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# Improving the solid-phase extraction of “quat” pesticides from water samples Removal of interferences

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## Abstract

A novel strategy, based on the addition of a cationic surfactant, for preventing the interferences associated with a diminution in the efficacy of solid-phase extraction (SPE) with silica cartridges of diquat, paraquat and difenzoquat in water is developed. Conditions for extraction are optimised with respect to pH, cationic surfactant and its concentration. Humic acids, anionic surfactants, inorganic salts and other organic contaminants like pesticides, phenols, polycyclic aromatic hydrocarbons and polychlorinated biphenyls produce the studied interferences. The best performance is shown in the improvement of the “quats” recovery from waters with high levels of humic acids and anionic surfactants (recovery is increased from ca. 30% to more than 80%). Unfortunately, the strong interference from inorganic salts remains. The presence in the water sample of other organic contaminants only affected the extraction efficiency of difenzoquat at high concentrations (more than 1 mg/l). Analytic utility is illustrated by selective measurements of the three herbicides, in real water samples. Overall, the results show that in spite of its drawbacks, SPE is a useful technique that allows the detection and quantification of the “quats” at limits below 100 ng/l as established by the European Union. © 1998 Elsevier Science B.V. All rights reserved.

**Keywords:** Water analysis; Extraction methods; Pesticides; Diquat; Paraquat; Difenzoquat

## 1. Introduction

Diquat (1,1'-ethylene-2,2'-bipyridylium ion), paraquat (1,1'-dimethyl-4,4'-bipyridylium ion) and difenzoquat (1,2-dimethyl-3,5-diphenyl-1H-pyrazolium) are included in a priority list of herbicides of potential concern established for the Mediterranean countries by the European Union (EU), due to their widespread usage in this area [1]. Consequently, they may be present as residues in surface waters, and some of them are found in drinking water [2,3]. Although there are few studies on difenzoquat

toxicity [4], diquat and paraquat are extremely toxic and are often encountered in cases of accidental and suicidal poisoning [5,6]. As a result, there is a need for analytical procedures for their identification and screening.

Bipyridylium herbicides are polar and nonvolatile, properties that point at liquid chromatography (LC) as the preferred approach [7–9]. However, this technique frequently requires enrichment and isolation of the analytes prior to the determination [10].

In environmental analysis, solid-phase extraction (SPE) is a very useful preconcentration technique, which allows both extraction of pesticide residues with high efficiency and their concentration at such

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levels that the limits set by the EU for pesticides in drinking water are really achieved [11–13]. Advantages associated with this technique are rapidity, economy, versatility and potential for automatization. In addition, these herbicides are fairly soluble in water and so less amenable to extraction with organic solvents. SPE cartridges packed with silica [14–18], Dowex [19,20] and graphitized carbon black [21] have been used for isolation and concentration of diquat, paraquat and difenzoquat from waters. The basic mechanism of analyte retention is ionic interactions between solute and solid-phase.

In spite of the SPE procedures increasingly being preferred, it has been observed that the presence of common contaminants—naturals or xenobiotics—in natural waters, like humic acids, surfactants, inorganic salts, phenols, polycyclic aromatic hydrocarbons (PAHs), other pesticides or related compounds, could affect in the negative the analysis performance, significantly diminishing the recovery efficacy or significantly interfering in the posterior determination [22–26]. Although, these undesirable effects originated by the sample composition are well known, there is only an analytical study focused on to avoid them [27]. It is mainly devoted to decreasing the coextraction of humic acids and to removal of the interferences that appear in the determination of acidic pesticides by LC–UV detection.

