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Determination of acid herbicides in aqueous samples by liquid–solid disk extraction and capillary gas chromatography

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ABSTRACT

A simplified procedure for extraction and analysis of chlorinated acid herbicides in aqueous matrices using modern filter disk extraction technology is presented. An acidified water sample is extracted with a 47-mm polystyrene–divinylbenzene filter disk and the analytes are eluted with a mixed methanol–methyl *tert.*-butyl ether solvent. After extract drying, the analytes are esterified with diazomethane and analyzed by gas chromatography with electron-capture detection. The discussion includes extraction disk selection, sample acidity and salting requirements, elution volume requirements and the effect of sample volume on recovery. Method detection limits are given as well as accuracy and precision data on four fortified matrices —reagent water, dechlorinated tap water, biologically active surface water and high humectant ground water.

INTRODUCTION

The Safe Drinking Water Act as amended in 1986 [1] required promulgation of maximum contaminant levels and recommended treatment technologies for 83 contaminants in drinking water in three time-based phases. Final regulations for the phenoxyacid herbicides, 2,4-D and silvex, were published in January 1991 [2]. This same rule contained monitoring requirements for the unregulated herbicides dalapon, dicamba, dinoseb and picloram. Regulation for pentachlorophenol was published in July 1991 [3]. In addition, the following acid herbicides are scheduled for regulation in a future phase: acifluorfen (blazer), bentazon, dacthal and dicamba. Inherent in the regulations are requirements for sound analytical methods.

The current US Environmental Protection Agency (EPA) method for the analysis of phenoxyacid and other acid herbicides in drinking water is EPA Method 515.1 [4]. The analyte list of Method 515.1 contains 17 compounds, including all those discussed above. This method was originally developed for use during the National Pesticide Survey [5]. During this extensive study, four of the analytes were not determined quantitatively because of lack of control of precision, namely dalapon, chloramben, acifluorfen and 4-nitrophenol. Two of these

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compounds are not appropriate candidates for Method 515.1 or the technique discussed below. Dalapon is a hydrophilic molecule, which does not partition favorably from aqueous solutions by liquid–liquid or reversed-phase extraction and 4-nitrophenol does not methylate. Method 515.1 is a complex liquid–liquid extraction procedure employing large volumes of organic solvents, which are usually vented to the atmosphere during preconcentration. Our objectives in these capillary gas chromatography (GC) methods development activities were to simplify the methodology and minimize solvent consumption by means of liquid–solid extraction (LSE).

Numerous reports on the use of LSE techniques for the analysis of organic acids in aqueous solutions have been published over the past decade. Some of the more recent and pertinent ones are cited here. Most of these have employed extraction cartridges (*e.g.* Carbopack, reversed phase) for analyte preconcentration and subsequent analysis by high-performance liquid chromatography [6–10]. There have been some very interesting publications on ion-exchange procedures for the extraction of organic acids from aqueous samples for subsequent analysis by GC or GC–mass spectrometry [11–13]. Our original approach for the acid herbicides was in fact ion-exchange extraction. We did sufficient work with a strong anion exchanger (Bio-Rad AG1-X8) to demonstrate feasibility for both the herbicides and haloacetic acids [14]. An ion-exchange technique for dalapon and the haloacetic acids is under concurrent development (EPA Method 552.1). However, we found this to be a more complicated and time-consuming approach for the analysis of the herbicides than the filter disk extraction procedure presented below.

Recent reports have appeared on the use of reversed-phase extraction disks for the rapid extraction of organics from water [14–17]. Advantages of these disks over extraction cartridges have been discussed by Markell *et al.* [18]. These include high flow-rates, elimination of the potential for flow channeling and improved capability for handling dirty samples. The alternative use of disk technology has already been incorporated into several EPA drinking water methods.

