ELSEVIER

Journal of Chromatography A, 723 (1996) 169–177

JOURNAL OF CHROMATOGRAPHY A

Separation of *s*-triazine herbicides and their metabolites by capillary zone electrophoresis as a function of pH

Ph. Schmitt[a,*], A.W. Garrison[b], D. Freitag[a], A. Kettrup[a]

[a]*Institut für Ökologische Chemie–G.S.F., Schulstraße 10, D-85356 Attaching/Freising, Germany*

[b]*Ecosystems Research Division, National Exposure Research Laboratory, U.S. Environmental Protection Agency, 960 College Station Road, Athens, GA 30605, USA*

First received 9 September 1994; revised manuscript received 13 July 1995; accepted 20 July 1995

Abstract

The effects of buffer pH on electrophoretic mobility of various *s*-triazines (chloro-, hydroxy-, methoxy- and thiomethyl-*s*-triazines) in light of their chemical properties have been studied. Good separation was achieved for each class of *s*-triazines as cations, except for the chlorotriazines, with buffer pH around the pK_a of the herbicides, as well as at a pH of $pK_a - 2$. Migration times were correlated with molecular masses (as a first approximation of molecular size and shape). Possible hydrophobic wall interactions were detected at acidic pH and low voltage. Separation of hydroxytriazine metabolites as anions could also be achieved at a high pH of around 8. The detection level calculated for most of these *s*-triazines was 0.05 μg/ml of analyte in the injection solution.

Keywords: Capillary electrophoresis; *s*-Triazines; Herbicides

1. Introduction

Over the last 30 years the use of pesticides has increased–32 570 tons were used in 1992 in the Federal Republic of Germany; herbicides accounted for 48% of total pesticides [1]. There does not yet seem to be any general tendency towards restricted application of these products [2]. The *s*-triazine derivatives are among the most important selective herbicides and have many other industrial uses, e.g., as fungicides, dyes, pharmaceuticals, etc. These herbicides are 1,3,5-triazines (symmetrical triazines) substituted in the 2-, 4- and 6-positions. The 4- and 6-positions are substituted with different aminoalkyl groups. The substituent in the 2-position gives the triazine its specific selectivity and determines the name ends of the commercial products: chlorine (ending with -azine), methoxy (-tone) and thiomethyl (-tryne). Atrazine is the main representative of the *s*-triazines and was the most commonly used herbicide in the United States in 1993 [3]. Because of environmental pollution, the commercial use of atrazine has been forbidden in Germany since 1991 [4]; atrazine has been replaced by terbuthylazine.

Depending on their application, triazine her-

* Corresponding author. Present address: U.S. Environmental Protection Agency, Athens Environmental Research Laboratory, 960 College Station Road, Athens, GA 30605, USA.

0021-9673/96/$15.00
SSDI 0021-9673(95)00805-5

bicides are subjected to various degradation processes (photolysis, oxidation, hydrolysis, biodegradation, etc.), leading primarily to dealkylation of the amine groups in positions 4 and 6 and/or hydrolysis of the substituent in position 2; the latter process gives the corresponding hydroxytriazines, which are found as contaminants in stream, lake and well water [5]. Some of the parent triazines and their degradation products are highly resistant in soils; thus the analysis of their residues, the kinetics of their degradation, and their sorption/mobility in soil systems are important environmental problems that require efficient and definitive analytical techniques. The lack of routine non-radioactive methods for the quantitation of hydroxylated *s*-triazines from environmental samples [3] makes this an important analytical problem.

High-performance capillary electrophoresis (HPCE, CE) has developed rapidly since its introduction in the middle 1980s, and adds a separation tool of greater efficiency to the more conventional chromatographic instrumentation [6]. CE has been applied to a number of biomedical separation problems [7], but only a few articles report applications to pesticides or environmental samples [8]. CE has been successfully applied to the separation of phenoxy-acid herbicides (MCPA, MCPP, 2,4-D, Fenoprop, Dichlorprop) and their enantiomers [9–11], pyrethroids (alphametryne, cypermetryne) [12], organophosphates (glyphosate, MPA, ENPA, PMPA, ...) [13], bipyridinium salts (diquat and paraquat) [14,15], sulfonylureas (metsulfuron and chlorsulfuron) [16] and chloroanilines [17].

