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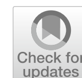

Micellar Electrokinetic Chromatography Method Development for Sensitive Monitoring of Rotenone in Lake Waters

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Abstract

Rotenone, a naturally occurring isoflavone compound, is applied to water as a piscicide to manage undesired fish populations in lakes, ponds, rivers and in aquaculture. A rapid and sensitive method based on solid-phase extraction (SPE) combined with large-volume sample stacking with polarity switching (LVSS) and micellar electrokinetic chromatography (MEKC) has been developed for the identification and quantification of rotenone in lake water. Several experimental parameters for MEKC, LVSS and SPE were investigated to achieve the optimum conditions necessary for the analysis. The optimized conditions which included a background electrolyte containing 20 mM sodium borate and 25 mM sodium dodecyl sulfate (SDS) at pH 10 were used to successfully detect rotenone within 17 min. Using a combined SPE and LVSS approach, the rotenone signal was enhanced by 1000-fold compared with a normal capillary electrophoresis analysis, and limits of detection and quantification obtained were 3 and 10 µg L^{-1}, respectively. The calibration curve was linear for rotenone concentration over the range of 10–100 µg L^{-1} and the method was highly reproducible with the relative standard deviation of the peak areas and migration times for method intra-day repeatability ($n=6$) found to be 5.4% and 0.6%, respectively. Quantitative recoveries ranging from 85 to 88% were obtained in the lake water matrices. The potential of the proposed method to be used for quantitative determination of rotenone at trace level concentrations in water samples was demonstrated by analyzing lake water samples including surface (1 m) and bottom (13 m), which makes it a suitable practical method for analyzing rotenone residues in water.

Keywords Rotenone · Micellar electrokinetic chromatography · Large-volume sample stacking · Solid-phase extraction · Lake water

Introduction

Rotenone is a naturally occurring flavonoid compound that has insecticidal, acaricidal and piscicidal properties, its molecular formula is $C_{23}H_{22}O_6$, molecular weight 394.42, log K_{ow} 4.10 and water solubility (20 °C) 0.296 mg L^{-1} [1].

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It is extracted mainly from the roots, but also from the seeds and leaves of many subtropical and tropical plants, mainly belonging to the genus *Lonchocarpus*, *Tephrosia* or *Derris*. Rotenone is used worldwide as a crop insecticide to control flying and crawling insects, as well as a fish eradicator in the management of bodies of water. Fish are highly susceptible because rotenone exerts its toxic action by directly inhibiting cellular respiration by blocking electron transport, and it enters efficiently and quickly in the bloodstream via the gills. When using a rotenone treatment, it has been found that majority of the fish die within 24–36 h following the treatment. In addition, rotenone has a short half-life (between 1 and 3 days) in soil and water and is broken down rapidly when subjected to UV radiation, which comes from sunlight, resulting in a loss of its toxic effects, [2, 3]. However, it is important to monitor rotenone because it can have toxic effects on non-target organisms such as insects [4], amphibians [5] and macroinvertebrates [6]. In addition,

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piscicides can potentially have direct environmental impact on esthetics, hydrology and water quality, recreation and biological resources [7].

Various bodies of water (lakes, ponds, rivers, streams, among others) have been treated with rotenone to eradicate invasive fish species. [8, 9]. During and after treatment, the most common technique to determine rotenone residues in water is liquid chromatography with ultraviolet detector (LC–UV) [10, 11]. More recently, liquid chromatography coupled with mass spectrometry (LC–MS) or tandem mass spectrometry (LC–MS/MS) has also been used due to its high sensitivity and selectivity [12–14]. However, LC–MS technique involves laborious cleanup and complicated sample pretreatments, and also it requires large volume of sample and solvents. In contrast, capillary electrophoresis (CE) is a technique that offers a more suitable alternative because of its higher efficiency, rapid time analysis and low reagent and sample consumption. Generally, CE separates charged molecules based on the differences in their electrophoretic mobilities under the influence of an electric field with separation performed in background electrolyte (buffer solution) inside a narrow bore capillary. Different modes of CE are available, such as micellar electrokinetic chromatography (MEKC). This mode is a powerful technique for analyzing neutral molecules in which surfactants are added to the buffer solution to form micelles. The main separation mechanism in MEKC is based on solute partitioning between a micellar phase and the aqueous buffer phase. In recent years, MEKC analysis has been employed to determine steroids [15], fluoroquinolones [16], hormones [17], hormone antagonists [18], phthalate esters [19], and artificial sweeteners [20], among others in water.

