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Solid-phase extraction and sample stacking–capillary electrophoresis for the determination of quaternary ammonium herbicides in drinking water☆

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Abstract

Conditions for the simultaneous determination of paraquat, diquat and difenzoquat by capillary zone electrophoresis were established by combining two preconcentration procedures. Off-line solid-phase extraction was used for the isolation and preconcentration of quats in drinking water. Quats were then analysed by capillary electrophoresis using sample stacking with matrix removal as on-column preconcentration procedure. Two different porous graphitic carbon cartridges were compared. The breakthrough volumes of the three herbicides were calculated and the loading capacity of the sorbents was compared. Recoveries higher than 80% for difenzoquat and around 40% for paraquat and diquat were obtained when a sample volume of 250 ml was percolated. For the stacking–capillary electrophoresis analysis of quats, 50 m*M* acetic acid–ammonium acetate (pH 4.0), 0.8 m*M* cetyltrimethylammonium bromide with 5% (v/v) methanol as carrier electrolyte was used. Detection limits, based on a signal-to-noise ratio of 3:1, were lower than 0.3 $\mu g\ l^{-1}$ for standards in Milli-Q water, and lower than 2.2 $\mu g\ l^{-1}$ for drinking water samples. Run-to-run and day-to-day precision of the method were established. The two preconcentration procedures used together was successfully applied to the analysis of the three herbicides in spiked drinking water at concentrations below the maximum admissible US Environmental Protection Agency levels.

Keywords: Sample stacking; Water analysis; Quaternary ammonium compounds; Pesticides

1. Introduction

Quaternary ammonium compounds form a group of herbicides commonly known as ‘‘quats’’, which are widely used in agriculture to boost productivity. Paraquat (PQ) and diquat (DQ) are used as non-selective contact herbicides for crop desiccation, pasture renovation, crop production with limited or no tillage and selective weed control. Difenzoquat (DF) is a selective herbicide used for post-emergence control of wild oats in cereal crops [1]. Quats are included in a European Union priority list of potentially dangerous herbicides in the Mediterranean countries, given their widespread use in this area [2]. The US Environmental Protection Agency (EPA) has included paraquat and diquat in a priority

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list of hazardous chemicals [3] and has established a maximum contamination level of 20 μg l^{-1} for DQ and a goal of 3 μg l^{-1} for PQ [4,5] in drinking water.

These herbicides are polar, easily soluble in water and have low volatility. Because of these properties, they are usually determined by ion-pair high-performance liquid chromatography (HPLC) with direct UV detection [6–8]. Liquid chromatography coupled to mass spectrometry (LC–MS) has also been used to analyse these compounds [9,10] in order to improve both selectivity and sensitivity. Due to the cationic character of the herbicides, capillary electrophoresis (CE) has also proved to be a promising alternative for their separation and/or analysis. Quats have been determined by CE in water [7,11–13] and other matrices such as serum, soil and urine [14,15] when using UV detection. For greater selectivity, CE together with mass spectrometry (CE–MS) has also been used to analyse quats in water samples [16–18]. However, CE has a less-than-desirable sensitivity based on concentration, as compared to HPLC. The concentration sensitivity problem comes from two sources, namely the low sample injection volume and the short optical path-length for on-capillary detection. So, to comply with the maximum legally permitted levels of quats in drinking water [5], enrichment procedures prior to determination have to be used.

Different techniques for on-column preconcentration of quaternary ammonium herbicides have been reported. Isotachophoresis (ITP), a discontinuous electrophoresis process, has been used as an on-line sample pre-treatment together with CE for the analysis of PQ and DQ in water [19]. Several techniques for on-column preconcentration in CE, known as sample stacking procedures, in which the concentration effect is based on the sudden change in analyte electrophoretic velocity brought about by the difference in the magnitude of the electric field, have been reported [20–23]. In a previous study [24] we used one of these stacking procedures to analyse quats in drinking water. This procedure involves field polarity reversal after the capillary has been filled with a large volume of sample of lower conductivity than is used for CE separation. Nevertheless, this method is only appropriate for the analysis of these compounds in highly contaminated water samples. Limits of detection (LODs) are between 18 and 154 μg l^{-1} [24], so other preconcentration methods are needed.

