

# MIDHS

## *Methods for the Determination of Hazardous Substances*

Health and Safety Laboratory



# 94

## Pesticides in air and/or on surfaces

Methods for the sampling and analysis of pesticides in air and/or on surfaces, using pumped filters/sorbent tubes and gas chromatography

February 1999

### Requirements of the COSHH Regulations

1 The Control of Substances Hazardous to Health (COSHH) Regulations<sup>1</sup> require assessment of the health risk created by work involving substances hazardous to health, and to prevent or control exposure to such substances. The COSHH Regulations also require that persons who may be exposed to substances hazardous to health receive suitable and sufficient information, instruction and training. Employers should therefore ensure that the requirements of the COSHH Regulations are fully satisfied before allowing employees to undertake any procedure described in this MDHS. Guidance is given in the Approved Codes of Practices (ACOP) for the Control of Substances Hazardous to Health, the General COSHH ACOP, and the Control of Carcinogenic Substances, the Carcinogens ACOP, which are included in a single publication with the COSHH Regulations.<sup>2</sup> This includes assessment of the risks in sampling pesticides.

### Definition

2 Unless otherwise stated, reference to 'pesticides' in this method includes compounds that can be present in both agricultural and non-agricultural formulations. These species may be present as either a vapour or a mixture of vapour and airborne particles.

### Properties and uses

3 The term *pesticides* has a very broad definition which embraces herbicides, fungicides, insecticides, rodenticides, soil-sterilants, wood preservatives and surface biocides among others. It can also include substances like growth regulators, defoliants, desiccants, fumigants and repellents/attractants.

4 Pesticides are used to reduce crop loss from disease and pest (plant and insect) attack, both before and after harvest. They are also used for public health to control various human pests and disease carriers. By the very nature of these functions, pesticides are released into occupied environments. A more complete definition and

details of pesticides which fall outside the scope of the legislation is given in Regulation 3 of the Control of Pesticides Regulations 1986.<sup>3</sup>

### Health effects

5 Pesticides are substances hazardous to health, designed to control pests, and should be treated as such. There are many possible complex symptoms resulting from exposure. They may cause symptoms such as headaches, dermatitis, muscle twitches, allergies, reproductive damage, cancer and even death. A recent review has put pesticide poisoning in perspective: 'The primary hazard of pesticide exposure is the development of acute toxic reactions as a result of dermal contact with, or inhalation of, a relatively large dose'.<sup>4</sup> Over-exposure by skin contact or breathing in pesticides can lead to toxic effects.

6 It is a requirement under RIDDOR that any cases of poisoning by pesticides must be reported without delay to the nearest office of the Health and Safety Executive (see Appendix 4).

### First aid

7 Measures appropriate in cases of suspected poisoning include:

- remove any protective or other contaminated clothing (taking care to avoid personal contamination);
- wash any contaminated areas carefully with water or with soap and water if available;
- in cases of eye contamination, flush with plenty of clean water for at least 15 minutes;
- lay the patient down, keep at rest and under shelter. Cover with one clean blanket or coat etc;
- avoid overheating;

- monitor level of consciousness, breathing and pulse-rate;
- if consciousness is lost, place the casualty in the recovery position (on their side, tilt the head back to ensure the airway remains open). Ensure that the mouth is clear of obstructions such as false teeth, that the breathing passages are clear, and that tight clothing around the neck, chest and waist has been loosened;
- DIAL 999 FOR AN AMBULANCE;
- monitor and record breathing and pulse every ten minutes until help arrives;
- if breathing ceases commence mouth to mouth resuscitation immediately, placing the casualty on their back. If a poisonous chemical has been swallowed, it is essential that the first aider is protected by the use of a resuscitation device;
- if there is no pulse commence chest compressions immediately, placing the casualty on their back.

### Exposure

8 Exposure to pesticide concentrates (often in organic solvent) is a greater risk than is exposure to dilutions in water for application. Splashes of concentrate on the skin should be avoided, whereas contamination by spray is of less concern.

### Exposure limits

9 A fundamental requirement of the COSHH Regulations is that exposure of employees to substances hazardous to health should be prevented or adequately controlled. Exposure by inhalation is a hazard, and in order to set standards for control of exposure by this route, various substances have been assigned occupational exposure limits.

10 There are two types of occupational exposure limits defined under COSHH: Occupational Exposure Standards (OES) and Maximum Exposure Limits (MEL). The key difference is that an OES is set at a level at which there is no indication of risk to health; for an MEL a residual risk may exist and the level takes socio-economic factors into account. In practice, MELs have been most often allocated to carcinogens and to other substances for which no threshold of effect can be identified and for which there is no doubt about the seriousness of the effects of exposure.

