HSE
Health and Safety Executive

Pesticides in air and on surfaces

Method for sampling and analysis of pesticides in air using pumped filters and sorbent tubes in series and on dermal surrogates using cotton pads and clothing. Analysis by gas chromatography

MDHS94/2

Methods for the Determination of Hazardous Substances

Health and Safety Laboratory

Scope

1 This method describes the determination of time-weighted average inhalable concentrations of pesticides in air. It can be applied to pesticides present in both agricultural and non-agricultural formulations present as either vapour or a mixture of vapour and airborne particles.

2 The analytical method can be applied to estimate surface or dermal contamination using cotton swabs, gloves or socks to sample body surface contamination.

Summary

3 A measured volume of air is drawn through a glass fibre filter and if required a sorbent back-up tube in series, to trap pesticides with significant vapour pressure. After sampling, the filter and sorbent tube are desorbed in ethyl acetate, acetone or other suitable solvent and analysed by gas chromatography with mass selective detection.

4 An estimate of potential dermal or surface exposure can be made using cotton gauze swabs, located on the worker's outer clothing. Similarly cotton gloves and socks against the skin may be used to determine actual hand and foot exposure.

5 The use of alternative methods not included in the MDHS series is acceptable provided they can demonstrate the accuracy and reliability appropriate to the application

Recommended sampling

6 Air monitoring should be carried out as described in MDHS14[1] for inhalable dust using an IOM sampler at 2 litres per minute. For pesticides with significant vapour pressures, a back-up tube can be placed in series after the filter, but the sampling efficiency for particulate matter may be compromised if the flow rate of 2 litres per minute is not maintained.

7 The method is suitable for airborne sampling over periods of 10 minutes to 8 hours in the concentration range of 10–1000 $\mu g.m^{-3}$.

8 Potential dermal exposure can be estimated using a modified sampling protocol using 10 x 10 cm cotton gauze swabs attached at seven locations on the workers clothing.[2]

9 Actual hand and foot contamination can be determined by the subject wearing thin cotton gloves and socks under protective gloves and boots.

Prerequisites

10 Users of this method will need to be familiar with the content of MDHS14.[1]

Safety

11 Users of this method should be familiar with standard laboratory practice and carry out a suitable risk assessment. It is the user's responsibility to establish appropriate health and safety practices and to ensure compliance with regulatory requirements.

Equipment

12 An inhalable dust sampler as described in MDHS14.[1] Clean the sampling heads before use as prescribed by the manufacturer.

13 Personal sampling pumps that meet the requirements of BS EN 13137.[3]

14 Binder free glass fibre filters (25 mm GF/A have been found suitable for the IOM samplers).

15 Two section sorbent tube containing Tenax®, 20 mg and 10 mg front and back sections respectively. This can be connected in series to the outlet of the inhalable sampling head using a short piece of flexible tubing or tube holder.

16 A portable flow meter, calibrated against a primary standard, with a measurement uncertainty typically less than ±2%.

17 Flexible plastic tubing for making a leak-proof connection from the sampling train to the pump; belts and harnesses to facilitate attachment of sampling apparatus to sample subjects; flat-tipped tweezers for loading and unloading the filters into samplers; and filter transport cassettes to transport samples to the laboratory.

18 Cotton swabs, thin cotton gloves and socks to be used as surrogates for dermal or surface sampling. These should be pre-cleaned by sonication in residue grade acetone or other suitable solvents and dried before use.

Laboratory apparatus and reagents

19 During the analysis only reagents of a recognised analytical grade should be used.

20 Residue quality solvents: Acetone, ethyl acetate or other solvents suitable for making analytical standards and extracting the pesticides of interest.

21 A selection of laboratory glassware and amber vials for carrying out solvent extractions of sampling media, volumetric flasks, Class A, complying with the requirements of BS EN ISO 1042.[4] As a precautionary measure it is recommended that all glassware be silanised[5] or use Nalgene or PTFE synthetic labware.

22 Syringe filters, 0.45 µm PTFE filters, for filtering sample extracts prior to analysis.

23 Positive displacement micropipettes complying with the requirements of BS EN 8655-6.[6]

24 Ultrasonic bath.

25 Sample concentrator.

26 A balance, calibrated against a primary standard, for the preparation of the calibration standards. The balance should be capable of weighing to ±0.1 mg over the range 0 to 100 g.

