

Development of a Solid-Phase Extraction Method for Phenoxy Acids and Bentazone in Water and Comparison to a Liquid–Liquid Extraction Method

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A rapid solid-phase extraction (SPE) method was developed for the determination of bentazone and the phenoxy acids 2,4-D, dichlorprop, MCPA, and mecoprop in Norwegian environmental water samples. Cartridges with a high-capacity cross-linked polystyrene-based polymer were used for off-line preconcentration. The effects of elution solvent, elution volume, sample volume, sorbent mass, pH, and flow rate on the recoveries of the pesticides were investigated using HPLC. Average recovery of >90% was achieved with 500 mg sorbents using 2 mL of methanol with 5% NH₃ as elution solvent. The recoveries were independent of sample pH in the tested range of pH 1–7. Using a sample volume of 200 mL, the limits of determination for the phenoxy acids and bentazone are 0.02 µg/L. Sample volumes up to 2000 mL at a flow rate of 60 mL/min could be handled without any loss of analytes, which makes it possible to lower the limits of determination. The SPE method was compared to a routinely used liquid–liquid extraction method. Three different water matrices spiked at 1.0 and 0.05 µg/L were extracted, and the quantification was performed by GC-MS. Both methods permitted the determination of phenoxy acids and bentazone in distilled water, creek water, and well water down to a level of 0.05 µg/L with recoveries >80% for 200 mL samples. Important advantages of the SPE method compared to the liquid–liquid extraction method were the short extraction times, lack of emulsions, use of disposable equipment, and reduced consumption of organic solvents.

Keywords: *Phenoxy acids; bentazone; solid-phase extraction; liquid–liquid extraction*

INTRODUCTION

Phenoxy acids, such as 2,4-D, dichlorprop, MCPA, and mecoprop, have extensively been used for control of weeds in agriculture. The high solubility of phenoxy acids in natural water promotes their entry into surface or ground waters by natural drainage or infiltration (Schuster and Gratzfeld-Hüsgen, 1991).

To meet the objectives for monitoring bentazone and phenoxy acids in water samples in Norway, a routine method with liquid–liquid extraction (LLE) has been used (Holen and Christiansen, 1994). Several methods for analysis of pesticide residues in water use dichloromethane for LLE (Durand et al., 1992). However, these methods can be time-consuming and require large volumes of hazardous organic solvents, which pose a risk with regard to both the environment and the health of the operators. Solid-phase extraction (SPE) has gained popularity for sample preparation of pesticides from water (Benfenati et al., 1990). It offers the advantages of short analysis time, cleaner extracts, enhanced trace enrichment, higher chemical selectivity, lack of emulsions, reduced consumption of organic solvents, and the possibility for automation. Several papers describe the use of C₁₈ bonded silica cartridges (Volmer and Levsen, 1994; Balinova, 1993), styrene–divinylbenzene

Empore extraction disks (Chiron et al., 1994; Hodgeson et al., 1994), and Carbopack cartridges (Di Corcia et al., 1993; Bucheli et al., 1997) for the extraction of acidic herbicides from water samples. The techniques of automated column switching (Geerdink et al., 1991; Hamann et al., 1989; Papadopoulou-Mourkido and Patsias, 1996; Scancho-Llopis et al., 1993) and on-line SPE coupled to liquid chromatography (Chiron et al., 1994; Chiron and Barcelo, 1993; Lee et al., 1999) have been reported for the determination of acidic herbicides both in drinking water and in surface water. Others have focused on the separation and quantification techniques for acidic pesticides (Schmitt et al., 1997; Stutz and Malissa, 1998). However, the sample preparation is the time-determining step in the whole procedure for analysis of pesticides.

The objectives of this work were (i) to develop a time effective SPE method for phenoxy acids and bentazone that can be used in the routine monitoring of drinking water and drainage water from agricultural fields in Norway and (ii) to compare the SPE method with an LLE method that has been used until now for routine analysis.

EXPERIMENTAL PROCEDURES

Chemicals. Methanol and acetonitrile far-UV were of HPLC grade, dichloromethane and tetrahydrofuran (THF) of pestiscan grade. All were obtained from Labscon (Dublin, Ireland). Orthophosphoric acid (H₃PO₄) 85%, ammonia solution (NH₃) 25%, hydrochloric acid fuming (HCl) 37%, formic acid (HCOOH) 98–100%, and anhydrous disodiumsulfate (Na₂SO₄),

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all of p.a. quality, were purchased from Merck (Darmstadt, Germany). Tetrabutylammoniumhydrogen sulfate, pentafluorobenzylbromide, and *n*-decane were from Fluka (Buchs, Switzerland). Potassium dihydrogenphosphate was obtained from Sigma (St. Louis, MO).