11 OESs and MELs are set on the recommendations of the Advisory Committee on Toxic Substances (ACTS). Full details are published by HSE in EH 40/98 *Occupational exposure limits 1998*.<sup>5</sup>

12 As far as pesticides are concerned, OESs and MELs have been set for relatively few active substances. This is partly because pesticide products usually contain

other substances in their formulation, including solvents, which may have their own OES/MEL.

### Analytical methods

13 This is not a 'reference' method in the strict analytical sense of the word. There may be alternative methods available for the determination of a particular analyte. With the exception of a few cases, where an exposure limit is linked to a specific method (eg rubber fume or asbestos), the use of methods not included in the MDHS series is acceptable provided that they have been shown to have the accuracy and reliability appropriate to the application.

14 This method has been validated to demonstrate that it is capable of meeting the stated performance parameters for the method.

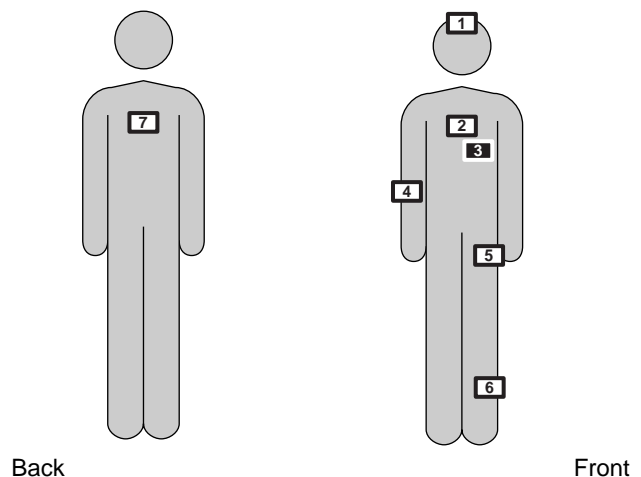
### PRINCIPLE

#### Air sampling

15 A measured volume of air is drawn through a 25 mm GF/A filter contained in a sampling head. A glass 'NIOSH' Tenax tube may be connected as a back-up, in series, to collect any of the more volatile pesticides which may pass through the filter (see paragraph 32). The sampling efficiency for particulate matter may be compromised if the filter/tube combination is employed, because flow rates lower than 2 l/min must be used. After sampling, the filter and tube packing is desorbed in either ethyl acetate or acetone for analysis. The resultant solutions are analysed using gas chromatography with mass spectrometric detection and quantified by comparison with a range of standard solutions.

#### Sampling potential dermal exposure

16 An estimate of dermal exposure is made by using 10 cm x 10 cm cotton gauze swabs, set in seven positions on the worker's outer clothing. The method used is modified from a protocol for field surveys of exposure to pesticides developed by WHO in 1982.<sup>6</sup>



- Position 1 On the hat as close as practicable to the top of the head
- Position 2 Over sternum on outside of normal clothing
- Position 3 On sternum, on inside of normal clothing
- Position 4 Upper surface of right forearm held with the elbow bent at right angles across the body, midway between elbow and wrist. On outside of normal clothing
- Position 5 Front of left leg, mid-thigh. On outside of normal clothing
- Position 6 Front of left leg, above ankle. On outside of normal clothing
- Position 7 On back between shoulder blades. On outside of normal clothing

17 To determine hand and foot contamination, thin cotton gloves and socks are worn under protective gloves and boots.

### SCOPE AND FIELD OF APPLICATION

18 The method described is for the determination of the time-weighted average inhalable concentrations of pesticides in workplace atmospheres. The method is suitable for sampling over periods in the range 10 minutes to 8 hours, with a concentration range from approximately 10 to 1000 µg/m<sup>3</sup> for samples of 10 litres of air.

19 This procedure is compatible with low flow rate personal sampling pumps and can be used for personal and fixed location sampling. It cannot be used to measure instantaneous or short-term fluctuations in concentration.

### Interferences

20 Organic components which have the same or nearly the same retention time as the analyte of interest during the gas chromatographic analysis will interfere. Interferences can be minimised by proper selection of chromatographic columns and conditions.

### Quality control

21 The procedure for spiked recoveries and storage stability tests described in this document acts as an internal quality control. This should be performed for every batch of filters and tubes. Analytical quality requirements, guidance on the establishment of a quality assurance programme and details of internal quality control and external quality assessment schemes are fully described in MDHS 71.<sup>7</sup>

### Detection limits

22 The detection limit for each individual pesticide will vary. A typical example would be that of carbaryl which has an OES of 100 µg/m<sup>3</sup> and a detection limit typically around 0.13 mg per sample. For a 10 l (20 min) volume air sample this corresponds to a detection limit of 13 µg/m<sup>3</sup>, and for a 240 l (8 hour) volume air sample this corresponds to a detection limit of 0.54 µg/m<sup>3</sup>.

