ULTRAVIOLET ABSORPTION SPECTRA AND DISSOCIATION CONSTANTS OF DIAMINO-1,3,5-TRIAZINES

Rafael PÉREZ[1], Rafael MARÍN GALVÍN[2] and
José M. RODRÍGUEZ MELLADO[3],*

Departamento de Química Física y Termodinámica Aplicada, Facultad de Ciencias,
Universidad de Córdoba, E-14004-Córdoba, Spain; e-mail: [1] *qf2pemor@uco.es,*
[2] *rmargal@emacsa.es,* [3] *qf1romej@uco.es*

This paper presents ultraviolet absorption spectra of two diamino-1,3,5-triazines, namely 1,3,5-triazine-2,4-diamine (DT) and 6-chloro-1,3,5-triazine-2,4-diamine (ClDT). The spectra were fitted to the log-normal distribution. In the more energetic zone of the spectrum both compounds presented common bands, placed around 204–205 and 223–226 nm (depending on the pH of the medium). At higher wavelengths the spectra were different, with bands appearing in the range 235–267 nm. From variations of the maximum absorbances of the individual bands, the pK_b values 3.5 ± 0.2 and 1.2 ± 0.1 were obtained for protonation of the ring nitrogen placed between the amine radicals of DT and ClDT, respectively, and 9.35 ± 0.2 and 11.5 ± 0.1 for dissociation of the amino groups of DT and ClDT, respectively.
Keywords: UV spectroscopy; Dissociation constants; 1,3,5-Triazine-2,4-diamines; Herbicides; Basicity; Determination.

The 1,3,5-triazine herbicides are continuously contaminating the environment due to their persistence in soils and hydric sediments, caused by their low solubilities in water and their strong sorption on carbonaceous materials and clays[1]. Some studies reported the use of various electrochemical techniques for determination of such herbicides[2–9] and the reductive cleavage of the Cl atom was also proposed. Skopalová and Kotouček[10] found that the reduction of the triazine ring yields an unstable intermediate, which loses HCl. A similar mechanism was also proposed by Pospíšil *et al.*[11,12] for the electroreduction of atrazine and terbutylazine on mercury electrodes, though the cleavage of an ethyl group was not excluded. Skopalová *et al.*[13] examined the electroreduction of prometryne and other methylsulfanyl-1,3,5-triazine herbicides finding that 4,6-bis(isopropylamino)-1,3,5-triazine is formed as an intermediate in the reduction, the end product being the protonated 4,6-bis(isopropylamino)dihydro-1,3,5-triazine. Electrochemical

reduction of hexazinone, 3-cyclohexyl-6-(dimethylamino)-1-methyl-1,3,5-triazine-2,4(1H,3H)-dione, was examined[14]. The reductive cleavage of dimethylamine followed by the two-electron reduction of the deaminated compound occurred in the same way as that proposed for the cleavage of Cl from chlorinated herbicides[11–13]. In previous works, the reductions of simazine and propazine on mercury electrodes[15,16] were studied. The electroreduction follows essentially the above proposed reaction scheme: after the first two-electron reduction, the herbicides undergo a cleavage of the Cl atom to yield the dechlorinated intermediates which are reduced through irreversible two-electron processes. Moreover, simazine is adsorbed on the electrode with the triazine ring parallel to the electrode surface. At pH values where both the protonated and unprotonated simazine coexist, both forms are co-adsorbed on the electrode[16]. In the reduction of the methylsulfanyl derivatives the cleavage of the methylsulfanyl group takes place to a higher or lower extent[17].