Standards. Certified reference standards of bentazone, 2,4-D, dichlorprop, MCPA, and mecoprop were supplied by Dr. Ehrenstorfer (Augsburg, Germany). For each pesticide, stock solutions of 1 mg/mL were made in 20 mM phosphate buffer, pH 3. They were used for preparation of diluted mixed standards. All solutions were stored in the dark at 4 °C. The mixed standard solutions were stable during the 16 weeks of the study.

Samples. Distilled water was used as sample in the method development work. Creek water, well water from the Aas area (Norway), and distilled water were used for comparison studies of SPE and LLE.

Equipment and Materials for Sample Preparation. An SPE vacuum manifold from Supelco (Bellefonte, PA) was used for SPE, and a standard Millipore 47 mm filtration apparatus (Bedford, MA) was used for extraction with disks. The cartridges used for preconcentration were 6 mL disposable extraction cartridges packed with 200 or 500 mg of styrene-divinylbenzene copolymer (SDB) from IST (Mid Glamorgan, U.K.). Empore extraction disks, 47 mm, with a C₁₈ phase and disposable C₁₈ cartridges (500 mg, 6 mL) from Varian (Harbor City, CA) were used in preliminary tests.

The eluates from the cartridges were evaporated to dryness using a centrifugal evaporator from Savant Instruments (Farmingdale, NY).

SPE Procedure. Samples were prepared by spiking 500 mL of distilled water with mixed standard solutions. During method development the sample pH was adjusted to 1 with 6 M HCl. The extraction cartridges were rinsed by passing 5 mL of methanol through the cartridge followed by 10 mL of water adjusted to the same pH as the sample. Teflon tubes were connected between sample reservoir and cartridges. Sample loading was performed at a flow rate of 5–10 mL/min under vacuum. The sorbent was never allowed to dry during the rinsing and sample loading procedures. After extraction, the cartridges were dried with a gentle stream of nitrogen. Elution was performed by gravity, but the vacuum was turned on at the end of elution. Different elution solvents and elution volumes were tested. The eluate was evaporated to dryness, redissolved in 1 mL of 20 mM phosphate buffer, pH 3, and analyzed by HPLC. Once the elution parameters were optimized, different retention parameters were tested.

For the method comparison study, 200 mL of distilled water, creek water, and well water was spiked with mixed standard solutions and the sample pH was adjusted to 7. The general procedure for SPE was as described above. SDB cartridges of 500 mg were used. The sample loading flow rate was 60 mL/min, and elution was performed with 2 mL of methanol with 5% NH₃. The eluate was evaporated to dryness, redissolved in 4 mL of phosphate buffer, pH 8, derivatized with pentafluorobenzyl bromide (Holen and Christiansen, 1994), and analyzed by GC-MS.

LLE Procedure. Two hundred milliliters of water was acidified to pH 1 by addition of 3 M HCl and extracted twice with dichloromethane (50 mL + 25 mL). The combined extracts were dried over anhydrous Na₂SO₄, evaporated to dryness, derivatized, and analyzed by GC-MS as previously described for SPE.

HPLC Analysis. The liquid chromatograph was composed of a Spectra-Physics model SP8000 pump, a SP4270 integrator (San Jose, CA), a Gilson autosampler (Middleton, WI) with a 50 μ L loop, and a Milton Roy UV detector (Staffordshire, U.K.) set at 200 nm. A C₈ analytical column of stainless steel, 25 cm \times 4.6 mm i.d., packed with Spherisorb 5 μ m particles from Phase Separations Ltd. (Deeside, U.K.), was used for HPLC analysis. The mobile phase was 20 mM phosphate buffer, pH 3/acetone (65:35 v/v) at a flow rate of 1 mL/min, and the injection volume was 50 μ L. Quantification was performed by external calibration by measuring the peak areas.