### Overall uncertainty

23 The overall uncertainty has been calculated using the following CEN<sup>8</sup> definition for each batch of samples:

$$\text{Overall uncertainty} = |\text{Bias}| + 2 \times (\text{precision})$$

For this method the bias was calculated as the possible bias of the flow-meter (2%) and the average difference between the stated and analysed concentration of a series of pesticides of known concentrations (2%). The precision, as a coefficient of variation, was calculated using the pump precision (5%) and the average precision of the analysis of a series of pesticides (8%). This gives an overall uncertainty of 23%.

### Analytical recoveries

24 The pesticide mixture detailed at paragraph 28 was used for this study. The carbaryl OES (from EH 40/98) of 0.1 mg/m<sup>3</sup> was used as a benchmark for all the compounds in the mixture. Spiking was carried out at five levels; 0.1 (x OES), 0.5, 1.0, 2.0 and 10.0. The spiked sampling devices were prepared for analysis using the method described in paragraphs 56 to 58. The only exception in this case was that the spikes at 2.0 and 10.0 (x OES) were desorbed in 5 ml and 20 ml, respectively, instead of the standard 2 ml of desorbing solvent. The analytical range of these spikes was 50 to 500 ng/ml of each pesticide. At each analytical level, 6 GF/A filters and 6 Tenax tubes were loaded, desorbed and subsequently analysed. The data showing the mean analytical recoveries is shown in a back-up data report to this method.<sup>9</sup>

### Storage stability tests

25 Laboratory tests on filters and tubes spiked with the mixture detailed at paragraph 28 were used to monitor each pesticide's stability over a 14-day period. A single load level of 1.0 x OES was used for all devices, which were stored at room temperature. The stabilities were monitored on day 0 (the day of spiking), day 3, day 7 and day 14. The results are summarised in Appendix 1, Tables 1 and 2.

### REAGENTS AND STANDARDS

26 The method is suitable for a range of organic pesticide compounds, either singly or in mixtures, and the chromatograph should be calibrated with the compound or compounds of interest. A mixture of 27 organic pesticides is used as an example; these are arranged to give resolved peaks on a HP-5MS gas chromatography column.

### Mixture solvents

#### *Ethyl acetate and acetone*

27 These should be of residue analysis quality and must be free from compounds co-eluting with the compound or compounds of interest.

### Pesticide mixture

28 The representative mixture of pesticides (made up in ethyl acetate) which can be analysed directly by GC is shown over the page.

<i>Pesticide name</i>	<i>Formulae</i>	<i>Chemical group</i>	<i>Use</i>
Bifenthrin	$C_{23}H_{22}ClF_3O_2$	Pyrethroid	Insecticide
Bromopropylate	$C_{17}H_{16}Br_2O_3$	Benzilate	Acaricide
Bupirimate	$C_{13}H_{24}N_4O_3S$	Pyrimidine	Fungicide
Captan	$C_9H_8Cl_3NO_2S$	Dicarboximide	Fungicide
Carbaryl	$C_{12}H_{11}NO_2$	Carbamate	Insecticide
Chlorfenvinphos	$C_{12}H_{14}Cl_3O_4P$	Organophosphate	Insecticide
Chlorothalonil	$C_8Cl_4N_2$	Organochlorine	Fungicide
Chlorpyrifos	$C_9H_{11}Cl_3NO_3PS$	Organophosphate	Insecticide
Chlorpyrifos-Methyl	$C_7H_7Cl_3NO_3PS$	Organophosphate	Insecticide
Cypermethrin	$C_{22}H_{19}Cl_2NO_3$	Pyrethroid	Insecticide
Deltamethrin	$C_{22}H_{19}Br_2NO_3$	Pyrethroid	Insecticide
Dichlofluanid	$C_9H_{11}Cl_2FN_2O_2S_2$	Sulfamide	Fungicide
Dimethoate	$C_5H_{12}NO_3PS_2$	Organophosphate	Insecticide
$\alpha$ -Endosulfan	$C_9H_6Cl_6O_3S$	Organochlorine	Insecticide
$\beta$ -Endosulfan	$C_9H_6Cl_6O_3S$	Organochlorine	Insecticide
Endosulfan-Sulphate	$C_9H_6Cl_6O_4S$	Organochlorine	Insecticide
Fenoxycarb	$C_{17}H_{19}NO_4$	Carbamate	Insecticide
Iprodione	$C_{13}H_{13}Cl_2N_3O_3$	Dicarboximide	Fungicide
Lindane	$C_6H_6Cl_6$	Organochlorine	Insecticide
Metalaxyl	$C_{15}H_{21}NO_4$	Acyalanine	Fungicide
Omethoate	$C_5H_{12}NO_4PS$	Organophosphate	Insecticide
Permethrin	$C_{21}H_{20}Cl_2O_3$	Pyrethroid	Insecticide
Phosalone	$C_{12}H_{15}ClNO_4PS_2$	Organophosphate	Insecticide
Pirimiphos-Methyl	$C_{11}H_{20}N_3O_3PS$	Organophosphate	Insecticide
Tetradiphon	$C_{12}H_6Cl_4O_2S$	Organochlorine	Acaricide
Tolyfluanid	$C_{10}H_{13}Cl_2FN_2O_2S_2$	Sulfamide	Fungicide
Triazophos	$C_{12}H_{16}N_3O_3PS$	Organophosphate	Insecticide

