Application of the Base-Promoted Esterification Procedure to the Chlorophenoxy Acid Herbicides of U.S. EPA Method 515.3

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Abstract

Determination of chlorinated phenoxyacid herbicides by gas chromatography is complicated by the fact that these compounds exhibit low volatilities due to the hydrogen bonding of their carboxylic acid and phenol functionalities. Furthermore, these functional groups can cause the parent molecule to adsorb on the stationary phase of the column, thus producing asymmetric peaks. Masking of these polar groups can significantly increase the volatility and reduce the adsorption effects of these compounds, yielding products that can undergo analysis by gas chromatography.

A variety of reactions have been employed in the preparation of less polar derivatives. Two categories are examined in this work: silylation and alkylation. Within the category of alkylation, derivatization techniques examined include acid-catalyzed esterification, extractive alkylation, and base-promoted esterification. Of all the investigated techniques, base-promoted esterification is determined to be the most effective. This paper reports the application of this procedure in the development of a sensitive method for the determination of a variety of phenoxyacid herbicides at concentrations below the microgram-per-liter level in water.

Introduction

Chlorinated phenoxyacids are used as selective herbicides in agriculture. Although chlorophenols are used as herbicides as well, they are also extensively used in anti-rotting agents for nonwoolen textiles, paints, and industrial biocides. (1) Due to their carboxylic acid and phenol functionalities, they are somewhat soluble in water. When applied to soils, they tend to leach into ground and surface water and may be found in drinking water. Because of their toxicity, phenoxyacid herbicides must be monitored at low concentration levels in drinking water.

A variety of reactions have been employed to reduce the polarity of the analytes listed in Table I (2–6). Current Environmental Protection Agency (EPA) methodologies require the use

of either diazomethane or trimethylsilyldiazomethane (TMSD) as derivatizing agents for the chlorinated phenoxyacid herbicides (7). The first, diazomethane, is considered extremely toxic; it and several of its precursors have been cited as carcinogens. It has also been known to explode in both gas and liquid form (8). The second, TMSD, produces a large background in the chromatograms, resulting in more difficult identification and detection of the target analytes. These drawbacks prompted the EPA to investigate alternative derivatization techniques.

Experimental

Instrumentation

A Hewlett-Packard (Palo Alto, CA) model 5880 gas chromatograph (GC) equipped with an electron-capture detector (ECD) was used. A DB-1701 fused-silica column (fused silica with chemically bonded [14% cyanopropylphenyl]methylpolysiloxane, 30 m × 0.25-mm i.d., 0.25-μm film thickness) was chosen for the primary analysis. A DB-5.625 fused-silica column (fused silica with chemically bonded [5% phenyl]-methylpolysiloxane, 30 m × 0.25-mm i.d., 0.25-μm film thickness) was chosen for the confirmation analysis. Splitless injection mode was employed with a 30-s split delay; helium linear velocity was measured at 25 cm/s. The temperature program utilized was set at 35°C for 10 min, increased to 150°C at 5°C/min, held for 10 min, increased to 222°C at 4°C/min, held for 5 min, increased to 260°C at 5°C/min, and held for 6 min.

Reagents

Analytical standards were purchased as ampulized solutions from Chem Service (West Chester, PA). Methyl iodide (catalog number 28,956-6), pentafluorobenzylbromide (PFB) (catalog number 10,1052), 1.0M tetrabutylammonium hydroxide in methanol (catalog number 23,018-9), tetramethylammonium hydroxide (catalog number 23,321-2), and potassium carbonate (catalog number 36,787-7) were obtained from Aldrich (Milwaukee, WI). Ampulized solutions of BF_3–methanol (catalog number 3-3020) and the silylating

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agent, 80% *N,O*-bis(trimethylsilyl)acetamide–20% trimethyl-chlorosilane (3-3018), were purchased from Supelco (Belle-fonte, PA). All solvents and reagents were of analytical grade.