We have evaluated C_{18} and polystyrene–divinylbenzene (PS–DVB) resin disks and present here a procedure for the extraction and analysis of acid herbicides in aqueous samples. This technology provides the basis for an improved, alternative method (EPA Method 515.2). Method performance data are presented for fortified reagent water and drinking water sources.

EXPERIMENTAL

Chemicals

Individual stock and calibration standard mixtures were prepared from pure materials obtained from the EPA Repository, Research Triangle Park, NC, USA. All solvents were high-purity pesticide quality (Burdick & Jackson) distributed by Baxter Scientific (Cincinnati, OH, USA). All other chemicals were ACS reagent grade or better.

Instrumentation and capillary column

A Hewlett-Packard 5890 (Kenneth Square, PA, USA) capillary gas chromatograph was fitted with a J & W Scientific (Folsom, CA, USA) DB-5 fused-silica capillary column (30 m × 0.32 mm I.D., 0.25 μm d_p). The gas chromatograph was also equipped with an electron-capture detector and a HP 7673 auto-sampler.

Analytical operating parameters

Helium carrier gas velocity was set at 25 cm/s (210°C). The detector make-up gas, methane–argon (5:95), was set at 30 ml/min. Initial oven temperature was set at 50°C and held for 5 min. The oven temperature was then ramped to 210°C at 10°C/min and held for 5 min, followed by a program to 230°C at 10°C/min and a final 10-min hold. A 2-μl sample size was injected in the splitless mode (purge off 30 s).

Other special equipment and materials

The extraction disks were Empore-3M 47-mm C_{18} and PS–DVB resin (Analytichem International, Harbor City, PA, USA). The extraction apparatus consisted of all-glass Kontes filter funnels (Cat. No. k953755-0000, Fisher Scientific, Pittsburgh, PA, USA) used with 1-l glass vacuum flasks. A Model 111 N-EVAP 12 (Or-

ganomations, South Berlin, MA, USA) was used for sample concentration.

Standard procedure

Summary of the method. The method analytes and surrogate compound (2,4-dichlorophenylacetic acid) are extracted from 250-ml aqueous samples by means of 47-mm filter extraction disks. The analytes are eluted with a minimal volume of a combination methanol–methyl *tert.*-butyl ether (MTBE) solvent and esterified with diazomethane. Analysis is accomplished by means of capillary GC with electron-capture detection.

Extraction. The samples were prepared for extraction by addition of 20% (w/w) anhydrous, reagent-grade sodium sulfate (previously heated to 400°C for 4 h) and adjustment of sample pH to 1.0 ± 0.1 with reagent-grade sulfuric acid. The extraction disks were conditioned by sequentially adding in a continuous manner the following series to the disk surface [380–500 Torr (1 Torr = 133.322 Pa): 20 ml methanol–MTBE (10:90), 5 min of room air, 20 ml methanol and 20 ml of reagent water. The sample is then added (without allowing the disk to dry) and the vacuum is adjusted to 630 Torr. After all the sample has passed through the disk, the vacuum is adjusted to 380–500 Torr and room air is passed through the disk for 20 min.

Elution. A 2-ml volume of methanol–MTBE (10:90) is placed on top of the disk, without vacuum, and allowed to sit for 1 min. The vacuum is then applied and the eluate is collected in a 60-ml test tube, which is placed inside the vacuum flask after extraction. This step is repeated and the sample flask is rinsed with 4 ml of pure MTBE, which is also passed through the disk.

Extract drying and derivatization. The eluent is dried by passing it through a large pasteur pipette containing 4 g acidified anhydrous sodium sulfate. Any visible water in the eluate must be excluded from the drying pipette to avoid clogging. The eluate collection tube is then rinsed with 2×1 ml aliquots of MTBE, which are also passed through the drying tube. Derivatization is accomplished by purging the sample directly with diazomethane gas using a micromolar generation procedure, which is described in detail in Method 515.1 [4]. The procedure is in turn based upon the esterification technique described by Schlenk and Gellerman [19].