Solid-phase extraction (SPE) has often been recommended for the isolation and concentration of quaternary ammonium herbicides [25]. Cation-exchange resins have been proposed to concentrate paraquat and diquat in drinking waters [26–28] and silica has also been extensively used for the isolation and preconcentration of quats in different matrices such as water [8,10,29–31], urine [32,33] and foods [32,33]. Non-polar phases such as C_8 and C_{18} [34,35] after addition of an ion pair reagent for the concentration of these compounds in water have also been reported.

Recently, the use of graphitic carbons for the SPE of organic compounds from liquid natural matrices or extracts has been proposed [36]. The surface characteristics of porous graphitic carbons are responsible for various types of interactions (hydrophobic, electronic and ion-exchange) with analytes. These sorbents have also been used for the isolation and concentration of quats in water [31,37].

In this study, conditions for the extraction and preconcentration of PQ, DQ and DF from water using different porous graphitic carbons (PGCs) as adsorbent materials, previous to CE analysis using sample stacking with matrix removal, are established. Quality parameters were obtained and the combination of SPE and sample stacking was applied to the analysis of tap and mineral water samples.

2. Experimental

2.1. Chemicals

Methanol and acetonitrile (both HPLC-gradient grade), acetic acid (100%), sodium hydroxide, hydrochloric acid (25%) and cetyltrimethylammonium bromide (CTAB) were obtained from Merck (Darmstadt, Germany); trifluoroacetic acid (TFA) from Sigma (St. Louis, MO, USA); and ammonium acetate from Fluka (Buchs, Switzerland). Water was purified using an Elix 3 coupled to a Milli-Q system (Millipore, Bedford, MA, USA).

The herbicides studied, which are shown in Fig. 1, were paraquat (1,1′-dimethyl-4,4′-bipyridylium ion)

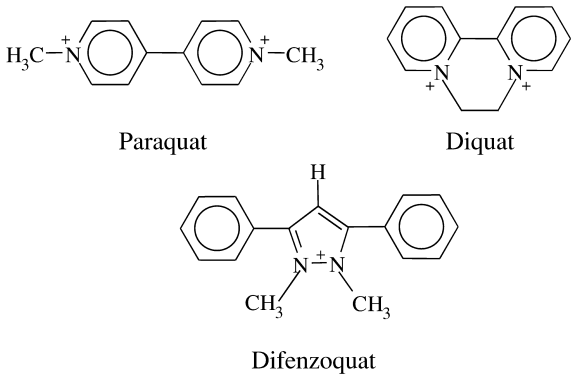

Fig. 1. Quaternary ammonium herbicide structures.

purchased from Sigma, and diquat (1,1′-ethylene-2,2′-bipyridylium ion) and difenzoquat (1,2-dimethyl-3,5-diphenylpyrazolium ion) obtained from Chemservice (West Chester, PA, USA).

Stock standard solutions of individual quats (1 mg ml^{-1}) were prepared in Milli-Q water and stored in plastic vials to prevent adsorption. Working solutions were obtained by dilution with 0.8 m*M* CTAB aqueous solution, and were filtered through a 0.45 μm nylon filter. Buffers were prepared from an aqueous solution of 400 m*M* acetic acid and pH 4.0 was obtained by adding ammonium acetate (400 m*M*). This buffer was diluted with Milli-Q water to 50 m*M* after the addition of CTAB and methanol to obtain the final carrier electrolyte.

Two PGC cartridges were used. Hypersep Hypercarb SPE cartridges (200 mg, 3 ml) were purchased from ThermoQuest (ThermoHypersil, Cheshire, UK) and Supelclean Envi-Carb SPE cartridges (250 mg, 3 ml) from Supelco (Bellefonte, PA, USA).

