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CONSTRUCTION AND CALIBRATION OF A PERSONAL PASSIVE DOSIMETER FOR SAMPLING ORGANIC GASES AND VAPOURS IN BREATHING ZONE AIR

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Abstract. A personal passive dosimeter of the permeation type has been constructed for sampling organic gases and vapours in breathing zone air. In the dosimeter, paper coated with silicone rubber serves as a permeation membrane. The device has been calibrated for 14 organic substances. The experimentally determined sampling rate values for investigated compounds were independent of face air velocity and in almost all cases of compounds' concentration in the air. No difference between sampling rates for single compounds and their mixtures has been observed.

INTRODUCTION

The most reliable information on workers' exposure to toxic substances is based on the results of measurements in their breathing zones. Such measurements have been possible since the introduction of personal pumps, which placed on the worker's clothes can collect air samples from his breathing zone over the entire period of exposure. Recently, a new personal sampling technique — passive sampling — has grown in popularity among industrial hygienists. The major features of a personal passive dosimeter are determined by the components of its name; personal, because it can be worn by the worker in close proximity to his breathing zone; passive, because no forced air movement is required and collection of toxic substances is due to passive diffusion; and dosimeter, because it provides quantitative information on the magnitude of the exposure. The device is very simple, light, inexpensive and its application is free of any calibration and maintenance problems.

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Passive dosimetry is based on a diffusion of gas or vapour through a stagnant air layer or through a membrane into an absorbent bed. The first quantitative device utilizing passive diffusion was described by Palmes and Gunnison in 1973 (6). Since that time, several types of dosimeter for different classes of compounds, and following different construction patterns, have become commercially available.

The theory and practical aspect of passive dosimetry have been described in detail in several review papers (1—4, 9, 10).

The purpose of this study was to construct a passive dosimeter for collecting organic gases and vapours from breathing zone air and to calibrate it for several classes of compounds, mostly organic solvents.

MATERIALS AND METHODS

1. Construction of a passive dosimeter

The authors decided to develop a permeation type dosimeter in order to minimize the influence of environmental parameters (temperature, humidity, air velocity etc.) on sampling performance. As a collecting medium, activated charcoal based sorbent in the form of pellets or strips seemed to be preferable. Granulated charcoal, although convenient to handle, could not be accepted as it causes occasional perforations in the membrane material.

The designed passive dosimeter is shown in Fig. 1. It consists of a polypropylene body, on which a sorbent pellet (activated charcoal pressed with silicone polymers) is placed. A membrane (paper impregnated with silicone rubber) is put on the sorbent and all screwed

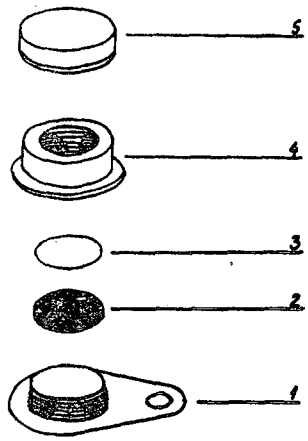

Fig. 1. Schematic of a passive dosimeter. 1 — dosimeter's body, 2 — sorbent pellet, 2 — membrane, 4 — ring nut, 5 — cap.

together to the sampler body by a plastic ring nut. The non-exposed sampler is protected by a plastic cap.

A silicone rubber impregnated paper was selected from other investigated membrane materials (cellulose acetate, silicone rubber, combinations of silicone rubber and chromatographic supports) as providing an adequate sampling rate and good reproducibility of results.

2. Calibration of passive dosimeters

In diffusion type dosimeters, mass transfer or sampling rates of investigated compounds can be calculated from the geometrical parameters of the dosimeter and diffusion coefficient (literature data) according to Fick's First Law of Diffusion (11). For permeation type devices, however, the permeation constant or sampling rate values for any substance should be determined experimentally by exposing the dosimeter under controlled conditions to known concentrations of the substance and determining the amount of collected material (5, 12). The value is characteristic for each substance and membrane material.

Testing and calibration of passive dosimeters was performed in a 14.5 l exposure chamber, in which known concentrations of investigated solvents were produced by a flow-dilution system. Known amounts of solvents were continuously injected by a low flow syringe pump into a controlled stream of clean air from a cylinder. The volume of solvent vapour — air mixture passing through the chamber — was controlled by precision valves. The concentration of a substance in the mixture was kept within $\pm 5\%$ of the required value. The temperature was 20°C and relative humidity 30%. The exposure chamber was equipped with a revolving plate whose speed could be controlled enabling study of the effect of air movement on the sampling rate if dosimeters on the plate were subjected to various rotation speeds.