The present study tries to develop an efficient strategy for preventing interactions between the cationic herbicides (diquat, paraquat and difenzoquat) and other contaminants present in water. The literature reveals that the majority of studies have been performed for pesticides and solid-phases of apolar character, whereas those carried out on the most polar ones are very limited [22–26]. The behaviour of the extraction efficiency, when organic matter or different surfactants (cationic, anionic, nonionic and zwitterionic) are present in water samples was studied in a previous work [17]. It was demonstrated that both types of pollutants have a negative influence in the extraction procedure, except for cationic surfactants that maintain, or even improve, the extraction efficacy. The anomalous behaviour of cationic surfactants has also been reported in studies about the interactions between them and other pesticides in water samples [28]. This has been attributed to their displaced capacity, avoiding the bound of pesticides with other molecules. The pur-

pose was to evaluate if cationic surfactants have the ability to eliminate interactions between the bipyridylum herbicides and other contaminants present in water samples, and also to provide acceptable recoveries in their presence. For this, the effect of the presence of humic acids, tensioactives, salts and other contaminants [phenols, carbamates, polychlorinated biphenyls (PCBs) or PAHs] has been checked and the influence of pH regulation, together with the addition of cationic surfactants to improve the efficiency of SPE, are studied.

## 2. Experimental

### 2.1. Chemicals

Diquat, paraquat and difenzoquat were purchased from Promochem (Wesel, Germany). Standard solutions of them were prepared in the mobile phase used in the LC gradient. To study the effect of pH, reaction solutions were prepared from NaAc–HAc (pH 3–5),  $\text{Na}_2\text{HPO}_4$ – $\text{NaH}_2\text{PO}_4$  (pH 6–9), and NaOH (pH 10–12).

Humic acids sodium salt was obtained from Aldrich (Milwaukee, WI, USA). Cetrimide (hexadecyltrimethyl ammonium bromide) was from Panreac (Barcelona, Spain), while cetylpyridinium (1-hexadecylpyridinium chloride), sodium lauryl sulphate (sodium dodecyl sulphate) and benzalkonium chloride were from Aldrich. Tetramethylammonium hydroxide (TMAOH) was from Fluka (Buchs, Switzerland).

PAHs (acenaphthene, benzo[*b*]fluoranthene, anthracene, indeno[1,2,3-*cd*]pyrene, benzo[*a*]pyrene and phenanthrene) were obtained from Aldrich, and their standard solution (500  $\mu\text{g}/\text{ml}$ ) prepared in acetonitrile. Aroclor 1016, 1221, 1242 and 1254 from Supelco (Bellefonte, PA, USA), were diluted in ethyl acetate to obtain a 1000  $\mu\text{g}/\text{ml}$  standard solution. Carbamates (carbaryl, iprodione, methomyl, carbosulfan, oxamyl and molinate) were purchased from Promochem, with purities as high as 99% and were prepared as a 1000  $\mu\text{g}/\text{ml}$  solution. In the same concentration *o*-cresol, 4-nitrophenol, 4-methoxyphenol, 4-chlorophenol and 4-chloro-3-methylphenol from Merck (Darmstadt, Germany), were prepared in distilled water.

Sodium chloride, calcium chloride, sodium sul-

phate anhydrous and aluminium chloride, all for analysis quality, were obtained from Panreac.

Commercial preconcentration silica Sep-Pak cartridges of 500 mg, 125 Å pore size and 55–105 µm particle size (Waters, Milford, MA, USA) were employed for “quats” extraction.

## 2.2. Apparatus

The LC system is mainly composed by a sample injector (Reodyne Model 7125, sample size 20 µl), a UV-Vis programmable detector L-4250 from Merck-Hitachi (Tokyo, Japan), and two LC-6A liquid chromatography pumps, a SCL-6B system controller and a C-R4A data processor, from Shimadzu (Kyoto, Japan). The analytical column is Spherisorb SW3 of 3 µm (Waters) (30 mm×4.6 mm I.D.).

