ELSEVIER

Analytica Chimica Acta 302 (1995) 9–19

ANALYTICA CHIMICA ACTA

Abilities of differentiation and partial least squares methods in the analysis by differential pulse polarography Simultaneous determination of furazolidone and furaltadone

Agustina Guiberteau Cabanillas *, Teresa Galeano Diaz, Anunciación Espinosa-Mansilla, Pedro Luis López-de-Alba [1], Francisco Salinas Lopez

Department of Analytical Chemistry, University of Extremadura, 06071 Badajoz, Spain

Received 10 February 1994; revised manuscript received 16 September 1994

Abstract

A comparison between the applicability of two multicomponent analysis methods, differentiation of signals and partial least squares (PLS) methods, to the resolution of overlapping differential pulse polarographic (DPP) peaks corresponding to the irreversible reduction process of two nitrofuran derivatives has been performed. The results show that the derivative DPP signals are not suitable for the resolution of mixtures of these system, by application of the zero-crossing method, because the zero-crossing potential is not independent of the concentration. However, PLS has the capacity of modelling the total evolution of the DPP peaks with the concentration. The PLS multivariate calibration method has been successfully applied to the simultaneous analysis of both compounds in a pharmaceutical formulation.

Keywords: Differential pulse polarography; Furazolidone; Furaltadone

1. Introduction

Differentiation of analytical signals and partial least squares methods have been extensively applied to improve results in different analytical techniques, mainly spectroscopic techniques [1–3]. However, these approaches have been scarcely used in electroanalytical techniques. Berzas and Rodríguez [4] have examined the possibilities of applying differentiation of the differential pulse polarographic (DPP) signal to the simultaneous determination of binary mixtures of inorganic ions. In the above mentioned work, binary mixtures of two well-known systems, cadmium(II)/indium(III) and thallium(I)/lead(II), were resolved, by the first-derivative of the differential pulse polarograms and measurement of the analytical signal, taking into account the zero-crossing technique [1,5].

Mixtures of these inorganic ions have been the subject of another paper [6], which reports and discusses the results obtained by a multicomponent

* Corresponding author.

[1] Present address: Instituto de Investigaciones Científicas, University of Guanajuato, Guanajuato, Guanajuato, 36000 México.

SSDI 0003-2670(94)00444-7

analysis method based on multiple regression procedures to resolve the highly overlapping peaks obtained by DPP. The quantification of lead(II), thallium(I), indium(III) and cadmium(II), in binary, ternary and quaternary mixtures was carried out by the multiple standard calibration method, and the proposed methodology was applied to determine these metals in drinking and waste water samples. A home-made program (MULTI3) [7] was used for the resolution of the multicomponent mixtures, based on a least squares multiple regression procedure. However, a serious constraint for its applicability is posed by the indium(III)/cadmium(II) mixtures containing dissimilar concentrations of the two ions, the half-wave potential of which differ by only 30 mV.

Another related paper has been reported [8] about the use of the Kalman filter for multicomponent analysis of linear sweep voltammograms. The method was also validated by using the cadmium(II)/indium(III) and the cadmium(II)/indium(III)/lead(II) systems. However, the Kalman filter has been scarcely used by other workers, probably because of its complex mathematical foundation and serious applicability constraints. In addition, the use of Fourier transformation in the least-squares methodology has been reported [9] and applied to the resolution of the thallium(I)/lead(II) mixture. However, Grabaric et al. [10] showed this technique to be much less efficient when the overlapping peaks correspond to processes involving a different number of electrons.

The applicability of multicomponent analysis to other electroanalytical techniques than DPP has been also examined. Hence, the above mentioned paper [6] discusses the results obtained by applying the multilinear regression procedure to anodic stripping voltammetry (ASV) signals for the resolution of the same metallic ions mixtures. In this case, it was necessary to apply a multiple standard addition method to address the problem posed by the small shift of the waves of the different analytes with each new stripping.