Generally, MEKC offers great resolving power and short analysis time; however, the short pathway for UV detection and the small injection volume yields poor sensitivity. On-line sample preconcentration represents a convenient way to enhance sensitivity in MEKC and one common preconcentration technique is large-volume sample stacking (LVSS). In LVSS, a large volume of a low conductivity sample is hydrodynamically injected into the capillary. Upon polarity switching, the sample plug is pumped out from the capillary by the electroosmotic flow, while the negatively charged micelles move back towards the inlet and they are compressed between the sample zone and the background electrolyte (BGE). The polarity is reversed when current reaches a value close to the normal value found for the separation BGE, and the analysis is continued in the normal MEKC mode [21]. The sensitivity in MEKC can be improved by performing a sample preparation technique like solid-phase extraction (SPE), which can extract and preconcentrate traces of the analytes and remove interfering compounds from the matrix. The SPE–MEKC method has been increasingly applied to determine at trace level a broad range of compounds in environmental waters such as surfactants, dyes, biogenic amines, pesticides and chlorophenols, among others [22].

The goal of this work was to develop a simple, precise and sensitive SPE–MEKC method to analyze rotenone in lake water as well as to investigate the enrichment of the analyte using LVSS, and ultimately provide a practical method which can be used to monitor trace levels of rotenone residues in environmental water samples.

Experimental

Chemicals and Reagents

Rotenone standard, sodium tetraborate decahydrate (borate), sodium dodecyl sulfate (SDS) and sodium hydroxide were purchased from Sigma Aldrich Chemical Co. (Oakville, ON, Canada). Acetonitrile was purchased from Anachemia (Montreal, QC, Canada) and methanol was obtained from Caledon (Georgetown, ON, Canada). All other reagents used were of analytical grade and 18 MΩ water was used to prepare the solutions. For SPE C_{18} bulk sorbent, Bond Elut empty cartridges (polypropylene, 6 mL) and frits (polyethylene, 20 µM, 12.7 mm) were obtained from Agilent Technologies (Mississauga, ON, Canada).

Preparation of Standards and CE Background Electrolytes

To prepare the background electrolyte (BGE) for each optimization, appropriate masses of sodium tetraborate decahydrate and SDS were weighed within ± 0.001 g and dissolved in 18 MΩ water to obtain the desired concentration. Buffers were shaken with a magnetic stirrer for complete dissolution and then adjusted to the required pH (± 0.01) by either 1 M NaOH or 1 M HCl.

Borate concentrations were varied from 20 to 140 mM (with increments of 20 mM) containing various SDS concentrations from 10 to 30 mM (with increments of 5 mM). These solutions were used for optimization studies.

A stock solution of rotenone (2500 µg mL^{-1}) was prepared in acetonitrile and stored in a plastic bottle at 4 °C. Calibration standards were prepared from the stock solution by appropriate dilutions with acetonitrile–water (20:80 v/v).