The separation of *s*-triazine herbicides and their solvolytic products has been demonstrated with CZE [18], and quantitative determination of chloro-*s*-triazines in tap water was accomplished by micellar electrokinetic capillary chromatography (MECC) after concentration by solid-phase extraction (SPE) [19]. The possibility of direct quantitation of hydroxylated metabolites of atrazine in humic-containing samples with CZE without cleanup was reported [20].

Because *s*-triazines and their degradation products exist as ionic species at certain pHs, they are good candidates for separation by CZE. In this research, we present CZE techniques and data for separation of the hydroxy-, methoxy- and thiomethyl-*s*-triazines, which have pK_as amenable to the usual CZE separation buffers. The low pK_as (<1.5) of the chloro-*s*-triazines caused them to be only partially separated by the CZE techniques applied here. In addition, we present results of studies on the effects of buffer pH on electrophoretic mobility of the various *s*-triazines in light of their chemical properties.

2. Experimental

Separations were performed with a Beckman P/ACE 2100 Series HPCE with Beckman System Gold chromatography software. The fused-silica CE column (75 μm I.D.; 375 μm O.D.; 50 cm length to detector and total length of 57 cm) was obtained from Beckman Instruments. The separation runs were done at constant temperature (30°C) and voltage (20 kV) with UV detection. The 230-nm filter was found to give the best signal of the seven available UV filters (200, 214, 230, 254, 280, 300 and 340 nm) of the P/ACE system, and was used for all following trials. Hydrodynamic sample injection for 15 s was used for sample introduction in all experiments. Each herbicide was first analyzed alone in the buffer system, before mixing with other herbicides. Acetate buffers (50 m*M*) were prepared by mixing acetic acid (0.1 *M*), sodium acetate (0.1 *M*), and deionized water to reach the desired molarity and a pH between 3.8 and 5.6. Citrate–phosphate buffers were prepared by mixing citric acid (0.1 *M*) and disodium hydrogenophosphate (0.2 *M*) to get a pH in the range 2.2–7.8. Citrate–HCl buffers in the pH range 1.2–5 were prepared by mixing disodium citrate (0.1 *M*) and HCl (0.1 *M*).

Herbicide stock solutions were prepared by dissolving 5.0 mg of herbicide in 100 ml of pesticide grade methanol. Acidification of solutions was necessary for the solubilization of the hydroxytriazines. When necessary, dilutions were done in water (for standard curves), and those solutions were immediately used for CE. All

buffers and stock solutions were kept under refrigeration.

Chemical sources and purity: methoxy-, chloro-, hydroxy- and thiomethyl-*s*-triazines were purchased in greater than 99% purity grade from Dr. Ehrenstorfer (Augsburg, Germany) or from Riedel de Haen (Pestanal grade; Munich, Germany). Hydrochloric acid, glacial acetic acid, sodium acetate, disodium hydrogen phosphate, disodium citrate, and citric acid, all p.a. grade, were obtained from Merck (Darmstadt, Germany).

3. Results and discussion

3.1. Separation

s-Triazines (Table 1) are basic polar compounds which can protonate at the aromatic-ring nitrogen in aqueous solution to give the corresponding cations [21]. The dissociation constants (pK_a) corresponding to this reaction for the compounds used in this study are given in Table 1 [21–24]. There are large differences in the pK_a-values found in the literature. Two groups of compounds are observed: the chlorotriazines (parent compounds and dealkylated metabolites) with low pK_as around 1.5 to 2, and the OH-, OCH_3- and SCH_3-substituted *s*-triazines with pK_as in the range 3.1–5.2. These pK_a-values follow the order given by Weber [24]:

average pK_a:	5.0	>	4.2	>	4.0	>	1.7
X substituent:	–OH	>	$-OCH_3$	>	$-SCH_3$	>	–Cl

Various buffer systems were used in this study to observe the influence of buffer pH on electrophoretic behavior of the pesticides in terms of relative separation and changes in migration time.

Hydroxytriazines

The separation of hydroxypropazine, hydroxysimazine, and all hydroxy-metabolites of atrazine and terbuthylazine was accomplished in this experiment.

First acetate buffer (50 m*M*) was used which gave baseline separation of five hydroxylated compounds (hydroxyterbuthylazine, hydroxyatrazine, hydroxydesisopropylatrazine, hydroxydesethylterbuthylazine, and hydroxydiaminotriazine) migrating as cations at a pH of 4.65. The use of this buffer in a quantitative study of atrazine hydroxy-metabolites is reported elsewhere [20]. Addition of methanol to the buffer did not increase resolution.

