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Note

NOTE

Derivative spectrophotometric determination of acetamiprid in the presence of 6-chloronicotinic acid

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Abstract: A simple first-order derivative spectrophotometric method was developed for the simultaneous determination of acetamiprid and 6-chloronicotinic acid (6-CNA) at pH 7.0. By using the zero-crossing approach, acetamiprid was determined at 269.0 nm and 6-CNA at 216.0 nm with detection limits of 7.19×10^{-7} and 8.25×10^{-7} mol dm^{-3}, respectively, and relative standard deviations not exceeding 1.2 % in the case of model systems.

Keywords: derivative spectrophotometry; acetamiprid; 6-chloronicotinic acid.

INTRODUCTION

Acetamiprid ((*E*)-N^1-[(6-chloro-3-pyridyl)methyl]-N^2-cyano-N^1-methylacetamidine, Fig. 1a) belongs to the most efficient class of insecticides nowadays, called neonicotinoids, which account for about 24 % of the total insecticide market.[1] Since its launch in the mid-1990s, products containing acetamiprid have gained registrations for over 60 agricultural crops, including cotton, vegetables, potato, orchards, vines, citrus, tea, and ornamentals.[1] In addition, acetamiprid is also of interest for the control of termites and household pests.[1] Acetamiprid is marketed under a variety of names, including Mospilan, Dyken, Fertilan, Masuta, Mospildate, Suntamiprid and Vapcomere.[2]

6-Chloronicotinic acid (6-CNA), Fig. 1b, represents one of the synthetic precursors,[3] and also an intermediate of acetamiprid decomposition.[4–8] These facts impose the need for reliable analytical methods for the determination of these two compounds in their mixtures. The analytical techniques used most widely for acetamiprid determination are gas chromatography[9,10] and liquid

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chromatography (LC) with diode array (DA),[4–7,11,12] mass spectrometric (MS),[6,7,13–20] and thermal lens spectrometric[21] detection. Some alternative techniques, such as enzyme-linked immunosorbent assay,[22] spectrophotometry,[23] colorimetry,[24] Fourier transform infrared spectroscopy[6] and voltammetry,[6,25] have also been employed to analyze different acetamiprid (and 6-CNA) containing samples.

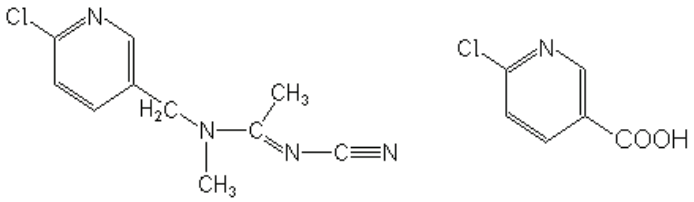

Fig. 1. Structural formula of a) acetamiprid and b) 6-CNA.

Due to the widespread availability of the instrumentation, simplicity of procedures, speed, precision and accuracy, spectrophotometric methods enjoy wide popularity. In addition, they are more economic and simpler, compared to methods such as chromatography and electrophoresis.[26] Except for a conference proceeding,[27] no spectrophotometric methods have hitherto been reported as papers for the simultaneous determination of acetamiprid and 6-CNA.

Several techniques have been proposed for the treatment of spectrophotometric data, with the objective of extracting the largest amount of analytical information from spectra composed of unresolved bands. Undoubtedly, a major success was achieved by the derivative treatment of the absorbance curves – plotting the first- or a higher-order mathematical derivative of the absorbance against wavelength ($dA/d\lambda$). Derivative spectrophotometry offers a convenient solution to a number of analytical problems, such as resolution of multicomponent systems, removal of sample turbidity, matrix background and enhancement of spectral details. For these reason, it has been applied in the analysis of different pharmaceuticals, foods, cosmetics and environmental samples.[26,28,29] The same method was also applied for the simultaneous determination of pesticides or pesticides and their degradation products.[30–36]

In this work, a rapid, environmentally acceptable and inexpensive first-order derivative spectrophotometric method was developed for the determination of acetamiprid and 6-CNA in their mixtures.