Instrumentation and LVSS–MEKC Method

CE analyses were performed on a P/ACE MDQ system (Beckman Coulter, Brea, CA, USA) equipped with a UV detector. Data acquisition was performed with the 32 Karat 8.0 software. Rotenone was detected at 214 nm using direct absorbance and a separation voltage of + 20 kV was

applied for 20 min. Separations were carried out on a 50 µm (I.D.) × 365 µm (O.D.) × 60 cm (L_T) bare-fused silica capillary (Polymicro Technologies, Phoenix, AZ, USA) housed in a cartridge with temperature controlled at 25 °C by a circulating liquid fluorocarbon coolant system. A new bare-fused silica capillary was first rinsed with methanol (30 psi, 10 min) to remove any debris or particulates. Then it was rinsed with 1 M NaOH (20 psi, 40 min), 0.1 M NaOH (20 psi, 20 min) and water (20 psi, 10 min). It was then flushed with buffer of 20 mM borate, 25 mM SDS at pH 10 (10 min, 20 psi).

The capillary was rinsed with 0.1 M NaOH (20 psi, 3 min), water (20 psi, 1 min) and with buffer (20 psi, 4 min) before injecting the sample with LVSS (15.0 psi, injection time 0.5 min, applied reverse potential 10 kV and time of reverse polarity 5 min). The capillary was filled with water and the ends immersed in vials of water when not in use.

Solid-Phase Extraction Procedure

SPE cartridges were packed with 600 mg of C_{18} sorbent. The cartridge was activated with 5 mL of methanol followed by 5 mL of deionized water at a flow rate of 1–2 mL min^{-1} using a manifold. A sample volume of 150 mL was passed through the cartridge. Then, it was dried with vacuum for 10 min. Then, rotenone was eluted with 1.5 mL of acetonitrile. The extract was evaporated to dryness with a gentle nitrogen flow and reconstituted with 1.2 mL of acetonitrile–water (20:80 v/v) to be analyzed using the LVSS–MEKC method.

SPE–LVSS–MEKC Method Validation

The following parameters were evaluated: precision, accuracy, linearity, limit of detection (LOD), limit of quantification (LOQ) and matrix effect. Precision, in terms of repeatability, was assessed by analyzing deionized water spiked at 10, 40 and 80 µg L^{-1}, triplicates were made at each concentration and relative standard deviation (RSD) was calculated. The accuracy and linearity were evaluated by analyzing deionized water spiked at 20, 40, 60, 80 and 100 µg L^{-1}. Each concentration level was measured in triplicate. For accuracy, the amount added was plotted against the amount recovered at each concentration, and the average recovery was calculated by multiplying the slope of the curve for 100. For linearity, the determination coefficient (R^2), slope and *y*-intercept of the calibration curve were calculated. Limit of detection (LOD) and limit of quantification (LOQ) of rotenone were determined as signal-to-noise ratio (S/N) of 3 and 10, respectively. To evaluate matrix effect, two different lake water samples (surface and bottom) were spiked at 40 µg L^{-1}, triplicates were made for each sample and the average recovery was calculated.

Results and Discussion

MEKC Method Optimization

MEKC was investigated as a method to determine rotenone. For the optimization, normal injection mode (5 s at 1 psi) was used. Several parameters including sample solvent, pH, concentration of borate and SDS would be discussed in the following sections.

The first parameter optimized was the solvent of the solutions. Standards at 500 µg mL^{-1} in ethanol, ethanol–borate buffer (75:25 v/v), acetonitrile and acetonitrile–water (20:80 v/v) were tested maintaining constant borate buffer of 100 mM (pH 9.0) and 20 mM SDS. When using ethanol, the current decreased markedly, probably because when it was mixed with BGE, air bubbles could be produced causing the current drops. When acetonitrile was used, the rotenone peak was not observed, so acetonitrile–water (20:80 v/v) was selected, this showed the best peak shape and lowest RSD values for area (10%, $n = 4$) and migration time (5%, $n = 4$), also the profile of the electropherograms was maintained between analysis in different days. With this solvent, a standard at 500 µg mL^{-1} was prepared to test the other optimization parameters (pH, borate and SDS concentrations).