GC-MS Analysis. All GC-MS measurements were performed with a Hewlett-Packard 5971A MSD combined with a Hewlett-Packard 5890A GC (Palo Alto, CA) fitted with a CP-SIL 5CB MS capillary column, 50 m \times 0.25 mm i.d. \times 0.40 μ m film thickness, from Chrompack (Middelburg, The Netherlands). The carrier gas was helium (Ultra Plus 6.0, Hydro gas, Oslo, Norway) set to a head column pressure of 18 psi at 80 °C (linear velocity = 29.9 cm/s). The injection volume was 2 μ L operating in the splitless mode (60 s). Injector and detector temperatures were 240 and 260 °C, respectively. The oven temperature was held at 80 °C for 1 min, then raised at 20 °C/min to 160 °C followed by 5 °C/min to 280 °C, and finally held for 5 min. The MSD was operated in the selected ion monitoring mode (SIM, 70 eV). Two characteristic ions were selected for each compound: mecoprop, *m/z* 394 and 396; MCPA, *m/z* 380 and 382; dichlorprop, *m/z* 414 and 416; 2,4-D, *m/z* 400 and 402; and bentazone, *m/z* 378 and 420. Quantification was performed by external calibration by measuring the peak areas.

RESULTS AND DISCUSSION

Choice of SPE Sorbent and Method Development. Most publications on extraction and cleanup of environmental samples with SPE describe the use of bonded silica sorbents, especially C₁₈ or C₈ (Heberer et al., 1995; Mattina, 1991; Butz et al., 1994). In a preliminary experiment C₁₈ cartridges and C₁₈ disks were tested with water with a high content of dissolved organic matter. However, the C₁₈ material was plugged immediately. SDB and divinylbenzene/vinylpyrrolidone sorbents have been reported to give good recoveries for polar pesticides and acidic herbicides from water (Pichon et al., 1996; K ppen and Spliid, 1998). SDB cartridges were tested with the same water containing a high content of dissolved organic matter and were found to work well without plugging. As our intention was to use the method also for samples with a high content of dissolved organic carbon, it was decided to use SDB cartridges for further method development. Plugging of the bonded silica sorbents is probably caused by the smaller particle size and wider particle size distribution of the silica, compared to SDB sorbents.

The SPE method development was performed in two major steps. First, the retention was held constant and the elution process was optimized by testing different elution solvents and elution volumes. Once the elution process was optimized, the variables controlling retention (sorbent mass, sample pH, sample volume, and flow) were tested and revised if necessary. As initial conditions for SPE of phenoxy acids and bentazone from aqueous environmental samples, the following parameters were selected: distilled water samples of pH 1 to suppress the ionization of the phenoxy acids and bentazone, which have pK_a values in the range 2.6–3.8 (Tomlin, 1994); a sample volume of 500 mL; a sorbent mass of 500 mg; a solute concentration of 20 μ g/L of each pesticide; a flow rate of 5–10 mL/min; and 5 mL of elution solvent.

Choice of Elution Solvent and Elution Volume. In this study, five elution solvents were tested: ethyl acetate/acetone (1:1) with 5% HCOOH, THF with 5% HCOOH, THF/methanol (1:4) with 5% HCOOH, methanol with 5% HCOOH, and methanol with 5% NH₃. HCOOH was used to increase elution solvent strength of the solvent due to higher ionic strength. Using elution volumes of 5 mL, the average recoveries for the pesticide mixture were in the range 83–95% with a relative standard deviation (RSD) of 3–11%. The highest mean recovery for the pesticides mixture was obtained using

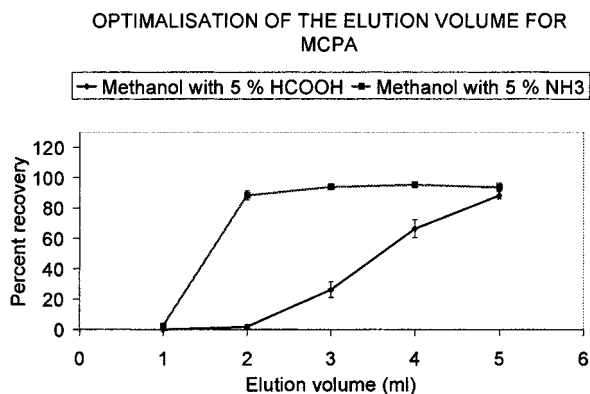


Figure 1. Percent recovery of MCPA as a function of elution volume of methanol with 5% HCOOH and methanol with 5% NH₃. A solute concentration of 20 µg/L in 500 mL distilled water samples at pH 1 was preconcentrated at a flow of 5–10 mL/min on 500 mg SDB extraction cartridges. (Error bars represent standard deviation, $n = 3$.)

methanol with 5% NH₃ and THF/methanol with 5% HCOOH (1:4) as elution solvents. The average recoveries for the pesticide mixture were 95 ± 3% for both of these elution solvents.

