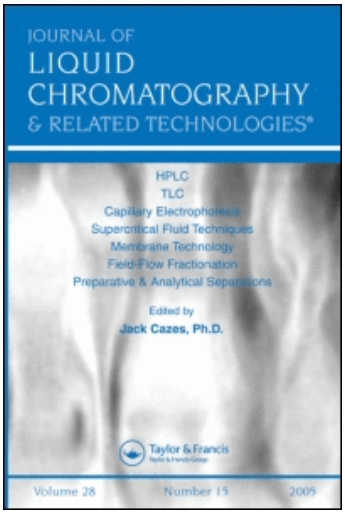

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ABSTRACT

A micellar electrokinetic chromatography (MEKC) procedure has been developed for the analysis of dimethoate (DM) in environmental water and soil samples, using solid phase extraction (SPE) as a clean-up and pre-concentration technique to improve selectivity and DM detection limits. The limit of quantification (LOQ) was 1 μg/mL for direct injection and 3 ng/mL after the SPE pre-concentration procedure. Within-run and

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between-day reproducibility studies performed at 0.02, 0.05, and 0.2 μg/mL indicated that the procedure was indeed reproducible. Quantification was by UV detection at 200 nm. The capillary electrophoresis (CE) method proposed uses sodium borate 100 mM with sodium dodecyl sulfate 50 mM, pH 8.4 as a buffer. The method was simple and fast, with good recoveries, which on average ranged from 82 to 92% with a relative standard deviation of 7% or less for water and soil samples fortified at 10, 20, 30, and 300 ng/mL. Our results show CE to be a powerful analytical tool for the determination of DM in environmental water and soil samples.

Key Words: Dimethoate; MEKC; Water analysis; Soil analysis; Solid-phase extraction.

INTRODUCTION

In the environmental field, capillary electrophoresis (CE) is becoming increasingly popular as a major analytical technique to complement chromatographic methods. The rapid growth of research into the instrumentation and applications of CE has proved it to be an interesting tool in many analytical separations and to be highly efficient at separating all kinds of polar and non-polar compounds, including a wide variety of pollutants.[1–11] It is widely described as a useful alternative to the more usual HPLC or GC for monitoring certain environmental pollutants.[1,10,12,13]

Capillary electrophoresis separations are typically performed in fused-silica capillaries with internal diameters of 25–100 μm, and provide high theoretical plate numbers. These diameters, however, and the fact that only a small sample volume can be injected, seriously impede the technique, resulting in poor sensitivity, particularly with UV absorbance detection. Sensitivity can be improved either by using a more sensitive detection method or by performing a pre-concentration step like solid-phase extraction (SPE) before separation. We used Oasis HLB (Hydrophilic–Lipophilic Balance) cartridges; the new reversed-phase for SPE formed by the macroporous copolymer poly(divinylbenzene-co-*N*-vinylpyrrolidone), which has both hydrophilic and lipophilic retention characteristics. Oasis HLB cartridges are water-wettable, so there is no need to ensure that they are wet before loading the aqueous sample.

One disadvantage of GC is that some pesticides, including dimethoate (DM) (Fig. 1), are difficult to analyze because of their lack of volatility or their thermal instability, so HPLC and CE techniques offer an alternative for their analysis.

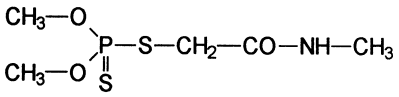

Figure 1. Structure of dimethoate.

The absorption bands of DM in the UV-vis region are very poor and the HPLC chromatograms obtained during the application of clean-up procedures to soil samples, by a UV detector at 200 nm, presented interferent peaks that were not completely eliminated. An excellent alternative for completely eliminating these peaks was the use of MEKC with a UV detector at 200 nm.

The aim of this research was to develop an micellar electrokinetic chromatography (MEKC) method using SPE, off-line, for the quantitative analysis of DM in water and soil samples as an alternative to GC[14–18] and HPLC[19–22] analysis. Solid-phase extraction was used as a clean-up and preconcentration technique in order to improve the selectivity and limit of quantification (LOQ) of DM.