Borate/SDS buffer was employed in this work because it is one of the most common buffers used in MEKC. A crucial point in the method development is to establish the optimum pH, as it affects the electroosmotic mobility, solubility and partitioning of analytes into the micellar phase. The pH of the borate/SDS buffer was varied from 9.0 to 11.0 at intervals of 0.5, maintaining constant concentrations of 100 mM borate and 20 mM SDS. Typically, increasing buffer pH leads to the decrease of analysis time due to the increase in the electroosmotic flow (EOF) of the buffer solution, but for rotenone at higher pH, analysis time and peak band broadening increased, and a shoulder appeared (Fig. 1a), which makes it less suitable for analyses. On the other hand, at lower pH values, it was observed that rotenone response decreased significantly. At pH 10.0, a decent size of rotenone peak was found with only a small shoulder and, therefore, pH 10.0 was selected as the optimum pH and used for other optimizations.

The effect of borate concentration was evaluated from 20 to 140 mM at intervals of 20 mM, maintaining constant pH 10.0 and SDS concentration at 20 mM. With increasing concentration of borate, a shoulder appeared in rotenone peak and analysis time was increased (Fig. 1b). The optimum peak shape (with no shoulder) and shorter analysis time was achieved with 20 mM sodium tetraborate. SDS concentration was evaluated from 10 to 30 mM at intervals of 5 mM, maintaining constant pH 10.0 and