2.2. Capillary electrophoresis conditions

A Beckman (Fullerton, CA, USA) P/ACE System 5500 CE instrument with diode array detection was used. This system was modified to control the removal of electrode polarity. Electrophoretic data were processed using the P/ACE Station software version 1.0. An uncoated fused-silica capillary (Supelco) of 57 cm (50 cm effective length)×50 μm I.D. was used. The temperature was held at 25 °C. Samples were loaded by pressure injection at 140 kPa and for 0.25 min. For sample matrix removal, +20 kV were applied and then the separation was performed by reversing the polarity at the same potential. Direct detection was performed at two wavelengths, 220 nm for DQ and 255 nm for PQ and DF. Electrophoretic separation was carried out using an acetic acid–ammonium acetate 50 m*M* buffer solution at pH 4.0 containing 5% methanol and 0.8 m*M* CTAB. Methanol was added in order to improve resolution between PQ and DQ while CTAB was added as wall capillary modifier to reverse the electroosmotic flow (EOF) allowing the application of the sample stacking with matrix removal procedure to the analysis of cationic compounds [24]. Carrier electrolyte was filtered through a 0.45 μm membrane filter and degassed before use.

2.3. Capillary conditioning

New capillaries were pre-treated with 0.1 *M* hydrochloric acid for 15 min, ultrapure water for 15 min, 1 *M* sodium hydroxide for 30 min, and finally rinsed with ultrapure water for 30 min. At the beginning of each session, the capillary was treated with 1 *M* sodium hydroxide for 15 min, then rinsed with ultrapure water for 15 min and, finally, with the carrier electrolyte for 60 min. The capillary was rinsed with the carrier electrolyte for 2 min before each run.

2.4. Sample treatment

Tap water and mineral water samples spiked with PQ, DQ and DF were treated using PGC cartridges (HyperSep Hypercarb and Supelclean Envi-Carb), following the procedure described by Carneiro et al. [31]. The cartridges were washed with 2 ml of MeOH, 2 ml of MeOH–water (1:1), 2 ml of water and finally with 2 ml of water at pH 9.0. Samples of 250 ml at concentration levels between 1.0 and 20 μg l^{-1} and adjusted to pH 9.0 with 1 *M* sodium hydroxide immediately before use were passed through the cartridges at a flow-rate of 2–3 ml min^{-1} using a Visiprep System (Supelco). The cartridge was dried with air and quats were eluted with 2 ml of acetonitrile–TFA (80:20, v/v) and the eluate was evaporated to dryness with N_2. Subsequent evapora-

tion steps after the addition of 0.5 ml of acetonitrile were performed to remove the TFA completely. Finally, the extract was re-dissolved in the appropriate amount (1–5 ml) of 0.8 m*M* CTAB solution.

2.5. Stacking procedure

The stacking procedure was developed in a previous study [24]. Briefly, the silica capillary was filled with the carrier electrolyte and then a long plug of sample was introduced under hydrodynamic pressure (140 kPa) for 0.25 min. A high voltage (+20 kV) was then applied and the sample matrix was removed from the capillary. After sample injection, the current decreased due to the high resistivity caused by the lower conductivity, but rose again when the sample matrix was removed from the capillary. The voltage was turned off and the polarity was switched to the separation configuration when the current was 95% of the original carrier electrolyte value.

3. Results and discussion

3.1. Preliminary study

A preliminary study was carried out using 250 ml of Milli-Q water spiked with PQ, DQ and DF at 0.8 μg l^{-1}, and using the Hypersep Hypercarb PGC cartridges. After the SPE preconcentration the sample was eluted with 2 ml of acetonitrile–TFA (80:20, v/v), evaporated to dryness with N_2, reconstituted with 1 ml of 0.8 m*M* CTAB aqueous solution, and directly injected into the capillary electrophoresis system using the stacking procedure. Fig. 2a shows the electropherogram obtained at two wavelengths, 220 and 255 nm. The presence of TFA in the reconstituted sample affected the electrophoretic separation when the stacking procedure was applied. When the TFA was not totally removed DF showed a double peak, probably due to the coexistence of both DF and the TFA–DF ion-pair under non-equilibrium conditions. Splitting of the peaks was