A study of variation in pesticide recovery as a function of elution solvent volume was carried out for all five elution solvents. The elution curves for MCPA using methanol with 5% HCOOH and methanol with 5% NH₃, respectively, are illustrated in Figure 1. The elution volumes producing adequate recovery are approached in the plateau region of the curve. Figure 1 shows that methanol with 5% HCOOH has less solvent strength for MCPA than methanol with 5% NH₃. Elution using methanol with 5% NH₃ gave 88 ± 3 and 94 ± 1 recoveries for MCPA with 2 and 3 mL elution volumes, respectively. Similar curves were made for every elution solvent and pesticide in the mixture (not shown). The curves illustrated that 2 mL of methanol with 5% NH₃ was sufficient to elute all of the pesticides from the sorbent. The higher recovery of the pesticides in the alkaline methanol compared to acidified methanol is probably due to a higher solubility of the pesticides and a higher effective ionic strength in the basic solution. It was observed that THF/methanol (1:4) with 5% HCOOH also has a high elution strength. However, THF may form explosive peroxides and is for safety reasons not preferable in routine analysis. The other elution solvents did not have the same elution strength and, therefore, 2 mL of methanol with 5% NH₃ was used for further experiments. Other methods with SDB sorbents use larger amounts of organic solvents before preconcentration and during elution (Chiron et al., 1994; Hodgeson et al., 1994; Pichon et al., 1996; Köppen and Spliid, 1998). It is important to reduce the total amount of organic chemicals, and therefore the method was optimized with regard to elution volume. In addition, the time used for evaporation of the eluate is reduced, which in turn, contributes to a faster sample preparation.

Sorbent Mass. The recoveries obtained using two different sorbent masses, 200 and 500 mg, are shown in Figure 2. The recoveries for the pesticide mixture were 100 ± 8 and 89 ± 3%, respectively. However, the developed method will be further applied to clean up and concentrate aqueous soil extracts with high contents of dissolved organic matter. Such samples may require a higher sorbent capacity, and it was therefore decided to maintain a sorbent mass of 500 mg.

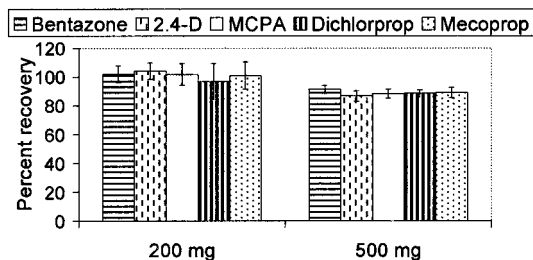


Figure 2. Recoveries obtained with 200 and 500 mg sorbent masses using 500 mL of distilled water at pH 1 spiked with 10 µg of each pesticide. Elution was performed with 2 mL of methanol with 5% NH₃. (Error bars represent standard deviation, $n = 3$.)

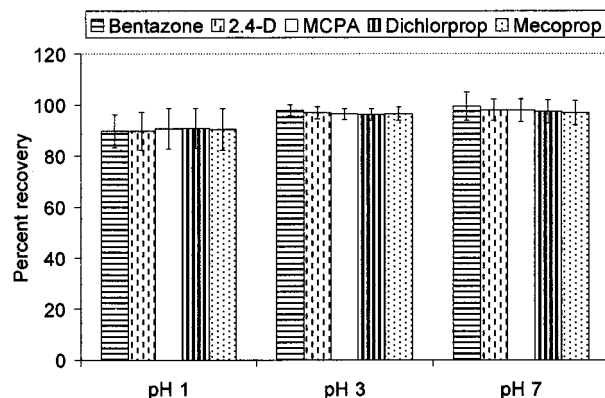


Figure 3. Recovery as a function of sample pH obtained on 500 mg SDB cartridges for 500 mL of distilled water spiked with 10 µg of each pesticide.