As can be seen, the dechlorinated compounds are in most cases interme-diates of the four-electron reduction. It was shown that the protonation of the ring nitrogen placed between the amine radicals is essential for the re-duction. Thus, it seems interesting to elucidate the reduction mechanism of such intermediates to contribute to the knowledge of overall reaction path-ways of the herbicides. But the knowledge of equilibrium constants of the above mentioned protonation reactions is essential. For this reason, the aim of this paper was to obtain the equilibrium constants of the acid-base reactions corresponding to two diamino-1,3,5-triazines by UV spectroscopy. The chemical structures of the compounds are:
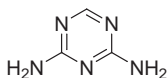
1,3,5-triazine-2,4-diamine
(DT)
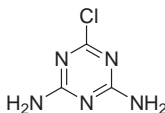
6-chloro-1,3,5-triazine-2,4-diamine
(ClDT)

EXPERIMENTAL

In all cases, Merck analytical grade reagents were used with the exception of DT, which was from Aldrich and ClDT which was from Supelco. All reactants were used without further purification. Solutions of either sulfuric acid, for pH < 1.2, 0.1 mol l^{-1} in both acetic and phosphoric acids, for 2 < pH < 8, and 0.1 mol l^{-1} in both phosphoric acid and sodium hydrogencarbonate for pH > 8 were used as solvents. For measurements made at pH < 1.2, the acidity function H_0 was used as a measure of pH (ref.[18]). In the same reference was found the correction for pH values of ethanol–water solutions (which, on the other hand,

were virtually the same for all pH values at a given ethanol content). Stock solutions of DT and ClDT were prepared in pure ethanol and stored in the dark at 277 K to avoid decomposition. The measurements were made at the 0.1–0.2% ethanol concentrations in the medium.

Measurements were made on a Perkin–Elmer Lambda 3b spectrophotometer with quartz cuvettes of pathlength 1.0 cm. pH values were determined with a Hanna Hi-848 pH-meter and a glass electrode.

RESULTS AND DISCUSSION

The absorption spectra as functions of the acidity for both DT and ClDT are shown in Fig. 1. The curves showed two main bands whose intensities (and, to a lower degree, positions) depended on pH of the solution. In the case of
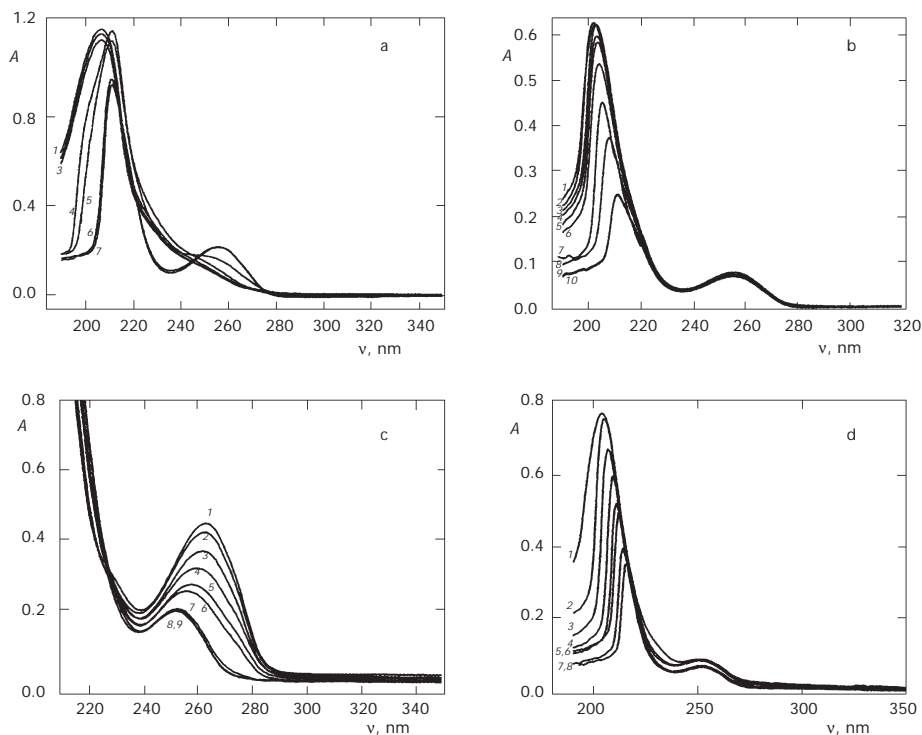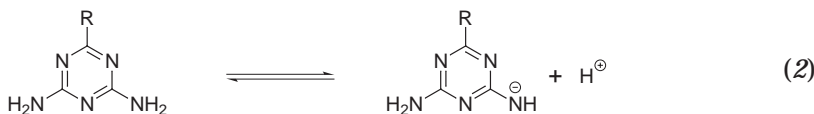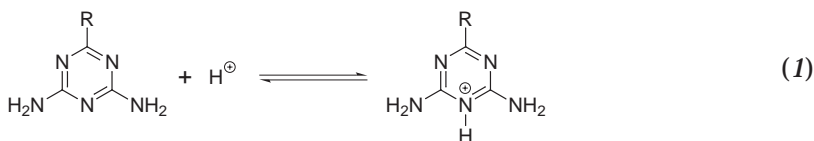

