MDHS 4
Methods for the Determination of Hazardous Substances

May 1986

Generation of test atmospheres of organic vapours by the permeation tube method

Apparatus for laboratory use

Health and Safety Executive: Occupational Medicine and Hygiene Laboratory

INTRODUCTION

1 Organic vapours are, in general, toxic and may also be flammable. Handle pure chemicals and concentrated solutions in a ventilated fume cupboard. The apparatus or vapour exit should be placed in a ventilated fume cupboard or suitably vented to outside atmosphere. Consult suitable source references for toxicity and first-aid advice.

SCOPE

2 This method is suitable for the generation of atmospheres of low- to medium-boiling liquids at the vol. ppm level and below. A 1 ppm atmosphere may be generated at rates of the order of 1 litre/min. Lower concentrations may be generated by dilution of the atmosphere.

Construction

3 The permeation device is a sealed polytetrafluoroethylene (PTFE) tube containing the test liquid. The device is housed in a thermostatted glass vessel. Diluting air is supplied in a glass system with ball and socket joints.

Accuracy

4 Assuming there are no leaks and the (dynamic) system has reached equilibrium, there are three main sources of error:

Temperature control

5 This should be better than ± 0.1°C. A temperature change of 0.1 results in a change in permeation rate of about 1%.

Weighing

This should be done under conditions of constant temperature and humidity.

Airflow

7 If rotameters are used, these have a specified precision of 1% measured as a relative standard deviation, provided temperature and pressure corrections are made.

Stability

8 After an initial stabilising period of the order of one week, provided temperature and primary airflow are kept constant, a stable atmosphere should result. Transient variations over time periods of the order of a few days may occur but are probably mostly accountable for in the variation of weighing conditions. After equilibration, stability is expected to be better than ± 5% (relative standard deviation) for the primary flow.

PRINCIPLE

9 The test liquid permeates through a PTFE membrane into an air or gas stream under controlled conditions.

10 The concentration of the generated atmosphere may be reduced by means of a second dilution stage.

11 The concentration of the generated atmosphere is calculated from the weight loss of the permeation device and the total dilution air volume.

REAGENTS

Compressed air

12 A compressor or compressed air cylinder may be used. The air should be filtered and purified before use.

Test liquid

13 This should be analytical grade of known purity.

APPARATUS

Permeation tube

14 The permeation tube consists of a short length (100mm) of 6.3mm OD PTFE tubing sealed at one end with a stainless steel ball of about 1½ times the diameter of the tube. The tube is filled two-thirds full

of test liquid and the open end sealed with a secondary ballbearing.

Thermostatted chamber and diluting air

15 The permeation tube chamber (essentially a waterjacketed condenser) and tubing and dilution chambers down-flow are constructed of borosilicate glass. Connecting tubing should be at least 9mm ID to minimise resistance to air flow. Joints are all ball and socket. Pressure regulators, needle valves, on-off valves and an air filtration and purification unit are required.

PROCEDURE

16 Place a freshly prepared permeation tube in the thermostatted chamber maintained at a constant temperature in the range 25 to 40°C.