EXPERIMENTAL

Chemicals and Reagents

Dimethoate (99.8%) was purchased from Riedel de Haën. Electrophoresis-grade sodium dodecylsulfate (SDS) and sodium borate were purchased from SIGMA of St. Louis, MO. Acetonitrile and methanol were HPLC-grade and purchased from Merck of Barcelona, Spain. Borate buffer was 100 mM boric acid/borate with 50 mM SDS (pH = 8.4). The pH of this solution was adjusted to 8.4 with freshly prepared 1 M sodium hydroxide solution. All buffers and stock solutions were prepared with distilled water, purified using a Milli-Q water purification system (18 MΩ resistance) (Millipore, Bedford, MA).

Equipment

The electrophoresis equipment used was a P/ACE System 2000 HPCE (Beckman Instruments, Palo Alto, CA) equipped with a UV detector. System Gold Nouveau Software (Beckman Instruments) was used to monitor the equipment, data acquisition and the analysis of the results.

For SPE, a Manifold (Waters, Milford, MA) was used and, for solvent evaporation, a SC110A Speed Vac Plus concentrator (Savant Instruments, Farmingdale, NY).

The column used for separation was an untreated fused-silica capillary tube (Beckman Instruments) of 75 μm I.D., 375 μm O.D., measuring 50 cm to the detector, and with an overall length of 57 cm.

Solid-phase extraction was carried out with Oasis HLB cartridges (200 mg–6 mL) (Waters, Milford, MA).

Electrophoretic Conditions

At the beginning of each day, the capillary was conditioned by flushing with 0.1 M NaOH for 5 min, followed by 5 min with de-ionized water, and 5 min with separation buffer (borate buffer). The capillary was washed with 0.1 M NaOH for 1 min and water for 2 min between runs. At the end of each day, the capillary was rinsed with 0.1 M NaOH for 5 min and then for 5 min with de-ionized water.

Standard/sample injections were made using pressure injection for 10 s (60 nL). The separations were performed at 30°C with a separation voltage of 18 kV, resulting in a current of 55 μA. Dimethoate was detected at 200 nm. Peak areas were used to draw a calibration curve and for the quantification of DM.

Preparation of Stock and Standard Solutions

Stock solution of DM was prepared by dissolving appropriate amounts of it in Milli-Q water to produce a concentration of 0.5 mg/mL. This stock solution was further diluted with Milli-Q water to prepare additional working solutions with final concentrations of 20, 10, and 0.1 μg/mL. Such working solutions were used to construct the calibration curve for water and soil samples. The stock and working solutions were stored in the dark at −20°C, and the calibration standards (with concentrations ranging from 1 to 30 μg/mL) were stored at 5°C for up to two days.

Preparation of Water Samples

The method was developed and optimized using a solution of DM in Milli-Q water, which was applied to ground, river, and drinking water samples collected from local sources, for which standard samples were prepared by adding appropriate amounts of working solutions of DM to 100 mL of Milli-Q, to give final concentrations in the range of 3–100 ng/mL.

Preparation of Soil Samples

The average soil composition for soil A was 49.9% sand, 29.9% silt, 20.2% clay, and 0.70% humic matter, and for soil B, 39.3% sand, 22.1% silt, 38.6% clay, and 0.43% humic matter.

Soil samples were spiked at the 3, 30, and 100 ng/g levels with DM working solutions and then mixed well by hand and shaken for 5 min. A 100 g spiked soil sample was extracted for 15 min by ultrasonic agitation with 100 mL of Milli-Q water. The suspensions were then centrifuged for 10 min at 2000 *g*, the supernatant removed, and filtered through a glass-fiber filter. To improve sensitivity, the aqueous soil extract was pre-concentrated by means of a solid-phase extraction process.

Solid-Phase Extraction Procedure

To improve sensitivity, the water samples and aqueous extracts from soil samples were pre-concentrated by means of the following solid-phase extraction process:

Conditioning Step

Passage of 6 mL of methanol/acetonitrile (50/50, v/v) through the SPE cartridge.

Equilibration Step

Passage of 6 mL of water in preparation for sample loading.