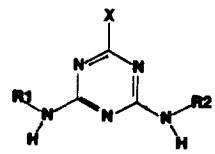
In a second trial, separation of all the hydroxy-metabolites of atrazine and terbuthylazine with a citrate–phosphate buffer, varying the pH between 2.7 and 6.7, was attempted. Migration times versus pH are given in Figs. 1a and 1b. In both cases the migration order is reversed in going from low to high pH. In the case of the atrazine metabolites, baseline separation with this citrate buffer was not as good as with the acetate buffer used earlier [20], indicating possible interaction of the analytes with the buffer system. The close pK_a-values of the hydroxy-metabolites of atrazine caused coelutions at certain pHs. The metabolites of terbuthylazine showed a good separation pattern. The best separation for each set of four compounds was obtained at two pH levels: between 2.7 and 3.2 and at about 4.7 (Fig. 2).

At $pH < pK_a - 2$ (pH 2.5 to 3), 99% of the molecules are protonated and migrate as cations with the electroosmotic flow (EOF) (toward the cathode). As all molecules carry the same charge, the separation order is governed by the molecular masses/size (Fig. 2a)

At $pH = pK_a$ (pH 4.5 to 5), 50% of the analyte molecules are protonated. The migration order is reversed from that at low pH and is a function of the charge-to-mass ratio governed by the pK_a-values (Fig. 2b). Because of the close pK_a-values of the analytes, their migration and separation are very sensitive to small buffer-pH variations.

At $pH > pK_a + 2$ (pH 6.5 to 7), 99% of all molecules are deprotonated and neutral. Their speed in the column is equal to the EOF and they coelute in one major peak, visible on the electropherogram as the "neutral" peak (Fig. 2c)

Table 1
pK_a values for *s*-triazines found in the literature [21–24]



	R1	R2	X	pK_a [21–24]	log *P*	M_r
Chloro-s-triazines						
Simazine	CH_2CH_3	CH_2CH_3	Cl	1.65–1.8	–	201.7
Atrazine	CH_2CH_3	$CH(CH_3)_2$	Cl	1.68–1.85	–	215.7
Propazine	$CH(CH_3)_2$	$CH(CH_3)_2$	Cl	1.5–1.85	–	229.8
Terbuthylazine	CH_2CH_3	$C(CH_3)_3$	Cl	1.94	–	229.8
Trietazine	CH_2CH_3	$(CH_2CH_3)_2$	Cl	1.88–1.9	–	229.8
Chloro-metabolites						
Desethylatrazine	H	$CH(CH_3)_2$	Cl	1.65	–	187.7
Desisopropylatrazine	CH_2CH_3	H	Cl	1.58	–	173.6
Desethylterbuthylazine	H	$C(CH_3)_3$	Cl	–	–	201.7
Chlorodiamino triazine	H	H	Cl	–	–	145.6
Hydroxy-s-triazines						
Hydroxysimazine	CH_2CH_3	CH_2CH_3	OH	–	0.79	183.3
Hydroxyatrazine	CH_2CH_3	$CH(CH_3)_2$	OH	5.15–5.2	1.55	197.3
Hydroxypropazine	$CH(CH_3)_2$	$CH(CH_3)_2$	OH	5.2	2.01	211.3
Hydroxyterbuthylazine	CH_2CH_3	$C(CH_3)_3$	OH	–	1.82	211.3
Hydroxy-metabolites						
OH-desethylatrazine	H	$CH(CH_3)_2$	OH	4.57–4.75	0.66	169.2
OH-desisopropylatrazine (OH-destbutylterbuthylazine)	CH_2CH_3	H	OH	4.65	−0.23	155.2
OH-desethylterbuthylazine	H	$C(CH_3)_3$	OH	–	0.93	183.3
Hydroxydiamino triazine (Ameline)	H	H	OH	–	−1.26	127.1
Methoxy-s-triazines						
Atraton	CH_2CH_3	$CH(CH_3)_2$	$O-CH_3$	4.2	1.82	211.3
Prometon	$CH(CH_3)_2$	$CH(CH_3)_2$	$O-CH_3$	4.2	2.28	225.3
Terbumeton	CH_2CH_3	$C(CH_3)_3$	$O-CH_3$	–	2.09	225.3
Secbumeton = Isobumeton	CH_2CH_3	$CH(CH_2CH_3)(CH_3)$	$O-CH_3$	–	2.31	225.3
Thiomethyl-s-triazines						
Desmetryn	CH_3	$CH(CH_3)_2$	$S-CH_3$	3.1–3.93	1.82	213.4
Ametryn	CH_2CH_3	$CH(CH_3)_2$	$S-CH_3$	4.0–4.1	2.24	227.4
Prometryn	$CH(CH_3)_2$	$CH(CH_3)_2$	$S-CH_3$	4.05–4.1	2.7	241.4
Terbutryn	CH_2CH_3	$C(CH_3)_3$	$S-CH_3$	4.4	2.51	241.4
Simetryn	CH_2CH_3	CH_2CH_3	$S-CH_3$	–	1.63	213.3
Aziprotyn	N_3	$CH(CH_3)_2$	$S-CH_3$	–	–	225.3
Dipropetryn	$CH(CH_3)_2$	$CH(CH_3)_2$	$S-C_2H_5$	–	3.12	255.4

