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Note

Determination of phenoxy acid herbicides using solid-phase extraction and high-performance liquid chromatography*

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Phenoxy acid herbicides are extensively used for weed control and ultimately find their way into lakes, streams and groundwater. Presently, the accepted procedure for determining 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and 2-(2,4,5-trichlorophenoxy)propionic acid (silvex) involves hydrolysis, extraction, and esterification prior to analysis by gas chromatography[1]. The main disadvantages of this method are the time-consuming sample preparation procedure and the hazards associated with handling organic solvents.

The recent introduction of solid-phase extraction materials is rapidly eliminating the need for liquid–liquid extraction in many procedures[2–5]. This paper describes a procedure for determining phenoxy acid herbicides using a Baker-10 SPE®** system for sample concentration and a high-performance liquid chromatograph for separation and quantitation.

EXPERIMENTAL

Apparatus

A Baker-10 SPE system was used to concentrate herbicide samples onto a Baker C_{18} HC (high capacity) solid-phase extraction column obtained from J. T. Baker (Phillipsburg, NJ, U.S.A.). Samples were analyzed on a Waters Assoc. (Milford, MA, U.S.A.) high-performance liquid chromatograph equipped with two Model M6000A pumps, a Model M450 variable-wavelength detector, a WISP 710B automatic sampler, a Model 720 systems controller and a Model 730 data module. The column used was a 25 cm × 4.6 mm I.D. Zorbax C_8 (DuPont, Wilmington, DE, U.S.A.) with a particle size of 6 μm.

Reagents

All herbicide esters were obtained from the Pesticides & Industrial Chemicals Repository [U.S. Environmental Protection Agency (USEPA), Research Triangle

* The views of the author do not purport to reflect the positions of the Department of the Army or the Department of Defense (Para. 4-3, AR 360-5)

** Use of trademarked name does not imply endorsement by the US Army, but is used only to assist in identification of a specific product.

Park, NC, U.S.A.]. The herbicide-free acids were obtained from Chem Services (West Chester, PA, U.S.A.). Methanol was of UV grade obtained from Burdick & Jackson Labs. (Muskegon, MI, U.S.A.). Acetic acid was of reagent grade obtained from Fisher Scientific (Pittsburgh, PA, U.S.A.). Water used for preparation of solutions was first distilled and then passed through a Millipore Milli-Q (Bedford, MA, U.S.A.) water purification system.

Procedure

Stock solutions of the free herbicide acids and the esters were prepared in methanol at approximately 1000 mg/l. Serial dilutions of the herbicide acids were prepared for calibrating the HPLC system. Esters of the herbicides were prepared similarly and diluted to the range 10–250 μg/l with water. A 50-ml water sample, spiked with the appropriate ester, was hydrolyzed at pH 11 for 1 h with sodium hydroxide. The pH was then adjusted to 2.5 with concentrated hydrochloric acid, and the sample was passed through a C_8 or C_{18} SPE column at a rate of 3–5 ml/min. Two 1-ml portions of methanol were used to elute the herbicides from the column. The eluate was diluted to 5 ml with distilled/deionized water to achieve a sample concentration factor of 10. The sample's solvent strength, therefore, was weak enough to permit a large injection volume. The HPLC conditions were as follows: mobile phase, methanol–1% aqueous acetic acid (68:32); flow-rate, 1.2 ml/min; detector wavelength, 280 nm (0.005 a.u.f.s.); injection volume, 200 μl.