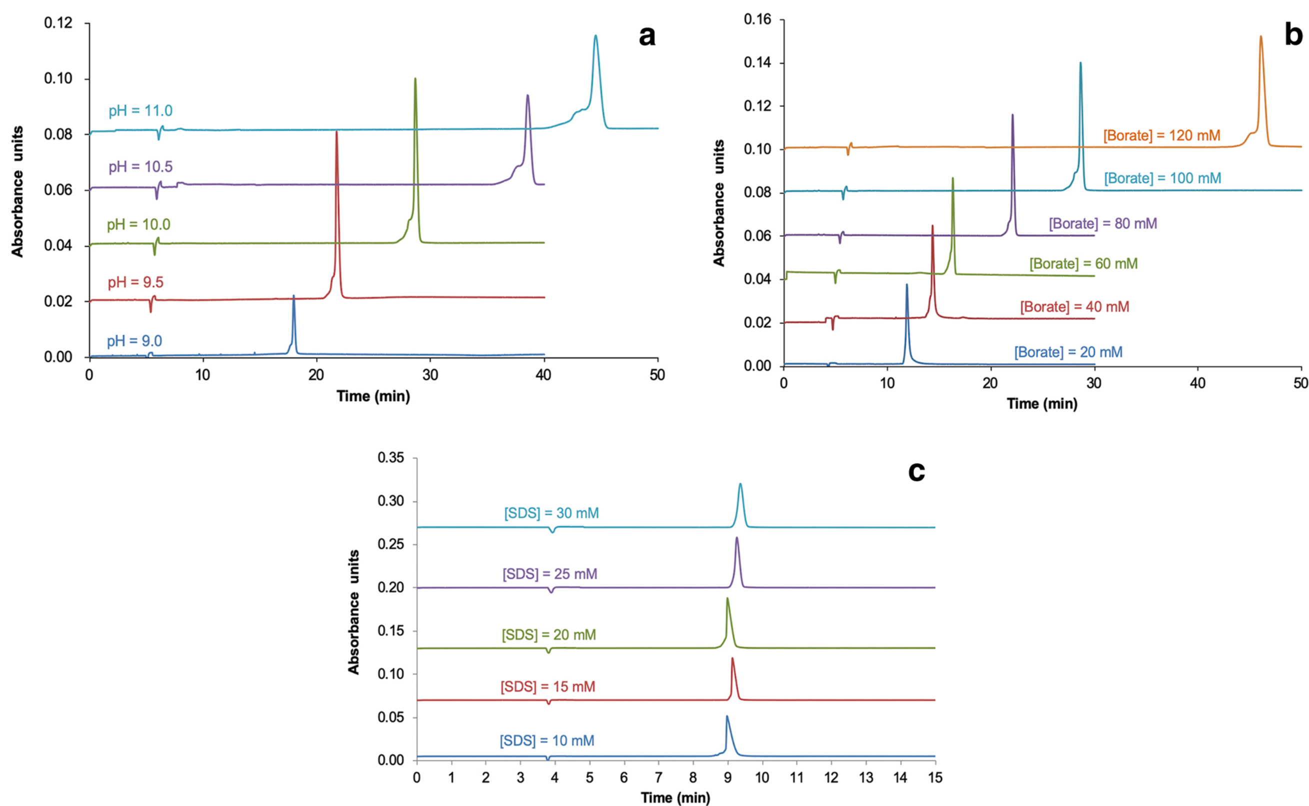

Fig. 1 Electropherograms obtained for: **a** pH optimization, **b** borate concentration optimization and **c** SDS concentration optimization, voltage + 20 kV

borate concentration at 20 mM. With decreasing SDS concentration, rotenone peak fronting was increased and when the SDS concentration increased band broadening was observed. As illustrated in Fig. 1c, the optimum peak shape and shorter analysis time was achieved with 25 mM SDS.

LVSS Optimization

LVSS with polarity switching was used as a preconcentration technique to increase the enrichment in CE for the analysis of rotenone. It was necessary to use LVSS with polarity switching to observe rotenone peak at trace level. In general, LVSS involves injecting a large volume of sample prepared in a low conductivity matrix. Then, a voltage at negative polarity is applied to focus the zones and remove the sample matrix. When the analyte is completely focused and most of the sample matrix is removed, the voltage is paused, and the polarity is reversed. This is done when the current has reached approximately 90% of its value. Development of an LVSS technique required optimization of several variables: the sample solvent water–acetonitrile (60:40 v/v and 80:20 v/v) and buffer–acetonitrile (60:40 v/v, borate buffer at 3, 10 and 20 mM), injection time (0.1, 0.2, 0.3, 0.5 and 1.5 min) and pressure (10, 15 and 20 psi) in the hydrodynamic mode, applied reverse potential (5, 10, 15 and 20 kV) to ensure enough stacking time to remove the sample from the capillary without losing the rotenone and time of reverse polarity (1, 2, 3, 4, 5 and 6 min) to increase analyte response.

For LVSS, a solution at 10 µg mL^{-1} in water–acetonitrile (80:20 v/v) was used, because with a higher content of acetonitrile, lack of repeatability was observed and with buffer–acetonitrile, the rotenone peak was not observed.

With increasing volume of the capillary filled with the sample the focusing step takes longer time, different percentages of capillary filling were tested to find optimal volume of the injected sample: 18% (15 psi, 0.1 min), 24% (20 psi, 0.1 min), 36% (15 psi, 0.2 min), 48% (20 psi, 0.2 min), 60% (15 psi, 0.3 min), 80% (20 psi, 0.3 min), 90% (15 psi, 0.5 min), and 100% (10 psi, 1.5 min). The pressure of 15.0 psi with 0.5 min leading to about 90% filling of the capillary was selected as optimal because it gave a gaussian peak shape for rotenone. These percentages were calculated based on the applied pressure, injection time, length and internal diameter of the capillary using Sciex CE expert Lite software (SCIEX, Concord, ON, Canada).

Another parameter optimized was the applied reverse potential; 5, 10, 15 and 20 kV were tested. With 5 kV, band

broadening and migration time of the rotenone peak were increased, also the height of the peak was not improved. When using 15 and 20 kV, there was no repeatability between injections, so the optimum reverse voltage was 10 kV. Finally, time of reverse polarity was optimized by monitoring the electric current during the preconcentration. Polarity is changed from reverse to normal when the current reaches a value close to the maximum found when the capillary is completely filled with the borate/SDS buffer (16 µA, 100%). Times tested were 1, 2, 3, 4, 5 and 6 min (87–91% of the maximum current), the optimum time of polarity switching was 5 min. Optimum conditions were pressure 15.0 psi, injection time 0.5 min, applied reverse potential 10 kV and time of reverse polarity 5 min. With these conditions, the area of the peak increased to 7 times, as shown in Fig. 2.