27 A gas chromatograph with mass selective detector (GC/MS). Alternatively, the use of specific detectors such as electron capture or nitrogen phosphorous detectors may increase sensitivity and specificity in some applications.

28 The gas chromatography column should be capable of separating the analytes of interest from other components in the sample matrix. Typical GC/MS conditions that have been found suitable are shown below.

Column	MS 30 m x 0.25 mm ID (0.25 µm film thickness) 5%-diphenyl – 95% dimethylsiloxane copolymer
Carrier	Helium: 1 $ml.min^{-1}$.
Temperature programme	Injector: 250 °C Detector: 280 °C Initial temperature: 60 °C for 1 min; ramp at 10 °C.min^{-1} to 295 °C; Hold 3.5 min

Sample collection

Air samples

29 Sampling should be carried out in accordance with the procedures described in MDHS14[1] for inhalable dusts. Remove both ends of the sorbent tube before sampling (if using) and place in series behind the filter head using a short piece of flexible tubing or tube holder. Maximising the air volume for the exposure period will improve the detection limit for the procedure.

30 After sampling, in a clean environment, remove the filter from the sampling head using flat-tipped tweezers, place in a labelled transport cassette for transfer to the laboratory. Sorbent tubes should be capped and transported with the filter cassettes. Keep separate from any bulk materials collected.

Dermal or surface exposure

31 An estimate of potential dermal exposure can be made using 10 cm x 10 cm cotton gauze swabs, set in seven positions on the worker's outer clothing as shown in Figure 1.

32 To determine actual hand and foot exposure, thin cotton gloves and socks can be worn under protective gloves and boots.

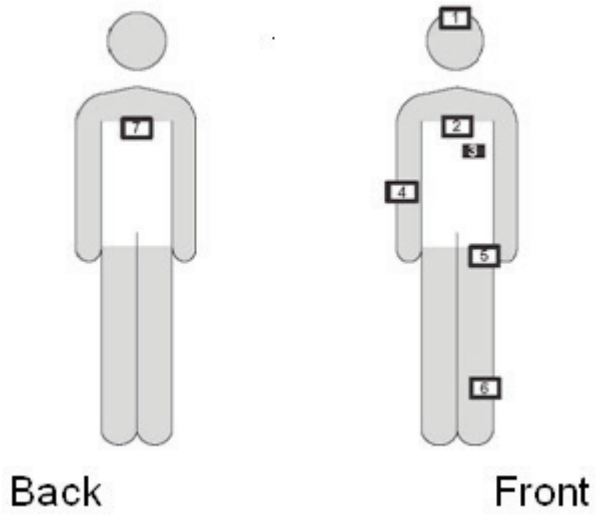

Figure 1 Position of cotton swabs on worker clothing
Position 1: on the hat close to the top of the head
Position 2: over sternum on outside of normal clothing
Position 3: on sternum inside of normal clothing
Position 4: upper surface of right forearm held with the elbow bent at right angles across the 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

33 After sampling, in a clean environment, transfer the swabs, gloves and socks to separate labelled plastic or glass bottles for transport to the laboratory. To avoid cross contamination wear clean disposal gloves for each sample. Keep separate from any bulk materials collected.

Blanks

34 With each batch of ten samples, submit at least two blanks from the same lot of each sampling medium. Subject these blanks to the same handling procedure as the samples apart from the period of sampling.

Calibration

35 Prepare at least four standard solutions of each pesticide or pesticide mixture, spanning the analytical range by dissolving a known mass of a certified standard of each pesticide in an appropriate solvent and dilute as appropriate. A typical pesticide mixture, soluble in ethyl acetate, is shown in Table 1.

36 Analyse each standard and measure the peak area of the target pesticide. Plot the peak areas against the corresponding pesticide concentration in $\mu g.ml^{-1}$, and construct the line of best fit. The slope of this line is the detector response (R_F) for the target pesticide.

Sample analysis

Air samples

37 Desorb each filter in a sealed glass bottle containing 2 ml of the appropriate solvent using sonication for 2 hours.

38 Carefully empty the packing from each sorbent tube (omit glass wool and any urethane pads) into a glass vial containing 2 ml of suitable solvent. Desorb as for filter.

