A METHOD FOR THE DETERMINATION OF TRINITROTOLUENE IN AIR

BY

J. MACKAY, K. W. HOLMES, and R. E. WILSON

From the Ministry of Supply

(RECEIVED FOR PUBLICATION MARCH 5, 1957)

Properties of Trinitrotoluene

Trinitrotoluene is the high explosive used as a main bursting charge in shells, mines, and bombs.

It is a potent poison for the liver, blood, and blood-forming organs, and fatalities have been recorded from toxic anaemia, toxic jaundice, and acute yellow atrophy of the liver. From 1916 to 1918 there were notified 403 cases of toxic jaundice, 105 (26%) being fatal, and 15 cases of toxic anaemia, all of which were fatal. In the second world war, toxic jaundice cases numbered 116, with 25 deaths (21.5%), and toxic anaemia cases 24, with 15 deaths. These figures take no account of the lesser degrees of intoxication where further deterioration was halted by timely intervention.

2:4:6-Trinitrotoluene is one of six isomers, and has the formula $C_6H_2(NO_2)_3CH_3$. It is obtained by nitration of the coal-tar product toluene and melts at 81 to 82° C. It is practically insoluble in water, but is soluble in fat and many organic solvents. The vapour pressure at room temperature is very low. Nevertheless, according to *Occupation and Health* (International Labour Office, 1934), it is capable in the dry state of giving off fumes into the atmosphere at a temperature as low as 32° C. Furthermore, the low vapour pressure means that any vapour arising from hot melted trinitrotoluene will readily condense into fume on meeting cooler air and collect as a fine powder on any surface colder than 70° C. Air pollution is for all practical purposes in the form of suspended solids.

Inhalation is by far the most important mode of entry to the body. Stewart, Witts, Higgins, and O'Brien (1945), in observations on persons exposed to contact of different kinds, found that the greatest effects occurred in those who were working in melt houses where there was the most intense exposure to fume. The maximum allowable concentration for an eight-hour day and with a normal amount of physical effort is fixed in America at 1.5 mg. per

cubic metre of air. In this country, however, it has generally been accepted that a figure of 2 mg. is permissible. These figures, of course, are always capable of modification when the nature of the work differs from average conditions.

Factors Influencing Dosage

Physical Exertion.—The maximum allowable concentration figures are calculated on the basis of an ordinary amount of physical exertion. When effort is intensified, as by frequently going up and down stairs, or by having to carry heavy loads, pulmonary ventilation is greatly increased. If this should coincide with periods of unduly heavy air contamination the worker will be exposed to the risk of inhaling a much greater quantity of dust and fume.

Davies (1952), in reviewing recent work on the alveolar retention of dust particles, concludes that the maximum retention—which is between 50 and 60% of the dust inhaled—occurs with particles of 1.5 to 2 μ diameter, and that the proportion of 5 μ particles retained falls to about 30% or less. It is generally agreed that still larger particles are for the most part held up in the upper respiratory tract and are rejected by the action of ciliated epithelium, but a fair proportion of these may ultimately be swallowed, and so, as far as trinitrotoluene is concerned, contribute to the effect of its toxicity.

Warner and Chrenko (1943) made some observations on particle size distributions of trinitrotoluene dust in filling shops. They found no particles larger than 5 μ in diameter and nearly all the particles measured were less than 2 μ in size. If this evidence be accepted, it follows that practically the whole of trinitrotoluene dust and fume may be considered as coming within the respirable range. If so, it becomes unnecessary to insist on isokinetic conditions when it comes to air sampling. Also mass concentration can be taken as a reasonably good

measure of the inhalation hazard. Some confirmation of this view is afforded by experiments carried out in 1944 to determine the amount of air-borne trinitrotoluene retained and expired by workers. Using a modified service respirator, it was found that on an average 76% of the trinitrotoluene originally in the inspired air was retained within the body, whether breathing was by nose or mouth. Similar figures have been obtained in other dusty occupations for particles of the same size (van Wijk and Patterson, 1940).

