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Note

Two methods for estimating terbutryne residues in water using high-pressure liquid chromatography and gas–liquid chromatography with a conductivity detector

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In late 1973 a slow release formulation of terbutryne (2-ethylamino-6-methylthio-4-*tert.*-butylamino-1,3,5-triazine) was introduced commercially for the control of water weeds (CIBA-Geigy (Clarosan)). Hence it will be of increasing importance for residue analysts to be able to detect low concentrations of this compound in surface waters. In the work reported here two methods are described, one, high-pressure liquid chromatography (HPLC)[1] using a UV detector, the other, conventional gas–liquid chromatography (GLC) coupled with a conductivity detector[2]. Although other methods are available for the estimation of this compound[3], the authors believe that the present work will be useful in extending the range of instruments that may be used.

MATERIALS AND METHODS

Water was obtained from three local sources: (1) an ornamental pond at the Weed Research Organization (W.R.O.), (2) an irrigation reservoir at W.R.O., and (3) a section of the Oxford Canal. The pH value, total chlorophyll content, and total dissolved solid content of each water were measured, and the resulting values are presented in Table I.

TABLE I

CHARACTERISTICS OF THE THREE WATERS

Sample	*Dissolved solids (mg/l)*	*Total chlorophyll content (μg/l)*	*pH at 25°*
W.R.O. pond	308	16.5	7.20
W.R.O. reservoir	263	5.8	7.80
Oxford Canal	544	3.6	7.75

Dissolved solids

1-l samples of filtered water (Whatman No. 42 paper) were evaporated to dryness by repeated small additions to a tared evaporating basin heated on a hotplate. The basin was reweighed and the weight gained taken as a measure of dissolved solids.

Total chlorophyll content

Total chlorophyll was measured fluorometrically using a Turner Model 110 fluorimeter, previously calibrated against a spectrophotometer for this determination. The excitation light was filtered through a Corning glass C5-5-60 filter and the fluorescence monitored through a CS-2-64 filter.

Fortification of the water

Solutions of the herbicide were prepared in methanol so that 3 ml of solution added to a 3-l sample of water gave the required concentration of herbicide. The water was fortified at four levels, 0.1 ppm, 0.05 ppm, 0.005 ppm, and 0.001 ppm. Control samples were prepared by adding 3 ml of methanol to 3 l of water.

Extraction procedure

The extractions were carried out on the same day as fortification without prior filtration of the water. Triplicate 1-l samples of the waters were basified by the addition of 1 ml of "0.880" ammonia solution and then shaken successively with 100-ml and 50-ml portions of dichloromethane. The separated solvent layers were run through a pad of anhydrous Na_2SO_4 into a 250-ml conical flask, and any emulsions formed were broken by running them onto the Na_2SO_4. No loss of efficiency occurred if sufficient Na_2SO_4 was used to absorb the aqueous phase. A further 50 ml of dichloromethane was used to wash the Na_2SO_4 and the combined extracts and washings were evaporated under reduced pressure at 35° on a water-bath. The flasks were removed from the water-bath when about 1 ml of solvent remained and this was removed with a gentle stream of dried air.

High-pressure liquid chromatography

A Perkin-Elmer Model 1240 instrument equipped with a 1.7-mm × 0.5 m stainless-steel column was used, with the following operating conditions: column, Permaphase ETH (DuPont, Wilmington, Del., U.S.A.); eluent, 20% methanol in water; column temperature, 65°; flow-rate, 0.4 ml/min; chart speed, 120 mm/h; injection volume, 5 μl. The 0.001-ppm, 0.005-ppm and 0.05-ppm residues were dissolved in 1.0 ml of methanol and the 0.1-ppm residues in 2.0 ml of methanol; 5 μl of the sample were injected with a high-pressure syringe through a silicone rubber septum directly onto the column. The sensitivity was set at 0.01 absorption units full scale deflection (a.u.f.s.d.) for the lowest concentration, 0.02 a.u.f.s.d. for the 0.005-ppm samples and 0.05 a.u.f.s.d. for the two higher concentrations. Standards were prepared in methanol from an analytically pure sample of the herbicide. It was found that the instrument gave a linear response to standards ranging from 5 ng/5 μl to 300 ng/5 μl. Suitable combinations of standards within this range were chosen to give calibration curves for the different levels of herbicide expected. All peak heights were measured vertically from the apex to a tangent skim baseline.

Gas chromatography

A Pye 104 gas chromatograph equipped with a Tracor Coulson electrolytic conductivity detector (CCD) was used. This type of detector is specific in its response to nitrogen when used in the reductive mode. Acid gases formed are removed by a strontium hydroxide packing placed in the pyrolyser tube adjacent to the exit. A PTFE cell insert[4] was fitted between the pyrolyser and the gas–liquid interface. The ion-exchange column of the detector was packed with 30 *g* of Duolite ARA 366 anion resin (Diamond Shamrock Chemical, Redwood City, Calif., U.S.A.) in the lower section and 15 g of Zerolit DM-F mixed resin (BDH, Poole, Great Britain) in the upper section. These resins maintained the cell water at pH 7.2. Deionised water was used to fill the reservoir. Chromatography was performed on a 1.5-m × 4-mm-I.D. glass column, using the following conditions. Column packing: 2% OV-17 on Chromosorb W-HP 80–100 mesh; flow-rates and gases: carrier, helium, 60 ml/min; sweep, hydrogen, 60 ml/min; reduction, hydrogen, 100 ml/min; temperatures: column, 215°; injection port, 250°; vent valve, 240°; C.C.D. pyrolyser, 850°; Detector: attenuation, 1; cell voltage, 30 V; background signal, 1.2 mV; Chart speed: 120 mm/h; injection volume: 3 μl.