39 Filter the extracts through 0.45 µm PTFE filters into amber glass GC vials.

Dermal samplers

40 Sonicate each swab, glove and sock in a sealed bottle containing 25 ml, 100 ml and 250 ml respectively of the desorbing solvent for 2 hours.

41 Take 1 ml of each of the resulting extracts and filter, as for air samples, into amber glass GC vials.

42 Analyse the sample and blank extracts using the same conditions as the standards. Measure the chromatographic peak area of the target compound in each sample and convert this peak area to a pesticide concentration, in $\mu g.ml^{-1}$, by dividing by the R_F value obtained from the calibration standards.

43 Calculate the mean concentration of the target pesticide, in $\mu g.ml^{-1}$ in the blank extracts. If necessary, this value can be used to blank correct the samples.

Calculations

Pesticide concentration in air samples

44 Calculate the volume, V_S, in m^3, of each air sample as outlined in MDHS14.[1]

45 The pesticide concentration in each air sample (filter and sorbent tube combined if using), C, in $\mu g.m^{-3}$ can then be calculated using the equation:

$C = M_T / V_S$

Where:

M_T = total mass of pesticide on air sampler (µg)

V_S = Volume of air sampled (m^3)

Pesticide mass on dermal samplers

46 Calculate the mass of pesticide found on the dermal sampler, M, in µg using the equation:

M = concentration of pesticide in extract ($\mu g.ml^{-1}$) x extract volume (ml)

47 Exposure to the corresponding body part can then be determined from the product of the mass of pesticide on a given patch and the ratio of the patch area to the body part area.[7] Body part areas may need to be corrected to account only for exposed areas.

Appendix: Additional information

Further information on dermal sampling

1 A comprehensive treatment of the use of patches for sampling has been published by Popendorf and Ness.[8] Further work detailing the principles of patch sampling and its alternatives is reported by Soutar et al.[9]

Detection limit of the method

2 The detection limit for each pesticide will vary. A typical example, carbaryl, for a 240 l air sample has a detection limit of 0.54 $\mu g.m^{-3}$.

Overall uncertainty

3 The overall uncertainty as defined by BS EN 482[10] was typically estimated to be around 23% for a wide range of pesticides (see Table 1).

Analytical recoveries for air samples

4 The pesticide standards used to calibrate the GC can be used in recovery determination. Spiking should be carried out at several appropriate levels on replicate (6) GF/A filters, sorbent tubes and dermal sampling devices.

Storage stability

5 Laboratory tests on filters and tubes spiked with pesticides were used to monitor stability over a 14-day period. One loading level was monitored for all sampling media stored at room temperature. The stability of specific pesticides was monitored immediately after spiking, then after 3, 7 and 14 days to inform how quickly analysis needs to be carried out after sampling. Typical data for a range of pesticides is shown in Table 1.

Table 1 Recovery (%) over time of pesticides spiked onto GFA filters and Tenax® sorbent tubes (values in brackets)

