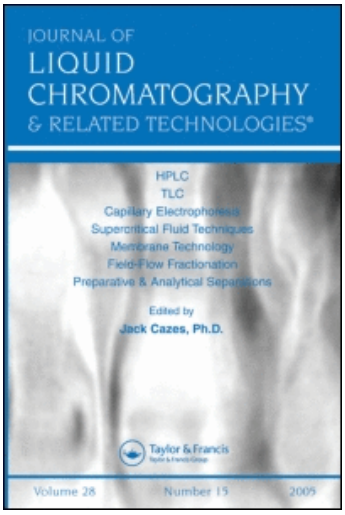

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CAPILLARY ZONE ELECTROPHORESIS OF TWO CATIONIC HERBICIDES, PARAQUAT AND DIQUAT

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ABSTRACT

Capillary zone electrophoresis with untreated fused-silica capillaries was evaluated in the separation and determination of paraquat and diquat, both are double quaternary ammonium ion herbicides. As high as 200,000-300,000 theoretical plates per meter were obtained for the separation of the two closely related herbicides over the pH range 3.5-9.5. At relatively high ionic strength in the running electrolyte, electrostatic interactions between the cationic herbicides and the negatively charged surface of the separation capillary were minimized. Under these conditions, the plot of average plate height versus the electroosmotic flow velocity indicated that longitudinal molecular diffusion is the major contributor to band broadening. The detection limits for paraquat and diquat were 15.4 and 16.8 femtomoles, respectively, with a UV detector.

INTRODUCTION

Over the last decade, high performance capillary electrophoresis (HPCE) has witnessed a rapid growth due to its promising analytical capabilities in the determination and separation of a wide variety of compounds. Currently, however, the separation and determination of non-volatile herbicides, pesticides and fungicides are mainly carried out by high performance liquid chromatography (HPLC), whereas gas chromatography is the

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chief technique for the determination of volatile pesticides and related species. The analysis of pesticides, herbicides and fungicides by GC, HPLC and other analytical techniques was recently reviewed by Sherma (1, 2).

This report is concerned with the investigation of the potential of capillary zone electrophoresis (CZE) in the separation and the determination of cationic herbicides, namely the double quaternary ammonium ions, paraquat and diquat. Paraquat and diquat are effective herbicides for terrestrial and aquatic plants, and are used at low concentrations (e.g., 1-5 μg/mL). Residues of these herbicides have been found in ground water (3), which can cause serious health problems (4-6). Their determination at low level is therefore important for the quality control of drinking water and rotational crops. As will be demonstrated in this report, CZE with its precision instrumentation and small sample requirements is well suited for the determination of these species. The methodologies developed in this study can be applied for a wider range of ionic pesticides.

EXPERIMENTAL

Instruments and Capillary Columns

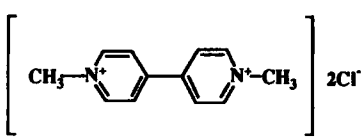
Experiments were carried out on an in-house built CE system (7). It consists of a 30-kV dc power supply of positive polarity (Model EH30P03, Glassman High Voltage Inc., Whitehouse Station, NJ, U.S.A.) and a UV-Vis variable wavelength detector equipped with a cell for on-column detection (Model 200, Linear Instruments, Reno, NV, U.S.A.). The electropherograms were recorded with a computing integrator (Model CR601, Shimadzu, Columbia, MD, U.S.A.).

The instrument for the UV spectrometry measurements was a UV-Visible Recording Spectrophotometer Model UV-160 from Shimadzu.

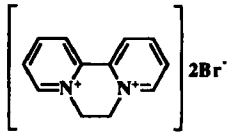
Fused-silica capillaries having an inner diameter of 50 μm and outer diameter of 375 μm were obtained from Polymicro Technology (Phoenix, AZ, USA). The untreated fused-silica capillary used in this study has 80 cm total length with a separation distance of 50 cm (*i.e.*, from the injection end to the detection point).

