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## Note

# Determination of 2-methoxy-3,6-dichlorobenzoic acid, 2,4-dichlorophenoxyacetic acid and 2-methyl-4-chlorophenoxyacetic acid in emulsifiable pesticide concentrates by high-performance liquid chromatography

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Emulsifiable concentrate formulations consisting of dicamba (2-methoxy-3,6-dichlorobenzoic acid), in combination with 2,4-D (sodium salt of 2,4-dichlorophenoxyacetic acid) or MCPA (2-methyl-4-chorophenoxyacetic acid) have found agricultural use for the control of a wide variety of broadleaf weeds.

For the routine quality control of manufactured concentrate formulations it is desirable to have a quick, simple and specific method for the simultaneous determination of each component. Most published analytical methods for the determination of dicamba, 2,4-D and MCPA are unsuitable for routine quality control monitoring of manufactured formulations either because they involve rather long and sometimes complicated procedures or because they lack specificity and/or sensitivity. Gas chromatographic procedures for these herbicides, almost without exception, involve some form of derivatisation prior to separation and detection[1–5]. Both ultraviolet (UV) and spectrophotometric methods involve extraction of the herbicides from their matrix prior to their determination[6,7]. While a few high-performance liquid chromatographic (HPLC) procedures have appeared in the literature for the determination of 2,4-D[8–10] literature on HPLC methods for dicamba and MCPA is scarce.

An HPLC method for the simultaneous analysis of emulsifiable concentrate formulations containing dicamba with either MCPA or 2,4-D has been developed which meets the requirements of speed, simplicity and specificity. The procedure, which involves no sample manipulation other than weighing and appropriate dilution, is based on the isocratic separation and UV detection at 254 nm of the two components in the concentrate. The recovery of each of the components based on peak height ratios of sample to external standard is in excess of 99%.

## EXPERIMENTAL

### *Apparatus*

The apparatus used consisted of a Waters Model 6000A pump, U6K injector

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and Model 450 variable wavelength UV detector (Waters Assoc., Sydney, Australia). An Altex Ultrasphere 5-$\mu$m ODS, 25 cm × 4.6 mm I.D. reversed-phase column was used (Edwards Instrument, Sydney, Australia). Chromatograms were recorded on an Omniscribe Model B5117-2 recorder (Activon Scientific Services, Granville, Australia).

*Reagents and standards*

Dicamba (87.0%) from Velsicol (Chicago, IL, U.S.A.), 2,4-D (83.0%) and MCPA (95.0%) from Universal Crop Potection (Great Britain). Methanol (HPLC Grade, Burdick & Jackson) from Alltech (Sydney, Australia). Tetrahydrofuran (HPLC Grade) from Waters. Tetrabutylammonium phosphate solution (HPLC Grade, Sigma) from Edwards Instrument.

*Preparation of concentrate formulations*

Aqueous formulations consisting of two different dicamba/2.4-D ratios and two different dicamba/MCPA ratios were prepared as shown in Table I.

TABLE I

EMULSIFIABLE HERBICIDE CONCENTRATES PREPARED AND ANALYSED

| *Component* | *% Added* | | | |
|---|---|---|---|---|
| | *1* | *2* | *3* | *4* |
| Dicamba | 20 | 25 | 20 | 25 |
| 2,4-D | 15 | 20 | 0 | 0 |
| MCPA | 0 | 0 | 15 | 20 |
| Surfactant | 8 | 8 | 8 | 8 |
| Water | 57 | 47 | 57 | 47 |

*Preparation of standards*

Two standards were prepared, one consisting of 0.050 g of dicamba and 0.040 g of 2,4-D per 100 ml of methanol and the other consisting of 0.050 g of dicamba and 0.040 g of MCPA per 100 ml of methanol.

*Preparation of sample*

A 0.25-g sample of each of the four concentrates was weighed and transferred to separate 100-ml volumetric flasks and each flask was then made to volume with methanol.

*Preparation of mobile phase*

The mobile phase was prepared by adding 580 ml of methanol, 20 ml of tetrahydrofuran (THF) and 1 vial (10 ml) of tetrabutylammonium phosphate solution to 390 ml of distilled water. After mixing the solution was degassed under vacuum.

*Chromatographic conditions*

Flow-rate: 1.0 ml $min^{-1}$. Detector settings: 254 nm and 0.1 a.u.f.s. Chart speed: 0.5 cm $min^{-1}$. Injection volume: 25 $\mu$l, each in duplicate.

