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Note

Sampling and determination of fenitrothion, dimethoate, mevinphos, linuron, metoxuron and trifluralin from air

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A variety of devices, such as impingers, bubblers, filters, solid sorbents and polyurethane foams, have been used for sampling pesticides from air[1–10]. The purpose of this study was to evaluate and/or develop procedures for sampling airborne pesticides used by garden product cultivators. Cultivations of considerable proportions are found in the south of Sweden (Skåne and Gotland). Relevant pesticides were selected after discussions with the Swedish Farmers Safety and Preventive Health Association in Kristianstad and with the cultivators themselves. The pesticides selected were fenitrothion, dimethoate, mevinphos, linuron, metoxuron and trifluralin.

Several methods for the sampling of fenitrothion may be found in the literature. A fritted-glass bubbler containing dimethylformamide (DMF)[10], a Florisil filter column linked in series with a bubbler containing DMF[12], and columns filled with Tenax GC[13] or OV 101 on Chromosorb[11] are examples. Gas chromatography (GC) is the usual analytical procedure and both nitrogen–phosphorus (NP)[10,13] and flame-photometric detection[11,12] may be used.

Sampling dimethoate by means of the impinger technique[2,14–15] or XAD-4 adsorption tubes[9] followed by analysis by GC with electron-capture (EC) or thermoionic[14] detection, has been described.

Sampling procedures for mevinphos employ Chromosorb 102[7] or XAD-4[9,16]. The analysis is performed with rubidium sulphate alkali flame ionization[16] or flame-photometric detection[7].

Several methods for the analysis of phenylurea herbicides have been described in the literature[17–26]. The major concern has been analysis; sampling of phenylureas from air has received much less attention. The GC analysis of phenylurea herbicides is complicated by the fact that some of these compounds decompose into isocyanates at high temperatures. Direct GC analysis is possible for linuron, whereas metoxuron decomposes[22]. This problem is overcome if the phenylureas are derivatized[17,18,21,23,25] or hydrolysed[27] before analysis. An alternative analytical procedure is high-performance liquid chromatography (HPLC). HPLC usually suffers from the drawback of low sensitivity but the sensitivity can be enhanced by using derivatization and/or specific detectors[23,26] or on-line preconcentration[28,29].

Trifluralin has been sampled with Chromosorb 102[30], XAD-4[31] and polyurethane foam[32]. Analysis is performed by GC–ECD[30–32].

EXPERIMENTAL

Chemicals

Hexane (Fisons; HPLC grade); acetone (Merck; p.a.); dichloromethane (Merck; p.a.); ethanol (Svensk sprit; 95%); linuron, metoxuron, trifluralin and dimethoate (Dr S. Ehrensdorfer, 99%); mevinphos and fenitrothion (Dr S. Ehrensdorfer, 98%); and heptafluorobutyric anhydride (HFBA) (Merck; GC grade) were used without further purification. Water was purified in an Elgastat water purifier.

Sampling equipment

Binder-free glass fiber filters (Millipore, AP 4003705, 37 mm) were housed in 37-mm filter holders (Millipore). Fritted-glass bubblers were filled with 10 ml ethanol (absorption solution). Amberlite XAD-4 (Rohm & Haas) is a cross-linked styrene–divinyl-benzene copolymer. For the elimination of salts and fines, the polymer was washed and decanted in 0.02 *M* hydrochloric acid and water. The polymer was then cleaned by Soxlet-extraction with acetone and finally dried overnight at 50°C. The adsorbent was filled in a glass tube, (120 × 5 mm) in two layers separated by a plug of silanized glass wool. The analytical and control layers each contained 200 mg XAD-4. The tube was stoppered at both ends with silanized glass wool.

Standard solutions

Fenitrothion, dimethoate, mevinphos and linuron were diluted in dichloromethane to 5, 50, 225 or 500 times the detectable quantity. The standard of the derivative of metoxuron and heptafluorobutyric anhydride (HFBA) was prepared as described in ref. 21. Trifluralin was diluted in acetone to 2, 50 and 500 times the detectable quantity.

