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Use of an automated thermal desorption system for gas chromatographic analysis of the herbicides trifluralin and triallate in air samples

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ABSTRACT

An automated solid particulate adsorption-based air sampling and thermal desorption gas chromatographic system has been evaluated for monitoring trifluralin and triallate vapours in air. Utilizing mini-tubes packed with Tenax-TA resin, capillary gas chromatographic separations of these herbicides with electron-capture detection were equivalent to those obtained with autosampler on-column injection. Linear detector responses and precision exhibiting standard deviations of $<1\%$ with respect to retention time and $<2\%$ with respect to peak area were obtained following thermal desorption of mini-tubes fortified with 0.1 to 50 ng of both compounds. Relative humidity (0–100%) of the air being sampled had little effect on mini-tube breakthrough, with $<1\%$ breakthrough of either herbicide following 28-h sampling periods with a flow-rate of 100 ml min^{-1}. Recoveries of trifluralin and triallate from fortified tubes maintained at room temperature for up to 168 h was quantitative with insignificant cross-contamination between mini-tubes stored in the sampling carousel over this time frame.

INTRODUCTION

Pesticide deposits may dissipate from soil or plant surfaces by volatilization [1] and it is now well established that significant off-target transport of pesticides occurs in the atmosphere as vapour drift [2]. Various air sampling procedures have been used to quantitate off-target vapour drift. Initial monitoring studies utilized liquid sampling trains to trap atmospheric residues [3–5]. Later, solid particulate sorbents, such as silica gel or XAD resins, were employed [6,7]. More recently, organic polymer foams, such as polyurethane foam, which have the advantage of sampling air at much higher flow-rates, have been utilized [8–10].

Each of the above sampling media offers advantages/disadvantages. Although liquid sorbents permit direct gas chromatographic (GC) analysis of sorbed pesticides, a preconcentration step is often required to enhance sensitivity. Polymer foams are the most convenient to use and permit air sampling at high flow-rates, however, as with solid particulate adsorbents, extensive solvent cleanup, usually by Soxhlet extraction, is required prior to sampling. Removal of the adsorbed pesticides from particulate or foam sorbents has typically been accomplished by solvent desorption which, in the case of foams, has generally involved Soxhlet extraction.

Thermal desorption has also been used to strip adsorbed analytes from particulate sorbents directly onto a GC column [11–14]. Since particulate sorbents can also be thermally conditioned prior to sampling and are effectively conditioned for reuse during subsequent analyses, solvent use is essentially eliminated. In addition, sensitivity is greatly enhanced because total analyte residues in the air sample are desorbed directly onto the GC column. Another advantage of thermal desorption is that the process can be automated. Recently, a system utilizing thermal desorption has been described that automates both the sampling and the analysis pro-

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cedures [15]. Integration of the field sampling and laboratory analysis was achieved through a sampling component common to both an automated air sampler and an automated thermal desorption unit mounted on a gas chromatograph. This component was a sample carousel capable of holding 50 mini-tubes packed with a particulate sorbent.

The objective of this study was to evaluate this system for its effectiveness in determining residues of the herbicides trifluralin and triallate in air with a view to utilizing the system in the aerodynamic gradient method of determining post-application herbicide vapour losses from treated fields [16,17].

EXPERIMENTAL

Mini-tube air sampling system (MASS)