SPE Optimization

Due to the low concentration of rotenone residues in environmental waters, a SPE procedure is necessary to preconcentrate the analyte. Rotenone is a lipophilic compound (log K_{ow} 4.10) and SPE using C_{18} cartridges has shown to be adequate in handling water samples containing this analyte [8]. SPE conditions were optimized by studying the C_{18} sorbent amount (200, 400 and 600 mg), sample volume (50, 100 and 150 mL) and the volume elution solvent (1, 1.5 and 2 mL of acetonitrile), these parameters were selected because they have a direct influence on analyte recovery. The conditions that gave the highest recovery and best sensitivity were cartridge packed with 600 mg of sorbent, 150 mL of water sample and 1.5 mL of acetonitrile as elution solvent.

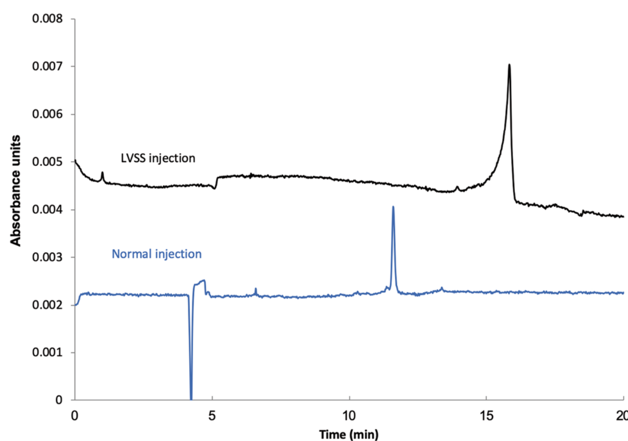

Fig. 2 Comparison between electropherograms of normal injection (1 psi, 5 s) and injection with LVSS with reverse polarity (15 psi, 0.5 min)

SPE–LVSS–MEKC Method Validation

With the method-optimized conditions, a Gaussian peak shape was obtained with rotenone migration time around 16.7 min. The method was validated (Table 1), and for the precision, RSD values < 10.6% were obtained. The average recovery for rotenone in water spiked between 20 and 100 µg L^{-1} was 102 ± 9% and it did not show dependence with concentration for the different spiked levels assayed. These results confirm the acceptable accuracy and precision of the SPE–LVSS–MEKC method. LOD and LOQ were found to be 3 and 10 µg L^{-1}, respectively. Linearity was suitable for rotenone determination with $R^2 > 0.98$. The recovery of spiked lake samples was 85–88%, so matrix effect was not significant since the recoveries are between 80 and 120%.

LC–UV and LC–MS/MS had been mostly used for rotenone analysis (Table 2), and such methods had low detection limit; however, they require large volumes of samples and organic solvents. The proposed SPE–LVSS–MEKC method is a useful alternative technique to HPLC for the analysis of rotenone in treated water bodies. It uses UV detection which yielded detection limits in the lower µg L^{-1} range, similar to those obtained with LC–UV, thus making it suitable to determine the allowable maximum rotenone concentration (40 µg L^{-1}) in waters with drinking water intakes, hydrologic connections to wells or water used for aquaculture [25].

Table 1 SPE–LVSS–MEKC validation data

Linearity[a]	r^2	Slope		Intercept
	0.9893	741 ± 141		4265 ± 9376
Accuracy (% average recovery)	102 ± 9			
Precision (% RSD, n = 3)	10 µg L^{-1}	40 µg L^{-1}		80 µg L^{-1}
	10.6	10.5		5.3
LOD (µg L^{-1})[b]	3			
LOQ (µg L^{-1})[b]	10			
Matrix effect (average recovery, n = 3)	Bottom		Surface	
	88 ± 5		85 ± 3	

[a]The linear range is 10–100 µg L^{-1} and each calibration point was measured in triplicate