On the other hand, Gerlach and Kowalski [11] applied multivariate methods to overcome problems in stripping voltammetry, and Henrion et al. [12] and Jagner et al. [13] applied multivariate methods, based on partial least squares (PLS), for resolving metallic interferences in ASV.

The PLS method is a technique based in factor analysis and PLS-1 and PLS-2 types have been described. PLS-2 differs from PLS-1 in the way used to perform the signal decomposition and the regression analysis. PLS-2 calculates the number of factors on all the components simultaneously and one pondered number of factors is optimized. PLS-1 performs the optimization of the number of factors for only one component at a time. The bibliographic data mainly refer to its application in spectroscopic techniques [14–17].

The basic concept of PLS regression was originally developed by Wold [18], and the use of the PLS method for chemical applications was pioneered by Wold et al. [19,20]. A detailed description of the mathematical principles of the PLS algorithms have been reported by Martens et al. [3].

This method needs a calibration step where the relationship between the signal and component concentration is deduced from a set of reference samples, followed by a prediction step in which the results of the calibration are used to determine the component concentrations for the sample signal.

PLS in relation with electroanalytical processes can be considered as a "full-voltammogram" method (all the experimental points of the voltammogram are used).

In the modelling process the first step is to select a optimum number of factors which depend on the number of independently varying chemical species present, as well as on other sources of systematic signal variation, such as the presence of randomly varying baselines, detector noise, interaction between pure components, changes in the shape of the component peaks from that of it's pure state, etc. Because of this, with an adequate design of the calibration matrix and optimization of the experiments, the above mentioned influences can be modeled.

In this paper, the PLS method is proposed for the resolution of binary mixtures of organic compounds exhibiting irreversible electroanalytical behaviour, in which small shifts of the waves along the potential axis, with the variation of the concentration, are observed. Both, derivative and PLS methods have been applied to DPP signals for a wide range of analyte concentrations and the results obtained are compared. The aim of this work is to propose a method applicable to real samples analysis.

The compounds that are object of our study are the nitrofuran derivatives furazolidone (FZ), 3-(5-nitrofurfurylideneamino)-2-oxazolidinone and furaltadone (FD), 5-morpholinomethyl-3-(5-nitrofurfurylideneamino)-2-oxazolidinone, that exhibit very similar chemical structures and properties. The nitrofuran derivatives are highly effective chemotherapeutic drugs, well known as antibacterial agents, and widely used to fight common infections to humans and animals or characteristic infections of domestic animals and, among these, FZ and FD are sometimes formulated together in our country. The polarographic behaviour of both compounds has been described in the bibliography [21,22]. They show a wave due to the irreversible reduction of the nitro group at very close potentials.

2. Experimental

2.1. Reagents

Furazolidone and furaltadone obtained from Sigma were used. Standard solutions of these were prepared by dissolving the appropriate amount in dimethylformamide (DMF). A stock Britton-Robinson buffer solution, which was 0.04 M with respect to boric, orthophosphoric and acetic acid, was prepared from analytical-reagent grade reagents. From this stock solution of buffer, solutions of various pH were prepared by the addition of 0.2 M sodium hydroxide solution. All other chemicals were of analytical-reagent grade.

2.2. Apparatus

An electroanalytical equipment formed by a computer controlled Autolab PSTAT10 potentiostat and a Metrohm 663VA stand, with a Ag/AgCl electrode reference, was used. The system is controlled from a Tystar PC 486 microcomputer equipped with the general purpose electrochemical system (GPES), version 3.0, software package.

A basic LAB-DU50 home-made program is used to convert the obtained ASCII DPP files into the adequate format for the Data Leader and Lab Calc software packages [23,24].

Beckman Data Leader Software package [23], version 3.0, was used for differentiation of data by the simplified least-squares procedure of Savitzky and Golay [25,26].

The Lab Calc software package, version A 1.01, and the PLSplus version 2.0 [24] were used for the statistical treatment of the data and the application of the PLS methods.

