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Determination of residues of 2,4,5-trichlorophenoxyacetic acid in soil by gas chromatography of the *n*-butyl ester

The herbicide 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) is recommended[1] for use in forests, for total weed control, for the control of woody weeds, *Urtica dioica* and *Tussilago farfara* and in mixtures with 2,4-D for weed control in established turf. It is more persistent in the soil than many other phenoxyalkanoic acids[1,2] yet little published information is available concerning the analysis of its residues in soil. The gas chromatographic determination of phenoxyalkanoic acids commonly involves the production of an ester derivative, usually the methyl ester (see for example MARQUARDT *et al.*[3]) although other esters have been used[4–8], in order to convert the acid into a more volatile form. In the method described here the *n*-butyl ester is employed as under the chromatographic conditions used, this ester, unlike the methyl and ethyl esters, elutes with a retention time that does not coincide with that of any co-extractives from the soils studied.

Experimental methods

Extraction. The solvent used was diethyl ether–chloroform–glacial acetic acid (25:25:1), the ether and chloroform being first distilled in glass. Soil samples (10 g) were ground with 10 g anhydrous Na_2SO_4 and shaken with 50 ml of solvent mixture in 250-ml conical flasks for 1 h on a wrist action shaker. For very wet soils ($> \sim 20\%$ water) more sodium sulphate was necessary in order to prevent the formation of a soil-water sludge at the bottom of the extraction flask. The exact quantity was determined experimentally; for soils with 50% water about 20 g Na_2SO_4 was sufficient.

Esterification. After shaking, the flask contents were allowed to settle and a 5-ml aliquot of the supernatant liquid was transferred to a 35-ml test tube fitted with a ground glass stopper. The solvent was removed with a stream of dry air on a water-bath at 35°. Residues from soils fortified with esters were dissolved in 5 ml 2,2,4-trimethylpentane and aliquots taken for gas chromatography. To residues from soils fortified with 2,4,5-T acid or from soils with unknown 2,4,5-T content, a 1-ml portion of *n*-butanol was added followed by three drops of concentrated sulphuric acid. The tube was stoppered and placed in a boiling water-bath for 30 min, the stopper being removed briefly to release the pressure after 2 or 3 min. The tube was allowed to cool, then 20 ml deionised water and 5 ml 2,2,4-trimethylpentane were added, after which the tube was shaken. The phases were allowed to separate and 5-μl aliquots of the organic layer were injected into the gas chromatograph.

Gas chromatography. The following conditions were used: Pye 104 gas chromatograph with a ^{63}Ni detector; column, 1.5 m × 4 mm I.D. glass packed with 1.5% XE 60 on 80–100 mesh Chromosorb W, HP; injector temperature, 275°; attenuation, 5×10^2; column temperature, 195°; detector voltage, pulse mode 150 μsec; detector temperature, 280°; carrier gas flow, 60 ml/min oxygen-free nitrogen.

Standards were prepared from 2,4,5-T acid which was taken through the butylation procedure. Quantities were used which gave concentrations in the organic layer in the range 0.005 ng–0.1 ng acid equivalent/5 μl. A graph of log peak area *vs.* log ng herbicide was linear over this range.

Results and discussion

It was necessary to use standards prepared by the butylation procedure rather than solutions made from standard amounts of 2,4,5-T butyl ester as the yield, though reproducible, was only 80%. Butyl ester residues were measured using standards prepared from pure 2,4,5-T butyl ester.

TABLE I

RECOVERY OF 2,4,5-TRICHLOROPHENOXYACETIC ACID FROM FORTIFIED SOILS

Soil	% *clay*	% *organic carbon*	*pH*	*2,4,5,-T added (p.p.m.)*	% *recovery (mean)*	
					Not butylated	*Butylated*
Sandy loam	15.2	1.63	7.7	0.1 butyl ester	88	73
				0.05	81.5	75
				0.01	90.5	58
				0.1 acid	—	89
				0.05	—	74.5
				0.01	—	66.5
Silt loam	22.6	3.45	6.2	0.1 butyl ester	91	71
				0.05	91.5	86
				0.01	90	56
				0.1 acid	—	101
				0.05	—	90
				0.01	—	73.5

Recoveries of 2,4,5-T from two soils fortified at three levels with both the acid and butyl ester are given in Table I and show that the method was capable of producing good recoveries of either form of 2,4,5-T. Comparison of 2,4,5-T butyl ester concentrations in extracts before and after butylation can be used to give an indication of the ratio of acid to ester following an application of a butyl ester formulation although butylation of the residues from soil fortified with butyl ester gave low recoveries as might be expected due to loss of the ester by volatilisation. Direct measurement of the ester was preferred.

There is effectively no background at the appropriate retention time so the limit of detection is largely determined by the sensitivity of the instrument. In our case this is about 0.005 ng, which, on the basis of a 10 g soil sample, is equivalent to 0.005 p.p.m. We have found that operation of the electron capture detector (^{63}Ni or ^{3}H) in the d.c. mode greatly reduces the sensitivity of the method. We have no experience of a ^{3}H detector operating in a pulse mode.

Since this work was completed a method has been described[9] which also uses the butyl ester of 2,4,5-T for its determination in soil, although the method of extraction is different and no details of detection limits or recoveries seem to have been given.

Current experiments in this laboratory which will be reported elsewhere have shown that application of butyl ester to several soils results in rapid hydrolysis of

the ester to the acid making its detection unlikely after a few days. The method described here is appropriate for soils containing both original and hydrolysed ester.

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