Dosimeters (5—6 in a series) containing charcoal pellets were placed on the rotating plate in the chamber and then exposed to a known concentration of a substance or mixture of substances for three hours. Substances adsorbed in each dosimeter were desorbed with carbon disulfide and determined by gas chromatography (Varian 2800, USA).

The concentration of the substance in the chamber was measured every 30 minutes during each exposure by taking 1 dm^3 air samples (charcoal tubes connected to SKC personal pumps). Collected vapours were desorbed with carbon disulfide, analyzed by gas chromatography and mean concentration of the substance calculated. In addition, one continuous air sample was taken over the entire exposure period.

Passive dosimeters were tested for 14 substances, representing the most frequently used industrial organic chemicals: benzene, toluene, m-xylene, ethyl acetate, n-propyl acetate, dichlorethane, dichlorpropane, trichlorethylene, tetrachlorethylene, vinyl chloride, cyclehexane, n-butanol, white spirit and extraction naphta. The influence of air movement, concentration of the compound, and presence of other compounds after collection by passive dosimeters or sampling rate, were also investigated.

RESULTS AND DISCUSSION

Examples of the relationship between the amount of a substance collected in a dosimeter and its concentration in chamber air are presented for white spirit in Fig. 2 and for cyclohexane in Fig. 3. Collected amounts were directly proportional to concentration. The sampling rate (SR), calculated from the experimental data according to the formula:

$$SR = \frac{m}{c \cdot t}$$

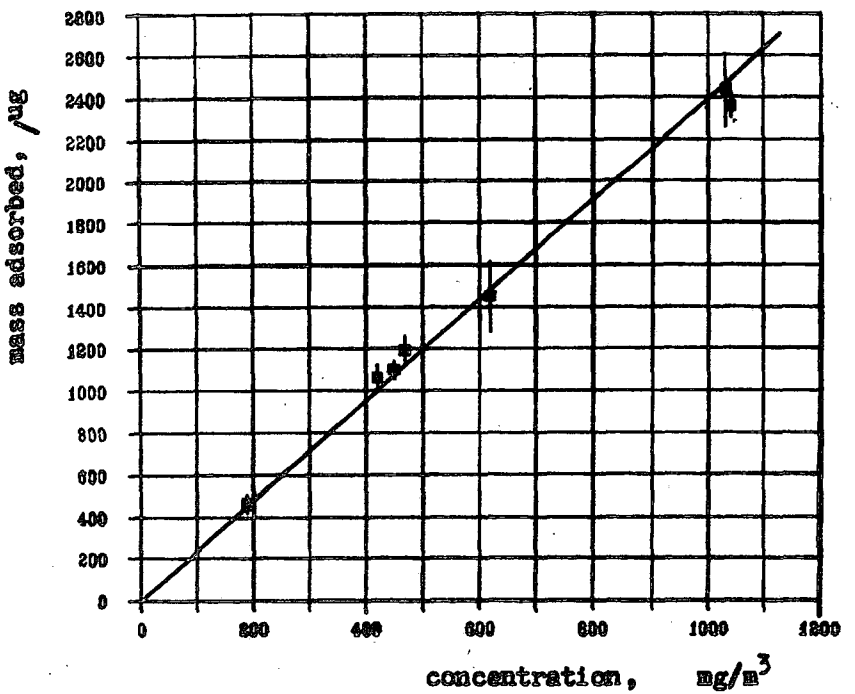

Fig. 2. The relationship between white spirit vapours collected in the dosimeter during 2 h exposure and its concentration in the air.