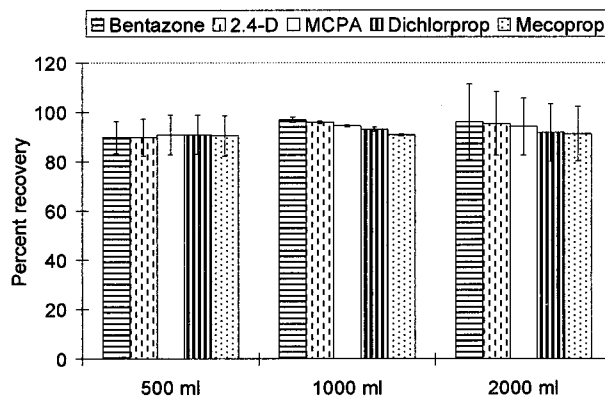


Figure 4. Recovery as a function of sample volume using 500, 1000 and 2000 mL of distilled water at pH 1 spiked with a constant amount of 10 µg of each pesticide.

Sample pH. The effect of sample pH on recovery was tested at three pH levels, 1, 3, and 7, and the results are presented in Figure 3. The average recoveries were good at all tested pH levels and were in the range 90–98%. It is therefore not required to acidify the samples before extraction of acidic herbicides using SDB polymer columns. High recoveries obtained when the pesticides are in their ionic form are due to an interaction between the aromatic, polymeric structure of the sorbent and the aromatic part of the molecule (Hodgeson et al., 1994). To check if variation of pH in environmental samples could affect the recovery, creek water rich in dissolved matter was adjusted to pH 1 and 7 before extraction. The average recovery for the pesticide mixture was 98 ± 9% at pH 1 and 103 ± 9% at pH 7, which showed that the variation of pH had no influence on the recovery. However, eluates of environmental samples

Table 1. Percent Recovery in the Comparison Study of SPE and LLE Using Distilled Water, Creek Water, and Well Water Spiked at 1.0 and 0.05 $\mu\text{g/L}$ ^a

		concn = 1 $\mu\text{g/L}$		concn = 0.05 $\mu\text{g/L}$	
		SPE	LLE	SPE	LLE
bentazone	distilled water	86.4 \pm 4.8	91.8 \pm 4.8	133.2 \pm 17.1	137.7 \pm 8.4
	creek water	96.2 \pm 2.8	102.5 \pm 4.1	104.7 \pm 12.7	110.2 \pm 19.3
	well water	83.2 \pm 0.9	95.8 \pm 4	123.6 \pm 6.7	149.1 \pm 5.0
2,4-D	distilled water	83.1 \pm 3.0	73.8 \pm 4.8	100.0 \pm 22.4	80.5 \pm 7.3
	creek water	97.5 \pm 5.6	90.2 \pm 2.7	92.7 \pm 11.1	98.3 \pm 7.7
	well water	94.4 \pm 1.2	81.2 \pm 7.5	113.6 \pm 5.6	98.0 \pm 21.4
MCPA	distilled water	77.8 \pm 2.9	73.8 \pm 4.9	96.7 \pm 7.5	78.5 \pm 8.5
	creek water	112.1 \pm 5.7	97.2 \pm 2.1	106.6 \pm 5.0	100.9 \pm 14.9
	well water	92.4 \pm 1.1	81.8 \pm 5.3	103.2 \pm 5.0	98.2 \pm 16.7
dichlorprop	distilled water	85.7 \pm 2.7	84.0 \pm 5.2	101.7 \pm 16.9	91.4 \pm 8.6
	creek water	94.6 \pm 3.7	90.8 \pm 1.7	94.1 \pm 10.2	87.4 \pm 11.4
	well water	92.7 \pm 0.7	90.1 \pm 6.8	106.9 \pm 3.9	106.0 \pm 12.2
mecoprop	distilled water	81.7 \pm 2.6	80.8 \pm 4.5	99.1 \pm 10.1	87.4 \pm 5.8
	creek water	90.0 \pm 4.3	83.6 \pm 2.2	93.0 \pm 5.6	98.8 \pm 4.8
	well water	90.3 \pm 0.9	87.3 \pm 4.5	100.6 \pm 7.8	100.0 \pm 1.9
average	distilled water	82.9 \pm 4.0	80.7 \pm 6.0	106.1 \pm 14.8	95.1 \pm 8.2
	creek water	98.1 \pm 4.6	92.9 \pm 2.9	97.9 \pm 10.2	99.1 \pm 13.1
	well water	90.6 \pm 1.1	87.2 \pm 6.6	109.6 \pm 5.4	110.3 \pm 12.3

^a Average of four replicates \pm standard deviation.