## 2.3. Procedure

The basic extraction procedure has been described previously [17]. Briefly, it consists in washing with a 0.5 M sulphuric acid solution, distilled water and a 2% (v/v) ammonium hydroxide solution, to condition the solid-phase. After passing 250 ml of water sample using vacuum, the cartridge is inverted and “quats” are eluted with 5 ml of a mixture (10:90) of methanol and a solution of 2 g of TMAOH and 30 g of ammonium sulphate in 1 l of water, adjusted to pH 3 with 5 M sulphuric acid. LC analysis is performed by gradient in the conditions described in a previous work [17]. The initial mobile phase composition was a 100% of the TMAOH solution used for the elution. The gradient was linearly programmed to mix with 50% methanol after 15 min and hold up during 10 min. The flow-rate of the mobile phase was 0.5 ml/min. The herbicides were monitored with a UV detector, set initially at 350 nm for diquat, at 260 nm after 6 min for paraquat and at 255 nm after 12 min for difenzoquat.

## 3. Results and discussion

### 3.1. Removal of interferences caused by humic acids and anionic surfactants

The significantly lower pesticide recoveries from

humic acids and/or anionic surfactants solutions, with the SPE procedure have been reported by several authors [22–26]. Humic acids are the largest compounds that can appear in the organic matter fraction dissolved in water (ca. 50%). The other 50% consists in small organic molecules (carboxylic acids, amino acids, carbohydrates etc.) [29]. On the other hand, the surfactants of major use in detergent formulations are anionic (ca. 70%), but there are other kinds used as nonionic, zwitterionic or cationic [17,23].

The effect of different concentrations of organic matter and surfactants present in water on the extraction and isolation of diquat, paraquat and difenzoquat, using silica, has already been evaluated in a preliminary study [17]. The results showed a negative effect of both on the recoveries of the three cationic herbicides. One exception is cationic surfactants, which do not reduce the extraction efficiency at any concentration studied.

Some authors argue that the interference may be caused because humic acids and surfactants saturate the sorptive sites of solid-phase, or because they are bound to the pesticides. The chemical species formed could either remain retained by solid-phase and not be desorbed during the elution, or passing unretained through it [17,22,24–28]. The bulk of available evidence indicates the interaction of quaternary ammonium groups of the herbicides, which bear positive charges, with the negative sites of humic or surfactant substances, such as the oxygen atoms of carboxyl and hydroxyl groups [17].

All of that stated above suggests that the addition of an “anionic groups blocker” to the water samples (as cationic surfactants) could prevent the undesirable effects of the humic acids and surfactants, since the cationic surfactant displaces the “quat” molecule from its binding with the humic acids and surfactant.

The effect of the presence of cationic surfactants in high content humic acids water on the extraction and isolation of “quats” was evaluated. Fig. 1 shows the recoveries of the three compounds at different pH from: distilled water; simulated water samples, prepared by adding humic acids until obtain a final concentration of 50 mg/l; and moreover, adding 30 mg/l of cetrimide to the simulated water samples in order to confirm if the cationic surfactant has the ability to improve the recovery.

All the recoveries obtained in this work were

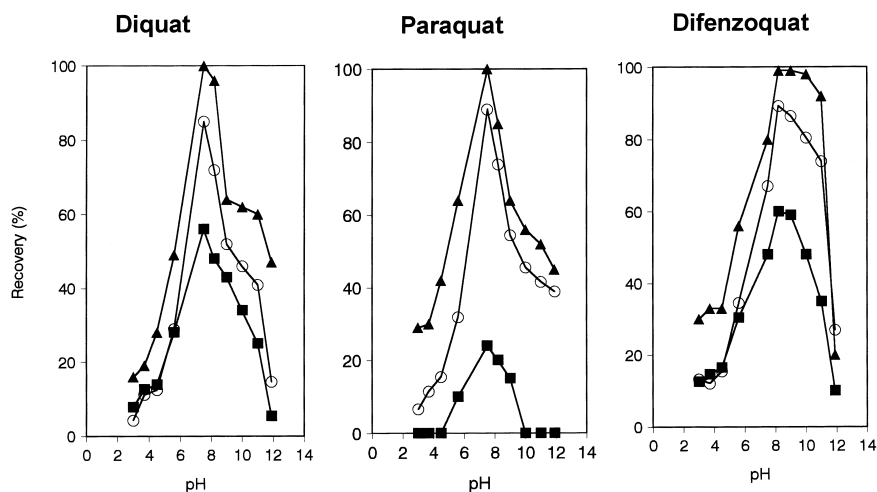


Fig. 1. Recovery at different pH of (▲) distilled water; (■) distilled water containing 50 mg/l of humic acids; (○) distilled water containing 50 mg/l of humic acids and 30 mg/l of cetrimide. The concentration of herbicides in water was 4  $\mu$ g/l of each.