## SAMPLING EQUIPMENT

### Swabs, gloves and socks

29 Cotton is the preferred fabric for all dermal sampling devices. If dermal sampling is to be used, all devices should be initially treated to a thorough cleaning process involving ultra-sonication in residue analysis grade acetone, and subsequent drying before undertaking any sampling strategy.

### Filters

30 Whatman 25 mm GF/A filters are used for this application. Care must be taken when handling these fragile filters. It is recommended that tweezers are used at all times when filters are to be transferred, eg between filter tin and sampling assembly.

### Pumped tubes

31 NIOSH-style Tenax tubes may be used. These consist of a glass tube with both ends flame sealed, 70 mm in length with 6 mm OD and 4 mm ID, containing two sections of 0.4-0.8 mm Tenax separated by a 2 mm portion of urethane foam. The sorbing section contains 30 mg of Tenax, and the back-up section contains 15 mg. A 3 mm portion of silylated glass wool is placed in front of the sorbing section. The pressure drop across the tube should be less than 3 kPa (25 mm of mercury) at an airflow of 0.5 l/min. The OSHA 'Versatile Sampler' (OVS) tube may also be suitable, but has not been evaluated by HSE for the present method. The tube is capable of sampling at a higher flow-rate than the Tenax tube, so may produce some improvement in sampling efficiency.

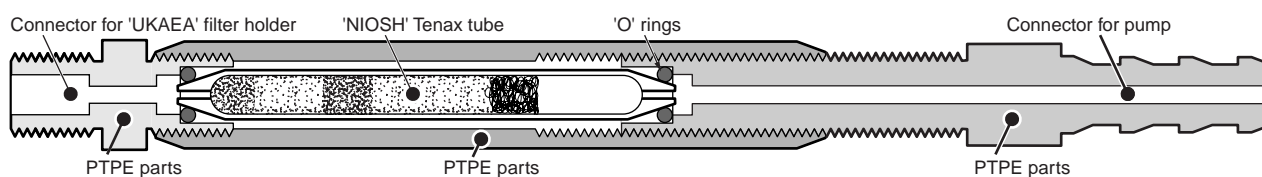


Figure 1 PTPE holder for Tenax back-up tube

## Sampling assembly

32 A suitable assembly for air sampling is illustrated in Figure 1. It utilises a 25 mm filter held within a sampling head (not shown), backed up by a PTFE tube holder containing the Tenax sorbent tube. This assembly is employed when sampling airborne mixtures of both vapours and aerosols. A 25 mm filter can also be used independently by mounting it in a multi-orifice sampling head with seven equispaced inlet holes. Other equivalent sampling heads may be used<sup>10</sup> (criteria for judging equivalence of other samplers is under discussion by standards organisations; on present information the IOM dust sampler will meet those requirements if pumped at 2 l/min).

## Sampling pump

33 The pump should be suitable to be worn by a person carrying out normal work, and should be capable of running continuously for 8 hours at the recommended flow rate (0.5 to 2 l/min). The total volume of air sampled by the pump over the sampling period should be within  $\pm 5\%$  of the calculated volume. A flow-stabilised pump, capable of continuous low-flow, may be necessary to achieve this. It is also recommended that a pump with a flow interruption indicator is used.

## Flow-meter

34 Flow-meter, portable, capable of measuring the appropriate flow rate (see paragraph 33) to within  $\pm 2\%$ , and calibrated against a primary standard.<sup>10</sup>

**Note 1:** *The flow-meter incorporated into the pump may be used provided that it has adequate sensitivity, that it has been calibrated against a primary standard with a loaded sampler in line, and that it is read in a vertical direction if it is the supported float type. However, it is important to ensure that there are no leaks in the sampling train between the sampling head and the flow-meter, since in this event a flow-meter in the pump or elsewhere in line will give an erroneous flow rate.*

**Note 2:** *A soap bubble flow-meter may be used as a primary standard, provided its accuracy is traceable to national standards (see Appendix 2).*

## Ancillary equipment

35 Flexible plastic tubing, of a diameter suitable for making a leakproof connection from the sampler to the sampling pump; belts or harnesses to which the sampling pump can conveniently be fixed, unless the pump is sufficiently small to fit in the worker's pocket; flat-tipped tweezers for loading and unloading the filters into samplers; tube breakers to open the Tenax sampling tubes; containers to hold filters while being transported.