Generation of standard atmospheres

Two methods for the generation of known amounts of pesticide were used:

(i) Direct injection of standard solution.

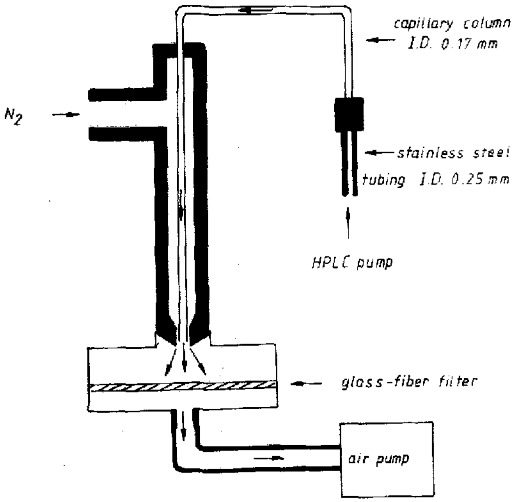

Fig. 1. Apparatus for "aerosol" generation.

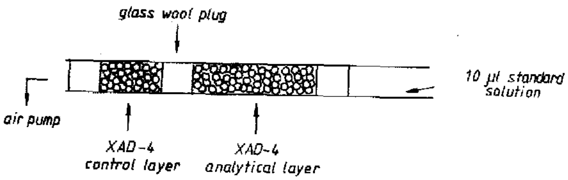

Fig. 2. Apparatus for generation of gaseous pesticide.

(ii) Generation of "aerosol": The apparatus used for the generation experiment[33] is shown in Fig. 1. The concentration of standard solution was 1–10 µg/ml and the flow through the HPLC system was 50–70 µl/min. The samplers were connected to an air pump with a flow of 1.5 l/min. The flow of nitrogen through the system was 1 l/min. Sampling was performed for a few minutes, after which the HPLC pump was stopped. The filter was disconnected after an additional 0.5 min.

Methods for sampling

Five methods for sampling were used:

(a) A standard solution (10 µl) was directly injected onto a glass-fiber filter.

(b) A standard solution (10 µl) was directly injected onto a glass-fiber filter, after which 15 l air was drawn through the filter.

(c) Pesticide was generated as an aerosol and sampled by means of a glass-fiber filter. A fritted-glass bubbler containing 10 ml ethanol was used as a back-up.

(d) A standard pesticide solution (10 µl) was added to 10 ml ethanol in a fritted-glass bubbler. A second bubbler was used as a back-up. Air (15 l) was drawn through the bubblers.

(e) A standard solution (10 µl) was injected in a glass tube and 15 l air was drawn through the XAD-4 layers. See Fig. 2.

Preparation of samples

The glass-fiber filters prepared with pesticide were desorbed with 2 ml dichloromethane or acetone, in an ultrasonic bath for 5 min. Filters containing metoxuron were desorbed in 2 ml dichloromethane in an ultrasonic bath for 5 min and then evaporated to dryness, after which 2 ml hexane was added and derivatization performed[21]. The fritted-glass bubbler samples were evaporated in a ventilated hood overnight, after which 2 ml dichloromethane was added and the samples were treated in an ultrasonic bath for 5 min. The analytical and control layers of the XAD-4 adsorption tubes were separately treated with 2 ml dichloromethane in an ultrasonic bath for 5 min. All samples were filtered before analysis.

Recovery studies

The recovery was determined by the use of an external standard. Linuron, mevinphos, fenitrothion and dimethoate were diluted in dichloromethane, and trifluralin in acetone. Metoxuron was diluted in hexane and then derivatized with HFBA. Three different concentration levels were examined. Each experimental set-up included six samples, standards, one solvent blank and one filter/XAD-4/fritted-glass bubbler blank.