Extraction and derivatization

It was intended that the final procedure be applicable to the determination of chlorinated phenoxyacid herbicides in

Table I. Analytes of U.S. EPA Method 515.3

Analyte	CAS number
Acifluorfen/lactofen*	50594-66-6
Bentazon	25057-89-0
Chloramben	133-90-4
2,4-D	94-75-7
Dalapon	75-99-0
2,4-DB	94-82-6
Dacthal/acid metabolites†	
Dicamba	1918-00-90
3,5-Dichlorobenzoic acid	51-36-5
Dichlorprop	120-36-5
Dinoseb	88-85-7
5-Hydroxydicamba	7600-50-2
4-Nitrophenol	100-02-7
Pentachlorophenol	87-86-5
Picloram	1918-02-1
2,4,5-T	93-76-5
2,4,5-TP (Silvex)	93-72-1

* Acifluorfen and lactofen are different esters of the same parent herbicide. Because of the saponification step prior to extraction in this method, they were quantitated together as a single analyte.

† Dacthal is a methyl diester; however, it is also used in its monoester/monocar-boxylic acid and dicarboxylic acid forms. Because of the saponification step prior to extraction in this method, all dacthal derivatives were quantitated together as a single analyte.

drinking water, ground water, raw source water, and water at any intermediate treatment stage. Because herbicides are applied as a variety of esters and salts, an initial saponification step was performed to ensure that all esters and salts were converted to the parent carboxylate ion, and therefore all forms were quantitated as a single analyte.

Extraction

The pH of the aqueous sample was lowered to below 2 followed by the addition of methyl *tert*-butyl ether (MTBE) to extract the chlorinated herbicides. Due to the EPA's commitment to pollution prevention, this procedure was designed as a microextraction to reduce solvent consumption. A 40-mL volume of water was extracted with a 4-mL volume of MTBE (9).

Derivatization

Acid-catalyzed esterification

Mineral acid-catalyzed esterification (Fisher esterification). A 1-mL volume of acidic methanol (10% concentrated H_2SO_4 in 90% methanol) was added to 3 mL of the MTBE extract. The extract was then heated at 50°C for 2 h. The resulting acidic extract was neutralized by a back-extraction with an aqueous solution of sodium bicarbonate, and an aliquot of the extract was injected onto the GC.

Lewis acid-catalyzed esterification. A 1-mL volume of BF_3–methanol was added to 31 mL of the MTBE extract. The extract was then heated at 50°C for 2 h. The resulting extract was washed with a solution of $NaCl$–H_2O, which pulled the remaining BF_3 into the aqueous phase and thus quenched the reaction. An aliquot of the extract was injected onto the GC.

Silylation

A 1-mL volume of the silylating agent, 80% *N,O*-bis(tri-methylsilyl)acetamide–20% trimethyl-chlorosilane, was added to 3 mL of the MTBE extract. The extract was then heated at 50°C for 4 h. After cooling, an aliquot of the extract was injected onto the GC.

Extractive alkylation

Tetramethylammonium hydroxide was added to a 40-mL water sample until the pH was greater than 10. A 40-µL volume of methyl iodide was added to a 4-mL volume of MTBE. The solvent was added to the aqueous sample and shaken for 5 min. The phases were allowed to separate for 5 min, and an aliquot from the upper MTBE layer was injected onto the GC.

Base-promoted procedure

Before methylation, the extract was thoroughly dried with acidified sodium sulfate. An 80-µL volume of 1.0M anhydrous tetrabutylammonium hydroxide in methanol was added to 3 mL of the dried extract followed by the addition of 40 µL of

Table II. Herbicide Recoveries in Chlorinated Surface Water

Analyte	Background concentration (µg/L)	Fortified concentration (µg/L)	Mean measured concentration (µg/L)	Standard deviation (µg/L)	Relative standard deviation (%)	Recovery (%)
Acifluorfen	< 0.38	3.75	4.08	0.63	15	109
Bentazon	< 1.2	7.50	6.98	0.58	8.3	93
Chloramben	< 0.14	3.75	3.22	0.26	8.1	86
2,4-D	< 0.36	7.50	6.85	0.55	8.0	91
Dalapon	< 1.2	7.50	8.06	0.39	4.8	108
2,4-DB	< 0.60	7.50	7.31	0.48	6.6	97
Dacthal/acid metabolites	< 0.38	7.50	6.71	0.70	10	90
Dicamba	< 0.20	3.75	3.69	0.14	3.6	98
3,5-Dichlorobenzoic acid	< 0.62	3.75	4.18	0.54	13	111
Dichlorprop	< 0.41	7.50	6.70	0.24	3.6	89
Dinoseb	< 1.2	7.50	8.81	1.8	20	117
5-Hydroxydicamba	< 0.21	3.75	0.180	0.048	26	5
4-Nitrophenol	< 1.2	7.50	6.63	0.78	12	88
Pentachlorophenol	< 0.021	0.750	0.771	0.071	9.2	103
Picloram	< 0.47	7.50	7.11	0.74	10	95
2,4,5-T	< 0.16	1.87	1.55	0.19	12	83
2,4,5-TP (Silvex)	< 0.072	1.87	1.69	0.13	7.6	90