3 μl of the sample were injected onto the column and the column effluent vented to the atmosphere for 30 sec. The gas flow was then switched to the CCD pyrolyser. The 0.001-ppm and 0.005-ppm residues were dissolved in 1.0 ml of methanol, the 0.05-ppm residues in 5.0 ml of methanol and the 0.10-ppm residues in 10.0 ml of methanol. These volumes were chosen to give a response within the linear range of the instrument. Standards were prepared in methanol from an analytically pure sample of the herbicide. The instrument was found to give a linear response with standards ranging from 3 ng/3 μl to 60 ng/3 μl. The vertical peak height to a tangent skim base line was used for all measurements.

TABLE II

SUMMARY OF RECOVERY DATA FROM BOTH METHODS

Water sample	*Fortification (ppm)*	*Method*			
		HPLC		*GLC conductivity detector*	
		Mean recovery (%)	*S.E. of mean (%)*	*Mean recovery (%)*	*S.E. of mean (%)*
W.R.O. pond	0.001	100.0	±4.62	96.7	±0.69
	0.005	90.0	±1.73	97.3	±2.01
	0.050	89.1	±2.24	98.0	±0.23
	0.100	94.5	±0.53	94.4	±1.44
W.R.O. reservoir	0.001	93.3	±3.33	95.0	±0.98
	0.005	100.0	0.00	92.3	±1.13
	0.050	95.3	±0.81	93.3	±0.80
	0.100	97.9	±0.17	92.3	±0.31
Oxford Canal	0.001	91.3	±5.21	96.2	±5.89
	0.005	95.3	±2.33	95.8	±0.83
	0.050	99.1	±0.93	98.4	±0.46
	0.100	95.1	±0.98	92.8	0.00
Overall mean recoveries		95.08% ± 1.07%		95.20% ± 1.55%	

RESULTS AND DISCUSSION

From Table II it can be seen that both methods give good results even at the lowest fortification of 0.001 ppm. As would be expected, the standard error becomes larger with increasing dilution of the herbicide. This is more marked with the HPLC method. Figs. 1a and 1b show typical chromatograms from both instruments. At the lowest concentration (0.001 ppm) the response is approximately twice the background signal and for practical purposes is the limit of detection for both methods. The results obtained justify the conclusion that these methods will form a useful extension of the means available for measuring this herbicide in an aquatic environment.

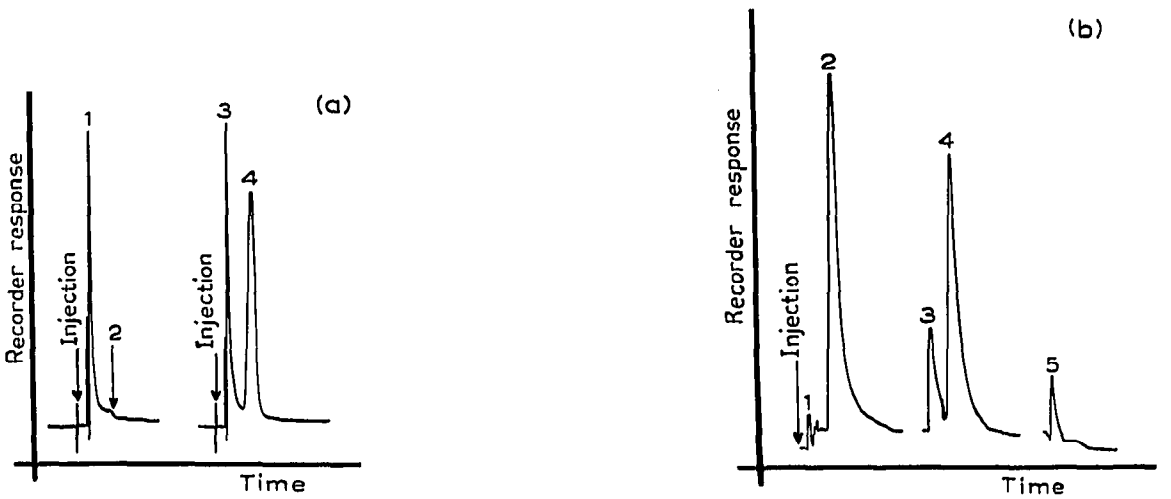

Fig. 1. Chromatograms of canal water control and 0.05-ppm fortification. (a) HPLC. 1 = Control (canal); 2 = terbutryne retention time (= 4.5 min); 3 = solvent response; 4 = terbutryne (0.05 ppm, canal). (b) GLC with conductivity detector. 1 = vent valve closed; 2 = terbutryne (30 ng, standard); 3 = vent valve closed; 4 = terbutryne (0.05 ppm, canal); 5 = vent valve closed (control, canal).

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