Sample Loading

Passage of 100 mL of sample through the cartridge at a flow rate of 10 mL/min. The sample volume may vary depending on the concentration of DM.

Elution Step

Elution of DM from the cartridge by passing 6 mL of methanol/acetonitrile (50/50, v/v) at 2 mL/min.

Evaporation and Reconstitution Step

The methanol was evaporated in a Speed Vac concentrator and the residue was reconstituted in 300 μL of Milli-Q water by sonicating for 1 min, and then analyzed. The efficiency of the SPE method tested was evaluated by comparison of the peak areas obtained in each case with those of the calibration lines of standard spiked solutions.

Quantification

External standard calibration was used for quantification of DM in water and soil samples, arrived at by means of calibration lines constructed with standards using the procedure described above. Unknown DM concentrations in water and soil samples were calculated by interpolation from the calibration graphs by a least-squares regression treatment. The linearity range was checked from 1 to 30 μg/mL.

Reproducibility

To determine within-run reproducibility, river water samples were spiked at 10, 50, and 100 ng/mL with DM, and analyzed six times. Between-day reproducibility was evaluated by analyzing water samples obtained on six different days, spiked at the same concentrations.

RESULTS AND DISCUSSION

Optimization of Electrophoretic Conditions

We studied the effects of several electrophoretic parameters, including such injection conditions as buffer, pH, buffer concentration, surfactant concentration (SDS), temperature, injection volume, and voltage. As the UV-detection wavelength was to be 200 nm, suggested by the UV spectra of DM in the analysis conditions, high-capacity buffers with low UV absorbance were required. The buffer salts investigated were sodium dihydrogenorthophosphate and sodium borate, the latter being the more suitable. Along with pH, running buffer concentrations between 40 and 120 mM were considered in the optimization of the CE method. As a compromise between assay speed and peak broadening due to Joule heating[23], a buffer with a concentration of 100 mM was chosen with 35,000 (N) theoretical plates for DM. The pH range

studied was between 8.2 and 9.2, as these values are within approximately ± 1 pK_a unit of the pK_a of the buffer, thus, ensuring consistent buffer capacity. Then, we analyzed the effect of pH on the asymmetry of the DM peak, current (μA), the number of theoretical plates and migration time, the results showing the optimum pH to be 8.4. Another parameter considered was SDS concentration, which was tested in the range 30–70 mM, as an increase in it implied an increase in the migration time of DM, while a concentration of 100 mM SDS provided good resolution.

The final parameter examined in optimizing the CE separations was the voltage applied to the capillary, which was varied from 10 to 24 KV, an optimal voltage of 18 KV being selected because the Joule heating was within the limits for the given type and length of capillary. An applied voltage of 18 KV resulted in a current of nearly 55 μA.

From the results obtained, we suggest that the optimized conditions for the analysis of DM in water and soil samples are: borate buffer 100 mM, 50 mM SDS (pH = 8.4), separation voltage 18 KV, cartridge temperature 30°C,[24] injection 10 s (60 nL), and detection with UV absorbance at 200 nm. Figure 2 shows typical electropherograms obtained in these conditions.

The next stage was to check that these parameters were indeed optimized by assessing the method's selectivity, recovery, reproducibility, linearity, and sensitivity.

Selectivity

Our results show the method developed to be highly selective in the analysis of DM in complex matrices, given that the electropherograms were obtained at 200 nm. Figures 2 and 3 show electropherograms from environmental water and soil samples spiked with DM at different concentrations; those of spiked and control samples showing no matrix interferences at the migration time, probably owing to clean-up of matrix interferences during the SPE of DM from water and soil samples, and to some interferences having longer migration times than DM.