## RESULTS AND DISCUSSION

A typical chromatogram of the concentrate containing dicamba and 2,4-D is shown in Fig. 1. The dicamba was found to have an impurity (possibly 3,5-dichloro-2-methoxybenzoic acid), which eluted after 5.5 min when using the eluent described. This same impurity peak is also seen in the chromatogram of the concentrate containing dicamba and MCPA, Fig. 2. As can be seen in Fig. 3, when using the mobile phase described it is not possible to separate 2,4-D from MCPA.

When initially developing the chromatographic conditions necessary to achieve the separation of the above components, it was found necessary to ion-pair the acid moiety with tetrabutylammonium phosphate (TBA) in order to increase their retention time on the reversed-phase column. Without TBA all three compounds eluted

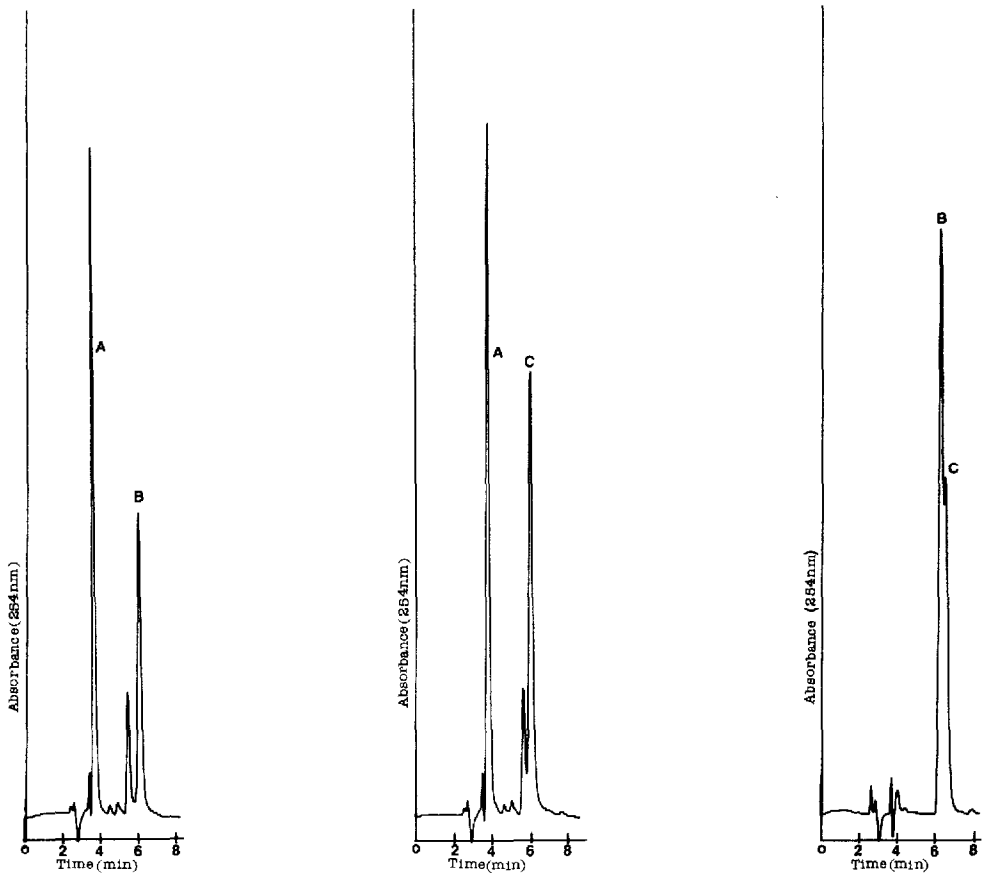


Fig. 1. Chromatogram of emulsifiable herbicide concentrate containing 25% dicamba (A) and 20% 2,4-D (B) when treated and chromatographed as described in Experimental section.

Fig. 2. Chromatogram of emulsifiable herbicide concentrate containing 25% dicamba (A) and 20% MCPA (C) when treated and chromatographed as described in Experimental section.

Fig. 3. Chromatogram of methanolic solution of 0.040% 2,4-D (B) and 0.040% MCPA (C). Chromatographic conditions as described in Experimental section.

