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Extraction of Four Chlorophenoxy Acid Herbicides and Picloram from Surface Wipes

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The method described in this paper was developed as a result of a request for analytical support for studies conducted at and around pest control shops at selected U.S. Army installations. As part of these studies, two adjacent wipe samples were collected from various surface locations (e.g., sinks, work benches, washrooms, desks, floors, doorknobs, etc.) within each shop. One wipe sample was submitted to us with the request for analysis of several ionic herbicides (2,4-D, silvex, 2,4,5-T, 2,4-DB, and picloram) and the adjacent wipe sample for analysis of other multi-class pesticides. This communication deals only with the procedure used for the extraction and analysis of the ionic herbicides.

Essentially, the wipe sample extraction involved the use of a potassium hydroxide (KOH) solution similar to that used by Leahy and Taylor (1967) and by McKone and Cotterill (1974) for picloram in soil. Extractions were performed in a heated sonic bath to facilitate hydrolysis of any ester forms of the herbicides studied. Following this extraction/hydrolysis, the alkali solution was washed first with petroleum ether and then with diethyl ether to remove possible interferences from nonionic pesticides and other contaminants. Leahy and Taylor used ethyl acetate as a wash while Purkayastha (1974) used chloroform. The next steps involved acidification of the sample and then extraction of the herbicide acids with diethyl ether. The ether extract was dried over acidified sodium sulfate, concentrated, methylated, and analyzed by electron-capture gas chromatography.

MATERIALS AND METHODS

With the aid of forceps, wipe samples were collected using a pre-extracted cotton ball premoistened with hexane. After the surface was wiped the cotton ball was placed into a 40-mL sample vial with a polytetrafluoroethylene (PTFE)-lined septum screw cap. A somewhat similar collection technique was employed by Leidy (1987) for organophosphorus insecticides that used cotton balls and dental wick material dipped in 2-propanol.

To simulate somewhat the condition under which field samples were received (i.e., some samples were still slightly moist with hexane, and others although appearing dry still had the odor of hexane), pre-extracted cotton balls for use in method recovery experiments were placed in clean 40-mL vials. Each ball was fortified with a total of 2 mL of hexane solution containing the herbicides. This addition was done in 1-mL increments to avoid over-saturation of the cotton ball. The fortification solutions were each prepared at two different fortification levels and consisted of a mixture containing 2,4-D (acid), silvex (propylene glycol butyl ether ester), 2,4,5-T (isooctyl ester), 2,4-DB (methyl ester), and single component solutions of picloram acid or picloram methyl ester. Control samples were fortified using 2 mL of hexane only. The vials were then sealed with PTFE-lined septum screw caps and the contents were allowed to equilibrate at room temperature for 24 hr. NOTE: All glassware, pipets, etc., that

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would come into contact with the acid form of the herbicides during this procedure were prerinsed with acidic water (pH 2), then rinsed with acetone, and allowed to dry.

After 24 hr the contents of the vials were dried using a gentle stream of nitrogen from a manifold system. Twenty-five (25) mL of KOH solution (0.75% w/v) was added to each vial. The vials were capped and placed in a fabricated wire basket. The basket was then suspended in a heated sonic bath for 2.5 hr at 58 $\pm$ 2 °C. Hoke et al. (1986) described a hydrolysis procedure for fortified water samples which took one hour at room temperature using NaOH to basify the sample to pH 11. Through experimentation we found that the esters used in this study required a longer hydrolysis time at the temperature limit of the sonic bath available to us (i.e., 58 $\pm$ 2 °C).