The MASS (Canadian Centre for Advanced Instrumentation, Saskatoon, Canada) consisted of a sequence programmable air sampling unit (Model SAM) and an automated thermal desorption unit (ATDU) together with a common 50-position carousel. The carousel was fitted with borosilicate glass mini-tubes (38 mm × 2 mm I.D.) packed with approximately 14 mg of Tenax-TA resin. The resin was centered within each tube and held in place by a pressed stainless-steel screen on either side. For the field study, the air pump in the SAM was operated at its maximum capacity which produced an air flow-rate of 0.1 l min^{-1} through the mini-tubes. The SAM was programmed for sampling time (15, 30, 60 and 120 min) and with respect to mini-tube position such that some positions were bypassed, these being filled with empty mini-tubes for the later insertion of mini-tubes fortified with standards. For mini-tube analysis, the ATDU was mounted onto a Hewlett-Packard Model 5890A gas chromatograph equipped with a ^{63}Ni electron-capture detector (ECD) and controlled with a Model 5895A data section. The ATDU, directly interfaced to the GC system via an HP-1 fused-silica column (Hewlett-Packard; 25 m × 0.53 mm I.D., 0.88 μm film thickness), was operated isothermally (desorption oven temperature, 210°C) with a desorption cycle time of 5 min. The column oven temperature program of the GC system was as follows: 70°C for 1 min, then 5°C min^{-1} to 270°C, and hold for 5 min. The carrier gas (helium UHP) flow-rate was 6.5 ml min^{-1} while the detector make-up gas (nitrogen UHP) flow-rate was maintained at 70 ml min^{-1}. ECD temperature was set at 350°C. Under the above operating conditions, trifluralin and triallate had retention times of 24.5 and 28.1 min, respectively.

Thermal conditioning of the mini-tubes

A manifold, constructed from stainless-steel tubing and Swagelok components to accomodate eight mini-tubes, was used for the preliminary conditioning of the mini-tubes. The manifold was housed in a GC oven maintained at 325°C (maximum recommended temperature for Tenax-TA) and helium passed through the mini-tubes at 25 ml min^{-1} for 2 h. Then, with the GC column removed, the mini-tubes were cycled three times using the ATDU–GC with an ATDU oven temperature of 210°C and a 10-min desorption cycle. With the GC column installed, this process was repeated with a 5-min desorption cycle until desired background interferences were obtained.

Desorption temperature optimization

Mini-tubes were fortified with trifluralin and triallate by adding to the Tenax-TA resin 1 ng each of both herbicides contained in 10 μl of hexane using a 10-μl syringe. The mini-tubes were then placed in the carousel such that the fortified end of the resin was towards the GC column when the carousel was positioned in the ATDU. The optimum ATDU oven temperature using a 5-min desorption cycle was determined by thermally desorbing the fortified mini-tubes using temperatures from 150 to 220°C at 10°C intervals.

ATDU–GC–ECD linearity/reproducibility

Six-point (0.1, 0.5, 1.5, 10 and 50 ng) calibration curves for the thermal desorption of both herbicides from fortified mini-tubes were determined using the ATDU–GC–ECD. Peak area and retention time reproducibilities were established following replication of the above experiment nine more times.

Carousel storage/cross-contamination study

A carousel was fitted with 8 thermally conditioned mini-tubes, wrapped in aluminum foil, and then placed in a polypropylene container (with screw-cap lid) at room temperature. At weekly intervals, the carousel was inserted into the ATDU–GC–ECD and a single mini-tube analysed to deter-

mine background interferences. To determine whether the carousel contributed to the mini-tube backgrounds, this study was repeated except that the mini-tubes were placed in a 20-ml glass scintillation vial and a mini-tube removed at weekly intervals for analysis using the ATDU–GC–ECD.

Trifluralin and triallate cross-contamination between mini-tubes was studied by interspacing in a carousel mini-tubes fortified with either 10 or 100 ng of each herbicide with unfortified thermally conditioned mini-tubes. The carousel was wrapped in aluminum foil and placed in a polypropylene container (with screw-cap lid) at room temperature for 2 weeks. A mini-tube fortified at each level along with an adjacent unfortified mini-tube were analyzed using the ATDU–GC–ECD at the following times: 0.5, 1, 2, 4, 6, 8, 12, 24, 48, 72, 96, 120, 144, 168 and 336 h.