TABLE II

RECOVERY OF DICAMBA, 2,4-D AND MCPA FROM EMULSIFIABLE HERBICIDE CONCENTRATES

Based on duplicate 25-μl injections and peak height ratios.

| | *Dicamba (%)* | | | *2,4-D (%)* | | | *MCPA (%)* | | |
|---|---|---|---|---|---|---|---|---|---|
| | *Added* | *Found* | *Recovery* | *Added* | *Found* | *Recovery* | *Added* | *Found* | *Recovery* |
| 1 | 20.0 | 19.8 | 99.0 | 15.0 | 15.0 | 100.0 | — | — | — |
| 2 | 25.0 | 24.9 | 99.6 | 20.0 | 19.9 | 99.5 | — | — | — |
| 3 | 20.0 | 19.7 | 98.5 | — | — | — | 15.0 | 15.2 | 101.3 |
| 4 | 25.0 | 24.9 | 99.6 | — | — | — | 20.0 | 20.2 | 101.0 |

Mean recovery: dicamba, 99.2%; 2,4-D, 99.8%; MCPA, 101.2%.

with the solvent front. In addition, it was found necessary to add THF to the eluent to achieve separation between the dicamba impurity and both 2,4-D and MCPA. The retention times of the three components of interest when using the recommended eluent are: dicamba, 3.7 min; MCPA, 6.1 min; 2,4-D, 6.2 min. The retention time of the dicamba impurity peak is 5.5 min. Furthermore, although it was of no immediate interest to apply the above procedure to the analysis of formulations containing the different esters and anionic salts of 2,4-D and MCPA, the retention times of the following compounds were determined as a check on possible interferences: 2,4-D acid (6.2 min); 2,4-D amine (7.6 min); 2,4-DB (2,4-dichlorophenoxybutyric acid)

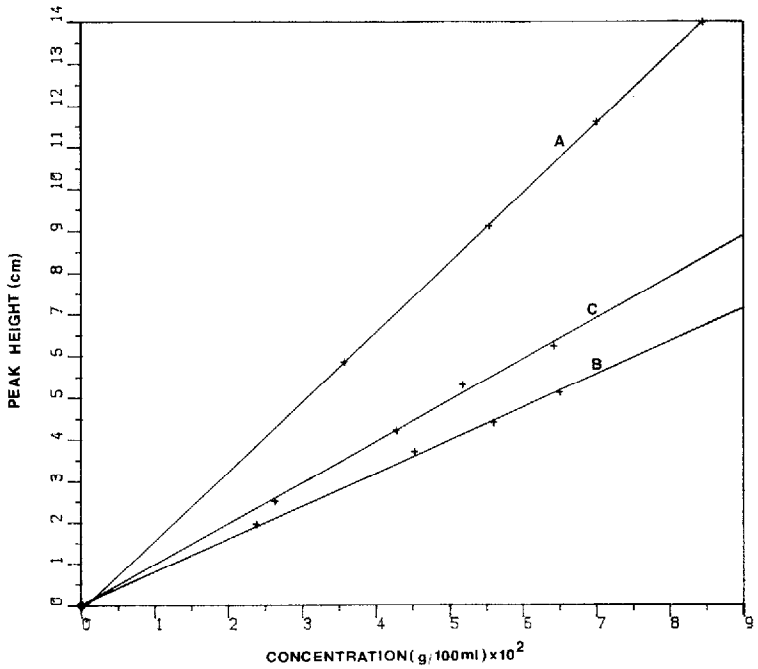


Fig. 4. Calibration curve of dicambal (A), 2,4-D (B) and MCPA (C).

(11.0 min) and 2,4-D ethyl ester (31.5 min). Hence the retention time of both 2,4-D and 2,4-D sodium salt is, as expected, the same (6.2 min).

Table II shows the average recovery of each component from the four formulations analysed. As can be seen the average recovery of MCPA is slightly above 100% due to the less than baseline separation of MCPA and the dicamba impurity peak.

Three methanolic solutions of dicamba, MCPA and 2,4-D were prepared covering the concentration range 0.0357–0.0844% (w/v) dicamba, 0.0290–0.0642% (w/v) MCPA and 0.0238–0.0650% (w/v) 2,4-D. These solutions, which correspond to formulations containing 14.28–33.76% dicamba, 11.60–25.68% MCPA and 0.52–26.00% 2,4-D when diluted as previously described, were used to construct the respective calibration curve of each component and so determine the linearity of detector response in the concentration range of interest. As can be seen in Fig. 4, linearity in the range investigated is excellent.

## CONCLUSION

The method described allows the simultaneous separation and quantitation of emulsifiable herbicide concentrates consisting of either dicamba and 2,4-D or dicamba and MCPA in less than 10 min with a recovery of 99% for dicamba, 100% for 2,4-D and 101% for MCPA. However, it should be noted that the eluent used does not achieve the separation of 2,4-D from MCPA.

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