A method for estimating Diuron (N'-(3,4-dichlorophenyl)-NN-dimethyl urea) in surface water by electron capture gas chromatography

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Diuron (N'-(3,4-dichlorophenyl)-NN-dimethyl urea) is used as an aquatic herbicide for water weed and algal control. (1,2,3,4). A method has been reported (5) for the estimation in water of several substituted urea herbicides including diuron. It involves hydrolysis of the herbicide to release an aniline which is determined colorimetrically after diazotisation and coupling to produce an azo dye. A recent paper (6) uses electron capture gas chromatography for the measurement of unchanged diuron in corn seedlings. The sensitivity of this method is scarcely adequate for routine residue analyses, however, as 10ng produced only 50% fsd at attenuation 2. The method described in this paper uses electron capture gas chromatography of the unchanged herbicide under the conditions reported previously (7).

Experimental method

Extraction procedure

The water was not filtered prior to analysis but

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any large pieces of flora or fauna were removed. One hundred ml of water was measured into a 250-ml separating funnel and vigorously extracted for 1 minute each with two 25-ml portions of dichloromethane. The lower organic layers together with any emulsion were combined in a 100-ml separating funnel. Five ml of glass-distilled water was added and the funnel was shaken for 30 seconds. In addition to washing the dichloromethane, this process was found to break any emulsions which may have formed. The dichloromethane was run into a 100-ml stoppered conical flask through a funnel containing a small plug of dichloromethane-washed cotton wool. The funnel and cotton wool were rinsed with 5ml dichloromethane. A clean glass bead was added and the solution concentrated to about 0.5ml under reduced pressure on a water bath at 35°. The flask was then taken from the water bath and the remaining solvent removed with a gentle stream of air. Five ml of saturated sodium chloride solution was added to the residue and the flask was shaken for 15 seconds. Five ml of 2,2,4-trimethylpentane was added with a pipette and the flask shaken vigorously for 1 minute. Aliquots of the upper 2,2,4-trimethylpentane layer were taken for gas chromatography.

Gas chromatography

A Varian Aerograph 1520 gas chromatograph was used fitted with the electron capture detector previously described in detail (7). The Aerograph electron capture detector is not suitable. The performance of other electron capture detectors has not been evaluated but it seems probable that any design which includes glass in its specification will not be suitable.

Operating Conditions

Column: 1.5m x 3.5mm O.D. stainless steel packed with 5% E301 (methyl silicone) on 60 to 80 mesh Gas Chrom Q.

Flow rate: 50 cc per minute oxygen-free nitrogen.

Injector temperature: 265° Sensitivity: X1

Column temperature: 155° Attenuation: 4 and 8

Detector temperature: 200° Recorder: 1mv L & N Speedomax W

Detector voltage: 90v Chart speed: 30 in/h

The ends of the column were packed with hexane-extracted steel wool. A stainless steel injector insert was fitted and injections were made with the tip of the needle just entering the column. It is essential to exclude glass from the system and to adhere strictly to the conditions described.

Calibration standard

A solution of diuron containing 1mg/ml was prepared in redistilled methanol. Using a Hamilton syringe, 50ul of the solution was transferred to a 100-ml volumetric flask and diluted to volume with 2,2,4-trimethylpentane. This solution, containing 2.5ng in 5ul was diluted with 2,2,4-trimethylpentane to give a range of standards containing 0.1ng to 1.0ng in 5ul. The graph of log peak height vs. log nanograms diuron was linear over the range 0.1ng to 1.0ng. One ng of diuron gave a peak height of 94% fsd at attenuation 8. The 2,2,4-trimethylpentane solutions obtained from extracts of the water were diluted where necessary so that the standard injection volume of 5ul contained a diuron concentration within the calibration range.

Fortification of the water

One ml of the 1mg/ml standard diuron in methanol solution was diluted to 1 litre with control water to give a 1 ppm fortified solution. Successive dilutions were prepared from this solution for the lower levels. The solutions were allowed to stand overnight before analysis.