The cell was thermostated by means of a Selecta Frigiterm thermostatic bath.

Solutions were purged with oxygen-free nitrogen for 7 min, before recording their voltammogram.

2.3. Procedures for the determination of furazolidone and furaltadone by PLS methods

General procedure

Samples are prepared in 25-ml volumetric flasks containing between 5×10^{-7} and 1×10^{-5} M of FZ and FD, 5% of DMF, 0.05% of gelatin, 10 ml of Britton-Robinson buffer solution (pH 6.8) and purified water (HPLC grade) to the mark. The DPP polarograms are obtained between +0.10 and −0.45 V with a 80 mV pulse amplitude, a 0.75 s drop time, a 35 ms modulation time and a 6.5 mV/s scan rate.

The polarograms are converted with the LAB-DU50 program and the optimized calibration matrix, calculated by the application of the PLS method, is applied to analyze the electrochemical data and to calculate the concentration of the two components in the problem samples.

Procedure for the analysis of furazolidone and furaltadone in the pharmaceutical formulation Trionic (Labiana lab).

Amounts of about 0.1 g of the formulation are accurately weighed and dissolved in 100 ml of DMF. Suitable aliquots of these solutions (< 1.25 ml) are pipetted to prepare the samples to carry out the analysis according to the general procedure.

3. Results and discussion

3.1. Influence of chemical variables

In a previous paper [22] an exhaustive study of the polarographic behaviour of furaltadone has been reported. This compound shows a DPP peak, due to

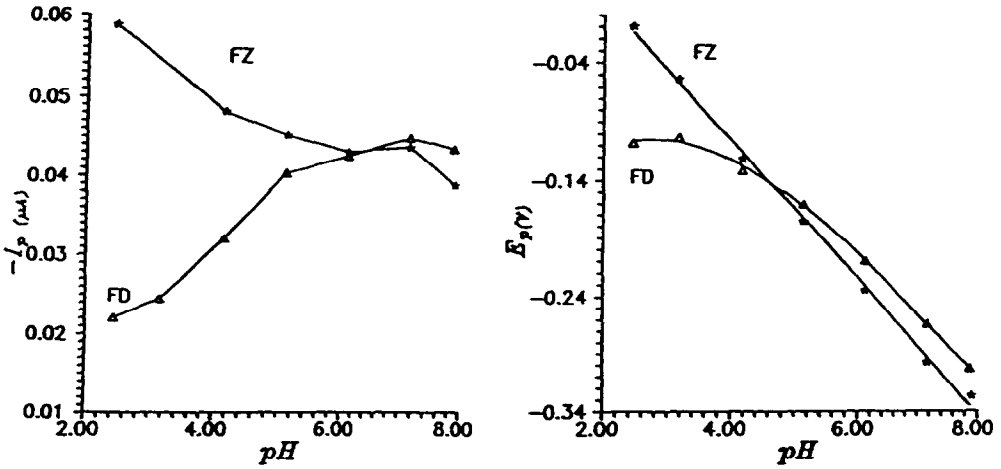

Fig. 1. Variation of I_p and E_p of furazolidone and furaltadone with pH.

the nitro group reduction, with an E_p value constant up to pH 4 whereas, at greater pH values, E_p changes to more negative potentials with a slope of 0.055 V/pH. On the other hand, in the direct current (DC) studies, it is observed that this wave shows a maximum which is suppressed by the addition of gelatin. The presence of DMF in the medium is also convenient due to the great solubility of furaltadone in this solvent.

With respect to furazolidone, no references have been found about its study and determination by DPP. Hence, we have studied the influence of pH on I_p and E_p for FZ and FD in the presence of 0.05% of gelatin and 5% of DMF, in order to compare the behavior of both compounds. Different Britton-Robinson buffer solutions are used to modify the pH value. In Fig. 1, the obtained results are shown. It can be observed that, above pH near 6, the ΔE_p value between FZ and FD remains practically constant (around 20 mV) and that the I_p of furaltadone reaches a maximum and practically constant value. Therefore, we have chosen a pH value of 6.8 for subsequent studies, obtained by the addition of 10 ml of Britton-Robinson buffer solution. The DPP peaks obtained in the above mentioned conditions are shown in Fig. 2.