calculated as an average value from, at least, three replicated analysis, each one with two injections. The pH influence in the extraction efficacy was tested at pH unit intervals between 3 and 12. It should be noted that pH values lower than 3 can affect the stability of the solid-phase employed, and pH values higher than 12 cause the degradation of diquat. The optimum pH for the sample extraction is 7.5 for diquat and paraquat and 8 for difenzoquat, but recoveries are rather acceptable in the pH 7.5–8 range, for the three compounds. Taking into account that at pH values higher than 7, the silanol groups of the stationary phase are ionized, at these pH values the cation-exchange capacity of the solid-phase will be increased.

The significant low recoveries from humic acids solutions and how the addition of cationic surfactants improve the recovery efficacy at pH values 5–10, almost at the values obtained for distilled water should be noted.

In principle, interactions of herbicides with humic organic matter are more complex than those described with the surfactant, due to the higher complexity of the molecule. They can range from van der Waals attraction forces up to direct reaction with functional groups, with steric effects also having to be considered. However, considering the molecular structure of cationic herbicides, charge transfer inter-

action seems to be more important, in the first instance the humic matter is acting as an electron donor via hydroxylic and carboxylic groups and aromatic structural units.

The effect of the presence of cetrimide on the recovery of diquat, paraquat and difenzoquat from water with high lauryl sulphate content was also assessed. Fig. 2 shows the results at different pH, of the “quats” extraction in presence of 3 mg/l of lauryl sulphate and when the anionic surfactant is mixed with the maximum cetrimide amount tested (30 mg/l). As can be seen, the presence of cetrimide in water compensates for the losses produced by the presence of anionic surfactants.

The interactions between anionic surfactant and cationic herbicides is explained by ion-pair formation, because they are generally present at concentrations below their critical micelle concentrations (ex. 404 mg/l for sodium lauryl sulphate).

Different cationic detergents at three concentrations were tested in presence of humic acids and lauryl sulphate. Recovery data are reported in Table 1. It is noteworthy that, in general, there were no significant differences between benzalkonium chloride and cetrimide recoveries whereas cetylpyridinium recoveries were lower. As can be seen, the highest concentration of cationic surfactant tested provides the best recoveries of the SPE. Concen-

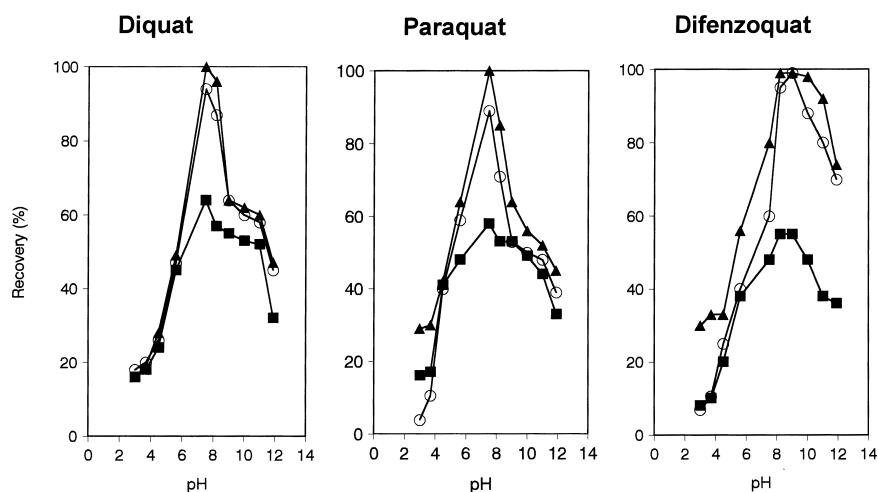


Fig. 2. Recovery at different pH of (▲) distilled water; (■) distilled water containing 3 mg/l of lauryl sulphate; (○) distilled water containing 3 mg/l of lauryl sulphate and 30 mg/l of cetrimide. The concentration of herbicides in water was 4  $\mu$ g/l of each.