Mini-tube retention/breakthrough study

The PTFE U-tube (Fig. 1) was fortified with 1000 ng each of trifluralin and triallate in 100 μl of hexane and then emersed in the water bath (50°C). Air at approximately 0, 65 or 100% relative humidity (monitored with a Model 911 Dew-All digital humidity analyzer; EG & G Environmental Equipment, Waltham, MA, USA) was continuously drawn through the U-tube at 0.1 l min^{-1} and subsequently through the two mini-tubes arranged in series. The down-stream mini-tube was analyzed using the ATDU–GC–ECD after the following times of continuous air flow: 2, 4, 8, 12, 14, 16, 18, 20, 24, 32 and 48 h. After 48 h, the U-tube was rinsed with 100 ml of hexane and the rinsing concentrated and analyzed by GC–ECD to determine the amount of each herbicide remaining in the U-tube. This experiment was repeated two more times using 5000 and 10 000 ng of each herbicide, except that, rather than fortifying the U-tube, the upstream mini-tube was fortified directly.

Field evaluation

The SAM was mounted at a 1.5-m height on a mast positioned approximately in the centre of a 7.1-ha circular plot. Immediately after surface application of a tank mix of trifluralin and triallate, each at 2.0 kg ha^{-1}, air sampling was commenced. Sampling times of 15 min were used immediately after application when large vapour losses were expected and then, as time after application increased, the sampling program included sampling times of increasing duration. After 120 h, the carousel was removed from the SAM and, after insertion of mini-tubes fortified with trifluralin and triallate standards, loaded into the ATDU–GC–ECD and the air samples analyzed.

RESULTS AND DISCUSSION

The SAM and the ATDU combine to make an integrated system because of the common sample carousel. Once air sampling has been completed,

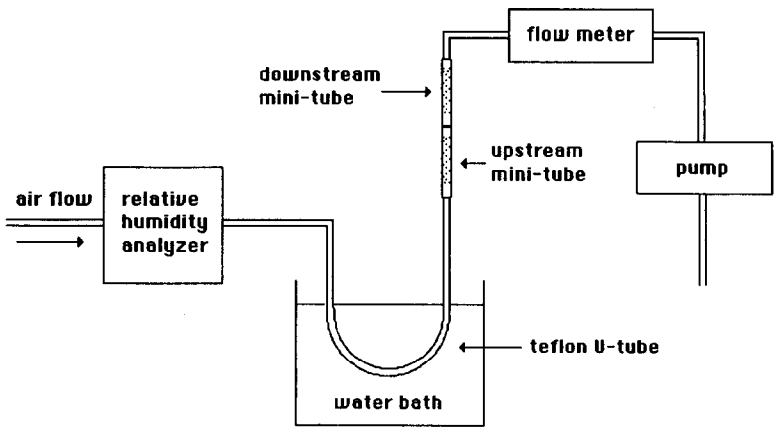

Fig. 1. Apparatus used to determine the breakthrough characteristics of the mini-tubes.

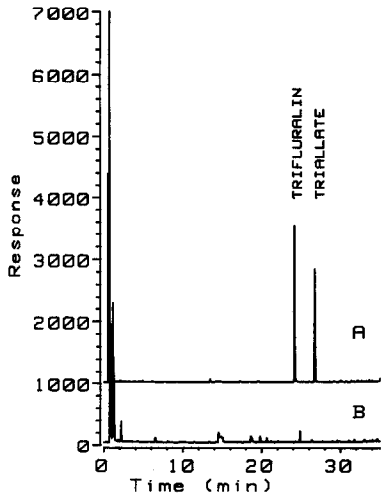

Fig. 2. Mini-tube backgrounds. (A) Background following the extended desorption procedure and three 10-min ATDU–GC desorption cycles at 210°C; (B) 5.0 ng of trifluralin and triallate, respectively.

the carousel is removed from the SAM and, after mini-tubes fortified with appropriate standards have been inserted, positioned in the ATDU on the gas chromatograph. The mini-tubes are then automatically sequentially desorbed onto the GC column.