EXPERIMENTAL

Chemicals and solutions

All chemicals used were of analytical reagent grade. Pestanal quality (Riedel de Haën, Germany) was employed as the analytical standard of acetamiprid and 6-CNA. Stock solu-

tions were prepared by dissolving the compounds in doubly distilled water to obtain a concentration of 5×10^{-4} mol dm^{-3}, which did not change over a long period when the solutions were kept in the dark at 4 °C. Britton–Robinson buffer solutions were prepared from a stock solution containing 0.04 mol dm^{-3} phosphoric, boric and acetic acids (all Merck), respectively, by adding 0.2 mol dm^{-3} sodium hydroxide (Merck) to the required pH values, covering the pH range of approx. 2–10.

Apparatus

Spectrophotometric measurements were performed on a PG Instruments T80+ UV–Vis double-beam spectrophotometer (PG Instruments, United Kingdom). A digital pH-meter (PHM 62, Radiometer, Denmark) and a combined glass electrode were used for pH measurements.

Procedures

Spectrophotometry. Characterization of the individual optical behavior of acetamiprid and 6-CNA was performed at the same molar concentration (4.34×10^{-5} mol dm^{-3}) in the pH range 2−10 and at wavelengths from 200 to 400 nm ($\Delta\lambda$ = 1 nm). Standard solutions for the calibration curves were prepared by the stepwise dilution of the stock solution to obtain concentrations in the range 3.69×10^{-6}–6.20×10^{-5} mol dm^{-3} for both compounds. Simultaneous derivative spectrophotometric determinations were realized at 269.0 nm (acetamiprid) and 216.0 nm (6-CNA).

pH Measurements. A digital pH-meter, a glass electrode and a saturated calomel electrode were used for all pH measurements. The glass electrode was previously calibrated using commercial buffer solutions (Hanna Instruments, USA) in two separate ranges 1.68−6.86 and 6.86−10.01.

Validation of the analytical method. The linearity for the developed derivative spectrophotometric method was checked in the concentration range of 3.69×10^{-6}–6.20×10^{-5} mol dm^{-3}. The limit of detection (*LOD*) and the limit of quantification (*LOQ*) were calculated using the following equations: $LOD = 3s/m$ and $LOQ = 10s/m$, where s is the standard deviation of the blank and m is the slope of the calibration curve.

Data processing. The experimental data were plotted using Origin 6.1 software package. The first derivative spectra were calculated using all data points in the range from 200 to 400 nm with $\Delta\lambda$ = 1 nm using the option differentiate. For noise reduction, the adjacent averaging method was tested using different smoothing factors (3, 5 and 9). Calibration equations were calculated using the linear fit option.

RESULTS AND DISCUSSION

To study the optical characteristics of the investigated compounds, the corresponding spectra were recorded in Britton–Robinson buffers (pH 2.0–10.0) in the wavelength range 200–400 nm. The representative spectra of acetamiprid and 6-CNA obtained at pH 7.0 are shown in Fig. 2. The spectrum of acetamiprid has two discrete absorption bands with maxima at 216.0 and 245.0 nm, of which the latter is much more intense. No significant changes in the absorption spectrum were observed in dependence on the pH of the solution. As was described earlier, the spectrum of 6-CNA also has two discrete, well-defined absorption bands with the maxima at 224.0 and 269.0 nm, the former band being more intense.[36,37] The shape of the 6-CNA spectra and the positions of its maxima depended signifi-

cantly on the pH value, especially at pH < 4.0.[36,37] At higher pH values, no significant change was observed.[36,37] In this context, pH 7.0 was selected for further investigations. As can be seen from Fig. 2, the strong overlapping of the spectra of the investigated compounds hinders their conventional spectrophotometric determination in a mixture. Hence, derivative spectrophotometry was investigated to develop a method for their simultaneous determination.[27] The derivative spectra of solutions containing the individual analytes were investigated in order to optimize the derivative order. The first-order derivative spectrum showed the highest sensitivity and a good resolution for the simultaneous determination of the compounds. Higher derivative orders were discarded because the noise attenuation was less effective and the signal became distorted.