methyl iodide. The extract was heated at 50°C for 1.5 h, resulting in the formation of a precipitate, tetrabutylammonium iodide. The methylated extract was passed through a florisil cleanup column and injected onto the GC.

Results and Discussion

Acid-catalyzed esterification

Fisher esterification is a mineral acid-catalyzed reaction of carboxylic acids with alcohols to form esters.

$$RCO_2H + R'OH \text{ ---------}H^+\text{---------} > RCO_2R' + H_2O$$
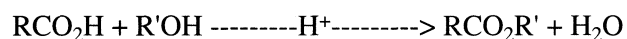
This is an equilibrium process; using an excess of the alcohol drives the reaction to completion.

This procedure worked well with the halogenated acetic acids formed in the disinfection of drinking water (9). However, several of the herbicides examined, namely dicamba, 5-hydroxydicamba, dinoseb, 4-nitrophenol, pentachlorophenol, and dacthal, were not derivatized by this procedure. It was determined through a literature search that dicamba and 5-hydroxydicamba did not derivatize due to steric bulk around the carboxylate moiety (both compounds contain substituents ortho to the carboxylic acid position) (10–26). The literature sources, however, did not offer an explanation for the lack of derivatization of the remaining four compounds. Dinoseb, 4-nitrophenol, and pentachlorophenol contain phenolic groups, and the dacthal compound is a diacid. It was assumed that the acidic methanol reagent was not vigorous enough to convert the phenols to ethers, nor to ensure the esterification of two carboxylic acid groups within the same molecule.

Similar results were obtained in the attempt to esterify dicamba using a Lewis acid, BF_3, as the catalyst. This was also noted by Frei and Lawrence (2) and attributed to steric hindrance of the o-chlorine atom.

Silylation

Silylation introduces a silyl group into a molecule, usually in substitution for an active hydrogen (5). The silylating reagent used in this work was 80% N,O-bis(trimethylsilyl)acetamide with 20% trimethylchlorosilane as a catalyst. This reagent was chosen because it was described as highly reactive in the silylation of carboxylic acids and phenols and also possessed the additional advantage of producing neutral reaction products. Initial work with the reagent produced chromatograms containing high background levels.

Due to the large number of compounds that was anticipated in this method, fur-

ther work was not pursued due to expected interference of the background with the elution of the analytes.

Extractive alkylation

In this procedure, simultaneous extraction and derivatization was performed. A carboxylic acid or phenol anion was partitioned from the aqueous phase into the organic phase, which contains the alkylating agent as an ion pair, by using a quaternary ammonium ion.

$$RCO_2H\text{-----}R'_4N^+OH^-\text{-----}> RCO_2^-N^+R'_4\text{-----}R''I\text{-----}> RCO_2R''$$

The choice of solvent was critical as it must provide low solvation of the extracted carboxylate anion to ensure that it easily reacted with an alkylating agent. Literature sources indicated good results using particular solvents, a primary choice being methylene chloride (10–15). Methylene chloride was not investigated as a potential solvent, however, because of the EPA's interest in eliminating its use from EPA methodologies due to its adverse health effects. Because the success of MTBE in the extraction of the target compounds had already been established, it was investigated as the solvent for the above reaction mechanism. However, the methylated herbicides of interest were not recovered with this change of solvent, and further work was not undertaken.