17 Connect up the ancillary equipment as illustrated in Fig 1.

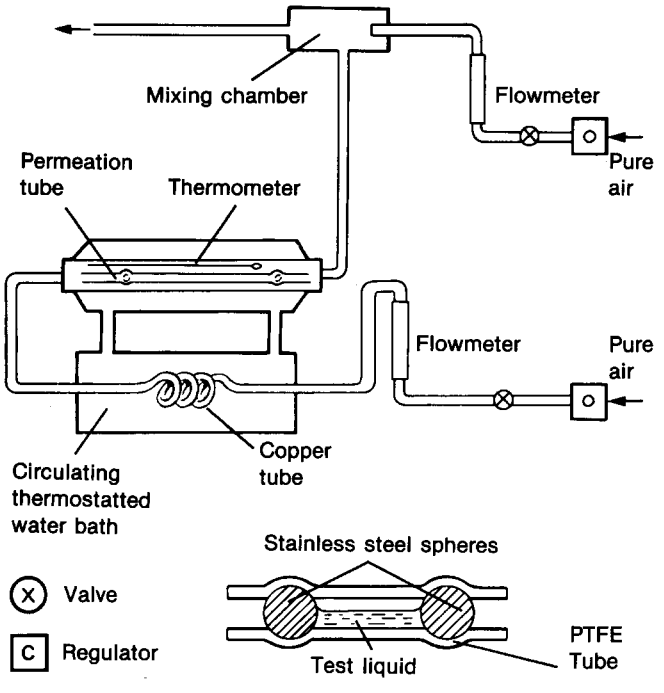

Fig 1 *Permeation tube*

18 Connect up the thermostatted chamber to the air supply and adjust the flow rate through the chamber to 100 ml/min.

19 Allow the system to stabilise over a period of at least one week.

20 Remove the tube and weigh on a five decimal place balance and weigh to ± 50 μg or better on a balance calibrated with test weights traceable to a recognised standard. Replace the tube in the thermostatted chamber. Repeat weighings at weekly intervals or at such time periods that the measured mass loss is at least 10mg. These weighings should ideally be carried out under the same environmental conditions (with respect to temperature and humidity) in which the tube is operated. Thermal shock and adsorption of water vapour during the weighing procedure must be avoided.

21 The concentration of test vapour at the exit point may be varied by means of the second dilution air flow. As an alternative to the arrangement shown in Fig 1, only part of the primary atmosphere could be diluted.

22 A number of methods are available for generating standard atmospheres, including others described in this series.[1] The use of other methods not included in this series is acceptable provided they have the accuracy and reliability appropriate to the application.

23 The Health and Safety Executive wishes, wherever possible, to improve the methods described in this series. Any comments that might lead to improvements would therefore be welcome and should be sent to the above address.

CALCULATIONS

24 The concentration of the generated atmosphere is

$$C = \frac{Q}{q} \times 10^3$$

where C = concentration of test vapour at exit point (mg/m^3)

Q = permeation rate (ng/min)

q = total dilutent gas flow (litres/min)

25 Alternatively, concentrations may be expressed by volume (ppm) where concentration (ppm) = concentration (mg/m^3) x $\frac{24.45}{MW} \times \frac{760}{P} \times \frac{T}{298}$

where 24.45 = molar volume (litres/mole) at 25°C and 760mm Hg

MW = molecular weight

T = experimental temperature K

P = experimental pressure (mm Hg)

ADVICE

Advice on this method and the equipment used may be obtained from the Health and Safety Executive, Occupational Medicine and Hygiene Laboratory, 403—405 Edgware Road, London NW2 6LN (telephone 01-450 8911).

Permeation tubes for some organic materials and portable thermostatted air-bath devices (as an alternative to the water bath described) are available commercially.

REFERENCES

1 Health and Safety Executive. Methods for the Determination of Hazardous Substances. *Generation of test atmospheres by the syringe injection method.* MDHS 3. HSE: London, 1981.

OTHER USEFUL REFERENCES

Health and Safety Executive. Methods for the Determination of Hazardous Substances Series. HSE: London.

American Public Health Association Intersociety Committee. *Methods of Air Sampling and Analysis.* (2nd Ed.) Ed. M. Katz. APHA: Washington DC, 1977.

Chemical Industries Association. *Permeation Tube Calibration.* Draft Analytical Note DAN 2. CIA: London.

Kirk-Othmer. *Encyclopedia of Chemical Technology.* Eds H F Mark *et al.,* 3rd Edition. Wiley — Interscience: New York, 1978.

Manufacturing Chemist's Association. *Chemical Safety Data Sheet* (various). MCA: Washington DC.

National Institute for Occupational Safety & Health. *Criteria for a Recommended Standard for Occupational Exposure to ...* (various). DHEW (NIOSH) Publication.

National Institute for Occupational Safety & Health. *Registry of Toxic Effects of Chemical Substances.* DHEW (NIOSH) Publication Nos 78-104A and 78-104B. 1977 Edition, 1978.

O'Keefe, AE and Ortman, GC. Primary Standards for Trace Gas Analysis. *Analyt. Chem.* 38 (1966) 760.
Patty, FA *Industrial Hygiene and Toxicology. Vol. 2: Toxicology.* Eds DW Fassett and DD Irish. 2nd Edition. Interscience: New York, 1963.

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