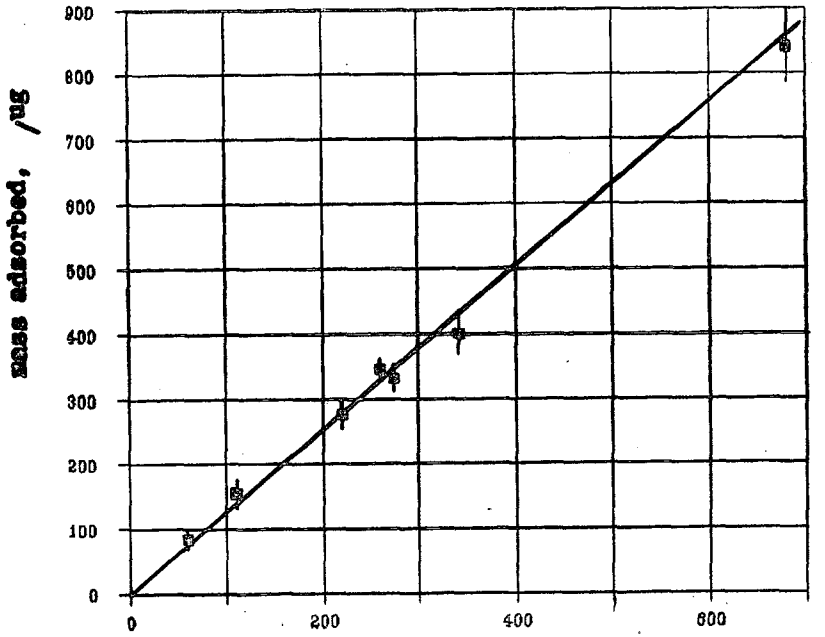

Fig. 3. The relationship between cyclohexane vapours collected in the dosimeter during 2 h exposure and its concentration in the air.

where: m — amount of the substance collected in the dosimeter
c — concentration of the chamber exposure
t — time of exposure

was independent of concentration within the investigated range, the mean values amounting to 20.6 cm^3/min (RSD = 0,072) for white spirit and 10.3 cm^3/min (RSD=0,105) for cyclehexane respectively. Similar results, indicating independence of concentration sampling rates, were obtained for all other substances, except butanol, for which lower efficiency of collection in the dosimeter was observed at higher concentrations, as shown in Fig. 4.

The dosimeters were tested under selected air velocity conditions. Air velocity at the face of the dosimeter was set at 26.7 cm/s or at 44.5 cm/s; no influence on the sampling rate for any substance was observed.

As mentioned above, differences between sampling rate values obtained for the same substance at different concentrations and air velocity were very small; it was necessary, however, to check whether they were statistically significant. This was done according to the procedure proposed by Remington and Schork (8) for differences between

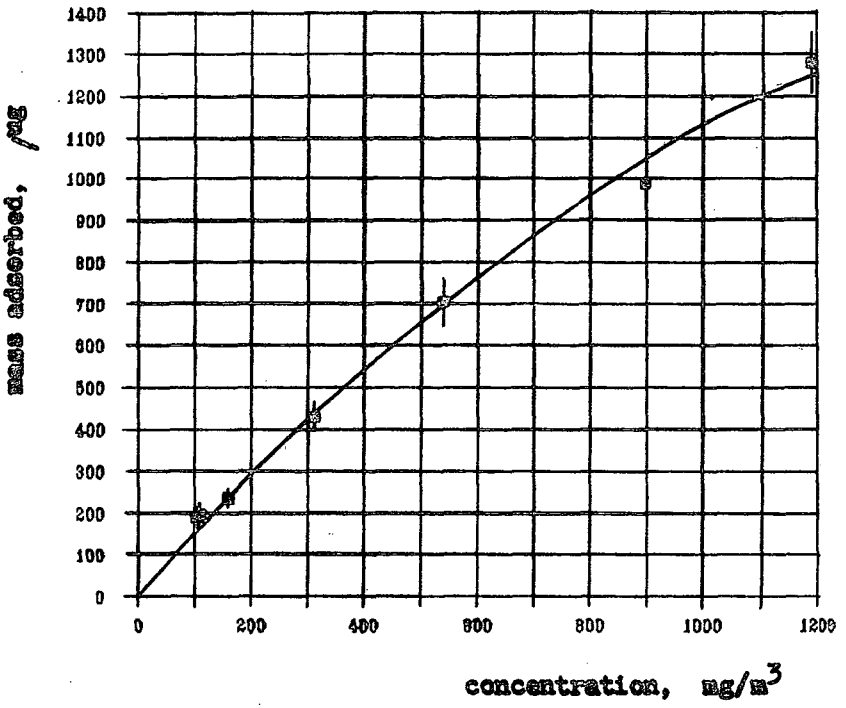

Fig. 4. The relationship between butanol vapours collected in the dosimeter during exposure and its concentration in the air.

the means, where variances are unknown and unequal. Statistical analysis proved that differences between the values for the same compound at different conditions were not statistically significant at the 0.95 confidence level. For butanol this statement is valid for concentrations below 300 mg/m³ (3 hour exposure); at higher concentrations the sampling rate decreases.

