Application and Techniques

A PROCEDURE FOR THE RAPID ASSESSMENT OF AERIAL SPRAY DEPOSITION PATTERNS

W.J. RAE

Ivon Watkins-Dow Ltd, New Plymouth

Summary

A rapid collection and sample analysis technique designed for the study of aerial swath patterns of phenoxy herbicide esters is described. Spray residues deposited on filter papers were extracted on site with a pre-measured volume of petroleum spirit. With no further sample preparation a determination was carried out by automated gas liquid chromatography using flame ionisation detection. Recoveries of 98 and 101% have been demonstrated with a precision of $\pm 2.5\%$ at 95% confidence levels. Detection levels were approximately 40 and 100 g/ha of 2,4-D and 2,5,5-T acid equivalent respectively.

INTRODUCTION

The method of assessment of spray patterns are many and diverse. Highly coloured or fluorescent dyes may be assessed visually on white paper strips or in the case of copper sprays the actual spray material may be developed and assessed (Hager and Collinge 1974, 1973).

In those cases where the workers chose to measure the actual pesticide rather than a tracer or a model spray, collection surfaces such as glass (Amsden 1968) or the polyester plastic Mylar (Yates 1974; Johnson *et al* 1978) have been used. The latter has the advantage of flexibility enabling it to be folded into a jar prior to extraction off site.

In using model dye sprays the assumption is made that the model spray has the same properties as a formulated material. In the case of a typical phenoxy herbicide emulsifiable concentrate (EC) containing surfactants an aqueous and oil component and a volatile ester active ingredient it was deemed desirable to assay the phenoxy ester spray residue directly.

Recent work by Warren (pers comm) Johnson and Wright (pers comm) have shown the utility of the Mylar collection card and Electron capture gas liquid chromatography (glc) analysis in studying drift patterns. However, the preparation and extraction of the Mylar target sample areas have tended to be very labour intensive. Also, non-volatile amine salt herbicides were studied.

In reviewing these methods it has become clear that application materials have been orientated towards the analytical technique. It was decided that what was required was a technique which was flexible enough to collect swath data with the current materials under commercial application conditions. As well as being more realistic to application conditions, such a technique would allow a direct linking of biological trial rating with the application data.

METHOD AND MATERIALS

A study was made of recovery patterns from aerial application of MCPB, 2,4-D and 2,4,5-T phenoxy esters. Spray was collected on a dense grade of filter paper (Whatman No. 5 or No. 6) which was then folded and inserted into a pre-measured volume of solvent and sealed in a screw cap vial. Analysis was done by glc, flame ionisation detection giving adequate sensitivity and eliminating clean up procedures necessary for the more sensitive electron capture detection.

With automatic injection, analysis of 100 samples could be completed in 36 hours involving a labour input (mostly data collation) of about eight hours.

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Field procedure

1. Screw cap vials 25 ml or 30 ml were pre-filled using an Oxford automatic repipette with 20 ml of 80/100 petroleum spirit.
2. One Whatman No. 5 or No. 6 or two No. 1 filter papers 12.5 cm diameter were attached to pinex squares with a drawing pin or paper clip and set out in the desired array.
3. Immediately after the spray had been applied, the filter papers were collected and placed in identified screw-cap vials. Cross contamination of filter papers during collection can be avoided using disposable plastic gloves.

Laboratory procedure

Equipment : Pye G.C.D. with S8 auto injector and Spectra Physics "Minigrator"
Column : 7' OV 225 5% on chromosorb W DMCS

Operating conditions : column 210 °C, detector 230 °C, injector 230 °C attenuation 4 x 1, chart speed 10 cm/hr, 10 microlitre injection sample.

An external standard was prepared from the spray EC actually used in the trial by dilution to an appropriate concentration with petroleum spirit.

Samples from the screw-cap vials were transferred by disposable Pasteur pipettes to the auto injector vials which were then sealed and numbered. Every fifth sample was an external standard. Injection and peak integration was then carried out automatically.

Recovery trial

1. A known weight of a known concentration of 2,4-D butyl ester EC was applied using a hand precision sprayer to a measured area of 24 m². Two superimposed swaths were applied in each direction at walking pace.
2. In the first precision hand application of 2,4-D butyl ester, collection from Whatman 12.5 cm No. 6 filter papers was compared with collection from glass surfaces. Eight replicates of each surface in a staggered array were used. A second precision application was made using only the filter paper collection surfaces.