FIG. 1

UV-VIS spectra. a 6.86 · 10⁻⁵ M DT; pH: 1.3 (*1*), 1.57 (*2*), 1.85 (*3*), 2.40 (*4*), 3.34 (*5*), 5.31 (*6*), 6.31 (*7*). b 1.1 · 10⁻⁵ M DT; pH: 7.11 (*1*), 7.48 (*2*), 8.53 (*3*), 9.05 (*4*), 9.55 (*5*), 9.88 (*6*), 10.56 (*7*), 10.95 (*8*), 11.12 (*9*), 11.76 (*10*). c 6.86 · 10⁻⁵ M ClDT; pH: 1.5 M H₂SO₄ (*1*), 0.4 M H₂SO₄ (*2*), 0.2 M H₂SO₄ (*3*), 1.06 (*4*), 1.18 (*5*), 1.30 (*6*), 2.09 (*7*), 3.05 (*8*), 4.01 (*9*). d 2.0 · 10⁻⁵ M ClDT; pH: 7.26 (*1*), 9.77 (*2*), 10.73 (*3*), 11.02 (*4*), 11.33 (*5*), 11.72 (*6*), 11.98 (*7*), 12.25 (*8*)

DT, the maxima were centered around 210 and 260 nm. The intensities of the higher energetic bands varied significantly with pH, whereas variation of the band appearing at higher wavelengths was much lower. In the case of ClDT, the situation was similar: in acidic media, the pH dependences were more marked for the 250 nm band, and, in basic media, the variations were observed mainly at lower wavelengths of the spectra.

The pH dependences of the spectra indicate that the reactants are involved in acid-base reactions. For both compounds, in very acidic media, the ring nitrogen between the amine radicals must be protonated, as it occurs in other compounds of the 1,3,5-triazine herbicides[19]. In fact, the pK_b values of this protonation reaction are about 2, for the herbicides with the chlorine atom in *para*-position to the nitrogen, and about 4.5 for herbicides substituted with a methylsulfanyl group in the same position. In alkaline media, the only reasonable acid-base reaction is the ionization of the amino groups. The corresponding reactions are shown in Eqs (*1*) and (*2*).

$$\text{(triazine structure)} + H^{\oplus} \;\rightleftharpoons\; \text{(protonated triazine structure)} \tag{1}$$

$$\text{(triazine structure)} \;\rightleftharpoons\; \text{(deprotonated triazine structure)} + H^{\oplus} \tag{2}$$

The absorption spectra were analysed using a computer program developed from Microsoft Visual Basic and based on other programs from our laboratory[20]. In this program it was assumed that the bands can be represented by a log-normal band shape, similarly to the spectra of substances corresponding to the vitamin B_6 group[21,22] and many pyridine derivatives[23–28]. This band shape can be described by the equation[29]:

$$A = A_0 \exp\left\{\ln 2\left[\frac{\ln[1 + 2b(\nu - \nu_0)/\Delta\nu_{1/2}]}{b}\right]^2\right\}, \tag{3}$$

where A is the absorbance at the frequency ν, A_0 and ν_0 are the coordinates of the maximum; $\Delta\nu_{1/2}$ is the band half-width; and b is a parameter which determines the degree of asymmetry of the curve. As b tends to zero, the curve is reduced to a Gaussian curve, *i.e.*, the band is symmetrical.