Reagents and Chemicals

All chemicals were of the analytical grade. Chemicals needed for the preparation of the electrolyte solutions were obtained from Fisher Scientific Co. (Pittsburgh, PA, U.S.A.). 2-Aminopyridine (Aldrich, Milwaukee, WI, U.S.A.) was used as the internal standard. Phenol (J.T. Baker Inc, Phillipsburg, NJ, U.S.A.) was used as the inert tracer to measure the electroosmotic flow. The herbicides, *i.e.*, paraquat and diquat, were purchased from Chem Service (West Chester, PA, U.S.A.). Their structures are as follows:



Paraquat



Diquat

All solutions were filtered with 0.2 μm Uniprep Syringeless filters from Genex Corp., (Gaithersburg, MD, U.S.A.) to avoid capillary plugging.

UV Spectrophotometry

Sample solutions were made by dissolving a small amount of paraquat, diquat and 2-aminopyridine in deionized water. Absorption spectra of the herbicides and 2-aminopyridine were obtained by scanning from 200 to 350 nm. The wavelengths of maximum absorbances, λ_{max}, the molar absorptivities, ε, and the correlation coefficient of the plots of absorbance versus concentration, for paraquat, diquat and 2-aminopyridine are listed in Table 1.

Other Procedures

Sample solutions were prepared by dissolving pure compounds in the running electrolyte. All injections were made by electromigration for 2-5 seconds, at an applied voltage that was the same as that for separation. The running voltage used for all the measurements was 15 kV. Electroosmotic flow was determined by measuring the migration time of phenol, which was considered as neutral under the experimental conditions.

The overall or net mobility of the solute, μ, which is the sum of electrophoretic (μ_{ep}) and electroosmotic (μ_{eo}) mobilities, was calculated from the electropherogram using the following equation:

$$\mu = \mu_{ep} + \mu_{eo} = \frac{l\,L}{V t_r}$$

where l is the separation distance, L is the total length of the capillary, t_r is the migration time of the solute and V is the applied voltage. The electroosmotic flow was determined from the migration time of phenol (an inert tracer), t_o, using the following equation:

$$\mu_{eo} = \frac{l\,L}{V t_o}$$

TABLE 1. Maximum wavelengths and molar absorptivity of paraquat, diquat and 2-aminopyridine.

Sample	λ_{max} (nm)	ε ($cm^{-1}M^{-1}$)	Correlation coefficient
Paraquat	258	1.72×10^4	0.9996
Diquat	308	1.62×10^4	0.9979
2-Aminopyridine	229, 290	NM	NM

NM, not measured

The electrophoretic mobility of the charged herbicides was estimated through the equation

$$\mu_{ep} = \mu - \mu_{eo} = \frac{l\,L}{V}\left(\frac{1}{t_r} - \frac{1}{t_o}\right)$$

RESULTS AND DISCUSSION

Figure 1A and B illustrates typical electropherograms of the separation of the two herbicides at pH 3.5 and 7.0, respectively. In both cases, sharp peaks with base-line resolution were obtained. The relatively shorter analysis time obtained at pH 7.0 is due to the increase in the magnitude of the electroosmotic flow as a consequence of increased ionization of the silanol groups of the capillary inner surface at this pH. The two quaternary ammonium ion herbicides having the same net charge (*i.e.*, +2) and similar molecular weights (184 for diquat and 186 for paraquat) separated on the basis of differences in their molecular shape.

As expected, the electrophoretic mobilities of paraquat and diquat were practically invariant over a wide range of pH, see Fig. 2. The average electrophoretic mobilities of paraquat and diquat were 5.86 (0.13) x 10^{-4} and 5.71 (0.10) x 10^{-4} $cm^2/V.s$, respectively. The constancy in electrophoretic mobilities may indicate that solute-wall interactions were minimized under the experimental conditions used in this study. At all