Pesticide-treated filters. XAD-4 adsorption tubes and fritted-glass bubbler

TABLE I

TEMPERATURE PROGRAMS USED FOR THE ANALYSIS OF LINURON, MEVINPHOS, FENITROTHION, DIMETHOATE, TRIFLURALIN AND METOXURON-HEPTAFLUOROBUTYRIC ANHYDRIDE DERIVATIVE

Sample	*Temp. (°C)*	*Time (min)*	*Progr. (°C/min)*	*Temp. (°C)*	*Progr. (°C/min)*	*Temp. (°C)*	*Time (min)*
Linuron*	100	0.1	30	–	–	230	10
Mevinphos*	100	0.1	30	–	–	200	10
Fenitrothion*	120	0.1	30	–	–	250	10
Dimethoate*	100	0.1	30	200	5	230	10
Trifluralin**	100	0.1	20	–	–	230	10
Methoxuron***	125	0.1	10	–	–	230	10

* Analysed with NPD.

** Analysed with ECD.

*** Analysed as derivative with heptafluorobutyric anhydride.

samples were stored in the dark at –20°C for at least three weeks before analysis. Filters were stored with and without solvent. To the solvent-containing samples, 0.5 g sodium sulphate was added as drying agent. Fritted-glass bubbler samples were stored with and without drying agent.

Analysis

The chromatographic runs were performed on a Hewlett-Packard (HP) 5880 gas chromatograph with electrone-capture and nitrogen–phosphorus detectors. The instrument was equipped with an autoinjector (HP, 7671 A) and the injection volume was 2 μl. An SE-30 capillary column (25 m × 0.32 mm I.D.) was used for the analysis of fenitrothion, linuron, metoxuron and trifluralin, and a capillary column containing cross-linked methyl silicone (25 m × 0.20 mm I.D.) for the analysis of dimethoate and mevinphos. The detector temperature was 300°C (NPD) and 200°C (ECD), and the injector temperature was 250°C (NPD) and 300°C (ECD). The temperature programs used are shown in Table I.

RESULTS AND DISCUSSION

Minimum detectable quantity

The minimum detectable quantity (signal to noise ratio 3:1) was determined as 3 pg for fenitrothion, dimethoate and mevinphos, 30 pg for linuron and 1 pg for metoxuron-HFBA derivative and trifluralin.

Recovery experiments

Table II shows that the recoveries of fenitrothion, dimethoate, linuron, metoxuron and trifluralin were high when sampling took place with a glass-fiber filter. The compounds were also effectively retained on the filter when 15 l air was drawn through the sample and no breakthrough occurred in the "aerosol" experiments. The influence of storage was studied on one level for each of these compounds. Except for metoxuron, neither the dry nor the solvent-desorbed glass-fiber filters showed any

TABLE II

RECOVERIES OF FENITROTHION, DIMETHOATE, MEVINPHOS, LINURON, METOXURON AND TRIFLURALIN SAMPLED WITH GLASS-FIBER FILTER

Sample	*Amount added (ng)*	*Recovery (%)*	*R.S.D.* (%)*	*Note***
Fenitrothion	8	103	4	A
	88	100	5	A
	970	93	8	A
	1140	100	7	A + 15 l air
	88	102	7	B stored dry
	88	102	7	B Na_2SO_4, solvent
	320	104	8	C no breakthrough
Dimethoate	10	94	5	A
	110	101	4	A
	450	101	6	A
	572	105	6	A + 15 l air
	110	96	4	B stored dry
	110	96	6	B Na_2SO_4, solvent
	160	102	6	C no breakthrough
Mevinphos	10	100	5	A
	100	103	13	A
	500	42	5	A
	572	47	8	A + 15 l air
	110	29	15	B stored dry
	110	61	22	B Na_2SO_4, solvent
Linuron	104	100	4	A
	1040	99	4	A
	5120	102	6	A
	5120	105	8	A + 15 l air
	104	94	4	B stored dry
	104	96	3	B Na_2SO_4, solvent
	1500	100	5	C no breakthrough
Metoxuron	10	83	4	A
	100	85	4	A
	1000	86	7	A
	1000	93	4	A + 15 l air
	100	92	2	A stored dry
	100	78	29	A Na_2SO_4, solvent
	100	106	5	C no breakthrough
Trifluralin	4	106	4	A
	84	103	5	A
	910	103	7	A
	84	95	7	A + 15 l air
	84	97	7	B stored dry
	84	93	7	B Na_2SO_4 + solvent
	196	98	5	C no breakthrough

* Relative standard deviation.