Prior to the thermal desorption of a mini-tube, carrier gas is routed through the ATDU via a switching valve into the GC column. Once a mini-tube has been inserted into the desorption oven, the valve position is changed and the carrier gas is routed sequentially through the mini-tube and then into the GC column. The mini-tube is inserted into the carrier gas stream such that the end of the mini-tube through which the air was sampled is placed towards the GC column. The desorption oven can be operated isothermally, or temperature programmed once the mini-tube is in place. Pesticide residues sorbed on the particulate sorbent are thermally desorbed and then focussed at the head of the GC-column, essentially effecting a cool on-column injection.

Extensive thermal conditioning of the Tenax-TA resin in the mini-tubes was necessary prior to evaluation of the effectiveness of the mini-tubes for air sampling and analysis of trifluralin and triallate. After the extended desorption procedure and three 10-min ATDU–GC desorption cycles at 210°C, backgrounds acceptable for the quantitation of 1 ng amounts of both herbicides were obtained (Fig. 2). However, several (4–5) additional 5-min cycles were required to obtain backgrounds acceptable for the detection of 100 pg of both herbicides (Fig. 3). Thus, longer desorption [14] at the maximum recommended temperature for Tenax-TA may have more effectively conditioned the resin. A major background peak occurred for all mini-tubes at 35.8 min (Figs. 3 and 5) and, thus far, the compound responsible for this peak has not been identified.

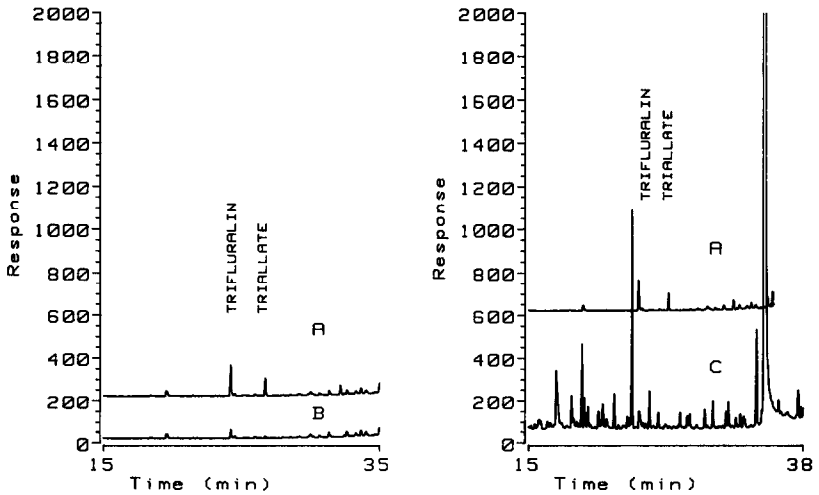

Fig. 3. Mini-tube backgrounds. (A) 0.1 ng trifluralin and triallate, respectively; (B) background following the additional four to five 5-min desorption cycles; (C) background after 8 weeks storage at room temperature in carousel wrapped in aluminum foil.

Following storage at room temperature in a carousel wrapped in aluminum foil, background peaks in the chromatograms of thermally conditioned mini-tubes increased somewhat after 8 weeks (Fig. 3). Interfering background peaks at the retention times for trifluralin and triallate remained small, being less than the equivalent of 100 pg. Similar results were obtained when the mini-tubes were stored in a glass scintillation vial over the same storage period except that, at 8 weeks, interfering peaks were smaller and none were detected at the retention times for trifluralin and triallate. Thus, it seems that during storage of the mini-tubes in the carousel, some of the increased background interferences may have originated from the carousel. This would indicate that when analytes in amounts of 100 pg or less are to be quantitated, the time intervals between thermal conditioning and air sampling, and air sampling and analysis should kept as short as possible.