[b]The limit of detection (LOD) and limit of quantification (LOQ) were defined as the concentration where the signal-to-noise ratio is 3 and 10, respectively

Table 2 Rotenone analysis in water with LC and CE

Matrix	Extraction	Analysis	LOD or LOQ (μg L^{-1})	References
River water	SPE or preconcentration step using Spin-X centrifuge filters	LC–UV	LOQ: 1	[8]
River water	Preconcentration step using Spin-X centrifuge filters	LC–UV	LOQ: 1	[9]
Water	SPE	LC–UV	LOD: 0.3	[10]
Lake water	SPE	LC–MS/MS	LOD: 0.05	[14]
River water	On-line SPE	LC–UV LC–MS/MS	LOD: 0.1 LOD: 0.01	[23]
Water	Molecularly imprinted polymer	UV–Vis spectrophotometry	LOD: 0.5	[24]

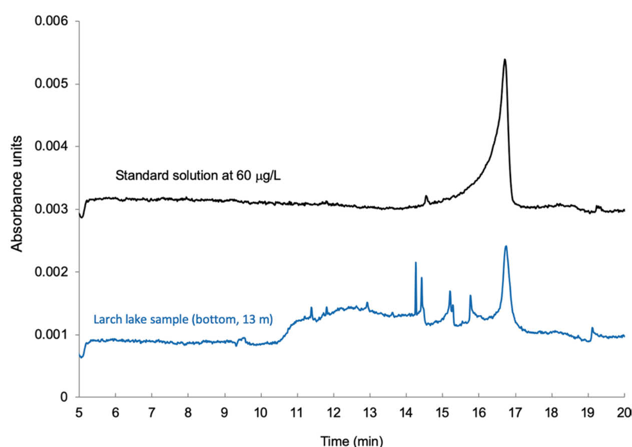

Fig. 3 Comparison between electropherograms of a standard of rotenone at 60 μg L^{-1} and the lake sample from the bottom

Analysis of Real Samples

To demonstrate the applicability of the validated method, two samples from Larch lake, that had previously been treated with rotenone, were analyzed. The samples were obtained from the British Columbia Ministry of Forests, Lands, Natural Resource Operations (BC MFLNRO), Canada. The rotenone concentration found was 142 μg L^{-1} for the sample from the surface (1 m) and 19 μg L^{-1} for the other sample from the bottom (13 m). The first sample was diluted 50:50 with acetonitrile–water (20:80 v/v) to obtain a response included in the linear range evaluated. Figure 3 shows the electropherograms of a standard at 60 μg L^{-1} and the bottom lake sample. It can be observed that the method is able to separate rotenone and the coextracted compounds from the matrix, also the migration time is not affected by the presence of the matrix. This demonstrates that the developed method is useful for detecting rotenone concentration in post-treated water below the United States Environmental Protection Agency (USEPA) level of concern of 40 μg L^{-1} to mitigate human health risk [25].

Conclusions

A rapid, sensitive and inexpensive SPE–LVSS–MEKC method has been successfully developed and validated for the identification and quantitation of rotenone in water samples. Our developed method is comparable to other articles published (Table 2). However, our method uses small sample and reagent size, is relatively easy to use and less time-consuming. Rotenone could be detected in less than 20 min and suitable precision and accuracy were obtained, limits of detection (LOD) and quantification (LOQ) were in the lower μg L^{-1}. Optimized method was successfully applied to lake water samples from the surface and bottom. This study offers the combination of SPE with on-line preconcentration using LVSS with switching polarity, for the improvement of sensitivity to make it suitable for monitoring rotenone at trace level during and after treatment in lakes, so it can be used to detect rotenone at concentrations below the USEPA level of concern. SPE combined with LVSS–MEKC is a powerful analytical tool for routine rotenone residue monitoring in laboratories.

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Compliance with Ethical Standards

Conflict of Interest No potential conflict of interest was reported by the authors.

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