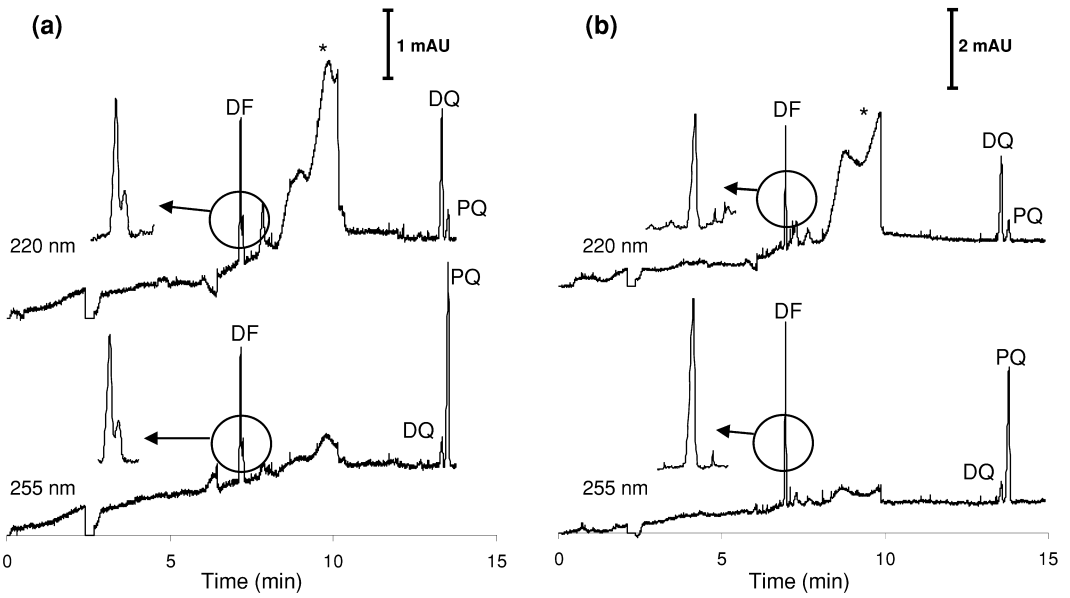

Fig. 2. Effect of TFA on the electrophoretic separation of quats. Electropherograms of 250 ml Milli-Q water spiked with quats at a concentration of 0.8 μg l^{-1}. (a) After the SPE preconcentration step. (b) Same as (a) after the complete removal of TFA. *, system peak. Electrophoretic conditions: carrier electrolyte, acetic acid–ammonium acetate 50 m*M* (pH 4.0), 0.8 m*M* CTAB/5% methanol; injection time, 0.25 min at 140 kPa; voltage during sample matrix removal, +20 kV; separation voltage, −20 kV.

not observed for PQ and DQ, because their migration times were too high for their equilibrium to be reach. In order to remove the TFA completely, small volumes of acetonitrile (0.5 ml, five times) were added to the extract, which was consecutively evaporated to dryness. When the TFA was totally removed, the double peak for DF disappeared (Fig. 2b).

3.2. Breakthrough volume

For off-line SPE preconcentration two different porous graphitic sorbents (PGC), Hypersep Hypercarb and Supelclean Envi-Carb, were tested. In SPE the breakthrough volume is an important feature to take into account since it determines the detection limit that can be reached. For determining the breakthrough and the recoveries, the method described by Hennion et al. [38] was applied. Only Milli-Q water was used to study breakthrough, since several authors have reported [39,40] that breakthrough volumes using different types of water do not show significant variations. Milli-Q water was spiked with quats at various concentration levels with the sample amount kept constant (200 ng). Therefore, the sample volume was increased (2–500 ml) and the concentration of quats was decreased (100–0.4 μg l^{-1}). Sample volumes higher than 500 ml were not studied because the total analysis time would have been too long. After preconcentration, samples were injected into the CE system using the stacking procedure and peak areas were measured and the recoveries were calculated by comparing the peak areas with those of a control sample (200 μg l^{-1}) representing 100% recovery.