The spectra were decomposed into sets of bands integrated by the minimum number of bands possible, and with the condition that the band parameters were independent of both the pH and concentration (with the obvious exception of the absorbance). Figure 2 shows a comparison between theoretical and experimental results for both compounds. As can be seen, different bands were obtained; their characteristic parameters are shown in Table I. These parameters remained virtually unchanged in the pH range studied. Obviously, the bands did not appear simultaneously at any pH value, but the intensities of some bands varied with pH of the medium ranging between maximum and minimum values (sometimes zero). Such variations are shown in Fig. 3.

If the pH dependence of the maximum absorbance of individual bands is due to the acid-base equilibria represented by reactions (*1*) and (*2*), the following equation must be fulfilled:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{b} + \log \frac{A_\mathrm{max} - A}{A - A_\mathrm{min}} \,, \tag{4}$$

TABLE I
Values of the parameters obtained in deconvolution of the UV spectra. The half-widths are given in kiloKaisers (kK)

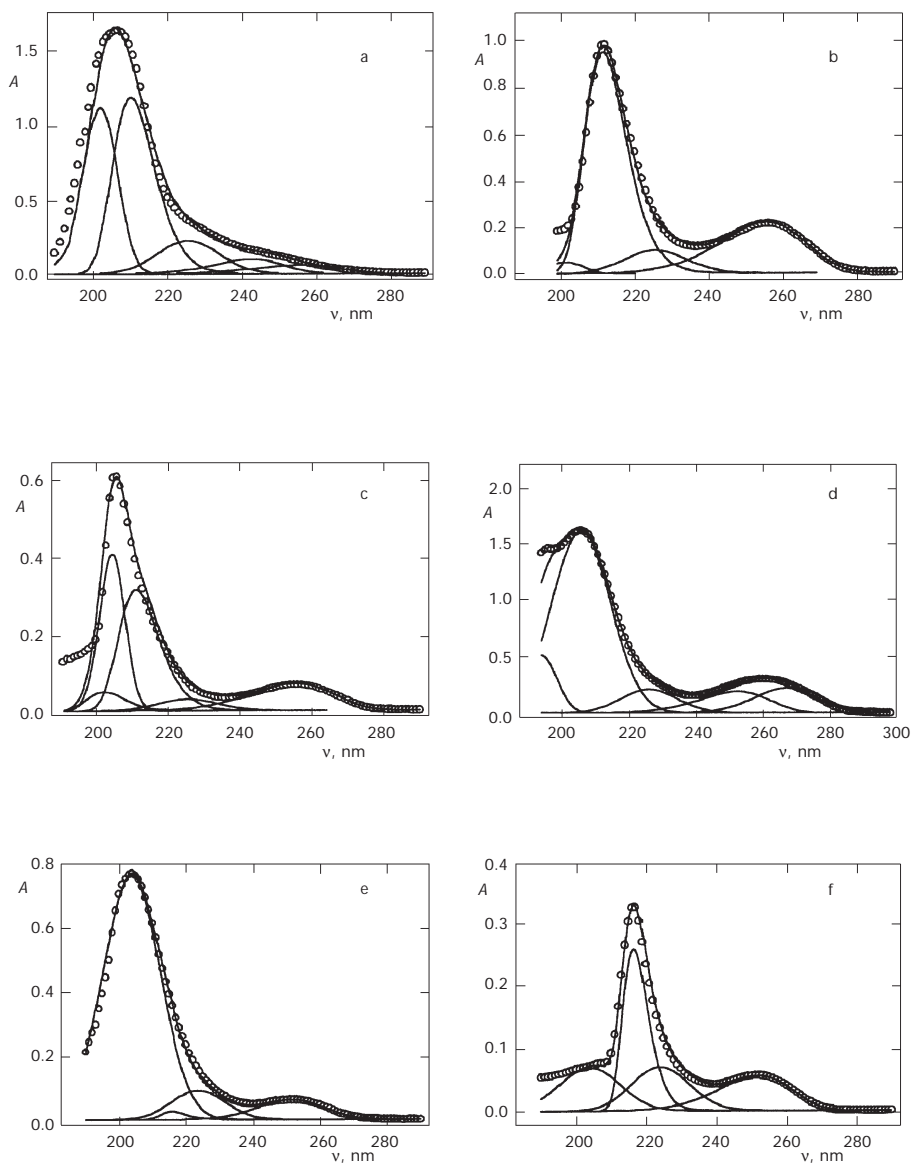| Compound	λ_max, nm	$W_{1/2}$, kK	b
DT	201.5 ± 0.5	1.8	0.1
	204.5 ± 0.5	1.2	0.2
	211.0 ± 1	1.95	-0.12
	216.5 ± 0.5	1.2	-0.15
	225.5 ± 0.5	2.5	0.05
	242.5 ± 0.5	2.5	0.2
	255.5 ± 0.5	2.7	0.2
CIDT	194.0 ± 0.5	2	0.1
	205.5 ± 0.5	3.2	0.08
	215.0 ± 0.5	1.3	-0.15
	226.0 ± 0.5	2.5	0.05
	252.0 ± 0.5	2.5	0.1
	267.0 ± 0.5	2	0.1