** (A) 10 μl standard solution directly injected onto glass-fiber filter. (B) Samples prepared as A and stored in the dark for three weeks at −20°C. (C) Sample generated as an "aerosol".

TABLE III

RECOVERIES OF FENITROTHION, DIMETHOATE, MEVINPHOS AND LINURON SAMPLED WITH FRITTED-GLASS BUBBLER CONTAINING 10 ml ETHANOL AS ABSORPTION SOLUTION

Sample	*Amount added (ng)*	*Recovery (%)*	*R.S.D.* (%)*	*Note***
Fenitrothion	12	45	48	A
	114	44	5	A
	1040	48	44	A
Dimethoate	120	95	10	A
	570	101	5	A
	120	39	68	B
	120	92	8	B + Na_2SO_4
Mevinphos	110	23	51	A
	570	20	50	A
Linuron	104	97	5	A
	1040	106	5	A
	5120	102	6	A
	1040	98	12	B
	1040	96	6	B + Na_2SO_4

* Relative standard deviation.

** (A) 10 μl standard solution directly injected into a fritted-glass bubbler containing 10 ml ethanol; 15 l air was drawn through the absorption solution; no breakthrough occurred. (B) Samples prepared as above but stored for 3 weeks in the dark at −20°C.

significant loss of substance when stored in the dark at −20°C for three weeks. Metoxuron required drying agent for storage stability. The recovery of mevinphos was poor, however, for the highest amount added and the samples were not stable to storage.

Comparative sampling with fritted-glass bubbler samplers was performed for fenitrothion, dimethoate, mevinphos and linuron. The results are shown in Table III. Recovery of fenithrothion and mevinphos was poor. The dimethoate samples required the addition of drying agent for storage stability. Sampling by means of a fritted-glass bubbler can thus not be recommended.

TABLE IV

RECOVERY OF MEVINPHOS SAMPLED WITH XAD-4 ADSORPTION TUBES

Amount added (ng)	*Recovery (%)*	*R.S.D.* (%)*	*Note***
11	92	6	A no breakthrough
108	96	4	A no breakthrough
267	94	6	A no breakthrough
100	100	4	B no breakthrough

* Relative standard deviation.

** (A) 10 μl standard solution directly injected into an adsorption tube, after which 15 l air was drawn through the tube. (B) Samples prepared as A, and then stored in the dark at −20°C for 3 weeks.

Linuron, however, showed recoveries between 96 and 106% and was stable to storage. Linuron can be sampled successfully by means of either a fritted-glass bubbler or a glass-fiber filter. As the fritted-glass bubbler gave poor results for three of the four compounds examined, no further experiments were performed with this kind of sampler.

Glass-fiber filters proved to be excellent samplers for all the pesticides examined except mevinphos. Thus, an alternative sampling procedure had to be used for this substance. Sampling of mevinphos on XAD-4 adsorption tubes gave recoveries between 92 and 100%. All of the mevinphos was found in the analytical layer and no breakthrough occurred. The samples were stable to storage for three weeks. See Table IV.