trations higher than 30 mg/l of cetrimide in water with high humic acids content form a precipitate that can hardly be passed through the cartridge.

A summary of the recovery data obtained at different amounts of humic acids added at the maximum amount of cetrimide (30 mg/l) is reported in Table 2. As this shows, in real water samples the organic matter content occurs at levels ranging

between 1.4 and 17.2 mg  $O_2$ /l, which are equivalent to humic acids concentrations ranging between 2.5 and 25 mg/l [17–22]. Then, the addition of cetrimide allowed recoveries in water with usual contents of organic matter, nearly to those obtained for distilled water. Concentrations of humic acids up to 50 mg/l gave recoveries between 84–88% that could be considered almost quantitative. Although at high-

Table 1

Recovery of bipyridylium herbicides from 250 ml distilled water samples spiked with humic acids and lauryl sulphate at increasing concentrations of various cationic surfactants

Cationic surfactant and concentration	Recovery (%) <sup>a</sup>					
	50 mg/l Humic acids			3 mg/l Lauryl sulphate		
	Diquat	Paraquat	Difenzoquat	Diquat	Paraquat	Difenzoquat
<b>Benzalkonium</b>						
0.3 mg/l	58	29	63	57	53	55
3 mg/l	78	47	75	71	75	68
30 mg/l	95	92	78	93	89	86
<b>Cetylpyridinium</b>						
0.3 mg/l	47	29	60	67	44	29
3 mg/l	76	45	63	88	62	46
30 mg/l	82	71	73	92	72	78
<b>Cetrimide</b>						
0.3 mg/l	42	23	48	40	54	47
3 mg/l	77	51	76	54	63	76
30 mg/l	85	88	84	93	97	84

<sup>a</sup> Mean values were calculated from three determinations.

Table 2

Recovery of bipyridylum herbicides from 250 ml distilled water samples, with added cetrimide (30 mg/l) at increasing concentrations of humic acids (spiked level: 4 µg/l)

Humic acids concentrations (mg/l)	Recovery (%) <sup>a</sup>		
	Diquat	Paraquat	Difenzoquat
0	101	99	92
2.5	94	91	87
5	96	94	88
10	90	90	87
20	86	85	86
50	85	88	84
100	76	56	74

<sup>a</sup> Mean values were calculated from three determinations.

er concentrations (100 mg/l) the recovery could be acceptable—higher than 50%—, the water permeability through the cartridge diminishes and the extraction of these herbicides from water requires too much time.

Table 3 shows the effect of different concentrations of lauryl sulphate in the presence of the maximum concentration of cetrimide added. Typical concentrations of linear alkylbenzenesulphonates (LASs) in surface water samples range from 5 to 300 µg/l, and these only rarely occur in higher concentrations [17–23]. The results indicate that the addition of cetrimide maintains pesticide recovery from water extracted with silica nearly quantitative up to 30 mg/l concentrations of lauryl sulphate, which is a concentration one hundred times greater than that present in surface waters. Concentrations of lauryl sulphate of 300 mg/l gave recoveries between 85–76% that could still be acceptable.