Fig. 3 shows the breakthrough curves obtained for the quats using both PGC sorbents. While both cartridges gave high and practically constant recoveries (up to 400 ml) for DF, PQ and DQ behaved differently. A considerable decrease in the recovery values of these two compounds was observed at small volumes, although, for the HyperSep HyperCarb cartridge, higher recoveries were obtained from 50 to 250 ml (e.g. for DQ, 37% against 15% for 50 ml). For this reason a volume of 250 ml and HyperSep HyperCarb as sorbent were chosen for the off-line SPE preconcentration. The recoveries were 80, 40 and 30% for DF, PQ and DQ, respectively.

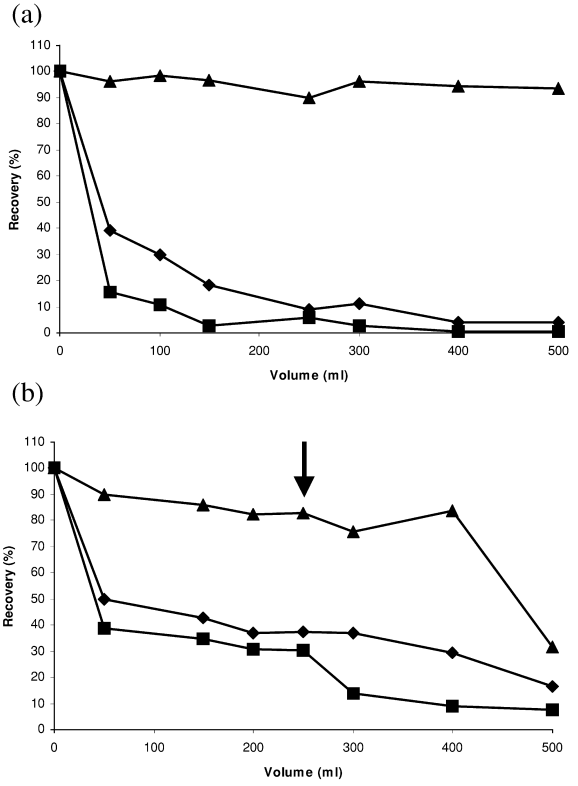

Fig. 3. Effect of sample volume on the recoveries of PQ, DQ and DF for both PGC sorbents. (a) Supelclean Envi-Carb cartridges; (b) HyperSep HypercCarb cartridges. ♦, PQ; ■, DQ; ▲, DF. Electrophoretic conditions as in Fig. 2.

3.3. Quality parameters with Milli-Q water

The limits of detection, linearity, run-to-run and day-to-day precision were obtained for quats using the method proposed. The results are summarised in Table 1. The LODs based on a signal-to-noise ratio of 3:1 and expressed as micrograms per liter of quaternary ammonium ion, were determined after preconcentration of 250 ml Milli-Q water spiked at low concentrations of quats. DF showed the lower LOD, 0.08 μg l^{-1}, while the figures for PQ and DQ were higher, 0.3 and 0.1 μg l^{-1}, respectively. These LODs are 35–185 times lower than those found in the earlier study using only sample stacking with matrix removal [24] and 10 times lower than those

Table 1
Quality parameters of the method (Milli-Q water)

Parameter	PQ[a]	DQ[b]	DF[a]
LOD ($\mu g\ l^{-1}$)	0.1	0.3	0.08
LOD Sample stacking ($\mu g\ l^{-1}$)[c]	10	11	15
Concentration (spiked level 5 $\mu g\ l^{-1}$)			
Run-to-run reproducibility, RSD (%) ($n=6$)	7.6	7.3	6.3
Day-to-day reproducibility, RSD (%) ($n=2\times3$)	12.3	11.7	11.6
Linearity (0.7–24.5 $\mu g\ l^{-1}$)			
Correlation coefficients	0.990	0.996	0.991