REFERENCES

1 E. C. Gundersson, *Chemical Hazards in the Work Place (ACS Symposium Series,*Vol. 149), American Chemical Society, Washington, DC, 1981, p. 301.
2 J. W. Miles, L. E. Fetzer and G. W. Pearce, *Environ. Sci. Technol.*, 4 (1970) 420.
3 *NIOSH Manual of Analytical Methods*, Vol. 1–3, National Institute of Occupational Safety and Health, 2nd ed., Cincinnati, OH, 1977.
4 *NIOSH Manual of Analytical Methods*, Vol. 4, National Institute of Occupational Safety and Health, 2nd ed., Cincinnati, OH, 1978.
5 *NIOSH Manual of Analytical Methods*, Vol. 5, National Institute of Occupational Safety and Health, 2nd ed., Cincinnati, OH, 1979.
6 *NIOSH Manual of Analytical Methods*, Vol. 6, National Institute of Occupational Safety and Health, 2nd ed., Cincinnati, OH, 1980.
7 *NIOSH Manual of Analytical Methods*, Vol. 7, National Institute of Occupational Safety and Health, 2nd ed., Cincinnati, OH, 1981.
8 J. N. Seiber, J. E. Woodrow, T. M. Shafik and H. F. Enos, in R. Haque and V. H. Freed (Editors), *Environmental Dynamics of Pesticides*, Plenum Press, New York, 1975, p. 17.
9 J. N. Seiber, G.-A. Ferreira, B. Hermann and J. E. Woodrow, in J. Harvey and G. Zweig (Editors), *Pesticide Analytical Methodology, ACS Symp. Ser.*, 136, 1980, p. 177.
10 K. M. S. Sundarom, *J. Environ. Sci. Health Part B*, 19 (1984) 409.
11 K. E. Krzymien, *Laboratory Report National Research Council Canada*, Unsteady Aerodynamics Lab., Ottawa, 1979, p. 1.
12 W. N. Yule, A. F. W. Cole and I. Hoffman, *Bull. Environ. Contam. Toxicol.*, 6 (1971) 289.
13 M. E. Krzymien, *ASTM Spec. Tech. Publ.*, 786 (1982) 35.
14 I. Baunok, *Suid-Afrikaanse Tydskrif vir Wetenskap*, 80 (1984) 277.
15 G. E. Carman, Y. Iwata, J. L. Pappas, J. R. ONeal and F. A. Gunther, *Arch. Environ. Contam. Toxicol.*, 11 (1982) 651.
16 J. E. Woodrow and J. N. Seiber, *Anal. Chem.*, 50 (1978) 1229.
17 U. A. Th. Brinkman, A. de Kok and R. B. Geerdink, *J. Chromatogr.*, 283 (1984) 113.
18 A. Buchert and H. Løkke, *J. Chromatogr.*, 115 (1975) 682.
19 J. de Jong, H. J. van Nieuwkerk, A. H. M. T. Scholten, U. A. Th. Brinkman and R. W. Frei, *J. Chromatogr.*, 166 (1978) 233.
20 A. de Kok, Y. J. Vos, C. van Garderen, T. de Jong, M. van Opstal, R. W. Frei, R. B. Geerdink and U. A. Th. Brinkman, *J. Chromatogr.*, 288 (1984) 71.
21 P. de Voogt, N. Haak, R. B. Geerdink and U. A. Th. Brinkman, *Chemosphere*, 11 (1984) 1193.
22 K. Jr. Grob, *J. Chromatogr.*, 208 (1981) 217.
23 J. Lantos, U. A. Brinkman and R. W. Frei, *J. Chromatogr.*, 292 (1984) 117.
24 J. F. Lawrence, *J. Chromatogr.*, 121 (1976) 85.
25 J. F. Lawrence, C. van Buuren, U. A. Th. Brinkman and R. W. Frei, *J. Agric. Food Chem.*, 28 (1980) 630.
26 S. M. Walters, *J. Chromatogr.*, 259 (1983) 227.
27 D. J. Caverly and R. C. Denney, *Analyst (London)*, 103 (1978) 368.

28 M. W. F. Nielen, G. Koomen, R. W. Frei and U. A. Th. Brinkman, *J. Liq. Chromatogr.*, 8 (1985) 315.
29 C. E. Goewie, P. Kwakman, R. W. Frei, U. A. Th. Brinkman, W. Maasfeld, T. Seshadri and A. Kettrup, *J. Chromatogr.*, 284 (1984) 73.
30 T. C. Thomas and J. N. Seiber, *Bull. Environ. Contam. Toxicol.*, 12 (1974) 17.
31 J. E. Woodrow, D. G. Crosby, T. Mast, K. W. Moilanen and J. N. Seiber, *J. Agric. Food Chem.*, 26 (1978) 1312.
32 B. C. Turner and D. E. Glotfelty, *Anal. Chem.*, 49 (1977) 7.
33 G. O. Nelson, *Controlled Test Atmospheres, Principles and Techniques,* Ann Arbor Science Publishers, Ann Arbor, MI, 1971.