A trial at pH 8.33 (with the addition of NaOH¶ to the citrate–phosphate buffer) showed four peaks (Fig. 2d) after a neutral peak, corresponding to the same compounds now migrating as anions with the same elution order as at pH 4.62. At higher pH the hydroxyl proton is lost and the hydroxytriazines are attracted as anions towards the anode; they are finally swept with the EOF toward the cathode in the reverse order of their hydroxyl group pK_as.

To summarize, the best buffer pH for the separation of these *s*-triazines can be given as $pH = pK_a$ or $pH = pK_{a,min} - 2$ (where $pK_{a,min}$ is the smallest pK_a-value of all analytes). Changing

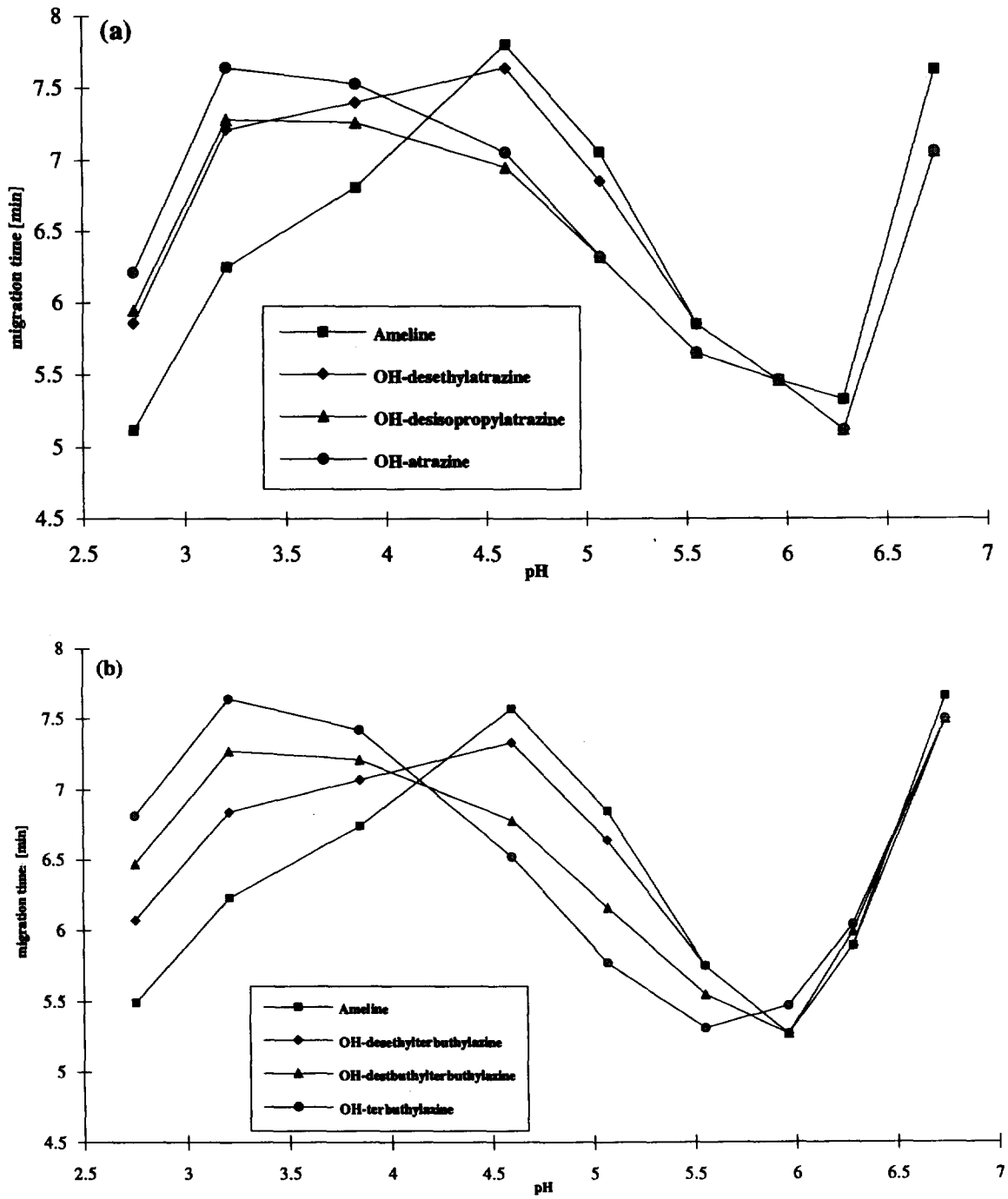


Fig. 1. Variation of migration time as a function of buffer pH. (a) Hydroxyatrazine and metabolites, (b) hydroxyterbuthylazine and metabolites (citrate–phosphate buffer, 20 kV, 30°C).

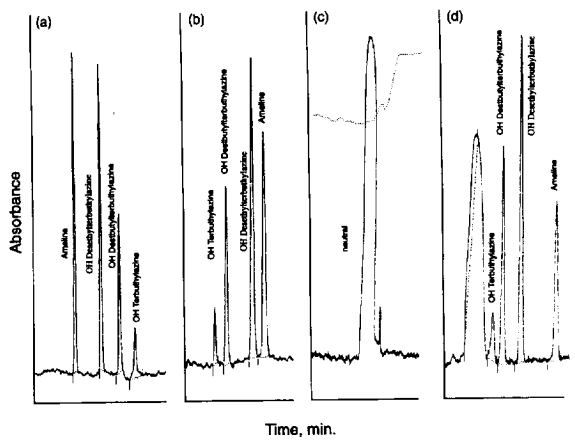


Fig. 2. Separation of the four hydroxy-metabolites of terbuthylazine. (a) pH 2.75, as cations; (b) pH 4.62, as cations with inversion in migration order; (c) pH 6.76, as neutral species with no separation; (d) pH 8.3, as anions.