Using a 5-min desorption cycle, the lowest oven temperature at which quantitative recovery of both trifluralin and triallate was obtained from fortified mini-tubes was 210°C. Because these herbicides have similar vapour pressures (trifluralin, 14.80 mPa [18]; triallate, 25.73 mPa [19], programming the ATDU oven temperature was not necessary and an isothermal desorption cycle was used. ATDU–GC–ECD analysis of fortified mini-tubes under these operating conditions produced trifluralin and triallate peaks which were equivalent to those obtained with on-column injection (Fig. 4). This would indicate that, under these conditions, both herbicides were efficiently focussed at the head of the GC column by the desorption process. These desorption parameters were then used for all other analyses.

A linear ECD response was observed for both trifluralin and triallate following thermal desorption of mini-tubes fortified with amounts of the two herbicides ranging from 0.1 to 50 ng (r^2 = 0.998 for both herbicides). The reproducibility of the retention times and area counts for both herbicides over this fortification range was very good. Standard deviations (n = 10 at each fortification level) of retention times were generally < 0.2%, whereas those for area counts were < 2% (Table I).

Cross-contamination between mini-tubes stored at room temperature for 2 weeks in a carousel wrapped in aluminum foil was minimal. At the 100-ng fortification level, cross-contamination between fortified and unfortified adjacent mini-tubes after 2 weeks was < 0.1% for trifluralin and < 0.2% for triallate. Somewhat higher percentages cross-contamination were observed at the 10-ng level, and this may reflect the presence of small interfering

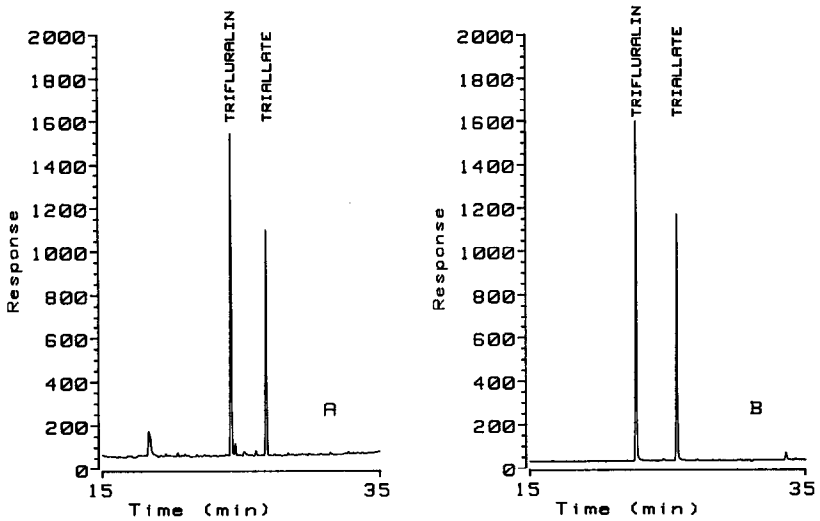

Fig. 4. Comparison of mini-tube thermal desorption and on-column injection for analysis of 1.0 ng each of trifluralin and triallate. (A) Mini-tube thermal desorption; (B) on-column injection.

TABLE I

REPRODUCIBILITY OF AREA COUNTS AND RETENTION TIMES FOR THE ATDU–GC–ECD ANALYSIS OF TRIFLURALIN AND TRIALLATE OVER A MINI-TUBE FORTIFICATION RANGE OF 0.1 TO 50 ng

Fortification level (ng)	Number of replicates (n)	Area counts · 10^{-3} (mean ± S.D.)		Retention times (min) (mean ± S.D.)	
		Trifluralin	Triallate	Trifluralin	Triallate
0.1	10	8.48 ± 0.11	6.22 ± 0.07	24.38 ± 0.01	26.94 ± 0.02
0.5	10	29.60 ± 0.46	22.42 ± 0.18	24.37 ± 0.02	26.92 ± 0.02
1	10	50.24 ± 0.69	38.11 ± 0.40	24.36 ± 0.03	26.91 ± 0.02
5	10	203.5 ± 1.7	153.4 ± 1.3	24.51 ± 0.02	27.07 ± 0.04
10	10	411.8 ± 2.8	309.9 ± 2.9	24.46 ± 0.16	27.06 ± 0.04
50	10	1200 ± 7.7	1157 ± 5.0	24.57 ± 0.03	27.13 ± 0.03

background peaks from the thermally conditioned mini-tubes at the retention times for trifluralin and triallate.