Base-promoted procedure

The base-promoted procedure entailed the abstraction of the acidic hydrogen by a base followed by the attack of the nucleophilic carboxylate ion on an alkyl halide in an SN_2 fashion (phenolic analytes were converted to their corresponding alkyl ethers). Literature sources indicated good results with the use of this technique in various applications

Table III. Herbicide Recoveries in Chlorinated Ground Water

Analyte	Background concentration (µg/L)	Fortified concentration (µg/L)	Mean measured concentration (µg/L)	Standard deviation (µg/L)	Relative standard deviation (%)	Recovery (%)
Acifluorfen	< 0.38	3.75	4.17	0.46	11	111
Bentazon	< 1.2	7.50	7.88	0.46	5.8	105
Chloramben	< 0.14	3.75	3.84	0.30	7.8	102
2,4-D	< 0.36	7.50	6.67	0.17	2.6	89
Dalapon	< 1.2	7.50	7.33	0.65	8.9	98
2,4-DB	< 0.60	7.50	7.74	0.54	7.0	103
Dacthal/acid metabolites	< 0.38	7.50	6.82	0.39	5.7	91
Dicamba	< 0.20	3.75	3.96	0.12	3.0	106
3,5-Dichlorobenzoic acid	< 0.62	3.75	4.25	0.29	6.8	113
Dichlorprop	< 0.41	7.50	7.11	0.74	10	95
Dinoseb	< 1.2	7.50	7.45	0.72	9.7	99
5-Hydroxydicamba	< 0.21	3.75	3.62	0.12	3.4	96
4-Nitrophenol	< 1.2	7.50	7.90	0.51	6.4	105
Pentachlorophenol	< 0.021	0.750	1.0	0.068	6.8	134
Picloram	< 0.47	7.50	6.15	0.63	10	82
2,4,5-T	< 0.16	1.87	1.65	0.074	4.5	88
2,4,5-TP (Silvex)	< 0.072	1.87	1.80	0.081	4.5	96

including food, pharmaceutical, and environmental chemistries (16–26).

$$RCO_2H \text{-----} R'_4N^+OH^- \text{------}> RCO_2^- \text{-----}R''I \text{-----}> RCO_2R''$$

Several bases were reported to work well in this reaction. Those investigated included potassium carbonate, tetramethylammonium hydroxide, and tetrabutylammonium hydroxide. Initial work began with the use of anhydrous K_2CO_3 as the base. However, the lower recoveries of methylated compounds led to concern regarding whether the dry base was effectively mixing with the MTBE extract upon addition. The use of tetramethylammonium hydroxide was investigated next. The chromatograms produced with this base yielded an interferant peak that coeluted with one of the analytes (dalapon) as well as other extraneous peaks. Literature sources indicated that anhydrous conditions were essential because the presence of moisture in the reaction vessel yielded artifact peaks in the sample chromatogram and further resulted in incomplete methylation of the target analytes (10–26). Because this base could not be purchased in anhydrous form, attention was directed toward tetrabutylammonium hydroxide as it was available in an anhydrous methanolic solution. The use of this base proved satisfactory, and it was chosen as the reagent for the final procedure.

The alkyl halide can be varied as well as the base in this base-promoted derivatization reaction. Much of the work reported to date has centered around the use of the alkyl halide PFB in an effort to obtain enhanced ECD signals. In this study, we employed methyl iodide as the alkylating agent because the additional sensitivity was not a priority, and iodide was expected to be an efficient leaving group in the SN_2 reaction. For this application, methyl iodide offered the additional advantages of shortening the chromatographic run (because the methyl derivatives are more volatile than their PFB counterparts) and eliminating the cleanup step required with the PFB procedure to remove excess reagent.

A reaction time of 1.5 h was utilized to ensure complete methylation of all target analytes in the presence of other organic compounds coextracted from the water sample. Several water matrices were examined in this respect including chlorinated surface water from a local utility, chlorinated ground water from a water source displaying a hardness of 460 mg/L (as $CaCO_3$), reagent water fortified at 1.0 mg/L with fulvic acid extracted from Ohio River water (intended to simulate high TOC). In each set of experiments, seven replicates were fortified with the entire list of chlorinated herbicides at the concentration of the mid-level of the calibration range. The results from these studies are presented in Tables II–IV. Additionally, extraction/methylation efficiencies were calculated by comparing the responses obtained from fortified reagent water taken through the established procedure to commercially prepared methyl derivatives; these results are in Table V.