F IG. 2

Fitting of the log-normal plots to experimental data shown in Fig. 1. DT at pH: 1.03 (a), 5.10 (b), 10.95 (c); ClDT at pH: 1.06 (d), 7.26 (e), 11.98 (f)

where A_{max} and A_{min} are the maximum absorbances measured at the maximum and minimum pH values of the curve, respectively. The plots of $\log[(A_{max} - A)/(A - A_{min})]$ vs pH should give straight lines with intercept equal to pK_b. When the bands increase with pH, the slope of the straight line obtained must be +1, whereas in the opposite case the slope must be –1. Figure 4 shows these plots for both compounds in the acid and alkaline pH ranges. The pK_b values obtained from these plots are given in Table II.

The pK_b value obtained for the protonation of the N3 nitrogen of DT lies between those corresponding to chlorinated and methysulfanyl-substituted 1,3,5-triazines. Nevertheless, when the molecule has a Cl atom in position 2 (*i.e.*, in position *para* to the heterocyclic nitrogen participating in the acid-base reaction), the pK_b value decreases by more than two units. In alkaline media, the effect of the presence of the Cl atom is opposite: pK_b
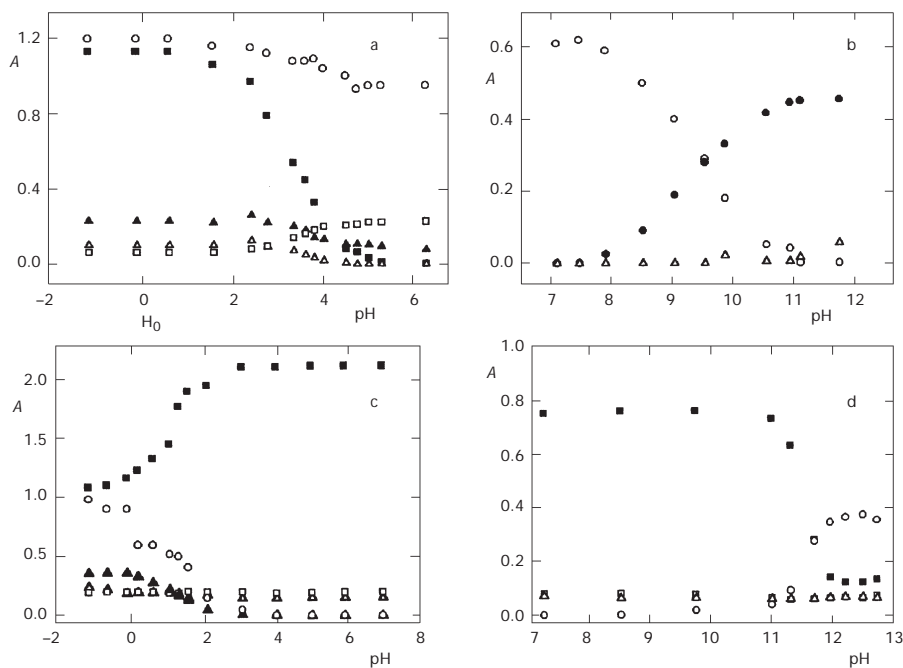