the buffer ionic strength and the voltage did not improve separation, but only changed the EOF and shifted migration times.

Another mixture of four hydroxytriazinic pesticides was also subjected to CE separation at pHs varying from 2.2 to 4 with the citrate–phosphate buffer. The best separation of the mixture of hydroxysimazine, hydroxypropazine, hydroxyatrazine, and hydroxyterbuthylazine was found at $pH < 3.3$, where $pH = pK_a - 2$. Hydroxyatrazine and hydroxyterbuthylazine have very similar electrophoretic behavior and were not separated under these conditions; their pK_a-values must be very close. A trial at pH 8.3 (citrate + NaOH), where the analytes are present as anions, also resulted in separation of only three of the four pesticides, with less efficiency than at pH 3.3.

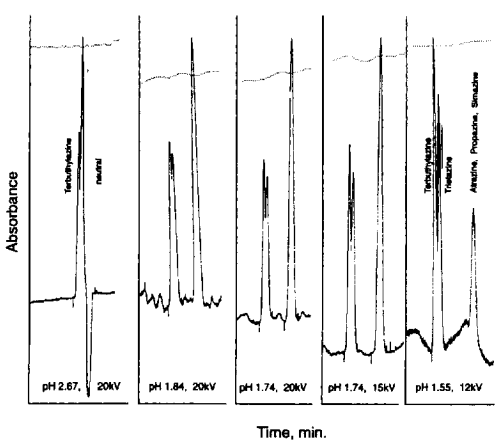


Fig. 3. Attempted separation of chloro-*s*-triazines at low pH (citrate–HCl buffer). At pH 2.67, only one triazine is separated from the neutral peak; at the other pHs, all three visible peaks are triazines (the neutral peak is not shown).