## LABORATORY APPARATUS

### Glassware

36 A selection of laboratory glassware, including pipettes, beakers, measuring cylinders and volumetric

flasks, all class A, complying with the requirements of BS 1792.<sup>11</sup>

37 As a precautionary measure it is recommended that all glassware should be pre-silanised.<sup>12</sup> An alternative to this is to use Nalgene synthetic labware where appropriate. All laboratory glassware should be prewashed with residue analysis grade acetone prior to commencing experimental work.

### Micropipettes

38 A set of adjustable positive displacement micropipettes, calibrated against a primary standard, for preparation of calibration and sample solutions.<sup>13</sup>

### Balance

39 A balance, calibrated against a primary standard, for the preparation of the calibration solutions. The balance should be capable of weighing to  $\pm 0.1$  mg over the range 0 to 100 g.

### Disposable gloves

40 Disposable gloves, impermeable, to avoid the possibility of contamination from the hands and to protect them from harmful substances. Vinyl or nitrile gloves are suitable.

### Miscellaneous

41 Other equipment needed for this analysis is:

- ultrasonic bath;
- sample concentration unit;
- a range of micro-syringes in the range 1  $\mu$ l to 500  $\mu$ l;
- glass sample vials.

### Gas chromatograph

42 A gas chromatograph (GC) fitted with a mass spectrometric detector is the preferred method of analysis, as this gives the highest amount of selectivity. Alternatively, a GC fitted with electron capture/nitrogen phosphorous detection can be used.

43 The selection of a GC column capable of separating the analytes of interest from other components is most important. A 30 m HP-5MS (low bleed (5%)-diphenyl-(95%)-dimethylsiloxane copolymer) with internal diameter of 0.25 mm and a film thickness of 0.25  $\mu$ m, has been found suitable for this analysis.

## SAMPLING PROCEDURE

### Calibration of sampling pumps

44 Measurement of the volume of air sampled may be a significant source of error in the final calculation of pesticide concentrations. About 15 minutes before sampling is to begin, connect the pump to a filter holder

(with a filter in place) by means of a flexible tube, and adjust the flow rate to the desired value by attaching a suitable calibrated airflow meter to the front of the filter holder. The pump should then be allowed to run for 15 minutes to stabilise the flow rate. Before taking the actual sample, a filter holder with a clean filter is fitted, with a Tenax tube in line if required, and the flow rate readjusted to its original value. The meter should also be used to check the flow rate at the end of the sampling period.

## Collection of samples

### *Air samples*

45 Connect the sampling assembly to the pump as described above. The filters should be handled with tweezers, and the ends broken from the Tenax tubes carefully, to avoid damage to the 'O' ring seals. When used for personal sampling, the sampler should be mounted in the worker's breathing zone (within 30 cm of the nose/mouth region), for example on the lapel, with the filter surface approximately vertical. The pump is attached to the worker as appropriate to minimise inconvenience. When used for fixed location sampling, a suitable sampling site is chosen.

46 When ready to begin sampling, remove the protective cover from the sampling head and switch on the pump. Record the time at the start of the sampling period, and if the pump is equipped with an elapsed time indicator, ensure that it is set to zero. Draw a measured volume of air through the GF/A filter paper. The recommended air sample volume is 200 l, and the sampling rate 2 l/min. Take a separate sample for each 100-minute period. If Tenax tubes are connected in series, the maximum achievable flow rate is 0.5 l/min, or 1 l/min if OVS tubes are used.

47 Since it is possible for a filter to become clogged, monitor the performance of the sampler periodically, a minimum of every two hours (or more frequently if heavy filter loadings are suspected). Measure the flow rate with the calibrated flow-meter and record the measured value. Terminate sampling and consider the sample to be invalid if the flow rate is not maintained to within  $\pm 5\%$  of the nominal value throughout the sampling period.<sup>10</sup>

**Note 3:** *If a flow fault indicator is fitted to the pump, regular observation of this indicator is an acceptable means of ensuring that the flow rate of flow-stabilised pumps is maintained satisfactorily, provided that the flow fault indicator indicates malfunction when the flow rate is outside  $\pm 5\%$  of the nominal value.*

48 At the end of the sampling period, measure the flow rate with an accuracy of  $\pm 5\%$  using the calibrated flow-meter (paragraph 34), switch off the sampling pump, and record the flow time and the time. Also observe the reading on the elapsed time indicator, where fitted, and consider the sample to be invalid if the reading on the elapsed time indicator and the timed interval between switching on and switching off the sampling pump do not agree to within  $\pm 5\%$ , since this may suggest that the sampling pump has not been operating throughout the

sampling period. Reseal the sampler with its protective cover and disconnect it from the sampling pump.

49 Carefully record the sample identity using a unique sample number and all relevant sampling data (see Appendix 3). Calculate the mean flow rate by averaging the flow rate measurements throughout the sampling period and calculate the volume of air sampled, in litres, by multiplying the flow rate in l/min by the sampling time in minutes.