Results and discussion

The Table shows the diuron recovery from three

surface waters and distilled water at four levels. Algal concentrations obtained using the Lund nannoplankton counting chamber (8) for the W.R.O. pond water, Oxford canal and Thames backwater were 5200/ml, 7400/ml and 8550/ml respectively. The corresponding pH figures were 8.9, 8.2 and 7.85. The three waters used in this work were all taken from typical sites where diuron might be used to control algae and aquatic vegetation.

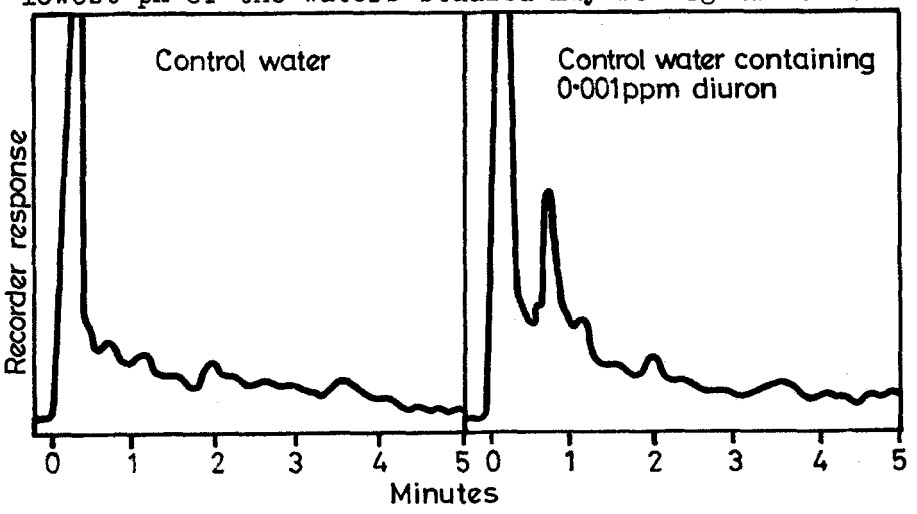
TABLE

RECOVERY OF DIURON IN P.P.M.

Water		Initial Concentration			
		0.001	0.01	0.1	1.0
W.R.O. Pond		0.00096*	0.0097	0.092	0.87
Oxford Canal		0.00085	0.0094	0.091	0.87
Thames backwater		0.00110	0.0110	0.097	0.86
Distilled		0.00092	0.0093	0.095	0.94
% Recovery	Mean	95.7	98.5	93.7	88.5
	S.D.	17.8	7.3	7.0	6.0
No. of determinations		14	12	12	18

* Corrected for blank

The overall mean recovery calculated from 56 results was 94%. The standard deviation of the percentage recovery at the 0.01, 0.1 and the 1.0ppm levels was on average 6.8%, corresponding to a coefficient of variation of 7.2%. Since replicate injections of standards gave a coefficient of variation of 5.5% it appears that most of the variation in the percentage recovery can be assigned to the final measurement and probably reflects the chromatographic stability of this compound. To achieve this level of reproducibility it is essential to use only the column packing and conditions described as previously noted (7) and to exclude glass from the system. The higher standard deviation recorded for the 0.001 ppm level is due mainly to some inexplicably high recovery figures obtained with the Thames water. The fact that this had the highest algal content and the lowest pH of the waters studied may be significant.



The Figure shows the chromatograms obtained from control Oxford canal water and this water fortified with 0.001 ppm diuron.

During the early development of the method blanks ranged from 0.004 to 0.024 ppm but this was reduced to an average 0.0005 ppm by scrupulously rinsing all glassware used, with distilled solvents immediately prior to use. The blank values for all the waters are extremely low (mean of 11 determinations = 0.00051 ppm) with a standard deviation of 0.00009 and they probably derive from the reagents rather than the water.

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