Methoxytriazines

The best separation of methoxytriazines (three pesticides of four) was obtained at a pH around 3.0. At pH lower than 2.5 atraton and terbumeton coeluted, as well as prometon and secbumeton. The pK_as of the latter two compounds must be very close, so that their separation is difficult with this method.

Thiomethyltriazines

The best separation of the thiomethyltriazines was at pH lower than 2.5; still, only five peaks were observed on the electropherogram for seven herbicides. Ametryn and terbutryn as well as simetryn and desmetryn coeluted. As the pH increased, the EOF became higher and analyte separation deteriorated. Aziprotyn is not detected as well as the other thiomethyltriazines because its maximum absorbance is not at 230 nm.

Chlorotriazines

The pK_a-values of the chlorotriazines are between 1.5 and 2, according to the literature. To affect protonation of these molecules and possible separation as cations, the background electrolyte must have a pH considerably lower than 2. Under such conditions, measurements were unstable because the EOF was almost non-existent and migration times were longer. Upon increasing the voltage to compensate for the low EOF, the buffer system degraded, as indicated by the decrease of the current to zero. Decreasing the voltage from 20 to 15 kV almost doubled retention times but did result in better separation. Five chlorotriazines were mixed and tested with HCl–citrate buffers at pHs ranging from 1.55 to 2.67 (Fig. 3). The best separation was found with the combination of low voltage (15

kV) and a low enough pH (1.74) to allow maximum protonation with a reasonable EOF.

This experiment illustrates the difficulties of applying CZE to low-pK_a compounds like chlorotriazines. A recent study showed the application of MECC to the determination of atrazine and simazine in river water after solid-phase extraction [19]. Other techniques (HPLC, GC, ELISA tests) have been successfully used for the analysis of chlorotriazines at detection levels as low as parts per trillion [25]; CZE apparently does not have applications to the routine analysis of chlorotriazines.

Mixture of 19 triazines

To expand the capability of these CZE separation methods, we mixed all these triazines (except the chlorotriazines) and analyzed them at various pHs to determine the best separation. At a pH of 2.2 with the citrate–HCl buffer, twelve distinct peaks were observed on the electropherogram, all migrating within 11 min. Several analytes coeluted (Fig. 4). At this low pH all these triazines can be considered to be completely protonated. As they carry the same charge (+1), their separation is governed only by their molecular mass (M_r) and shape. As shown in Fig. 5, the electrophoretic mobility (μ, in citrate–HCl buffer, pH 2.2) as a function of $1/M_r^{2/3}$ has been found to give a good linear correlation (with $r^2 = 0.979$); i.e., the migration times are directly proportional to $1/M_r$. This model considers all molecules to be spherical with the same density. The real shape of the pesticides is determined by their alkyl-substituents in the 4- and 6-positions and explains the differences in electrophoretic mobilities found for the same molecular masses.

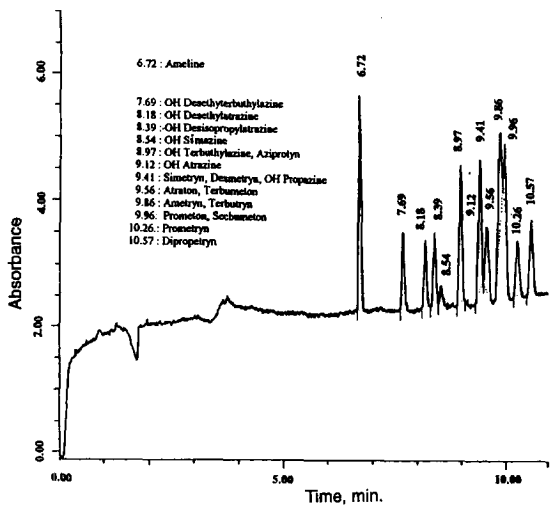


Fig. 4. Attempted separation of a mixture of 19 *s*-triazines (citrate–HCl buffer, pH 2.2, 20 kV, 30°C).