### Blanks

50 With each batch of ten samples, submit for analysis at least two unused filters/tubes from the same lot of sampling devices used for sample collection.

51 Sample blanks should be prepared by using filters, tubes and dermal samplers identical to those used for sampling and subjecting them to the same handling procedure except for the actual period of sampling. Label these as blanks.

52 For transport back to the laboratory, seal the filters in individual tins and replace the end-caps on the tenax tubes. Any dermal samplers should be sealed in individual polythene bags. Samples should be kept cool (dry ice containment if possible) during transport, stored in a freezer and analysed within 1 week.

## ANALYSIS

### Preparation of samples for analysis

#### *Air samplers*

53 *GFA filters* - Desorb each filter in a sealed glass bottle containing 2 ml of the desorbing solution (see paragraph 27) for 2 hours under sonication.

54 *Tenax tubes* - Carefully empty the packing (omit the glass wool and urethane pads) from each Tenax tube into glass bottles which contain 2 ml of the desorbing solution. Desorb as per filter.

55 After desorption, carefully filter the extracts with 0.45  $\mu\text{m}$  PTFE filters and place into amber glass GC vials for analysis.

#### *Dermal samplers*

56 Desorb each swab, glove and sock in sealed glass bottles containing 25 ml, 100 ml and 250 ml respectively of the desorbing solution for 2 hours under sonication.

57 After desorption, take 1 ml of each of the resulting extracts and filter using 0.45  $\mu\text{m}$  PTFE filters. The clean solutions can be placed directly into amber glass GC vials and analysed.

58 If the samples initially prove to be lower than the calibration range, a method of sample concentration can be used. This would normally involve taking 10 ml of

filtered solution and concentrating down to 0.5 ml. This allows the sample to be made up to 1 ml, giving a 10-fold concentration from the initial solution.

#### Blank samples

59 Blank samples are subjected to the same analytical procedure as the other samples in the set (paragraphs 53 to 58).

#### Preparation of calibration standards

60 At least four standard solutions of each pesticide, spanning the analytical range, should be prepared by dissolving a known amount of a certified standard in solvent and diluting as appropriate.

#### Chromatography

61 Gas chromatographic conditions that have been found to be suitable for analysis are:

Column dimensions	30 m x 0.25 mm ID (0.25 µm film thickness)
Column packing	HP-5MS (5%-Diphenyl / 95%-dimethylsiloxane copolymer)
Temperature programme	Injector: 250°C Detector: 280°C Initial temp: 60°C for 1 min Ramp at 10°C/min to 295°C; hold for 3.5 min
Carrier gas	Helium
Flow rate	1 ml/min

#### CALCULATIONS

##### Pesticide concentrations on dermal samples

62 Calculate the concentration of pesticide found on the dermal sampler by comparison with the graph of the calibration standards. This will give an analytical result for the sample in µg/ml or ppm. This result can then be adjusted for each sample volume, eg:

- Ai Analytical result (µg/ml) x 25 (ml) = µg on swab sample
- Aii Analytical result (µg/ml) x 2.5 (ml) = µg on swab sample (if concentrated)
- Bi Analytical result (µg/ml) x 100 (ml) = µg on glove sample
- Bii Analytical result (µg/ml) x 10 (ml) = µg on glove sample (if concentrated)
- Ci Analytical result (µg/ml) x 250 (ml) = µg on sock sample
- Cii Analytical result (µg/ml) x 25 (ml) = µg on sock sample (if concentrated)

63 By carrying out spiked recoveries (paragraph 24) of individual pesticides on each sample type, a profile can be made as to how much adjustment is necessary to results which carry a low percentage recovery. This is also true of the air samples.

#### Volume of air sample

64 Calculate the volume, V, in litres, of each air sample (paragraph 49).

#### Pesticide concentrations on air samples

65 Calculate the concentration of pesticide found on the air sampler by comparison with the graph of the calibration standards. This will give an analytical result for the sample in µg/ml. This result can then be adjusted for each sample to take into account the air volume sampled, eg:

$$C = \frac{A \times S \times 1000}{V}$$

where C = Pesticide concentration (µg/m<sup>3</sup>)  
A = Analytical result (µg/ml)  
S = Volume of desorbing solvent (ml)  
V = Volume of air sampled (l)

#### TEST REPORT

66 Appendix 3 gives recommendations for information to be included in the test report.

#### ADVICE

Advice on this method and the equipment used can be obtained from the Health and Safety Executive, Health and Safety Laboratory, Broad Lane, Sheffield, S3 7HQ (telephone 0114 289 2000, fax 0114 289 2500, email info@hsl.gov.uk).

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.