The addition of cetrimide to the water samples to

Table 3

Recovery of bipyridylum herbicides from 250 ml distilled water samples, with added cetrimide (30 mg/l) at increasing concentrations of lauryl sulphate (spiked level: 4 µg/l)

Lauryl sulphate (mg/l)	Recovery (%) <sup>a</sup>		
	Diquat	Paraquat	Difenzoquat
0	101	99	92
0.005	91	92	97
0.05	95	93	88
0.3	99	92	87
3	92	95	83
30	93	97	84
100	76	85	83

<sup>a</sup> Mean values were calculated from three determinations.

avoid the negative effect of humic acids and anionic surfactants is a very promising technique. It seems to actuate blocking the active sites of both compounds. Interactions between these chemicals and other pesticides have been extensively reported, and the authors suggest that the mechanism involved is also the ionic interaction between functional groups. Then the addition of cetrimide could increase SPE efficiency, not only for the cationic herbicides but also for other pesticides.

### 3.2. Influence of the salt concentration and of the presence of other organic pollutants

Different authors studying whether the ionic strength can affect the extraction of pesticides from water samples have assayed the addition of some salts to the water. The reported results indicate that an increase in the ionic strength can indistinctly improve or worsen the recovery, depending on the pesticide polarity and the mechanisms involved in the SPE [22,23,28].

The effect of the salts present in the waters in the SPE of diquat, paraquat and difenzoquat was studied. Fig. 3A illustrates the recoveries obtained at different levels of NaCl in spiked waters. Recoveries suffer an important decrease when the salt concentration is increased. Although this adverse effect takes place, the recoveries are higher than 50% at a salt concentration of 5 g/l. This phenomenon is expected and confirms the ion-exchange process between the cationic herbicides and the silanol groups of the solid-phase.

The ion-exchangers have been described as very

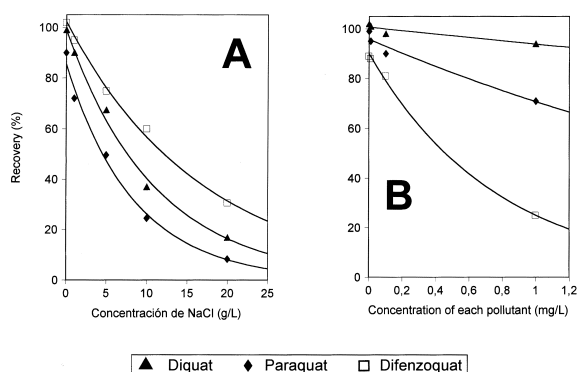


Fig. 3. Effect on the recovery of NaCl concentration (A) and a mixture of 20 organic pollutants (B).

useful materials for selectively extracting ionogenic organic compounds from aqueous solution, but their extraction efficiency is strictly dependent upon the ionic strength of the water sample [24,26]. From a practical point of view, a deep study of the most modern methods proposed for diquat, paraquat and difenzoquat shows that strong interferences from ions are evident [3,26].

The influence of the charge number of the salt cations was considered. Water samples spiked with 2 g/l of  $\text{CaCl}_2$  or  $\text{AlCl}_3$  were extracted. The recoveries obtained ranged from 38–46% for the  $\text{CaCl}_2$  or 5–10% for the  $\text{AlCl}_3$ . The interference of trivalent or divalent cations is higher than monovalent ones because they have more active centers.

The influence of the anion with respect to its interference was tested using  $\text{Na}_2\text{SO}_4$  salt at 2 g/l. Recoveries near the values obtained with water spiked with NaCl at the same concentration demonstrate that the nature of the anion has not the same impact as that of the cation.

The addition of cetrime to water with high salt content had no effect on the diminution of the recovery. Other mechanisms, mainly focused to decrease the ionic strength of the water sample, were tested. Addition of 5% of methanol, 15 ml of diethyl ether and 22 ml of 1-butanol, these lasts in their limits of aqueous saturation, showed no improvement on the recovery. Because of this interference, the saline concentration of the water samples must be measured for pesticide quantification.

Many other compounds can be present in environmental waters. Some of them are pollutants

derived from industry (PAHs, PCBs, and phenols) or agricultural use (carbamates). These compounds may influence the identification and quantification of diquat, paraquat and difenzoquat in two ways. First, they could affect the recoveries because they may interact with the “quats” since they have functional groups such as hydroxylic and carboxylic groups and also act as electron donors via aromatic structural unit forming compounds, which are not retained by the solid-phase. Second, they could result in severe interference in the determination of “quats” considering that PAHs, PCBs, phenols and carbamates are also analyzed using SPE and LC determination as for “quats” [11–13,22–24,27].