Recovery

The solvent used in the ultrasonic extraction of DM from soil samples was Milli-Q water, for two reasons: (1) DM is a water-soluble polar organophosphorus pesticide and (2) in SPE an aqueous sample is typically passed through a cartridge.[25]

The recoveries obtained for the extraction of the DM from spiked soil samples with the ultrasonic method, ranged from 90–95%. Recoveries of DM

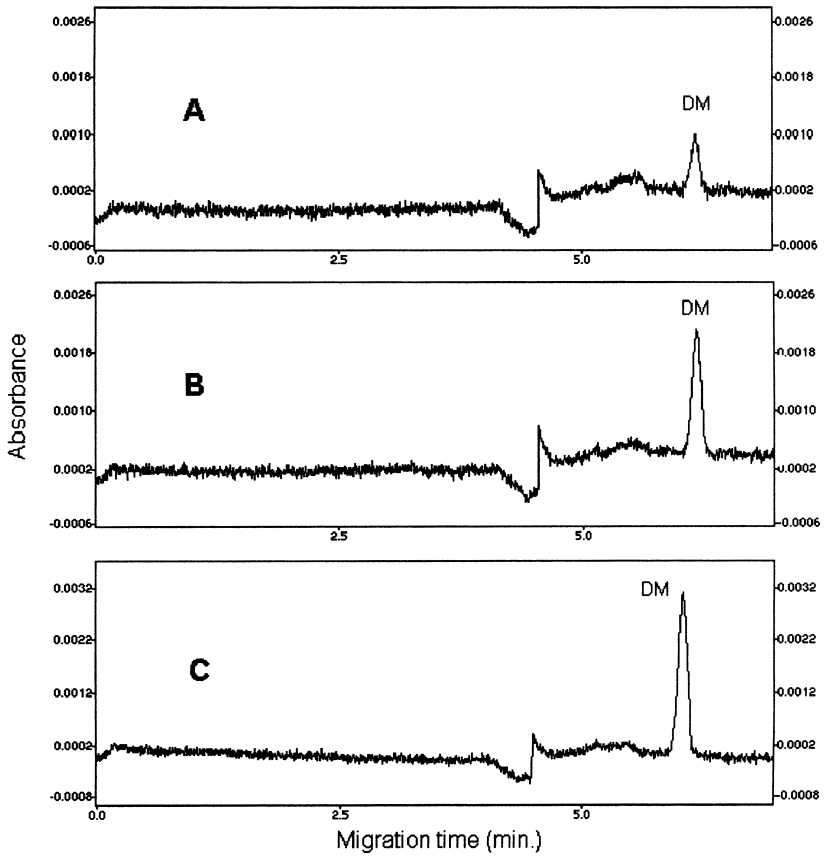

Figure 2. Micellar electrokinetic chromatography–Electropherograms for environmental water samples spiked with DM and preconcentrated by SPE. (A) Drinking water 5 ng/mL. (B) Ground water (10 ng/mL). (C) River water (20 ng/mL). Analysis conditions: 50 cm × 75 μm I.D. capillary column; pressure injection (10 s = 60 nL); 100 mM sodium borate + 50 mM SDS (pH 8.4) buffer; 18 kV (55 μA); 200 nm UV absorbance.

in SPE were measured for water and soil samples spiked with different concentrations of it. The detector responses to spiked samples were compared with responses to calibration standards with identical concentrations of DM. Such parameters as flow-rate during sample injection into the cartridge, elution strength, and eluent are typically optimized for the maximum recovery of DM. Table 1 shows the recoveries of DM from spiked water and soil samples