## APPENDIX 1

**Table 1** The stability of various pesticides over a 14-day period after being spiked onto GF/A filters

<i>Pesticide</i>	<i>Day 0 % remaining</i>	<i>Day 3 % remaining</i>	<i>Day 7 % remaining</i>	<i>Day 14 % remaining</i>	<i>Vapour pressure mPa</i>
Bifenthrin	83.1	92.2	92.6	82.2	0.024 (25°C)
Bromopropylate	87.9	92.2	91.5	84.2	0.011 (20°C)
Bupirimate	86.6	91.8	90.7	83.8	0.100 (25°C)
Captan	92.5	85	82.3	75.2	<1.30 (25°C)
Carbaryl	106.4	88.3	68.2	59.5	0.041 (23.5°C)
Chlorfenvinphos	88.6	85.5	84.4	70	0.530 (20°C)
Chlorothalonil	89.7	81.9	70	45.9	0.076 (25°C)
Chlorpyrifos	87.6	59	36.9	< 10	2.700 (25°C)
Chlorpyrifos-Methyl	88.8	19.7	< 10	< 10	3.000 (25°C)
Cypermethrin	96.9	92.9	93.8	74.9	1.8x10 <sup>-4</sup> to 0.023 (20°C)
Deltamethrin	98.2	92.4	96.3	79.1	1.24x10 <sup>-5</sup> (25°C)
Dichlofluanid	83.7	20	< 10	< 10	0.015 (20°C)
Dimethoate	102.6	94	83.7	70.7	0.250 (25°C)
α - Endosulfan	88.5	62.3	49.9	32.2	0.830 (20°C)
β - Endosulfan	89.8	88.7	86.2	68.1	0.830 (20°C)
Endosulfan-sulphate	87.1	93.5	92.2	81.1	—
Fenoxycarb	98.3	88.5	83.1	76.3	8.67x10 <sup>-4</sup> (25°C)
Iprodione	95	85.3	81.4	72.6	5.00x10 <sup>-4</sup> (25°C)
Lindane	91	22.5	11.9	< 10	5.600 (20°C)
Metalaxyl	85.6	87.2	85.8	74.7	0.750 (25°C)
Omethoate	100.5	86	76	72.2	3.300 (20°C)
Permethrin	85.8	90.4	90.9	80.1	0.070 (20°C)
Phosalone	90.4	93.9	92.6	85.3	<0.06 (25°C)
Pirimiphos-Methyl	89.8	71.4	46	12.6	2.000 (30°C)
Tetradifon	87.2	97	92.2	88.1	3.20x10 <sup>-5</sup> (20°C)
Tolyfluanid	81.6	45.6	13.1	< 10	0.020 (20°C)
Triazophos	90.6	88	80.2	68.9	0.390 (30°C)

**Table 2** The stability of various pesticides over a 14-day period after being spiked onto NIOSH Tenax tubes

<i>Pesticide</i>	<i>Day 0 % remaining</i>	<i>Day 3 % remaining</i>	<i>Day 7 % remaining</i>	<i>Day 14 % remaining</i>	<i>Vapour pressure mPa</i>
Bifenthrin	86.8	86.9	83.2	80	0.024 (25°C)
Bromopropylate	81.4	92.5	90.1	87	0.011 (20°C)
Bupirimate	93.5	94.3	94.3	94.4	0.100 (25°C)
Captan	93.7	76.4	75.1	69.3	<1.30 (25°C)
Carbaryl	113.4	108.5	93.7	88.9	0.041 (23.5°C)
Chlorfenvinphos	87.6	85.1	81.5	76.7	0.530 (20°C)
Chlorothalonil	87.3	78.5	77.5	63.4	0.076 (25°C)
Chlorpyrifos	88.7	85.9	81.5	66.3	2.700 (25°C)
Chlorpyrifos-Methyl	91.2	85.6	83.3	61.6	3.000 (25°C)
Cypermethrin	110	97.5	90.2	80.3	1.8x10 <sup>-4</sup> to 0.023 (20°C)
Deltamethrin	109.1	91.7	92.7	75.5	1.24x10 <sup>-5</sup> (25°C)
Dichlofluanid	93.8	80.4	80.8	75.2	0.015 (20°C)
Dimethoate	—	—	—	—	0.250 (25°C)
α - Endosulfan	90.9	93	92.4	82	0.830 (20°C)
β - Endosulfan	88.9	87	86.8	75.9	0.830 (20°C)
Endosulfan-sulphate	90.4	92.9	92.3	85.2	—
Fenoxycarb	84.9	81.4	78.1	65.2	8.67x10 <sup>-4</sup> (25°C)
Iprodione	98.8	86.8	79.2	68.4	5.00x10 <sup>-4</sup> (25°C)
Lindane	87.6	91.1	86.5	61.2	5.600 (20°C)
Metalaxyl	86.1	89	83	74.2	0.750 (25°C)
Omethoate	—	—	—	—	3.300 (20°C)
Permethrin	88.1	88.3	85	77.8	0.070 (20°C)
Phosalone	98.3	89.8	88.4	80.8	<0.06 (25°C)
Pirimiphos-Methyl	89.7	86	85	59.8	2.000 (30°C)
Tetradifon	90.3	92.3	88.5	83.8	3.20x10 <sup>-5</sup> (20°C)
Tolyfluanid	92.1	81.7	81.5	58.7	0.020 (20°C)
Triazophos	97.7	93.8	80.8	73.1	0.390 (30°C)