Next, the alkaline sample extracts were transferred to 125-mL separatory funnels. The contents of each extraction vial were then rinsed with 25 mL of the KOH solution, and this rinse was added to the funnel. The excess solution remaining in the cotton ball of each vial was removed by pressing the cotton ball against the inside wall of each vial with the aid of a stainless steel spatula. This solution was then decanted into the funnel. Each basic solution was washed 2X with 50 mL of petroleum ether and once with 25 mL of diethyl ether (unpreserved and peroxide free); each wash was discarded. After this wash step, each basic solution was acidified to a pH between 1 and 2 with 25% aqueous sulfuric acid (approximately 3.5 mL), then extracted 3X with 50 mL of diethyl ether. The extracts were collected in 500-mL Erlenmeyer flasks containing 4g of hexane-washed sodium sulfate. The flasks were stoppered and then shaken for 1 min. After venting the flasks, the stoppers were replaced, and the extracts were allowed to stand for 15 min. The extracts were then decanted into 250-mL Kuderna-Danish (K-D) flasks; the flasks were fitted with 3-ball macro Snyder columns and placed on a 57-60 °C water bath. The extracts were concentrated to ca. 4 mL and then removed from the bath and allowed to cool for several minutes. The ampules (10 mL, graduated) were removed from the K-D flasks, fitted with 2-ball micro Snyder columns, placed back on the same water bath and further concentrated to 0.2-0.5 mL. Once cool, the remaining extract in each ampule was evaporated just to dryness using a gentle stream of nitrogen.

One milliliter of boron trifluoride-methanol (Supelco,Inc.) was added to each ampule in such a manner as to wash down the entire inner wall. The 2-ball micro Snyder columns were placed back on the ampules, and the ampules were placed on a 95-100 °C water bath for 10 min. The ampules were then removed from the bath and cooled to room temperature. The contents of each ampule were reduced to $\leq$0.2 mL with a gentle stream of nitrogen. Four milliliters of toluene followed by 0.35 mL of 5% neutral sodium sulfate solution were added to each ampule. The ampules were stoppered, vigorously shaken for 1 min, and then allowed to stand for 3 min. The toluene layer in each ampule was then pipetted onto a micro drying column. Each column was made from a Pasteur pipet plugged with a small wad of hexane-washed glass wool and filled to a height of 4 cm with hexane-washed sodium sulfate. Each ampule was rinsed with 0.5 mL portions of toluene, and each rinse was transferred to the column. The column eluate and rinses were collected to exactly 5 mL in volumetric flasks.

Two Hewlett-Packard 5880A gas chromatographs equipped with Ni-63 electron-capture detectors and Level IV terminals were used. The first instrument was used for the analysis of the four chlorophenoxy acid herbicides and the second instrument for picloram. Listed below are the parameters and chromatographic columns used for each instrument:

Gas chromatograph #1:

detector temperature - 325 °C
inlet temperature - 220 °C
column temperature - 200 °C
carrier gas - argon/methane (95/5) at 60 mL/min
detector attenuation - 2^5

column - 6 ft, 1/4 inch O.D., 4 mm I.D., glass, packed with GP 1.5% SP-2250 + 1.95% SP-2401 on 100/120 Supelcoport.

Gas chromatograph #2:

detector temperature - 325 °C
inlet temperature - 220 °C
column temperature - 190 °C
carrier gas - argon/methane (95/5) at 60 mL/min
detector attenuation - 2^5

column - 6 ft, 1/4 inch O.D., 4 mm I.D., glass, packed with 100/120 mesh Ultra-Bond 20M coated with 0.5% OV-210 + 0.65% OV-17.

Injections of 4 μL were made for both standards and samples using a Hewlett-Packard 7673A Automatic Sampler. Multilevel calibration standards containing a mixture of methyl esters of 2,4-D, 2,4-DB, silvex, and 2,4,5-T were prepared in toluene at seven different concentrations. The concentration range for each of the chlorophenoxy acid esters were: 2,4-D (5-10000 pg/μL), silvex and 2,4,-T (2.5-5000 pg/μL), and 2,4-DB (10-20000 pg/μL). Multilevel calibration standards were not prepared for the methyl ester of picloram. The resulting picloram peaks from the derivatized samples were diluted to within $\pm$ 30% of the area of either a 10 or 20 pg/μL standard (prepared in toluene) and then quantitated.

RESULTS AND DISCUSSION

Initially, calcium hydroxide was tested as the extraction/hydrolysis medium since it was previously used with success in our laboratory for soil samples. However, calcium hydroxide was discarded in favor of KOH because less precipitates were produced during the procedure. Table 1 presents recovery data at two different fortification levels using calcium hydroxide as the extraction/hydrolysis medium. Analogous recovery data for KOH as the extraction/hydrolysis medium are presented in Table 2.