Pesticide	Day 0	Day 3	Day 7	Day 14	Vapour pressure (mPa)
Bifenthrin	83.1 (86.8)	92.2 (86.9)	92.6 (83.2)	82.2 (80)	(0.024) (25 °C)
Bromopropylate	87.9 (81.4)	92.2 (92.5)	91.5 (90.1)	84.2 (87)	0.011 (20 °C)
Bupirimate	86.6 (93.5)	91.8 (94.3)	90.7 (94.3)	83.8 (94.4)	0.1 (25 °C)
Captan	92.5 (93.7)	85 (76.4)	82.3 (75.1)	75.2 (69.3)	<1.3 (25 °C)
Carbaryl	106.4 (113.4)	88.3 (108.5)	68.2 (93.7)	59.5 (88.9)	0.041 (23.5 °C)
Chlorfenvinphos	88.6 (87.6)	85.5 (85.1)	84.4 (81.5)	70 (76.7)	0.53 (20 °C)
Chlorothalonil	89.7 (87.3)	81.9 (78.5)	70 (77.5)	45.9 (63.4)	0.076 (25 °C)
Chlorpyriphos	87.6 (88.7)	59 (85.9)	36.9 (81.5)	<10 (66.3)	2.7 (25 °C)
Chlorpyriphos-Methyl	88.8 (91.2)	19.7 (85.6)	<10 (83.3)	<10 (61.6)	3.0 (25 °C)
Cypermethrin	96.9 (110)	92.9 (97.5)	93.8 (90.2)	74.9 (80.3)	<0.023 (20 °C)
Deltamethrin	98.2 (109.1)	92.4 (91.7)	96.3 (92.7)	79.1 (75.5)	1.2×10^{-5} (25 °C)
Dichlofluanid	83.7 (93.8)	20 (80.4)	<10 (80.8)	<10 (75.2)	0.015 (20 °C)
Dimethoate	102.6 (-)	94 (-)	83.7 (-)	70.7 (-)	0.25 (25 °C)
Alpha - Endosulfan	88.5 (90.9)	62.3 (93)	49.9 (92.4)	32.2 (82)	0.83 (20 °C)
Beta-Endosulfan	89.8 (88.9)	88.7 (87)	86.2 (86.8)	68.1 (75.9)	0.83 (20 °C)
Endosulfan-sulphate	87.1 (90.4)	93.5 (92.9)	92.2 (92.3)	81.1 (85.2)	(-)
Fenoxycarb	98.3 (84.9)	88.5 (81.4)	83.1 (78.1)	76.3 (65.2)	8.67×10^{-4} (25 °C)
Iprodione	95.0 (98.8)	85.3 (86.8)	81.4 (79.2)	72.6 (68.4)	5×10^{-4} (25 °C)
Lindane	91.0 (87.6)	22.5 (91.1)	11.9 (86.5)	<10 (61.2)	5.6 (20 °C)
Metalaxyl	85.6 (86.1)	87.2 (89)	85.8 (83)	74.7 (74.2)	0.75 (25 °C)
Omethoate	100.5 (-)	86 (-)	76 (-)	72.2 (-)	3.3 (20 °C)
Permethrin	85.8 (88.1)	90.4 (88.3)	90.9 (85)	80.1 (77.8)	0.07 (25 °C)
Phosalone	90.4 (98.3)	93.9 (89.8)	92.6 (88.4)	85.3 (80.8)	<0.06 (25 °C)
Pirimiphos-Methyl	89.8 (89.7)	71.4 (86)	46 (85)	12.6 (59.8)	2.0 (30 °C)
Tetradifon	87.2 (90.3)	97 (92.3)	92.2 (88.5)	88.1 (83.8)	3.2×10^{-5} (20 °C)
Tolylfluanid	81.6 (92.1)	45.6 (81.7)	13.1 (81.5)	<10 (58.7)	0.02 (20 °C)
Triazophos	90.6 (97.7)	88 (93.8)	80.2 (80.8)	68.9 (73.1)	0.39 (30 °C)

References

1 *General methods for sampling and gravimetric analysis of respirable, thoracic and inhalable aerosols* MDHS14/4 HSE 2014 www.hse.gov.uk/pubns/mdhs/index.htm

2 World Health Organisation *Field surveys of exposure to pesticides: Standard Protocol* Unpublished WHO document VBC/82.1 (1982)

3 BS EN 13137:2013 *Workplace atmospheres. Pumps for personal sampling of chemical and biological agents. Requirements and test methods* British Standards Institution

4 BS EN ISO 1042:2000 *Laboratory glassware. One-mark volumetric flasks* British Standards Institution

5 Rimmer D A, Johnson P D and Brown R H *Determination of phenoxy acid herbicides in vegetation, utilising gel chromatographic clean-up and methylation with trimethylsilyldiazomethane prior to gaschromatographic analysis with mass selective detection* J Chromatogr A 755 1996 245–50

6 BS EN ISO 8655-6:2002 *Piston-operated volumetric apparatus. Gravimetric methods for the determination of measurement error* British Standards Institution

7 US Environmental Protection Agency *Exposure Factors Handbook 2011* Edition EPA/600/R-09/052F (2011)

8 Popendorf WJ and Ness SA *Pad dosimetry methods In surface and dermal monitoring for toxic exposures 1994* ed Ness SA 321–344 John Wiley & Sons New York

9 Soutar A, Semple S, Aitken RJ and Robertson A 'Use of patches and whole body sampling for the assessment of dermal exposure' *Ann Occ Hyg* 2000 **44** (7) 511–518

10 BS EN 482:2012 *Workplace exposure. General requirements for the performance of procedures for the measurement of chemical agents* British Standards Institution

You should use the current edition of any standards listed.

Further information

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