## APPENDIX 2

### Primary standard for calibration of portable flow-meter

The primary standard must be a flow-meter whose accuracy is traceable to national standards, used with careful attention to the conditions of the calibration certificate. A bubble flow-meter may also be used. This is an arrangement whereby the pump under test draws a soap film up a calibrated tube. The passage of the film is accurately timed between two marks whose separation defines a known volume. The volume between the marks can be checked by filling the burette with water, allowing temperatures to stabilise, drawing off a known volume and weighing the water, making allowance for the dependence of volume on temperature. A suitable bubble solution can be made by mixing one part of concentrated washing-up liquid, two parts glycerol and four parts water. The burette must be thoroughly wetted with the solution and several attempts at drawing the film up the tube may be necessary before the tube is wet enough for this to be achieved consistently. Traceability of the calibration will require checking of the clocks and use of certificated weights.

## APPENDIX 3

### Recommendations for the test report

It is recommended that the test report should include the following information:

- a complete identification of the air sample using a unique sample number, the date of sampling, the place of sampling, and the identity of the individual whose breathing zone was sampled;
- a reference to this MDHS and a description of any deviation from the procedures described;
- the type and diameter of filter used, and the type of sampling head;
- the type of sampling pump and flow-meter used, the primary standard against which it was calibrated, and the range of flow rates for which the flow-meter was calibrated;
- the duration of the sampling period in minutes and/or the time at the start and at the end of the sampling period;
- the volume of air sampled, in litres;
- the name of the person who collected the samples;
- the time-weighted average sample concentration found in the air sample, in milligrams per cubic metre and/or the mass collected on the filter, in milligrams;
- the overall uncertainty of the method;
- the name of the analyst;
- the date of the analysis;
- any unusual features with the analysis;
- recovery data.

## APPENDIX 4

### Alphabetical list of HSE field offices

Office name	HSE region	Telephone no
Aberdeen	Scotland	01224 252500
Ashford	London & SE	01233 624658
Basingstoke	Home Counties	01256 404000
<b>Birmingham *</b>	<b>Midlands</b>	<b>0121 607 6200</b>
Bootle	North West	0151 479 2200
Bristol	Wales & West	0117 988 6000
<b>Cardiff *</b>	<b>Wales &amp; West</b>	<b>01222 263000</b>
Carlisle	North West	01228 539321
Carmarthen	Wales & West	01267 232823
Chelmsford	Home Counties	01245 706200
East Grinstead	London & SE	01342 334200
<b>Edinburgh *</b>	<b>Scotland</b>	<b>0131 247 2000</b>
Glasgow	Scotland	0141 275 3000
<b>Horsforth *</b>	<b>Yorkshire &amp; NE</b>	<b>0113 283 4200</b>
Hull	Yorkshire & NE	01482 223487
Inverness	Scotland	01463 718101
Leeds	Yorkshire & NE	0113 283 4200
<b>Luton *</b>	<b>Home Counties</b>	<b>01582 444200</b>
<b>Manchester *</b>	<b>North West</b>	<b>0161 952 8200</b>
Newcastle-U-Lyme	Wales & West	01782 602300
Newcastle-U-Tyne	Yorkshire & NE	0191 202 6200
Northampton	Midlands	01604 738300
Norwich	Home Counties	01603 615711
Nottingham	Midlands	0115 971 2800
Plymouth	Wales & West	01752 668481
Poole	Home Counties	01202 667219
Preston	North West	01772 836200
Sheffield	Yorkshire & NE	0114 291 2300
<b>Southwark *</b>	<b>London &amp; SE</b>	<b>0171 556 2100</b>
Stoneleigh	Midlands	01203 696518
Worcester	Wales & West	01905 723406
Wrexham	Wales & West	01978 290500

\* Also Regional HQ

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| 28   | Chlorinated hydrocarbons charcoal tube/GC   | 76   | Cristobalite in respirable dusts X-ray diffraction (direct method)                             |
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| 30/2 | Cobalt AA   | 78   | Formaldehyde diffusive/solvent desorption/liquid chromatography                                |
| 31   | Styrene pumped thermal desorption/GC  | 79   | Peroxodisulphate salts mobile phase ion chromatography   |
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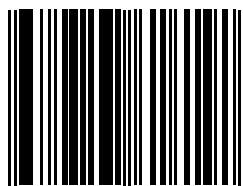
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