RESULTS

Run 1

1. EC dilution 31 ml/litres of a 2,4-D butyl ester EC containing 360 g/litre of 2,4-D acid equivalent.
2. Applied rate : 1050 g/24m² equivalent to 4.84 kg/ha

Recoveries

Glass

kg/ha	4.94	4.48	5.07	4.60	5.07	4.64	5.09	4.58
% recovery	102	93	105	95	105	96	105	95
mean rate	4.81	(99.4% recovery)						

Filter papers

kg/ha	4.92	4.50	5.16	4.58	4.67	4.69	4.85	4.63
% recovery	102	93	107	95	96	97	100	96
mean rate	4.75	(98% recovery)						

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Run II

Applied rate: 4.66 kg/ha

Recoveries

Filter papers

kg/ha	4.41	4.43	4.53	4.59	5.5	4.9	4.57	4.70
% recovery	95	95	97	98	118	105	98	101
mean rate	4.70 kg/ha (101% recovery)							

Detection limits

Detection limits estimated from field data and standard solutions are :

2,4-D	acid equivalent as the butyl ester	40 g/ha
2,4,5-T	acid equivalent as the butyl ester	100 g/ha

Measurement of precision

MCPB butyl ester in petroleum spirit 8.15 mg/100 ml was dispensed in 20 ml vials and then analysed as previously described using an external standard and automatic injection.

Results

Sample No.	1	2	3	4	5	6
Determination (mg/100 ml)	Standard	8.23	8.12	8.12	8.09	Standard
Sample No.	7	8	9	10	11	
Determination (mg/100 ml)	8.19	8.30	8.24	8.11	Standard	

Mean = 8.18; s.d. = 0.076 (t test)

Precision of a single determination $\pm$ 2.5% error at 95% confidence level.

DISCUSSION

External standardisation as the preferred technique is described. In this procedure separate injections of a known concentration of phenoxy ester and the unknown samples are compared. Because the flame ionisation detection is linear over a wide range, concentrations are in direct proportion to the relative areas of the chosen phenoxy ester peaks.

Internal standardisation has also been used for 2,4-D butyl esters and found satisfactory. In this procedure MCPB butyl ester of a known concentration is diluted in the extraction solvent and occurs as a well resolved single peak in every injection. Within the same injection the MCPB concentration may be compared with the unknown concentration of recovered 2,4-D butyl ester. Calibration of detector response MCPB butyl ester vs 2,4-D butyl ester is a necessary prerequisite.

In the case of 2,4-D/2,4,5-T 50/50 proprietary blend, however, the phenoxy acid equivalent may occur in a complex mixture of isooctyl and butyl esters. The use of an internal standard involves time consuming and involved calibration. By using an external standard of the EC with known total phenoxy acid equivalent of the same batch number and, therefore, the same proportion of esters the total phenoxy acid equivalent of the unknown and the standard can be simply and directly related. The greater simplicity of the external standard makes it the most practical analysis procedure.

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Detection limits

The detection limit for 2,4-D butyl ester has been established at 10⁻⁶g which corresponds to a rate which can be detected on a 12.5 cm filter paper of 40 g/ha. The detection limit of the mixed iso and *n*-butyl esters of 2,4,5-T are correspondingly less.

The described analysis technique has been applied to measure the spray deposition of a Hiller helicopter under varying conditions as well as estimating spray deposition in gorse canopy (G.W. Woon pers comm).

Extension of the procedure to other pesticides is limited only by their stability to glc analysis and their substantivity to cellulose fibres. The speed with which the sample can be 'fixed' offers considerable advantages over existing techniques when studying volatile pesticide components.

The pinex squares although completely covered by the filter paper can be a source of contamination unless replaced frequently. Extractives from the gummed paper inserts of the vials do appear on the glc trace but are well resolved from the peaks of interest.

Solvent loss during transfer to and from the field site has occurred in about 1% of the samples taken. Leakage is readily detected by odour and reduced solvent levels. Such vials are discarded and the date interpolated.

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