Ventilation.—This prevalence of dust and fume of a dangerous respirable character demands adequate ventilation. Trinitrotoluene is a powerful explosive, so that the shops in which it is handled are all surrounded by high earth banks and blast walls. These very materially reduce natural ventilation. Since all shops are not necessarily treated alike it is not impossible to have two of similar construction, carrying out identical processes, and yet varying markedly in the degree of air pollution. Weather conditions contribute to the difficulties, and there may be alterations almost from hour to hour. Changes of wind direction are not so important as the effects of the protective banking, but rises in temperature and in relative humidity are both capable of leading to noticeable variations. Within the shops the distribution of dust and fume is by no means uniform. The highest concentrations are generally found in the upper levels. Investigations in 1952 demonstrated that in enclosed spaces there was a tendency for trinitrotoluene to exist in the atmosphere in strata, so that it was quite possible to find a layer rich in dust and another layer poor in dust relatively close to each other.

The processes themselves and the layouts in the shops vary. The exposure of workers can vary according to the stage of the cycle of work on which they are engaged, and it is essential to evaluate concentrations at different points within the shop. The efficiency of local exhaust ventilation is necessarily subject to the over-riding demands of safety from explosion. Moreover, on occasion, the technical requirements of the process are such that it is imperative to maintain the shop temperature at a fixed level for a period and every effort is then made to exclude all draughts from outside. On such occasions ventilation is virtually non-existent. When night shifts were worked and blackout regulations observed, ventilation was further restricted. Observations made during the second world war showed that the concentration of air-borne trinitrotoluene in filling shops was often four or more times as high under blackout conditions as during day operations.

Description of Sampler

The problem of controlling the hazard is basically the prevention of air pollution. This means having a simple method of estimating the concentration of air-borne trinitrotoluene. It must be of an acceptable degree of accuracy, and it must be completely safe, because of the explosive risk. Earlier methods had included the use of the DSIR hand-pump (DSIR Leaflet No. 5, Nitrous Fumes, 1940), along with a varying choice of solvents—solid naphthalene pellets, acetone, different alcohols, a mixture of cyclohexanone and methyl ethyl ketone, and 2-diethylaminoethanol. A variety of reasons precluded the adoption of any one of these procedures as being completely satisfactory. In particular, it was desired to use an automatic means of obtaining the air samples. Because of the risk of explosion an electric motor and vacuum pump could not be used, and recourse was had at first to a water suction pump, with a gas meter to measure the volume of air sampled. But a source of water power was not always sufficiently convenient, and inordinate lengths of rubber tubing frequently became necessary. To overcome these difficulties the collecting unit to be described was evolved by the Chemical Inspectorate and Engineering Departments of R.O.F., Chorley, Ministry of Supply.

Basically, the principle is that of an egg-timer (Fig. 1). The unit consists of two large glass aspirators (*A*) one above the other, interchangeable and interconnected, so that when the known volume of water from the top one is allowed to drain into the lower one an equal volume of air is drawn into the top aspirator. An adjustable assembly (*B*) for containing an absorption train (*C*) (Fig. 2) is fitted, together with a revolution counter (*D*) to record the number of times, during a run, that the aspiration positions are reversed. A small glass cylinder (*E*) (Fig. 4) is fitted to the water outlet of each aspirator in order to ensure a sudden cessation of suction in preference to the gradual decrease which is normally evident. The complete apparatus is tested and calibrated, the rate of suction being controlled by a valve (*F*) (Fig. 3) connected to the suction outlet of the apparatus. The volume of air drawn through the system by each aspirator varies according to the rate of air flow. This is because the reduction in pressure when the water flow rate is increased is not fully compensated by the increase in bubble rate. Since, on completion of the cycle, the internal pressure is automatically equilibrated with atmospheric pressure, the total volume of air entrained is less per cycle than at lower flow rates. Ideally, a very slow flow rate would give the maximum volume entrained per cycle. In practice the flow is maintained at an approximately constant rate of 1 to 2 cubic feet per hour (faster rates tend to cause splashing in a bubbling tube that contains a sintered disc of G.I porosity) so that the variation is insignificant, provided the apparatus is calibrated at this particular flow rate. The usual practice is to reverse the aspirations about 10 times over a period of 45 to 60 minutes. The total volume of air sampled is usually around 1½ to 2 cubic feet (40 to 56 litres). The absorption train consists of two absorption vessels, inter-connected by polythene tubing (*G*) and attached to the main apparatus by rubber tubing (*H*). The first vessel has the sintered glass plate (*I*)

FIG. 2.—Sketch of the arrangements in the absorption train (Fig. 1).

