass plate and soaked with water in order to obtain the greatest possible constancy in the visual evaluation of the gray-coloring. The experiment was carried out at a room temperature of 23.0 ± 0.2°C and an atmospheric pressure of 1010 ± 10 millibar.

3. Preparation of a gray-color scale. $PdCl_2$ impregnated filter paper was suspended in saturated mercury vapour for ¼, ½, 1 or 2 hours under conditions as specified above. For each period 5 pieces of paper were reacted, but only one piece at a time. Selection of time for each piece of paper was randomized, and 1 to 8 hours elapsed between each test.

4. Preparation of a graphite gray-color scale. Aquadag colloidal graphite (H. Struers Chemical Laboratory, Copenhagen) was dispersed in 30 % ammonia water; the solution was diluted with ammonia water until $PdCl_2$ testing paper impregnated with the solution showed the same gray-color as after one hour in saturated mercury vapour. Thereafter graphite solutions were made with a concentration which was ¼, ½ or twice the concentration of the first solution, and the test paper was impregnated with these solutions.

5. Detection of mercury vapour in air over mercury covered with water or paraffin oil. Mercury with a surface area of about 5 cm^2 in a 250 ml glass bowl was covered either with 1 cm water or 1 cm paraffin oil. $PdCl_2$ test paper was suspended in the bowl which was sealed hermetically. Temperature and atmospheric pressure were as mentioned under paragraph 2. The exposure time was 48 hours. For comparison an experiment was made where the mercury was not covered with any liquid.

RESULTS

Re 1. The $PdCl_2$ impregnated filter paper showed a uniform light brown color; only the margins were somewhat darker.

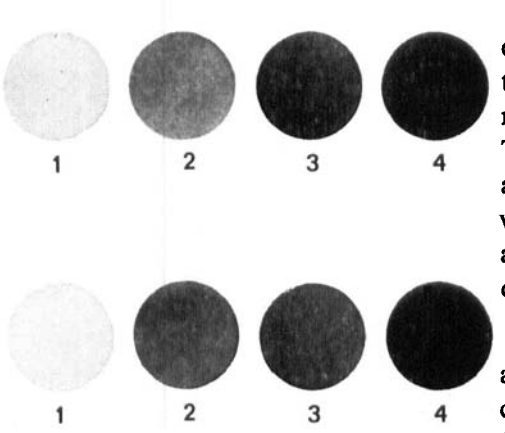

Fig. 1. Gradual gray discoloration of $PdCl_2$ test paper after exposure to saturated mercury vapour at 23°C for varying periods of time. 1, control. 2, exposure time ½ hour. 3, exposure time 1 hour. 4, exposure time 2 hours. The gray shades of this illustration cannot be safely used in the colorimetric analysis.

Fig. 2. Gray discoloration of $PdCl_2$ test paper over 5 cm^3 Hg covered with 1 cm liquid in a closed 250 ml container. 1, control. 2, water. 3, paraffin oil. 4, free mercury. Exposure time 48 hours.

A number of papers with structure faults like parallel stripes or bands were discarded.

Re 2. During the first hours after closing the bottle a one hour exposure of the test paper showed an increasing gray discoloration, reaching a constant value after abt. 5 hours. The atmosphere in the bottle was from that time considered saturated with mercury vapour (16.8 mg Hg per m^3 air under the conditions specified).

Re 3. The test paper showed a gray discoloration increasing with the exposure time (Fig. 1). Within each group of 5 pieces of test paper no shade difference could be detected by visual inspection.

Re 4. Test paper impregnated with graphite solutions with concentrations ¼, ½ or twice the concentration corresponding to the gray discoloration 1 hour in saturated mercury vapour at 23°C, showed gray-shades of the same intensity as test paper exposed for ¼, ½ and 2 hours, respectively, to saturated mercury vapour. This observation confirms indirectly the aforementioned proportionality formula which implies that the gray discoloration accumulates proportionally with the time of exposure.

Re 5. The results of the experiments appear from Fig. 2 and show that mercury vapour penetrates water and paraffin oil.

DISCUSSION

The method described seems to be adequate for semiquantitative detection of mercury vapour in air since the reaction between $PdCl_2$ and mercury vapour is accumulative and irreversible.

If a gray shade of the test paper one hour in saturated mercury vapour at 23°C is used as a basis for the colorimetric analysis, k in the formula given in the introduction will be $16.8 \cdot 1 = 16.8$. If the same shade is reached after one week (168 hours) in an atmosphere with an unknown concentration of mercury vapour, this concentration can be calculated as $x \cdot 168 = 16.8$, showing x to be 0.1 mg/m^3. If the said shade is reached only after e.g. 4 weeks, this corresponds to a mean concentration of 0.025 mg/m^3.

Correspondingly, if a shade of test paper ½ hour in saturated mercury vapour at 23°C is used as a basis for the analysis, the x values in the atmosphere with unknown concentrations of mercury vapour will be 0.05 mg/m^3 (one week) and 0.0125 mg/m^3 (four weeks), respectively.

It is evident that the method described can be only semiquantitative since the gray shade of an experimental test paper normally will be rated as lying between

two shades in a standard gray scale, or slightly above or below a shade in such a scale.

It should be noticed that also carbon monoxide reacts with $PdCl_2$ under formation of a gray or black shade. Therefore, differential analysis must be considered for each individual positive test. It is not likely, however, that carbon monoxide could be present in a dental office in concentrations sufficient to cause a discernible gray discoloration of the $PdCl_2$ test paper.

REFERENCES

Feigl, F. 1960. Tüpfelanalyse. Bd. 1., p. 365. 4. Aufl. Akademische Verlagsgesellschaft. Frankfurt a.M.