RESULTS AND DISCUSSION

Early experiments indicated that the methyl esters of 2,4-D, 2,4,5-T and silvex

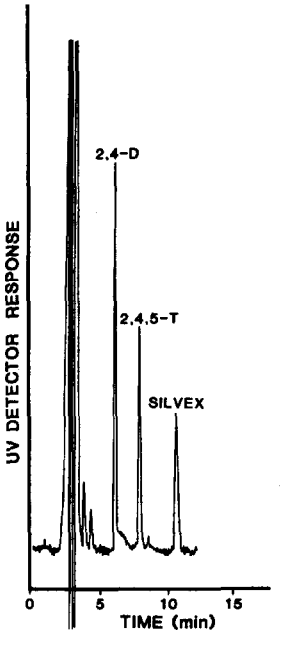

Fig. 1. High-performance liquid chromatogram of 2,4-D, 2,4,5-T and silvex standards at approximately 0.4 mg/l.

were hydrolyzed almost instantaneously at room temperature and pH 11. The 2-ethylhexyl ester of 2,4-D was also hydrolyzed in a few minutes; therefore, all samples were adjusted to pH 11, stirred and arbitrarily allowed to stand for 1 h to ensure complete hydrolysis.

Although the C_8 and C_{18} SPE columns showed comparable recoveries for the herbicides, the C_{18} HC columns were chosen because of recommendations by the supplier. Columns are normally prepared for extraction by passing 5 ml of methanol through, followed by 5 ml of water. For this study, a much cleaner baseline was obtained when the columns were first treated with 5 ml of acetone followed by the 5 ml of methanol and 5 ml of water. We have also found that columns could be re-used following this cleanup procedure with no apparent effect on their performance.

The two absorption maxima of these herbicides were both considered for UV detection. Although 235 nm gave the highest sensitivity, 280 nm was used because it produced the cleanest baseline. A typical chromatogram of the three herbicides is shown in Fig. 1.

TABLE I

RECOVERY OF PHENOXY ACID HERBICIDES FROM WATER USING 6-ml HC C_{18} SPE COLUMNS

M = Milli-Q water; R = Monocacy River water; S = Carroll Creek tributary water.

Herbicide	*Level of spike (μg/l)*	*Recovery (%)*	*R.S.D. (%) (n = 7)*	*Matrix**
2,4-D	20**	80	5.1	M
	200**	105	2.6	M
	15	29	11.4	R
	15	41	11.8	S
	50	55	1.1	R
	50	54	6.7	S
	250	63	1.9	R
	250	63	3.2	S
2,4,5-T	20**	100	6.8	M
	200**	99	3.4	M
	15	63	8.1	R
	15	53	10.6	S
	50	62	2.5	R
	50	61	5.6	S
	250	69	3.2	R
	250	68	4.6	S
Silvex	20**	100	7.9	M
	200**	95	5.0	M
	15	70	6.8	R
	15	74	10.7	S
	50	74	3.8	R
	50	74	4.4	S
	250	76	4.3	R
	250	74	6.0	S

* R and S passed through effective 1.67-μm filter prior to spiking.

** Free acids.

Sample preparation time was approximately 90 min for 15 samples in addition to 1 h for hydrolysis.

Compounds such as dicamba, chlorophenol and phenol did not interfere with the method.

Table I demonstrates the performance of the method when distilled water and local environmental water samples were spiked with each of the three herbicides. River water samples were very turbid, whereas the creek water samples were clear. The detection limit for each of the herbicides was approximately 10 μg/l which represented an observable peak of twice the level of the background noise. In tests involving distilled water, good recoveries and precision were obtained below the 100 μg/l drinking water limits set by the USEPA[6].

Evidently the herbicides were tightly bound to trace organics, when environmental water was used, as evidenced by the lower recoveries. Passing the sample through a 0.45-μm filter prior to spiking did not improve recovery. No herbicides were recovered from a second SPE column placed beneath the first. The addition of sodium chloride (300 g/l) to the sample, prior to passing it through the SPE column, did not produce an overall significant increase in recovery.

Although recoveries are somewhat low for environmental waters, this analytical method has sufficient sensitivity to be of value as a rapid scanning technique for the presence of these herbicides in drinking water. It is also less hazardous, easier to perform and less time consuming than the existing recommended gas chromatography method.

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