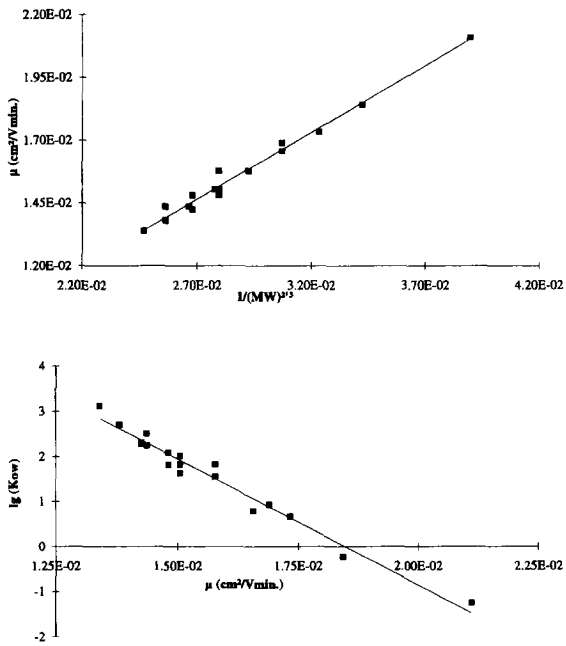


Fig. 5. Linear correlation between electrophoretic mobilities, μ, of 19 *s*-triazines at pH 2.2 (citrate–HCl buffer, 20 kV, 30°C) with (a) molecular mass; (b) log K_{ow}.

The addition to the buffer (citrate–HCl, pH 2.2) of increasing concentrations of methanol or acetonitrile increased analyte migration times, because of decreased electroosmotic flow, but did not improve separation. With both organic solvents, hydroxysimazine coeluted with hydroxydesisopropylatrazine, while the migration time of hydroxypropazine was reduced, giving an isolated peak. Atraton and terbumeton coeluted with the simetryn/desmetryn peak. All other pesticides migrated in the same elution order as in Fig. 4.

Lowering the voltage from 20 to 15 kV (with citrate–HCl buffer at pH 2.2) caused significant increases in migration times (lower EOF), as was

also observed with the chlorotriazines, and resulted in complete loss of resolution for compounds with high migration times (over 15 min). This implies interactions with the capillary wall surfaces. The log P values (log of the octanol–water partition coefficient) given in Table 1 were calculated with the Software PALLAS Ver. 1.1, PROLOG. A negative linear correlation ($r^2 = 0.970$) was found between the electrophoretic mobilities of the pesticides (from the electropherogram in Fig. 4) and the calculated octanol–water partition coefficients (log K_{ow}). The compounds with longer migration times (lower μ) are the ones with higher hydrophobicities. Apparently these more hydrophobic compounds completely disappear from the electropherograms as the voltage is lowered from 20 to 15 kV and below. Although it can not be proven, one explanation of the loss is complete sorption of these compounds on the partially neutralized capillary wall surface at low pH. This is enhanced by the fact that the solubilities of the compounds decrease with lower voltage because the electrolyte is cooler than at high voltage.

3.2. Reproducibility and detection levels

Hydrodynamic sample injections of hydroxyatazine were done for 1 to 90 s and variations in migration time, peak area, and peak height were plotted. Migration times for a mixture of these triazines were reproducible, with relative standard deviations (R.S.D.) under 0.5% ($n = 6$). The R.S.D. increases with increasing migration time. Fair linear correlations of peak area and height with injection time (analyte quantity) were found with injections up to 60 s. An injection time of 90 s gave values out of the linear range. The detection limit for hydroxyatrazine was found to be 0.05 μg/ml for a 10-s injection time at a signal-to-noise ratio of 2. The detection limits for several of the triazines were similar to that for hydroxyatrazine under these conditions. This level could be decreased to 0.01 μg/ml by choosing the optimum wavelength for each herbicide (e.g., with a diode-array or UV-scanning detector) and/or by increasing the sample injection time to 60 s. The use of electrokinetic injection has been successfully applied to preconcentrate the sample in the capillary before separation.

4. Conclusions

Good separation was achieved for each class of *s*-triazines, except for the chlorotriazines, with a citrate–HCl buffer at a pH around the pK_a of the herbicides, as well as at a pH of p$K_a - 2$, and a voltage of 20 kV at 30°C, with good reproducibility in migration times, peak areas, and peak heights.