FIG. 3
pH variation of the maximum absorbance for the fitted bands. a 6.86 · 10⁻⁵ M DT; λ (nm): ■ 202, ○ 210, ▲ 225, △ 243, □ 255. b 1.1 · 10⁻⁵ M DT; λ (nm): △ 204, ○ 216, ● 255. c 6.86 · 10⁻⁵ M ClDT; λ (nm): ○ 195, ■ 206, △ 226, □ 253, ▲ 267. d 2.0 · 10⁻⁵ M ClDT; λ (nm): ■ 205, ○ 215, □ 225, △ 252

pK_b values obtained for the studied compounds

Compound	pK_b
DT	3.5 ± 0.2
	9.35 ± 0.15
ClDT	1.2 ± 0.1
	11.5 ± 0.1^a

^{a} The slopes of the straight lines are close to 2.
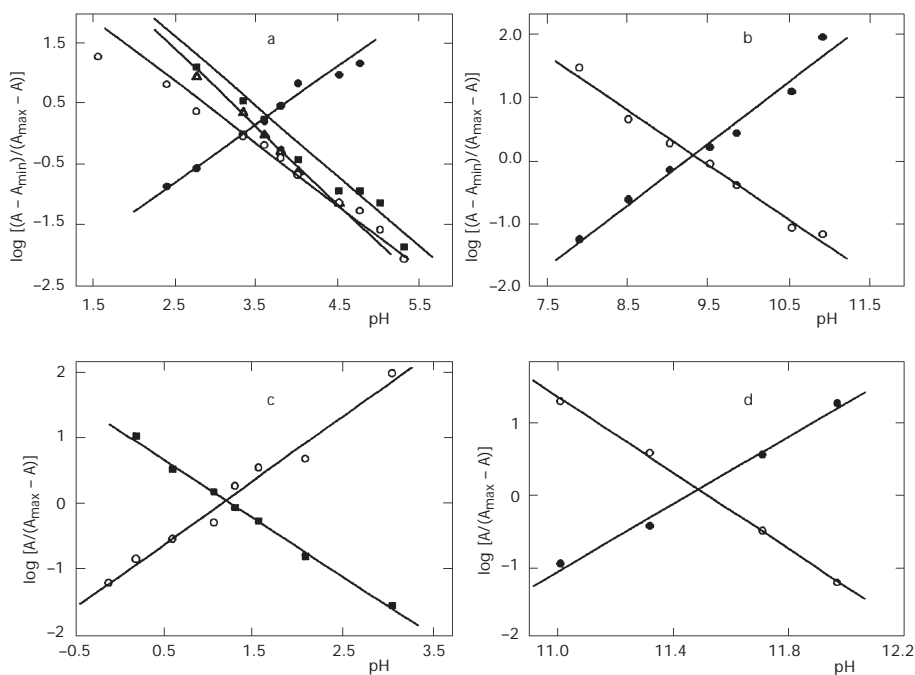

FIG. 4

Plot of log $[(A - A_{min})/(A_{max} - A)]$ (a, b) and log $[A/(A_{max} - A)]$ (c, d) *versus* pH. a $6.86 \cdot 10^{-5}$ M DT; λ (nm): ○ 202, ■ 225, △ 243, ● 255. b $1.1 \cdot 10^{-5}$ M DT; λ (nm): ○ 216, ● 255. c $6.86 \cdot 10^{-5}$ M ClDT; λ (nm): ● 206, ○ 267. d $2.0 \cdot 10^{-5}$ M ClDT; λ (nm): ● 205, ○ 215

of ionization of the NH_2 groups is more than two units higher for ClDT than for DT.

It must be noted that the plots of Eq. (*4*) had slopes close to unity (in absolute values) with the exception of those corresponding to ClDT in alkaline solutions, whose slopes were around two, in absolute values (see Fig. 4d). This agrees with the narrow pH-range of variation of maximum absorbances observed in Fig. 3d. The only plausible explanation assumes that the dissociation of the two amino groups can take place at very close pH values, this being compatible with the experimental results.