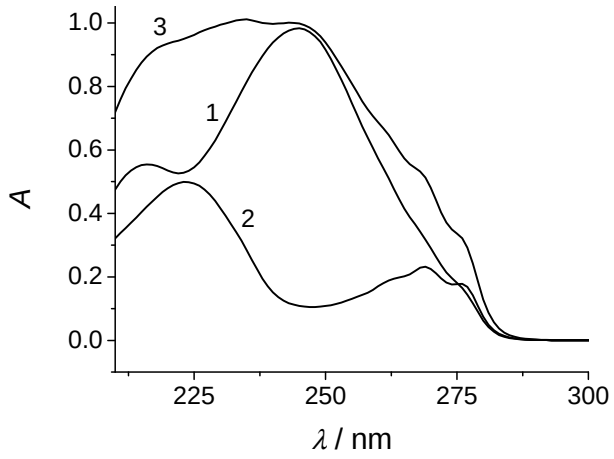

Fig. 2. Absorption spectra of acetamiprid (1), 6-CNA (2) and their mixture (3). Measurement parameters: $c_1 = c_2 = 4.34\times10^{-5}$ mol dm^{-3}, pH 7.0.

The main disadvantage of the derivative technique is that the signal/noise ratio becomes worse as the order of the derivative increases. Therefore, in practice, the derivative technique includes a certain degree of low-pass filtering or smoothing, to control the noise increase, which is an inevitable consequence of differentiation of the noise signal. The effect of smoothing of a peak-type signal is to reduce the noise, which is desirable. However, it distorts the signal, which is undesirable but unavoidable.[29] Thus, optimization of the smoothing factor is very important for obtaining the appropriate signals. In the present study, the adjacent averaging method was tested using smoothing factors of 3, 5 and 9, and the obtained curves were compared with the unsmoothed ones (Fig. 3). Smoothing factor 5 was selected, because this yielded good sensitivity, without significant sacrifice of the signal/noise ratio.

The smoothed first derivative spectrum of both compounds has more zero-crossings, of which those at 216.0 nm in case of acetamiprid and 269.0 nm in case of 6-CNA offer better sensitivity for the determination of the second compound (Fig. 3c). At these wavelengths, all the absorption is attributed to a single

compound. The effect of the concentration of the analytes on both zero-crossing points was studied in the range of 3.69×10^{-6}–6.20×10^{-5} mol dm^{-3}. The zero-crossing values selected were independent of the concentration.