Analysis. The samples were analyzed by capillary GC–electron-capture detection using a Hewlett-Packard 5890 GC equipped with a Model 7673A autosampler. A Waters Maxima data system was used for collecting and processing chromatographic data.

RESULTS AND DISCUSSION

During the course of the development of this method, the following parameters or variables were evaluated: column selection, extraction disk selection, sample acidity and salting requirements, sample volume and extraction time, and elution solvent selection and volume. Following method optimization, method validation data were obtained on fortified reagent water, dechlorinated tap water, biologically active surface water and high humectant ground water. These activities are described in some detail below.

All of the Method 515.1 analytes cannot be resolved by capillary GC using 30-m columns. Thus, we have separated the analytes into two groups for the methods development and validation activities. This was also standard practice during the National Pesticide Survey. The analytes are listed in Table I in the relative retention order observed for the primary column. These compounds are aromatic organic acids or phenols (dinoseb and pentachlorophenol) and usually contain chlorine substitution on the aromatic ring. Reference is made to the Pesticides Manual [20] or the Farm Chemicals Handbook [21] for details on chemical structure.

Since the acid herbicides are extracted by a reversed phase, the analytes must be in the molecular form for efficient recovery. This is accomplished by reducing the pH to 1.0 ± 0.1 with concentrated sulfuric acid. Recovery is also markedly enhanced by the addition of salt to attain a high ionic strength sample. Table II presents preliminary recovery data from fortified, unsalted 100-ml reagent water samples extracted with C_{18} and resin. The use of sodium sulfate gave somewhat higher recoveries than extractions by addition of the same mass per-

TABLE I

RELATIVE RETENTION ORDER

Analyte	Group[a]
3,5-Dichlorobenzoic acid	A
2,4-Dichlorophenylacetic acid[b]	A, B
Dicamba	B
Dichlorprop	A
2,4-D	B
4,4'-Dibromooctafluorobiphenyl (I.S.)	A,B
Pentachlorophenol	A
Silvex	B
5-Hydroxydicamba	B
2,4,5-T	A
2,4-DB[c]	B
Dinoseb	A
Bentazon	B
Picloram	B
Dacthal	A
Acifluorfen	B

[a] Analytes were divided into two groups during method development to avoid chromatographic overlap.
[b] Surrogate analyte.
[c] 2,4-DB = 4-(2,4-dichlorophenoxy)butyric acid.

centage of sodium chloride. For unsalted reagent water, the resin recovery data are significantly higher for dalapon, dacthal and picloram. Nevertheless, recovery is negligible or poor for several of the analytes. Salting the water dramatically improves the recovery for all of the analytes to acceptable levels, except for dalapon, and largely removes recovery differences between C_{18} and resin recovery data. The exception was dacthal, for which recovery remained significantly lower with C_{18} extraction.

Initial studies on elution volumes employed a moderately polar dye compound, Red Disperse 1, methanol elution and photometric measurement of recovery. With three successive 2-ml aliquots, recoveries of 80, 15 and 3% were obtained. The dye appeared to be almost quantitatively eluted from the disk with the first aliquot. However, the glass frit supporting the disk has a considerable surface area, which must be washed with additional solvent. The acid herbicides were eluted with the mixed methanol–MTBE solvent as described above. The analytes