Fig. 3B shows the effect on the recovery of those contaminants in a water sample spiked with 1 mg/l of each individual compound: five phenols, four aroclors, five PAHs and six carbamates. As can be deduced from the figure an important decrease in the recoveries (50%) was observed for difenzoquat at 0.5 mg/l. The different pollutants were checked separately to establish which was responsible for the difenzoquat losses. The results demonstrated that the four types of pollutants are capable of causing it. The mechanism for the influence mentioned is not clear and the addition of cetrime to the water samples does not result in any improvement in the results.

The determination of the “quats” by LC is not affected by the presence of other pollutants in water. In the chromatograms obtained, extraneous peaks do not appear during the analysis time. The prolongation of the chromatographic gradient demonstrated that no compound was eluted to the analytical column. It suggests that other contaminants were not extracted efficiently by the proposed method.

### 3.3. Repeatability, reproducibility and limits of detection

The recovery and within-run precision of this method of adding 30 mg/l of cetrime to the water samples were calculated from ten replicate analyses. For this purpose, simulated water samples were prepared from distilled water adding humic acids, lauryl sulphate, NaCl and phenols at concentrations of 20 mg/l, 300  $\mu\text{g/l}$ , 100 mg/l and 4  $\mu\text{g/l}$ , respectively. These conditions simulate highly contaminated surface water. Samples were spiked at low

(0.4 µg/l) and high (4 µg/l) concentrations of the three herbicides. The mean recovery was ranged from 99–89% for diquat, 91–85% for paraquat, and 92–88% for difenzoquat. The recovery efficiency was independent of the herbicide concentration. The precision of the measurements ranged from 4.3–10.4%. Limits of detection (signal-to-noise ratio=3) were 0.05 µg/l for diquat and 0.08 µg/l for paraquat and difenzoquat.

### 3.4. Application to real water samples

The analytical utility of the proposed method was assessed by applying it to the determination of diquat, paraquat and difenzoquat in surface waters. They were taken from different sources to get samples with different characteristics: sample A was tap water, sample B was taken from an irrigation channel, and samples C to E were from a marsh with high salinity levels. Sample D was taken in the point where a factory spilled waste waters. The content in organic matter, sodium chloride and phenols were determined by official analytical methods [30]. It was also confirmed that samples contained none of the studied herbicides, so they were spiked with the bipyridylum herbicides. Other water characteristics or possible presence of contaminants were not monitored.

Sample volume of 250 ml were added with cetrimide (30 mg/l) and analyzed following the procedure described. Results are summarized in Table 4. Apparently, the negative effect of the organic matter (see waters A and B) is almost

negligible. However, the adverse influence of high salt concentration is clearly noticeable (see waters C, D and E) and the decrease in the recovery of difenzoquat, originated by the high concentration of other organic compounds, also appears.

The herbicide peaks are clearly displayed for the water samples in the chromatograms obtained for the real samples as shown in Fig. 4. Although the negative effect on the recovery of the salt concentration in water is not eliminated, the good resolution of the chromatographic peaks, and the absence of compounds that interfere with LC–UV determination, allowed the detection and quantification of the bipyridylum herbicides at limits below 100 ng/l, as established by the EU. These results provide evidence of the high feasibility of SPE for determining diquat, paraquat and difenzoquat in real water samples.

## 4. Conclusion

The results show that the addition of a cationic surfactant to the water samples in the determination of trace of paraquat, diquat and difenzoquat avoids the negative influence on SPE of humic acids and anionic surfactants. It can be considered as the first step for a simple removal of interferences that prevents the losses in the extraction procedure.