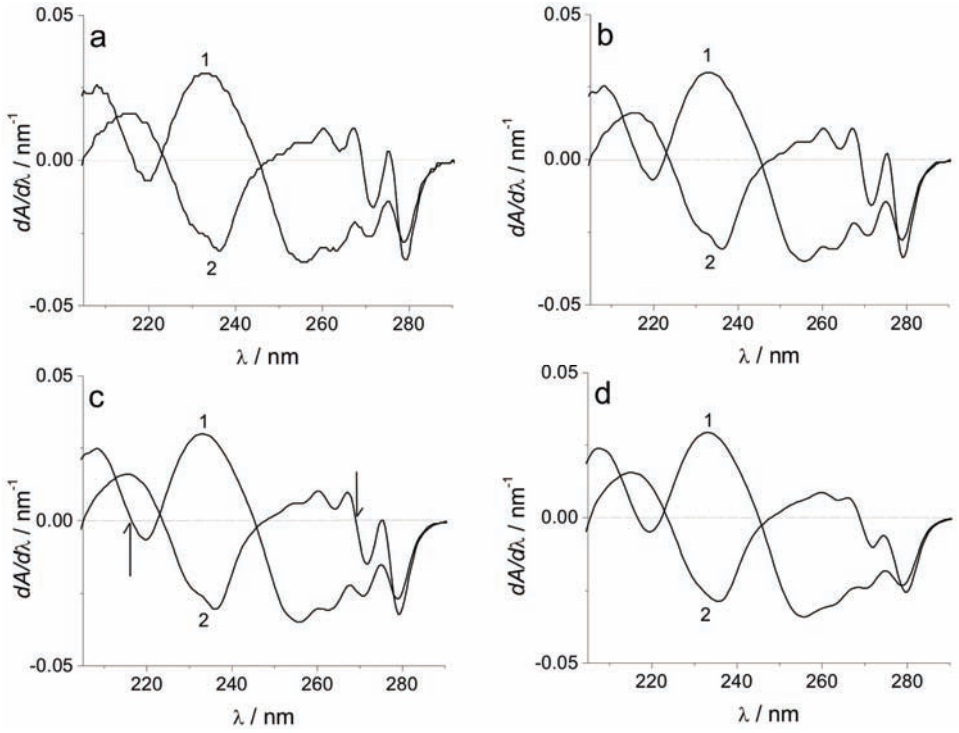

Fig. 3. Unsmoothed (a) and smoothed (b–d) first-order derivative spectra of acetamiprid (1) and 6-CNA (2). Measurement parameters: $c_1 = c_2 = 4.34\times10^{-5}$ mol dm^{-3}, pH 7.0; smoothing factors: 3 (b), 5 (c) and 9 (d).

Using the selected conditions, linear graphs of d*A*/dλ *vs*. analyte concentration were obtained in the concentration range of 3.69×10^{-6}–6.20×10^{-5} mol dm^{-3} for both analytes. The calculated values of the *LOD* were 7.19×10^{-7} and 8.25×10^{-7} for acetamiprid and 6-CNA, respectively. The relative standard deviation (*RSD*) values did not exceed 1.2 % (1.0 % for 6-CNA and 1.2 % for acetamiprid).

The good recoveries and low *RSD* values reflect the high accuracy and precision of the proposed derivative spectrophotometric method. The method is sensitive, simple, rapid and inexpensive, thus making it a convenient alternative tool for the determination of acetamiprid and 6-CNA in their mixtures.

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ИЗВОД

ДЕРИВАТИВНО СПЕКТРОФОТОМЕТРИЈСКО ОДРЕЂИВАЊЕ АЦЕТАМИПРИДА У ПРИСУСТВУ 6-ХЛОРНИКОТИНСКЕ КИСЕЛИНЕ

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Предложена је једноставна деривативна спектрофотометријска метода за истовремено одређивање ацетамиприда и 6-хлорникотинске киселине (6-CNA) при pH 7,0. Примењујући приступ нултог пресека ацетамиприд је одређиван у модел систему на 269,0 nm а 6-CNA на 216,0 nm, са границама детекције од $7{,}19\times10^{-7}$ и $8{,}25\times10^{-7}$ mol dm^{-3}, редом, и стандардном девијацијом мањом од 1,2 %.

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REFERENCES

1. P. Jeschke, R. Nauen, M. Schindler, A. Elbert, *J. Agric. Food Chem.* **59** (2011) 2897
2. C. D. S. Tomlin, Ed., *The Pesticide Manual: A World Compendium*, 15th ed., British Crop Protection Council, Farnham, Surrey, UK, 2009
3. N. V. Kovganko, Zh. N. Kashkan, *Russ. J. Org. Chem.* **40** (2004) 1759
4. M. L. Dell'Arciprete, L. Santos-Juanes, A. Arques, R. Vicente, A. M. Amat, J. P. Furlong, D. O. Mártire, M. C. Gonzalez, *Photochem. Photobiol. Sci.* **8** (2009) 1016
5. M. L. Dell'Arciprete, L. Santos-Juanes, A. Arques, R. F. Vercher, A. M. Amat, J. P. Furlong, D. O. Mártire, M. C. Gonzalez, *Catal. Today* **151** (2010) 137
6. V. Guzsvány, M. Kádár, Zs. Papp, L. Bjelica, F. Gaál, K. Tóth, *Electroanalysis* **20** (2008) 291
7. V. Guzsvány, J. Csanádi, S. Lazić, F. Gaál, *J. Braz. Chem. Soc.* **20** (2009) 152
8. V. Guzsvány, Lj. Rajić, B. Jović, D. Orčić, J. Csanádi, S. Lazić, B. Abramović, *J. Environ. Sci. Heal., B* **47** (2012) 1919
9. M. Mateu-Sánchez, M. Moreno, F. J. Arrebola, J. L. Martinez-Vidal, *Anal. Sci.* **19** (2003) 701
10. M. Tokieda, M. Ozawa, S. Kobayashi, T. Gomyo, *J. Pest. Sci.* **22** (1999) 77
11. E. Watanabe, K. Baba, H. Eun, *J. Agric. Food Chem.* **55** (2007) 3798
12. S. Seccia, P. Fidente, D. Montesano, P. Morrica, *J. Chromatogr., A* **1214** (2008) 115
13. H. Obana, M. Okihashi, K. Akutsu, Y. Kitagawa, S. Hori, *J. Agric. Food Chem.* **51** (2003) 2501
14. I. Ferrer, E. M. Thurman, A. R. Fernandez-Alba, *Anal. Chem.* **77** (2005) 2818
15. S. Seccia, P. Fidente, D. A. Barbini, P. Moricca, *Anal. Chim. Acta* **553** (2005) 21
16. P. Fidente, S. Seccia, F. Vanni, P. Morrica, *J. Chromatogr., A* **1094** (2005) 175
17. A. Di Muccio, P. Fidente, D. A. Barbini, R. Dommarco, S. Seccia, P. Morrica, *J. Chromatogr., A* **1108** (2006) 1
18. S. Liu, Z. Zheng, F. Wei, Y. Ren, W. Gui, H. Wu, G. Zhu, *J. Agric. Food Chem.* **58** (2010) 3271
19. J.-Y. Park, J.-H. Choi, B.-M. Kim, J.-H. Park, S.-K. Cho, M. W. Ghafar, A. M. Abd El-Aty, J.-H. Shim, *Biomed. Chromatogr.* **25** (2011) 136
20. Z. Xiao, X. Li, X. Wang, J. Shen, S. Ding, *J. Chromatogr., B* **879** (2011) 117