TABLE II

C_{18} AND RESIN RECOVERIES AND EFFECT OF SALTING

Analyte	Recoveries ± R.S.D.(%; $n = 3$)			
	C_{18}[a]	Resin[a]	C_{18}[b]	Resin[b]
Acifluorfen	77 ± 20	82 ± 5	104 ± 5	121 ± 1
Bentazon	0	No Data	90 ± 13	71 ± 5
Chloramben	8 ± 11	3 ± 15	72 ± 14	77 ± 7
2,4-D	86 ± 12	83 ± 6	81 ± 8	94 ± 15
Dalapon	0	42 ± 25	12 ± 75	31 ± 30
2,4-DB	81 ± 13	80 ± 14	118 ± 10	130 ± 8
Dacthal	53 ± 17	99 ± 8	67 ± 16	97 ± 5
Dicamba	73 ± 13	71 ± 14	83 ± 3	94 ± 15
3,5-Dichlorobenzoic acid	70 ± 17	76 ± 2	86 ± 25	107 ± 20
Dichloroprop	77 ± 11	78 ± 3	85 ± 9	94 ± 10
Dinoseb	72 ± 16	75 ± 5	92 ± 26	85 ± 6
Pentachlorophenol	69 ± 14	70 ± 2	65 ± 15	73 ± 8
Picloram	49 ± 19	74 ± 7	96 ± 24	99 ± 21
2,4,5-T	76 ± 11	75 ± 14	93 ± 10	89 ± 5
Silvex	73 ± 14	74 ± 14	82 ± 9	80 ± 5

[a] Fortified, unsalted reagent water.
[b] Fortified reagent water with 20% (w/w) Na_2SO_4.

TABLE III

SINGLE LABORATORY RECOVERY, PRECISION DATA AND METHOD DETECTION LIMIT (MDL) WITH FORTIFIED REAGENT WATER

Analyte	Fortified concentration (μg/l)	Mean recovery (%)[a]	R.S.D. (%)	MDL (μg/l)
Acifluorfen	0.50	70	21	0.25
Bentazon	2.50	70	11	0.63
2,4-D	0.25	96	38	0.28
2,4-DB	2.50	79	12	0.72
Dacthal[b]	0.25	96	16	0.13
Dicamba	0.75	109	11	0.28
3,5-Dichlorobenzoic acid	1.25	126	24	1.23
Dichlorprop	0.25	106	15	0.13
Dinoseb	0.50	87	22	0.28
5-Hydroxydicamba	0.75	90	12	0.25
Pentachlorophenol	0.25	103	18	0.16
Picloram	0.75	95	15	0.35
2,4,5-T	0.25	116	18	0.16
Silvex	0.25	98	9	0.06

[a] Based on the analyses of seven replicates by resin disk extraction.
[b] Measurement includes the mono- and diacid metabolites.

are effectively esterified in this solvent and no other solvents were evaluated.

Recovery *versus* sample volumes of 100, 250 and 500 ml and 1 l were determined for both C_{18} and resin extraction by analysis in triplicate for each sample volume. The mean recoveries averaged over all analytes were highest for the 100-ml volume, $88 \pm 13\%$ for C_{18} and $94 \pm 9\%$ for the resin disk. By contrast, the overall mean recoveries at 250 ml were $70 \pm 5\%$ for C_{18} and $77 \pm 7\%$ for the resin. With the exception of picloram and dacthal, analyte recoveries were remarkably constant for both C_{18} and resin over sample volumes from 250 to 1000 ml. At a volume of 250 ml, the C_{18} recoveries were unacceptably low for picloram (43%) and dacthal (25%). The resin recoveries at 250 ml were adequate for picloram (64%) and dacthal (93%) and remained greater than 80% at 1 l for dacthal. Considering all the analytes, the resin is the disk of choice. The overall superior performance of the resin is likely attributable to its aromatic, polymeric structure, which should have a greater affinity for the aromatic, moder-

TABLE IV

SINGLE-LABORATORY RECOVERY AND PRECISION DATA FOR FORTIFIED REAGENT WATER

Analyte	Fortified concentration (μg/l)	Mean recovery (%)[a]	R.S.D. (%)
Acifluorfen	2.0	59	13
Bentazon	10.0	68	8
2,4-D	1.0	90	20
2,4-DB	10.0	74	6
Dacthal[b]	1.0	60	10
Dicamba	3.0	75	9
3,5-Dichlorobenzoic acid	5.0	62	18
Dichlorprop	1.0	97	17
Dinoseb	2.0	63	10
5-Hydroxydicamba	3.0	77	8
Pentachlorophenol	1.0	69	11
Picloram	3.0	66	9
2,4,5-T	1.0	64	15
Silvex	1.0	68	8