Breakthrough of trifluralin and triallate through the mini-tubes was studied using the maximum air sampling flow-rate (0.1 l min^{-1}) possible with the SAM and relative humidities ranging from 0 to 100%. As observed previously for several workplace air pollutants [14], relative humidity had little effect on the breakthrough of either herbicide through the Tenax-TA resin. Less than 1% breakthrough of either herbicide was detected for each relative humidity level after 168 l of air (air flow-rate of 0.1 l min^{-1} for 28 h) was passed through each mini-tube. This magnitude of breakthrough was observed regardless of whether a 1000-, 5000- or 10 000-loading of each herbicide per mini-tube was used.

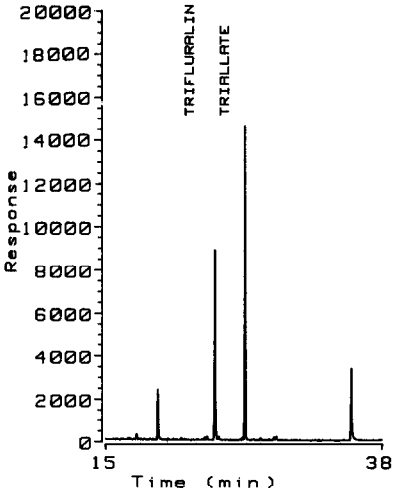

Fig. 5. Chromatogram resulting from the thermal desorption of a 120-min air sample collected 97.5–99.5 h after spraying the field with a surface application of a tank mixture of trifluralin and triallate at (2.0 + 2.0) kg ha^{-1}.

This study also confirmed the feasibility of using the mini-tube system for field sampling of herbicide vapours. In all air samples collected above the treated field over the 120-h sampling period following application, trifluralin and triallate peaks were large relative to atmospheric background peaks (Fig. 5). Thus, a sampling period longer than 120 h would have been required to determine the lowest level at which these herbicides could be realistically detected with a 2-h sample collection time. However, air sample analysis using the mini-tube system did show that herbicide vapour concentrations in the air were maximum immediately after application, and that increased vapour concentrations were present in the air during periods of dew deposition or after a rainfall, as would be expected [17].

As mentioned previously, one advantage of thermal desorption is that all of the analyte(s) in an air sample are desorbed onto the GC column and this can result in enhanced sensitivity. For example, a polyurethane foam sampler aspirated at 25 l min^{-1} will sample 3.0 m^3 over a 2-h sampling period. In contrast, a mini-tube sampling at 0.1 l min^{-1} over the same time period would sample only 0.012 m^3. In previous studies [16,17], the solvent extracts from the polyurethane foam samplers were concentrated to a volume of 10 ml. Thus, the GC analysis of 2.0 μl injection would represent only 0.0006 m^3 of sampled air. In this comparison, a 20-fold sensitivity

enhancement would be realized using the mini-tube technology. Presumably, sensitivity could be increased further with greater air sampling flow-rates through the mini-tubes.

In addition to enhanced sensitivity, the mini-tube based system: (i) offers automated/integrated sampling and analysis as well as convenient sample handling and transportation; (ii) essentially eliminates the use of organic solvents; and (iii) should provide field application for the simplified measurement of herbicide vapour concentrations in air. Studies are currently underway to compare the trapping efficiences of the mini-tubes with those of the polyurethane foam samplers currently used in herbicide vapour flux determinations using the aerodynamic gradient method of measurement.

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