Because good CE separation of triazines as cations can be achieved, it is expected that little cleanup would be required compared to that used for the more conventional chromatographic techniques, especially when it is necessary to analyze these compounds in environmental samples containing various anionic materials such as humic substances, biological compounds, or detergents. The triazines migrate before the neutral peak on the electropherogram, while the macromolecular anions migrate after this peak. CE has a distinct advantage over classical chromatographic methods, especially for the labile hydroxytriazines [20] which require cleanup and derivatization for GC analysis.

Further work is being conducted to compare the capillary electrophoretic behavior of the *s*-triazines, especially their experimentally observed pK_a and pI (isoelectric point) values, with values calculated using SPARC (Sparc Performs Automated Reasoning in Chemistry), a computer program that calculates physical and chemical reactivity parameters of molecules based on their molecular structures alone [26].

Acknowledgements

The authors appreciate the consultation of Sam Karickhoff and Mac Long of the Athens Environmental Research Laboratory, USEPA, on the ionization characteristics of *s*-triazines and the use of SPARC to estimate their pK_a- and pI-values.

References

[1] Biologische Bundesanstalt für Land- und Forstwirtschaft, Braunschweig, Germany.
[2] C. Stroetmann, in H. Frehse (Editor), Nature Conservation and Nuclear Safety, Pesticide Chemistry, Advances in International Research, Development and Legislation, VCH Verlag, Weinheim, 1991.
[3] R.N. Lerch and W.W. Donald, J. Agric. Food Chem., 42 (1994) 922–927.
[4] Pflanzenschutzanwendungsverordnung vom 22.03.1991, Bundestagesetzblatt 1, 1991, pp. 796–798.
[5] C.D. Adams and S.J. Randtke, Environ. Sci. Technol., 26 (1992) 2218–2227.
[6] B.L. Karger and F. Foret, in N.A. Guzman (Editor), Capillary Electrophoresis Technology, Marcel Dekker, New York, Basel, Hong Kong, 1993.
[7] H. Engelhardt, W. Beck, J. Kohr and T. Schmitt, Angew. Chem., 105 (1993) 659–680.
[8] Ph. Schmitt and A. Kettrup, GIT Fachz. Lab., (1994) 1312–1318.
[9] M.W.F. Nielen, J. Chromatogr., 637 (1993) 81–90.
[10] A.W. Garrison, Ph. Schmitt and A. Kettrup, J. Chromatogr. A, 688 (1994) 317–327.
[11] A.W. Garrison, Ph. Schmitt, D. Martens and A. Kettrup, Environ. Sci. Technol., (1995) submitted.
[12] V. Dombeck and Z. Stransky, Anal. Chem. Acta, 256 (1992) 69–73.
[13] R. Kostiainen, A.P. Bruins and V.M.A. Häkkinen, J. Chromatogr., 634 (1993) 113–118.
[14] M. Tomita, T. Okuyama and Y. Nigo, Biomed. Chromatogr., 6 (1992) 91–94.
[15] Z. Stransky, J. Chromatogr., 320 (1985) 219–231.
[16] G. Dinelli, A. Vicari and P. Catizone, J. Agric. Food Chem., 41 (1993) 742–746.
[17] S. Takeda, S.I. Wakida, M. Yamana, A. Kawahara and K. Highashi, J. Chromatogr. A, 653 (1993) 109–114.
[18] F. Foret, V. Sustacek and P. Bocek, Electrophoresis, 11 (1990) 95–97.
[19] C. Desiderio and S. Fanali, Electrophoresis, 13 (1992) 698–700.
[20] Ph. Schmitt, D. Freitag, Y. Sanlaville, J. Lintelman and A. Kettrup, J. Chromatogr. A, 709 (1995) 215–225.
[21] N.M.J. Vermeulen, Z. Apostolides, D.J.J. Potgieter, P.C. Nel and S.H. Smit, J. Chromatogr., 240 (1982) 247–253.
[22] H. Jork and B. Roth, J. Chromatogr., 144 (1977) 39–56.
[23] V. Pacakova, K. Stulik and M. Prihoda, J. Chromatogr., 442 (1988) 147–155.
[24] J.B. Weber, Spectrochem. Acta, 23A (1967) 458–461.
[25] E. Davoli, E. Benfenati, R. Bagnati and R. Fanelli, Chemosphere, 16 (1987) 1425–1430.
[26] S.L. Hilal, L.A. Carreira, G.L. Baughman, S.W. Karickhoff and C.M. Melton, J. Phys. Org. Chem., 7 (1994) 122–141.