A method detection limit (MDL) study was performed according to the EPA definition and standard procedure (27). To determine the MDL of each analyte, seven laboratory blanks were fortified at a level equal to 2–5 times the noise level and taken through the entire procedure. The MDL was calculated by multiplying the standard deviation for the seven replicates by the Student's t value at 99% confidence and $n - 1$ degrees of freedom (3.143 for seven replicates). The resultant MDLs are listed in Table VI. Also specified are estimated detection limit (EDL) values. The EDL is defined as either the MDL or the level of a compound in a sample yielding a peak in the final extract with a signal-to-noise ratio of approximately 5, whichever is greater.

Table IV. Herbicide Recoveries in with High TOC Content Water

Analyte	Background concentration (µg/L)	Fortified concentration (µg/L)	Mean measured concentration (µg/L)	Standard deviation (µg/L)	Relative standard deviation (%)	Recovery (%)
Acifluorfen	< 0.38	3.75	3.8967	0.4553	124	104
Bentazon	< 1.2	7.50	7.50	0.44	5.9	100
Chloramben	< 0.14	3.75	3.68	0.24	6.6	98
2,4-D	< 0.36	7.50	6.37	0.93	15	85
Dalapon	< 1.2	7.50	6.82	1.1	16	91
2,4-DB	< 0.60	7.50	8.01	0.42	5.2	107
Dacthal/acid metabolites	< 0.38	7.50	6.93	0.53	7.6	92
Dicamba	< 0.20	3.75	3.67	0.13	3.4	98
3,5-Dichlorobenzoic acid	< 0.62	3.75	3.86	0.33	8.5	103
Dichlorprop	< 0.41	7.50	7.24	0.52	7.2	97
Dinoseb	< 1.2	7.50	7.08	0.81	11	94
5-Hydroxydicamba	< 0.21	3.75	3.17	0.34	11	84
4-Nitrophenol	< 1.2	7.50	7.04	0.49	7.0	94
Pentachlorophenol	< 0.021	0.750	0.736	0.12	16	98
Picloram	< 0.47	7.50	5.66	1.0	18	75
2,4,5-T	< 0.16	1.87	1.49	0.29	20	79
2,4,5-TP (Silvex)	< 0.072	1.87	1.77	0.19	11	95

Conclusion

This work represents an attempt to develop an analytical method by which the chlorinated phenoxyacid herbicides can be measured in a safe and accurate manner. Several derivatization techniques were investigated. The acid-catalyzed procedure was found to be ineffective for several of the herbicide compounds, the silylation method produced a large number of extraneous peaks, and the extractive alkylation technique yielded no recoveries. The base-promoted esterification proved to be a safe and effective means of derivatization and was established as the basis of a new EPA method for the determination of herbicides in water. It is anticipated that the analysts utilizing this method will find it easy to understand as well as a means for obtaining accurate quantitation for the chlorophenoxy acids and phenols without the use of diazomethane or TMSD.

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Table V. Esterification Efficiencies

Analyte	Efficiency (%)
Acifluorfen/lactofen	91.2
Bentazon	77.3
Chloramben	87.7
2,4-D	94.1
Dalapon	91.2
2,4-DB	82.3
Dacthal/acid metabolites	83.4
Dicamba	92.6
3,5-Dichlorobenzoic Acid	86.4
Dichlorprop	89.3
Dinoseb	42.4
5-Hydroxydicamba	89.2
4-Nitrophenol	87.7
Pentachlorophenol	86.0
Picloram	46.2
2,4,5-T	94.6
2,4,5-TP (Silvex)	93.2

Table VI. Method Detection Limits and Estimated Detection Limits

Analyte	Method detection limit (µg/L)	Estimated detection limit (µg/L)
Acifluorfen/lactofen	0.38	0.38
Bentazon	0.50	1.2
Chloramben	0.14	0.14
2,4-D	0.36	0.36
Dalapon	0.53	1.2
2,4-DB	0.60	0.60
Dacthal/acid metabolites	0.38	0.38
Dicamba	0.20	0.20
3,5-Dichlorobenzoic Acid	0.13	0.62
Dichlorprop	0.41	0.41
Dinoseb	0.75	1.2
5-Hydroxydicamba	0.21	0.21
4-Nitrophenol	0.66	1.2
Pentachlorophenol	0.021	0.021
Picloram	0.47	0.47
2,4,5-T	0.16	0.16
2,4,5-TP (Silvex)	0.072	0.072