Low recoveries were obtained for the three herbicides from saline solutions and from natural water with high salt concentration. This phenomenon was expected and confirms the ion-exchange process

Table 4  
Recovery of bipyridylum herbicides extracted from 250 ml aliquots of different water samples

Compound	Recovery (%) <sup>a</sup>									
	Spiked at 4 µg/l level					Spiked at 0.4 µg/l level				
	A	B	C	D	E	A	B	C	D	E
Diquat	102	94	30	57	62	99	97	24	63	68
Paraquat	99	90	26	45	58	98	89	23	52	64
Difenzoquat	93	87	21	25	74	93	92	118	22	71

<sup>a</sup> Mean values were calculated from three determinations.

A=Drinking water with a organic matter concentration 1 mg O<sub>2</sub>/l (≡2 mg/l of humic acids) and 25 mg/l NaCl.

B=Water with a organic matter concentration of 10 mg O<sub>2</sub>/l (≡14.5 mg/l of humic acids) and 100 mg/l NaCl.

C=Water with a organic matter concentration of 12 mg O<sub>2</sub>/l (≡17.4 mg/l of humic acids) and 15 g/l NaCl.

D=Water with a organic matter concentration of 17 mg O<sub>2</sub>/l (≡25 mg/l humic acids), 5 g/l NaCl and phenol concentration of 1.5 mg/l.

E=Water with a organic matter concentration of 16 mg O<sub>2</sub>/l (≡23.3 mg/l humic acids) and 5 g/l NaCl.



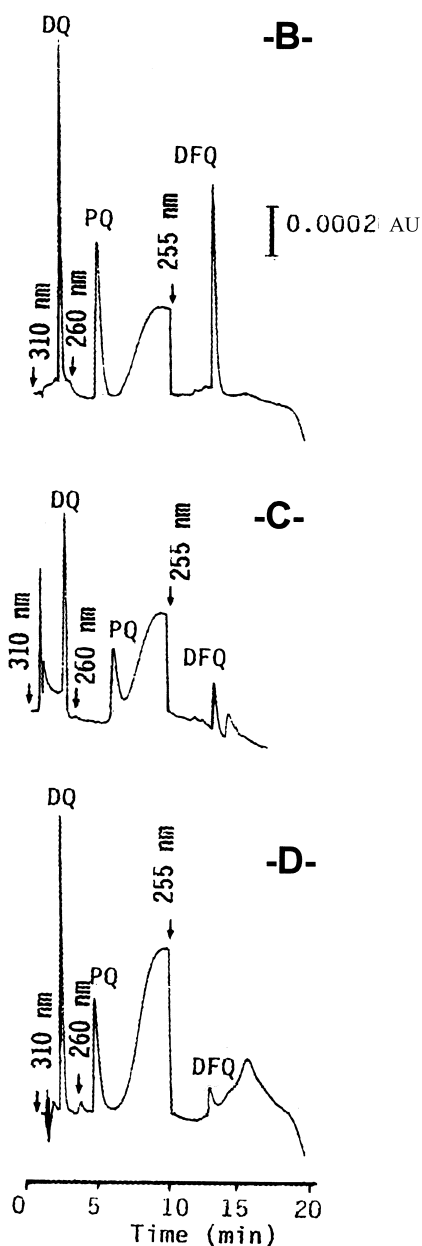


Fig. 4. Chromatograms of water samples B, C and D spiked at 0.4  $\mu\text{g}/\text{l}$  of each herbicide.

between the SPE and the bipyridylium ions. The SPE of selected pesticides generally is unaffected by the addition of other organic pollutants to the water samples. However the extraction of difenzoquat is negatively affected by the presence of these pollu-

tants at the 1 mg/l level, and this effect is reproduced in natural waters.

In spite of the drawbacks previously reported, SPE has proved to be a useful technique for determining diquat, paraquat and difenzoquat residues in natural water samples with LC–UV detection. The addition of cetrimide at 30 mg/l to the water samples avoids interferences and is a promising strategy. It can be used to eliminate the interactions between humic acids or surfactants and other organic compounds present in waters.

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