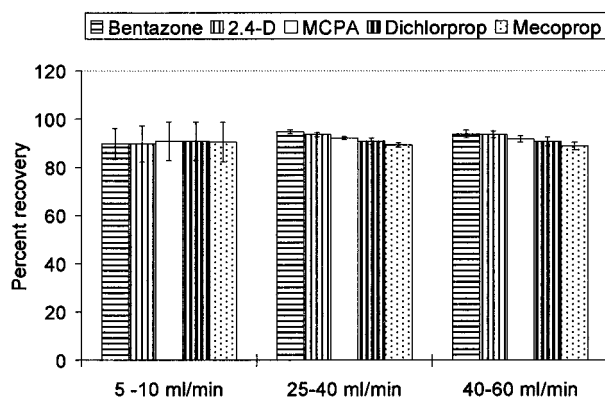


Figure 5. Recovery as a function of sample flow obtained by spiking 500 mL of distilled water at pH 1 with 10 μg of each pesticide.

were brown at a sample pH of 1 and colorless at a sample pH of 7, indicating that humic substances were retained and then coeluted at a sample pH of 1.

The possibility of using neutral pH in SPE avoids the coextraction of natural organic matter and results in cleaner extracts, which also has been reported by other authors (Pichon et al., 1996).

Sample Volume and Flow Rate. A test of recovery as a function of sample volume was carried out using sample volumes of 500, 1000, and 2000 mL. The average recoveries were $>90\%$ (Figure 4) for the pesticide mixture. Breakthrough using sample volumes >100 mL have been reported using SDB sorbents (Hodgeson et al., 1994). However, our studies showed that 2000 mL could be preconcentrated without breakthrough. The effect of flow rate on recovery was investigated at three different flow rates in the range 5–60 mL/min, and the results are shown in Figure 5. The average recovery for the pesticide mixture was in all cases $>90\%$, and the flow rate did not influence recovery. Other authors have used flow rates in the range 2–30 mL/min (Chiron et al., 1994; Pichon et al., 1996; Köppen and Spliid, 1998). However, lower flow rates increase the time needed for sample preparation, especially when large sample volumes are used.

Comparison of SPE and LLE (Table 1). The SPE method was compared to an LLE method applied in routine analysis. The comparison was performed with three different water matrices at two concentration levels, 1.0 and 0.05 $\mu\text{g/L}$. Spiked samples and blanks were divided in 200 mL portions and extracted by both methods. Acceptable mean recoveries with both methods for the pesticide mixture of $>80\%$ were obtained. There was in general no difference between the methods. At the highest concentration level the average recoveries were in the range 80–98% for all sample matrices. At the lowest level average recoveries were in the range 95–110% with both methods.

The study has shown that the two methods are comparable with respect to recovery of the pesticides. However, compared to LLE, SPE has several advantages, which can be summarized as follows: SPE is much faster than LLE, especially when handling samples with high amounts of dissolved organic carbon with which emulsion formation can cause problems during LLE. Furthermore, it is much more practical to extract many samples with SPE, and minor amounts of organic solvents are used with SPE compared to LLE, which involves large amounts of dichloromethane. Other important factors are that less time and less organic solvents are needed for cleaning of glass equipment, because disposable SPE cartridges are used for extraction. The SPE method was introduced to a laboratory that formerly used the described LLE method. After an in-house validation, the SPE method was accredited for routine analysis of environmental water samples down to a level of 0.02 $\mu\text{g/L}$. On the basis of the possibility to increase the sample volume from 200 to 2000 mL and use a flow rate of 60 mL/min, it can be feasible to lower the limit of determination.

Conclusion. The novelty of the work is the optimization of an SPE method for phenoxy acids and bentazone. Minor amounts of organic solvents are used, and high recoveries are obtained using large sample volumes and fast flow. The developed method using SDB cartridges is faster to perform than LLE. Good recoveries are obtained for phenoxy acids and bentazone in environ-

mental water samples. Very dirty samples can be handled without any plugging of the SDB cartridges, in contrast to the C₈/C₁₈ silica sorbents. The possibility of using neutral pH in SPE avoids the coextraction of natural organic matter and results in cleaner extracts. Using a sample volume of 200 mL, the limits of determination for the phenoxy acids and bentazone are 0.02 µg/L. It can be feasible to obtain lower limits of determination by increasing the sample volume to 2000 mL and using flow rates up to 60 mL/min.

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