[a] Based on the analyses of 6–7 replicates by resin disk extraction.
[b] Measurement includes the mono- and diacid metabolites.

ately polar analytes. Since the method detection limits [22] determined for a 250-ml sample (Table III) were more than adequate, this volume was chosen for the method performance data given below. If the analyte list of interest does not include picloram and dacthal, recoveries of 60% or greater may be anticipated for the remaining analytes for sample volumes up to 1 l by C_{18} or resin extraction.

The data of Table II represent overall analyte method recoveries, since the calibration standards were prepared in the final 5 ml extract. By contrast to Method 515.1, this method is sufficiently simple that aqueous standards are processed through the method in order to correct for recoveries. Accuracy and precision data have been obtained on three fortified matrices —reagent water, dechlorinated tap water and high humectant ground water. The complete set of performance data is contained in the method

TABLE V

SINGLE-LABORATORY RECOVERY AND PRECISION DATA FOR FORTIFIED, DECHLORINATED TAP WATER

Analyte	Fortified concentration (μg/l)	Mean recovery (%)[a]	R.S.D. (%)
Acifluorfen	2.0	150	7
Bentazon	10.0	112	9
2,4-D	1.0	90	16
2,4-DB	10.0	111	10
Dacthal[b]	1.0	118	8
Dicamba	3.0	86	10
3,5-Dichlorobenzoic acid	5.0	111	5
Dichlorprop	1.0	88	30
Dinoseb	2.0	121	6
5-Hydroxydicamba	3.0	96	6
Pentachlorophenol	1.0	96	6
Picloram	3.0	132	12
2,4,5-T	1.0	108	10
Silvex	1.0	115	7
2,4-Dichlorophenyl-acetic acid[c]	1.0	120	19

[a] Based on the analyses of 6–7 replicates by resin disk extraction.
[b] Measurement includes the mono- and diacid metabolites.
[c] Surrogate analyte.

TABLE VI

SINGLE-LABORATORY RECOVERY AND PRECISION DATA FOR FORTIFIED, HIGH HUMIC CONTENT SURFACE WATER

Analyte	Fortified concentration (μg/l)	Mean recovery (%)[a]	R.S.D. (%)
Acifluorfen	2.0	120	13
Bentazon	10.0	87	11
2,4-D	1.0	59	7
2,4-DB	10.0	80	14
Dacthal[b]	1.0	100	6
Dicamba	3.0	76	9
3,5-Dichlorobenzoic acid	5.0	87	4
Dichlorprop	1.0	110	22
Dinoseb	2.0	97	6
5-Hydroxydicamba	3.0	82	9
Pentachlorophenol	1.0	70	5
Picloram	3.0	124	9
2,4,5-T	1.0	101	4
Silvex	1.0	80	6

[a] Based on the analyses of 6–7 replicates by resin disk extraction.
[b] Measurement includes the mono- and diacid metabolites.

[23]. A set of representative data for each matrix is presented in Tables IV–VI. The data are based on the analysis of 6–7 replicates for each set. In obtaining these data, method blanks were routinely measured for the unfortified matrix. Thus, the high accuracy data observed for acifluorfen, dinoseb and picloram in the tap and surface waters may represent some unknown matrix effect. Nevertheless, these data are equivalent to or better than that obtained by Method 515.1 on real matrices. In general, the precision attained by this method is superior, probably because of increased method simplicity.

In summary, a LSE method has been developed for the analysis of acid herbicides in water matrices using modern filter disk extraction technology. The method is considerably simpler than conventional liquid–liquid extraction methods and the requirement for large volumes of organic solvents is eliminated. The analysis time, and thus cost, are decreased. A skilled analyst can process eight samples over two days by Method 515.1. The same number

can be processed in an 8-h period by the method described here.

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