Differences between sampling rate values determined for single compounds and their mixtures were also statistically insignificant at the 0.95 confidence level. For instance the sampling rate for toluene was 21.9 cm³/min (SD = 0.96, n = 12) for a single compound and 22.7 cm³/min (SD = 1,8, n = 45) when toluene vapours were mixed in the chamber with m-xylene vapours. It indicated that the substance was effectively collected by the dosimeter in the presence of other compounds at a rate not affected by their influence. Of course, other substances present would also be absorbed into the dosimeter at rates characteristic for each compound. Independence of the sampling rate of air velocity and the presence of other compounds was in agreement with reported data for permeation type dosimeters (5, 7, 9, 12).

Since no significant difference in the values of the sampling rate for one substance determined under different conditions was found, all experimental data for this substance can be regarded as belonging to the same population, and the mean sampling rate can be calculated from all obtained results. The determined mean sampling rates for 14 investigated compounds are presented in Table 1. Good reproducibility of

TABLE 1. Determined values of sampling rates for selected compounds in the constructed passive dosimeter

Substance	mean sampling rate (cm^3/min)	RSD (relative standard deviation)	n	maximum concentration tested (mg/m^3)
benzene	24.6	0.033	42	150
toluene	22.7	0.083	45	800
m-xylene	23.4	0.091	45	130
ethyl acetate	16.8	0.105	42	150
n-propyl acetate	17.3	0.109	42	160
dichlorethane	19.0	0.057	48	210
dichlorpropane	19.2	0.052	48	200
vinyl chloride	18.1	0.069	35	80
trichlorethulene	20.2	0.095	42	150
tetrachlorethylene	21.4	0.090	42	140
cyclohexane	10.3	0.105	42	600
n-butanol	12.9	0.096	24	300*
white spirit	20.6	0.072	42	1040
extraction naphta	19.6	0.065	36	1100

* for concentrations 300—1200 mg/m^3 the relationship between butanol and adsorbed-butanol concentration in air was not linear.

calibration results in the series of experiments (relative standard deviation below 0.1) indicates that constructed passive permeation dosimeters may be regarded as quantitative devices for taking breathing zone air samples. The experimentally determined values of the sampling rates of selected substances should be treated as dosimeter constants, enabling calculation of the concentration of exposure from the amount of a substance collected in the dosimeter and time of exposure.

The term "sampling rate" may be somewhat confusing from the theoretical point of view, since in passive dosimetry no air is in fact drawn through the dosimeter itself. The units of the calibration coefficient, however, cm^3/min, are exactly the same as for the sampling rate in traditional, active air sampling methods. The physical sense of sampling rate in passive dosimetry may be explained as the volume of air from which the sampled substance diffuses to the sorbent in a unit of time.

Listed in Table 1 are the upper values of concentrations of substances at which dosimeters were calibrated; these do not limit application of dosimeters. Charcoal pellets possess an absorption capacity

enabling continuous 8-hour sampling at concentrations even three or more times exceeding actual Maximum Allowable Concentration (MAC) values. In the case of toluene, for instance, dosimeters exposed for 8 hours at the concentration of 1800 mg/m^3 collected amounts of toluene vapour still within the linear range of the device and in good accordance with the determined sampling rate. Only for butanol the determined sampling rate may be applied only for 8 hour sampling at a concentration not exceeding 120 mg/m^3 (or shorter sampling at higher concentrations). Quantitative interpretation is, however, possible for higher exposures from the calibration graph butanol vapour collected vs air concentration x time.

CONCLUSIONS

1. The proposed construction of a permeation-type passive dosimeter with silicone rubber impregnated paper as a membrane was proved to be a convenient device for collection of breathing-zone air samples.

2. The elaborated sorbent, obtained by pressing activated charcoal with silicone polymers, traps efficiently organic vapours and gases entering the dosimeter by diffusion through the membrane.

3. The experimentally determined calibration constants — sampling rates — enable evaluation to be made of workers' exposure in industry to benzene, toluene, m-xylene, ethyl acetate, n-propyl acetate, dichlorethane, dichlorpropane, trichlorethylene, tetrachlorethylene, vinyl chloride, cyclehexane, n-butanol, white spirit and extraction naphta.

4. Independence of the determined sampling rate values of a compound's concentration and air velocity is of great practical importance for measurements in work environment.

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