21. V. Guzsvány, A. Madžgalj, P. Trebše, F. Gaál, M. Franko, *Environ. Chem. Lett.* **5** (2007) 203
22. S. Watanabe, S. Ito, Y. Kamata, N. Omoda, T. Yamazaki, H. Munakata, T. Kaneko, Y. Yuasa, *Anal. Chim. Acta* **427** (2001) 211
23. J. Fan, X.-J. Shao, Y.-F. Wei, J.-J. Wang, *Chin. J. Anal. Chem.* **36** (2008) 1411
24. Q. Xu, S. Du, G. Jin, H. Li, X. Y. Hu, *Microchim. Acta* **173** (2011) 323
25. F. F. Gaál, V. J. Guzsvány, L. J. Bjelica, *J. Serb. Chem. Soc.* **72** (2007) 1465
26. F. S. Rojas, C. B. Ojeda, *Anal. Chim. Acta* **635** (2009) 22
27. F. Gaál, V. Guzsvány, S. Lazić, N. Vidaković, in *Proceedings of the 12th Symposium on Analytical and Environmental Problems*, Szeged, Hungary, 2005, p. 88
28. C. B. Ojeda, F. S. Rojas, *Anal. Chim. Acta* **518** (2004) 1
29. G. V. Popović, L. B. Pfendt, V. M. Stefanović, *J. Serb. Chem. Soc.* **65** (2000) 457
30. B. F. Abramović, V. B. Anderluh, F. F. Gaál, D. V. Šojić, *J. Serb. Chem. Soc.* **72** (2007) 809
31. J. L. M. Vidal, M. D. G. Garcia, M. M. Galera, A. G. Frenich, *Anal. Lett.* **30** (1997) 2409
32. I. Baranowska, C. Pieszko, *Chem. Anal. (Warsaw)* **45** (2000) 583
33. I. Baranowska, C. Pieszko, *Anal. Lett.* **35** (2002) 473
34. T.-L. Kuo, D.-L. Lin, R. H. Liu, F. Moriya, Y. Hashimoto, *Forensic Sci. Int.* **121** (2001) 134
35. A. G. Frenich, M. M. Galera, J. L. M. Vidal, P. P. Vazquez, M. D. G. Garcia, *Anal. Lett.* **30** (1997) 341
36. V. Guzsvány, *PhD Thesis*, University of Novi Sad, Faculty of Sciences, 2006
37. V. J. Guzsvány, Zs. J. Papp, S. D. Lazić, F. F. Gaál, L. J. Bjelica, B. F. Abramović, *J. Serb. Chem. Soc.* **74** (2009) 1455.