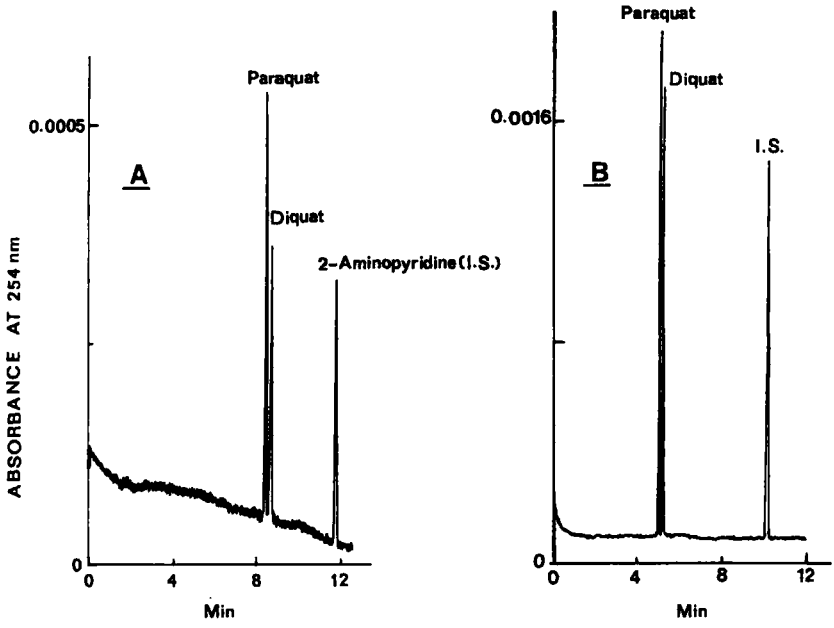


FIGURE 1. Typical electropherograms illustrating the rapid separation of herbicides by CZE. Separation capillary, untreated fused-silica, 50 cm (to the detection point), 80 cm (total length) x 50 μm I.D.; running electrolyte, 0.10 M sodium phosphate, pH 3.5 in A, pH 7.0 in B; sample injection, electromigration, 5 seconds; running voltage, 15 kV; internal standard, 2-aminopyridine; detection, 254 nm.

pH's, the ionic strengths of the running electrolytes were relatively high (i.e., 0.2 M NaCl), which lessened electrostatic interactions between the double quaternary ammonium ion herbicides and the negatively charged surface of the fused-silica capillary.

Another feature of Fig. 2, is that the overall or net mobilities of the two herbicides paralleled the electroosmotic flow, compare curves 4 and 5 to curve 1 in Fig 2. This is a unique characteristic for the migration of fully ionized species in the presence of an electroosmotic flow.

As can be seen in Fig. 2 (curve 1), the electroosmotic flow increased with increasing pH and consequently the overall or net velocities of the moving zones also increased. Figure 3 illustrates the plot of the average plate height versus the

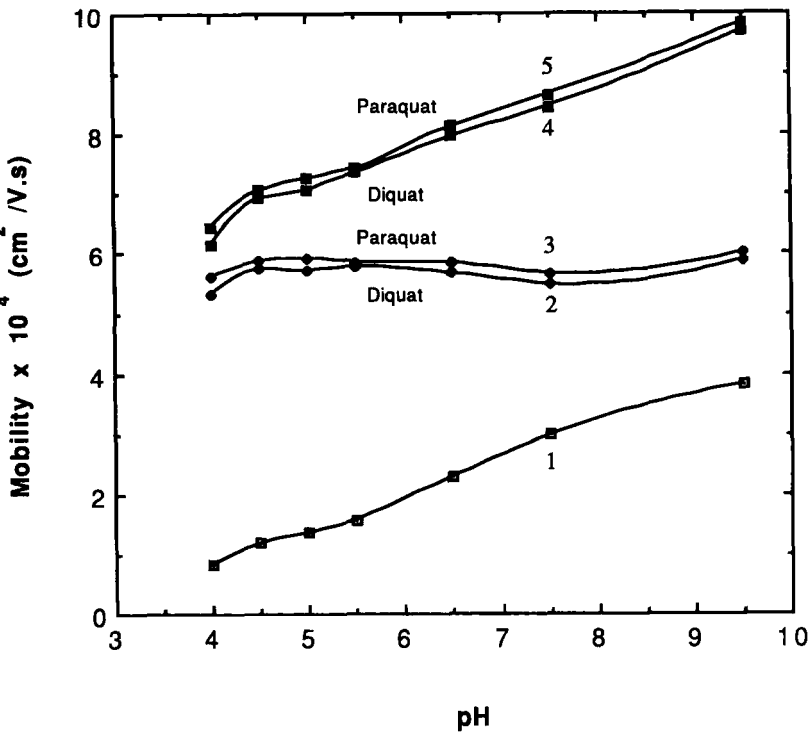


FIGURE 2. Mobilities of herbicides. Separation capillary, same as in Figure 2; running electrolytes: 5 mM acetate in the pH range 4.0-5.5, 5 mM phosphate in the pH range 6.0-8.0, 5 mM borate in the pH range pH 8.5-9.5. All electrolyte solutions contained 0.2 M NaCl. Sample injection, electromigration, 2 seconds; running voltage, 15 kV; detection, 254 nm. Symbols, 1, electroosmotic flow; 2 and 3, electrophoretic mobility; 4 and 5, overall or net mobility.

electroosmotic flow velocity (i.e., at various pH). This plot shows that the major cause of zone broadening is longitudinal molecular diffusion, whose effect is significantly higher at low flow velocity (i.e., low pH), see Fig. 3. This behavior may also indicate that the magnitude of adsorption of the cationic herbicides onto the the capillary wall is greatly reduced in the presence of 0.2 M NaCl in the running electrolytes.