REFERENCES

1. Ayele J., Levavasseur P., Mazet M.: *J. Water-SRT Aqua* **1996**, *45*, 28.
2. Hayes M. H. B., Stacey M., Thompson J. M.: *Chem. Ind. (London)* **1967**, 1222.
3. Hance R.: *Pestic. Sci.* **1970**, *1*, 113.
4. McKone C. E., Byast T. H., Hance R. J.: *Analyst (Amsterdam)* **1972**, *72*, 653.
5. Benadíková H., Kalvoda R.: *Anal. Lett.* **1984**, *17*, 1519.
6. Owens D. S., Sturrock P. E.: *Anal. Chim. Acta* **1986**, *188*, 269.
7. Lippolis M. T., Concialini V.: *Talanta* **1988**, *35*, 235.
8. Ignjatovic L. M., Markovic D. A., Veselinovic D. S., Besic B. R.: *Electroanalysis (N. Y.)* **1993**, *5*, 529.
9. Gálvez R., Pedrero M., Manuel de Villena F. J., Pingarrón J. M., Polo L. M.: *Anal. Chim. Acta* **1993**, *273*, 343.
10. Skopalová J., Kotouček M.: *Fresenius' J. Anal. Chem.* **1995**, *351*, 650.
11. Pospíšil L., Tršková R., Fuoco R., Colombini M. P.: *J. Electroanal. Chem.* **1995**, *395*, 189.
12. Pospíšil L., Tršková R., Záliš S., Colombini M. P., Fuoco R.: *Microchem. J.* **1996**, *54*, 367.
13. Skopalová J., Lemr K., Kotoueek M., Cap L., Ondra P.: *Electroanalysis (N. Y.)* **1998**, *10*, 331.
14. Privman M., Zuman P.: *J. Electroanal. Chem.* **1998**, *455*, 235.
15. Higuera M. J., Ruiz Montoya M., Rodríguez Mellado J. M.: *Electrochem. Commun.* **1999**, *1*, 184.
16. Higuera M. J., Ruiz Montoya M., Marín Galvín R., Rodríguez Mellado J. M.: *J. Electroanal. Chem.* **1999**, *474*, 174.
17. Ortiz R., Higuera M. J., Marín Galvín R., Rodríguez Mellado J. M.: *J. Electrochem. Soc.* **2001**, *148*, 419.
18. Bates R. G.: *Determination of pH. Theory and Practice*, p. 194. John Wiley, New York 1973.
19. Tomlin C. (Ed.): *The Pesticide Manual*. British Crop Protection Council, The Royal Society of Chemistry, London 1994.
20. Sevilla J. M., Domínguez M., García Blanco F., Blázquez M.: *Comput. Chem.* **1989**, *13*, 197.

21. Blázquez M., Sevilla J. M., Pérez J., Domínguez M., García Blanco F. in: *Biochemistry of Vitamin B$_6$* (T. Korpela and P. Christen, Eds), p. 355. Birkhausen, Basel 1987.
22. Blázquez M., Sevilla J. M., Pérez J., Domínguez M., García Blanco F.: *J. Chem. Soc., Perkin Trans. 2* **1989**, 1229.
23. Rodríguez Mellado J. M., Ruiz Montoya M.: *Gazz. Chim. Ital.* **1990**, *120*, 553.
24. Angulo M., Zón M. A., Rodríguez Mellado J. M.: *Anal. Quim.* **1993**, *89*, 647.
25. Zón M. A., Angulo M., Rodríguez Mellado J. M.: *J. Electroanal. Chem.* **1994**, *365*, 213.
26. Prieto I., Angulo M., Rodríguez Mellado J. M.: *J. Electroanal. Chem.* **1995**, *399*, 135.
27. Expósito E., Ruiz Montoya M., Angulo M., Rodríguez Mellado J. M.: *J. Electroanal. Chem.* **1996**, *402*, 211.
28. Ruiz Montoya M., Rodríguez Mellado J. M.: *J. Electroanal. Chem.* **1996**, *417*, 113.
29. Fraser R. P., Suzuki E. in: *Physical Principles of Protein Chemistry. Part C* (S. J. Leach, Ed.), Chap. 21. Academic Press, New York 1973.