Table 1. Recovery data for four chlorophenoxy acid herbicides and picloram from wipe samples using calcium hydroxide extraction/hydrolysis

Herbicide	Fort. Level Total μg as Acid Equiv./No. of Reps Per Level	Average % Recovery (All Reps)	Standard Deviation (All Reps)	Coeff. of Variability (All Reps)
2,4-D (Acid)	1.00/7 & 100.0/6	91.4	5.82	6.37
2,4-DB (ME)	0.99/7 & 99.4/6	85.5	4.48	5.24
2,4,5-T (IOE)	0.52/7 & 52.1/6	86.6	5.12	5.91
silvex (PGBEE)	0.52/7 & 51.9/6	85.2	5.67	6.65
picloram (Acid)	1.00/7 & 100.0/6	79.2	10.37	13.09

A comparison of these tables indicates the following: a) recovery and precision were generally satisfactory for the four chlorophenoxy acid herbicides using both calcium hydroxide and KOH; b) more specifically, recovery and precision data for picloram were

significantly improved ($p < 0.05$) and significantly reduced for 2,4-D ($p < 0.01$) using the KOH rather than calcium hydroxide for extraction/hydrolysis when compared using Student t test.

The average percent recovery (Table 2) for all compounds was greater than 80% while the coefficient of variability (CV) ranged from 4.76 to 7.87. Considering the range of herbicide forms used for fortification and the resulting data presented in Table 2, it appears that the procedure described in this paper is both rugged and reproducible. Table 2 does not show recovery or precision data for the individual fortification levels; however, in no case was the difference in average recovery greater than 7% between the two fortification levels for any of the herbicides. Also, the difference in the CV between levels did not exceed 3% for any herbicide.

Table 2. Recovery data for four chlorophenoxy acid herbicides and picloram from wipe samples using potassium hydroxide extraction/hydrolysis

Herbicide	Fort. Level Total μg as Acid Equiv./No. of Reps Per Level	Average % Recovery (All Reps)	Standard Deviation (All Reps)	Coeff. of Variability (All Reps)
2,4-D (Acid)	1.00/4 & 100.0/4	83.1	5.52	6.64
2,4-DB (ME)	0.99/4 & 99.4/4	84.5	4.14	4.90
2,4,5-T (IOE)	0.52/4 & 52.1/4	80.5	5.95	7.39
silvex (PGBEE)	0.52/4 & 51.9/4	84.0	4.00	4.76
picloram (Acid)	1.00/4 & 100.0/4	88.6	6.97	7.87

Table 3 summarizes the precision and accuracy data generated from analyses of intralaboratory quality control (QC) samples. These QC samples were fortified in the same manner and using the same fortification solutions as described above for the data presented in Tables 1 and 2. However, the QC samples were analyzed by several different analysts over a 9-mo period in conjunction with actual field samples. Also, Table 3 shows combined results from analyses of samples fortified with both picloram acid and methyl ester.

Overall, the results from QC sample analyses indicate average percent recovery values for most compounds comparable to those presented in Table 2; however, the average percent recovery values for 2,4-D ($p < 0.05$) and 2,4,5-T ($p < 0.01$) were significantly higher. This could be due to improved laboratory technique over time. The values for the CV were higher for the QC samples except for one compound (2,4,5-T). The larger CV values observed for QC samples can be attributed to the number of analysts involved in the extraction and analysis of these samples.

Table 3. Precision and accuracy data generated from QC samples analyzed in conjunction with actual field samples

Herbicide	Fort. Level Total μg as Acid Equiv./No. of Reps Per Level	Average % Recovery (All Reps)	Standard Deviation (All Reps)	Coeff. of Variability (All Reps)
2,4-D (Acid)	1.00/5 & 100.0/7	89.5	6.74	7.53
2,4-DB (ME)	0.99/5 & 99.4/7	85.3	10.30	12.08
2,4,5-T (IOE)	0.52/5 & 52.1/7	88.8	6.09	6.86
silvex (PGBEE)	0.52/5 & 51.9/7	88.1	7.26	8.24
picloram (Acid) (ME)	1.00/1 & 100.0/4 0.99/4 & 99.40/4	84.1	11.22	13.34

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