[a] λ: 255 nm.
[b] λ: 220 nm.
[c] Ref. [24].

published by Carneiro et al. [31] using off-line SPE and CE–UV. The LODs achieved are 8–200 times better than those obtained by electrokinetic injection and CE–MS using a quadrupole as analyser [16] and much lower than those with a time-of-flight [18].

Linearity was studied by preconcentrating through a HyperSep Hypercarb cartridge 250 ml of Milli-Q water spiked with quats at concentrations ranging from 0.7 to 24.5 $\mu g\ l^{-1}$. Calibration graphs were drawn and the calibration gave satisfactory correlation coefficients ($r^2>0.99$) for all the compounds.

For run-to-run precision, six replicas of 250 ml of Milli-Q water spiked at 5 $\mu g\ l^{-1}$ were determined. The relative standard deviations (RSDs) based on concentration ranged from 6.3 to 7.6%. For day-to-day precision, a total of six replicas of 250 ml of Milli-Q water spiked at 5 $\mu g\ l^{-1}$ were determined on 3 different days (two replicates each day). The RSDs based on concentration were lower than 12.3%. These values are good and similar to those obtained when only sample stacking with matrix removal was used: thus, off-line SPE did not introduce any great variation into the analysis.

3.4. Application

To show how the method can be applied to the analysis of real samples, tap water from Barcelona and mineral water were analysed with the proposed method. The water samples were spiked at 5 $\mu g\ l^{-1}$ with quats; 250 ml were preconcentrated using HyperSep Hypercarb cartridges; and the extracts were reconstituted in 1 ml of 0.8 m*M* CTAB solution. When these water samples underwent the stacking procedure, the capillary current was higher than for Milli-Q water due to these samples' higher salinity. As the stacking method requires a considerable difference between the sample and the carrier electrolyte conductivity, higher volumes of 0.8 m*M* CTAB solution had to be used to re-dissolve the extract. Fig. 4 shows the electropherograms obtained at 220 and 255 nm after the preconcentration of 250 ml of tap water spiked with PQ, DQ and DF (5 $\mu g\ l^{-1}$), when the sample was reconstituted with different volumes of 0.8 m*M* CTAB solution. When the sample was reconstituted using 1 ml of the CTAB solution (Fig. 4a), poor resolution between PQ and DQ was obtained and DF did not appear in the electropherogram. PQ/DQ resolution improved and DF was detected when a higher volume (5 ml) of CTAB was used (Fig. 4c). The dilution depends on the sample: for instance, a mineral water with lower salinity than Barcelona tap water only needed 2 ml of CTAB for the reconstitution of the SPE extract.

The limits of detection for real samples after a preconcentration step are always higher than those for standard solutions in Milli-Q water. Moreover, in the stacking technique the salinity of the sample must be taken into account because higher detection limits are obtained for samples with high salinity content. By using the combination of both preconcentration methods, off-line SPE and sample stacking, the limits of detection for quats in Barcelona tap water and mineral water samples were estimated. The LODs based on a signal-to-noise ratio of 3:1 are listed in Table 2. These were two to four times higher than the figures for Milli-Q water due to the salinity of the samples. Nevertheless, the figures are below the maximum admissible levels established by the EPA for PQ and DQ.