The detection limits of paraquat and diquat in terms of concentration and injected amount were determined, and the results are listed in Table 2. They were measured at the

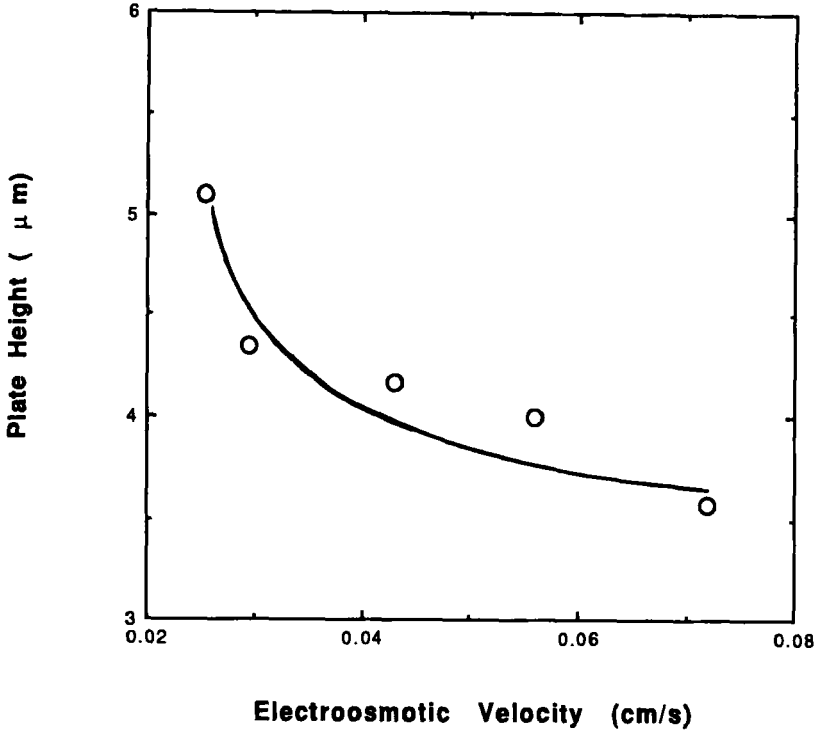


FIGURE 3. Plot of average plate height versus electroosmotic flow velocity. Separation distance, 50 cm. Experimental conditions are as in Fig. 2.

TABLE 2. Limits of detection for paraquat and diquat estimated on the basis of their chloride and bromide salts, respectively. Detection wavelengths: 308 nm for diquat, 254 nm for paraquat; other experimental conditions are as in Fig. 1A.

Sample	Limits of Detection				Correlation Coefficient
	Concentration		Injected Quantity		
	(μg/mL)	(μM)	(pg)	(femtomole)	
Paraquat	0.40	1.55	3.97	15.4	0.996
Diquat	0.50	1.45	5.78	16.8	0.996

wavelengths of maximum absorption, λ_{max}, that are listed in Table 1. To this end, several dilutions of standard solutions of paraquat and diquat containing 2-aminopyridine as the internal standard were analyzed by CZE using the conditions of Fig. 1A. 2-Aminopyridine is an excellent internal standard since it has two absorption bands extending in width over the wavelength regions where paraquat and diquat yielded maximum absorbances, see Table 1. For both paraquat and diquat, the calibration curves were linear with correlation coefficients of 0.999 and 0.998, respectively. The detection limits shown in Table 2, demonstrate that CZE is suitable for the quantitative analysis of femtomole quantities of these two herbicides. The molar absorptivities of both species were quite high, thus favoring the determination of the two herbicides at low level with UV detection.

The above studies have demonstrated that CZE is suitable for the separation and determination of minute amounts of fully ionized herbicides having the same net charge and similar molecular weights.

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