A = Polythene tubing
B = Air intake
C = G.I sinter
D = Solvent

FIG. 3.—Sketch of the arrangements in the inlet valve F (Fig. 1).

A = Suction
B = Water flow
C = Pressure release

FIG. 1.—The Chorley entraining unit.

A = Aspirator
B = Adjustable assembly
C = Absorption train
D = Revolution counter
E = Glass cylinder
F = Inlet valve
G = Polythene tubing
H = Rubber tubing
I = First vessel, with sintered glass plate
J = Second vessel

FIG. 4.—The water outlet tube of the aspirators with the cylinder surrounding it to ensure sudden cessation of suction.

(G.I porosity) to break up the air current and present as large a surface as possible to the solvent. The second vessel (*J*) is only a guard tube, and, in air concentrations of trinitrotoluene so far dealt with, has not been found necessary. The apparatus is very simple to use. It is set up wherever sampling is required, the absorption tubes filled with solvent (2 to 8 ml.), the adjustable arm is fixed at whatever point is desired, and suction is begun and continued by reversing the aspirators in turn at whatever rate of flow is wanted. The volume of air sampled throughout the test is calculated by multiplying the apparatus constant by the figure shown on the revolution counter. As a rule, this is about 1.5 cubic feet of air.

The solvent is ethylene glycol monoethyl ether ("cellosolve") which must be peroxide-free. It is claimed to give more accurate results than cyclohexanone/methyl

ethyl ketone and to permit a much more rapid determination than 2-diethylaminoethanol. Holmes and Wilson (1955) showed that the colour of the violet solution obtained after adding alkali is linearly related to concentrations of trinitrotoluene up to 16 $\mu\text{g.}$ per millilitre of solvent. Colour fading is not important, provided that the alkali is added after absorption of the trinitrotoluene in the solution, and the estimation made within an hour of adding the alkali. The moisture content of the air drawn through the sample was found to have no serious effect on the results.

The solvent is transferred from the bubbling tube to a 10-ml. glass-stoppered measuring cylinder, and 0.1 ml. of a 25% solution of potassium hydroxide added to produce a clear violet colour. The mixture is then made up to 10 ml. by the addition of ethylene glycol monoethyl ether which has been used to wash out the absorption tube. After shaking thoroughly, it is allowed to stand for 15 minutes before colorimetric estimation. Should the test sample produce too deep a colour, it may be diluted with ethylene glycol monoethyl ether, but the potassium hydroxide concentration must be maintained at 0.1 ml. of 25% potassium hydroxide per 10 ml. of sample.

Air samples can be taken as and when required, and can be submitted at leisure to colorimetric estimation. A Hilger photo-electric absorptiometer is used fitted with a tungsten filament lamp and "calorex" heat-resisting filters No. H.503. Using 1 cm. cells and Ilford 604 green filters, it is set at 1.0 with water against a blank consisting of ethylene glycol monoethyl ether plus 0.1 ml. of 25% potassium hydroxide per 10 ml. of solvent. A graph is prepared by measuring the estimation of a series of standards containing 2, 4, 8, 12, and 16 micrograms of trinitrotoluene per millilitre of solvent. From this graph and a knowledge of the volume of air sampled, the atmospheric trinitrotoluene concentration can be calculated.

By selecting a suitable solvent the apparatus can be used for determining the concentration of other air-borne contaminants, as has been done with tetryl.

Permission to publish this paper has been granted by the Ministry of Supply and our thanks are also due to Dr. T. Bedford for advice on its preparation.

REFERENCES

- Davies, C. N. (1952). *Brit. J. Industr. Med.*, 9, 120.
 Holmes, K. W., and Wilson, R. E. (1955). Ministry of Supply. Chemical Inspectorate Report No. 102.
 International Labour Office (1934). *Occupation and Health*. Geneva.
 Stewart, A., Wits, L. J., Higgins, G., and O'Brien, J. R. P. (1945). *Brit. J. Industr. Med.*, 2, 74.
 Warner, C. G., and Chrenko, F. A. (1943). Personal communication.
 Wijk, A. M. van, and Patterson, H. S. (1940). *J. Industr. Hyg.*, 22, 31