The method proposed was used to quantify tap water and mineral water samples spiked with quats at two concentration levels, the EPA level and a concentration below this figure (see Table 2). The recoveries for drinking water samples were similar to those for spiked Milli-Q water. Quantification was performed by external calibration using Milli-Q water spiked samples, with three replicas determined for each sample and spiked level. The results in

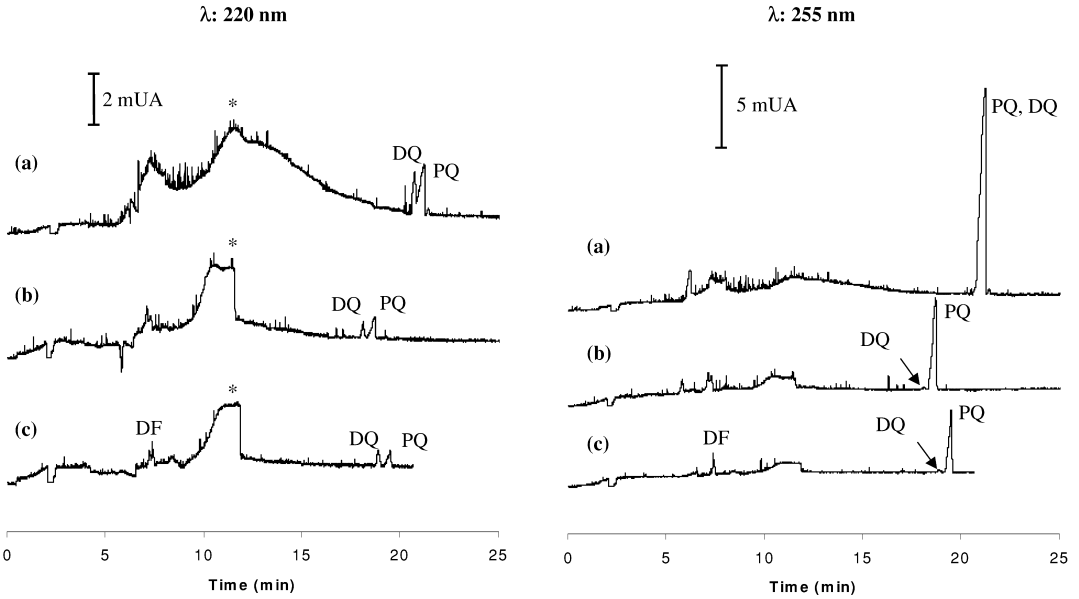

Fig. 4. Electropherograms of 250 ml tap water spiked at 5 μg l^{-1} with PQ, DQ and DF. After the off-line SPE preconcentration step, the sample was reconstituted with (a) 1 ml CTAB 0.8 m*M*, (b) 3 ml CTAB 0.8 m*M* and (c) 5 ml CTAB 0.8 m*M*. *, system peak. Electrophoretic conditions as in Fig. 2.

terms of concentration and standard deviations are given in Table 2. As we can see, good accuracy and precision were obtained.

4. Conclusions

The results of this study showed that the combination of solid-phase extraction with PGC cartridges and on-column sample stacking–capillary electrophoresis can be used to determine paraquat, diquat and difenzoquat in water samples. The highest recoveries were obtained using HyperSep HyperCarb cartridges but residues of TFA must be throughly eliminated to prevent peak splitting in the electropherogram. Detection limits, between 0.2 and 2.2 μg l^{-1}, were obtained, allowing the analysis of this compounds in drinking water samples at the levels established by the US Environmental Protection Agency.

Table 2
Water sample analysis

Quat	LOD (μg l^{-1})		Analysis at two spiked levels (n=3)					
	Tap water	Mineral water	Spiked level (μg l^{-1})	Tap water	Mineral water	Spiked level (μg l^{-1})	Tap water	Mineral water
PQ[a]	0.4	0.2	3.5[c]	3.2±0.3	3.5±0.2	1.2[d]	1.2±0.2	1.3±0.3
DQ[b]	2.2	1.8	20.3[c]	20.5±0.9	20.1±0.4	5.8[d]	5.3±0.6	5.6±0.2
DF[a]	1.1	0.4	5.7	5.2±0.6	5.3±0.4	2.7	2.8±0.2	2.5±0.2

[a] λ: 255 nm.
[b] λ: 220 nm.
[c] EPA level.
[d] Below EPA level.

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