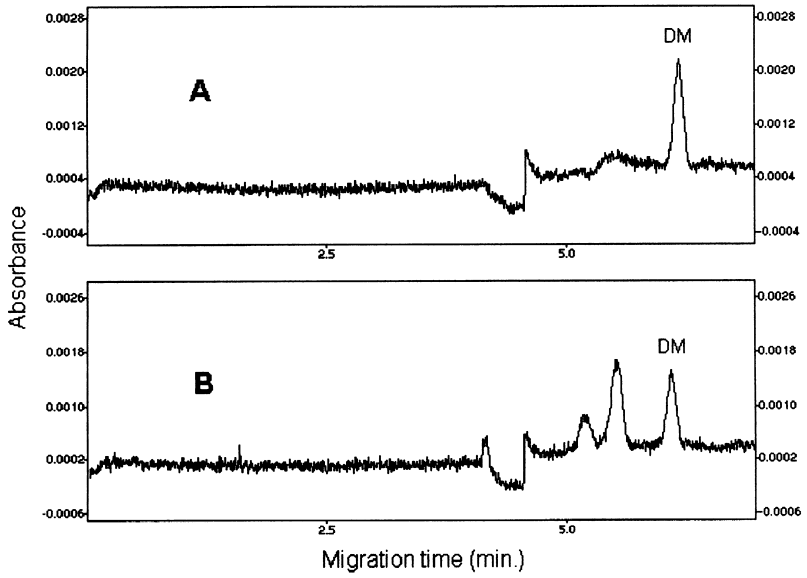

Figure 3. Micellar electrokinetic chromatography–Electropherograms obtained after ultrasonic extraction with Milli-Q water of soil spiked with DM followed by SPE from the aqueous extracts. (A) Soil A (10 ng/mL), (B) Soil B (7 ng/mL). For analysis conditions see Figure 2.

at different concentrations. The results show good recoveries ($\geq$ 82%) in both water and soil matrices using the SPE procedure.

Reproducibility

Six repeat injections of Milli-Q water samples at concentrations of 2 and 10 μg/mL were used to determine the reproducibility of the migration times and peak area on the same day (within-run) and on different days (between-day), the results indicating good reproducibility and quantitative accuracy for the method. Repeatability in the preparation of water samples was demonstrated by using three concentrations (10, 50, and 100 ng/mL) of dimethoate in samples of river water.

The resulting data (Table 2) reveal acceptable R.S.D. values for within-run and between-day reproducibility. For within-run results, the R.S.D. values were very low, ranging from 2.3 to 6.8% for river water spiked at different concentration levels, while between-day R.S.D. values varied from 5.3 to

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Table 1. Recoveries of dimethoate from spiked water and soil samples.

Sample	Concentration added (ng/mL)	Recovery rate (%)	R.S.D.[a] (%)
Milli-Q water	10	87	5.2
	100	92	4.0
River water	20	91	6.8
	100	84	3.1
Soil (A)	30	82	6.7
	100	86	5.4

[a]R.S.D. = Relative standard deviation.

14.3%. The greatest increases in the R.S.D. values are at low concentrations of DM in river water samples.

Linearity and Sensitivity

We found a good linear relationship between the peak–area ratios and DM concentrations in water and soil samples in the range of 3 to 1000 ng/g, with regression analysis of the data revealing a correlation coefficient of $r^2 \geq 0.991$. We estimated that the limit of quantification was 1 μg/mL for direct injection and 3 ng/g after the SPE pre-concentration procedure, this limit being determined by evaluating the level of DM necessary to produce a peak with a signal-to-noise ratio of 5, assuming a 100 mL sample aliquot and a 0.30 mL final volume of reconstituted extract.

Table 2. Reproducibility of dimethoate in spiked river water.

Concentration added (ng/mL)	R.S.D.[a] (%)	
	Within-run	Between-day
10	6.8	14.3
50	2.3	10.7
100	3.0	5.3

[a]R.S.D. = Relative standard deviation.

Analysis of Dimethoate in Environmental Samples

The method proposed was applied to the determination of DM levels in real samples of water and soil in order to observe the effect of the matrix on recoveries, separation, and interfering peaks. The electropherograms obtained were similar to those shown in Figs. 2 and 3. These analyses show a good separation between peaks and there are no matrix peaks interfering with that of the DM. Recovery of DM was over 83% from ground and river water, and over 85% from soil samples.

CONCLUSIONS

This study describes a CE method for the assay of DM in environmental water and soil samples at the ng/mL level. The ionic strength and pH of the electrolyte were shown to be the most critical parameters affecting the electrophoretic process. An off-line SPE system using HLB cartridges was developed for the pre-concentration of DM from environmental water and soil samples. Reproducibility, sensitivity, selectivity, and recovery are quite acceptable. The performance of the total analytical procedure was evaluated for three types of water: ground, river, and drinking water, and two types of soil.

The optimized methods were applied to ascertain the degradation kinetics of DM in soil samples in different physico-chemical conditions.

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