The linearity between I_p and concentration has been verified separately for both compounds in the range 5×10^{-7}–1×10^{-5} M, with the above mentioned chemical conditions and the instrumental parameters mentioned in the general procedure.

3.2. Differentiation of the DPP peaks

As mentioned in the Introduction, the differentiation of the DPP peaks has been used to resolve binary mixtures of metallic ions, whose electrochemical processes are reversible, by means of the zero-

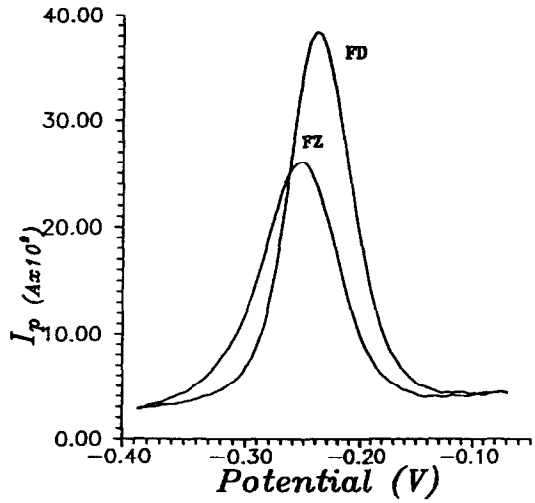

Fig. 2. DPP peaks of 2×10^{-6} M solutions of furazolidone and furaltadone at pH 6.8 (Britton-Robinson buffer) with 0.05% of gelatin and 5% of DMF.

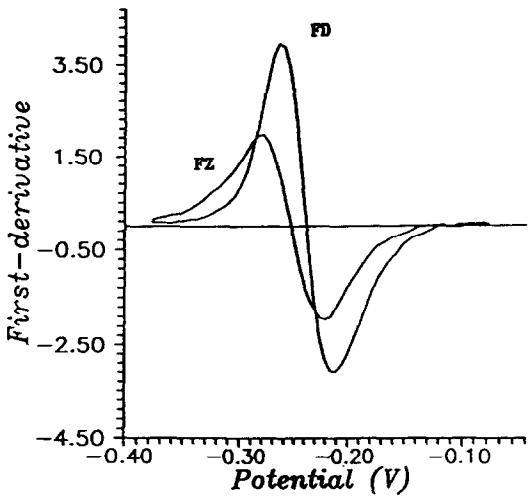

Fig. 3. First-derivative DPP peaks of 2×10^{-6} M solutions of furazolidone (FZ) and furaltadone (FD) at pH 6.8 and with 0.05% of gelatin and 5% of DMF.

crossing technique. We have studied the possibility of applying this approach to resolve the DPP peaks corresponding to the irreversible reduction processes of furaltadone and furazolidone.

The first-derivative DPP peaks have been calculated. For this purpose, the ASCII files provided by the GPES software package have been converted with a conversion program (LAB-DU50) to obtain adequate files for the Data Leader software package.

At first, the influence of the different instrumental parameters on the first-derivative peaks have been examined. We have found that the derivative amplitudes increase linearly with the pulse amplitude applied up to a value of 80 mV, whereas these signals decrease with the modulation time and the drop time. According to these results, a 80 mV pulse amplitude, a 35 ms modulation time and a 0.75 s drop time have been chosen.

The derivative amplitudes increase with an increase of scan rate, but excessively high scan rate values are not convenient due to the lower number of experimental points. We have fixed a 6.5 mV/s scan rate as the more appropriate.

The derivative peaks were obtained, by means of the quadratic equation of the Savitzky and Golay algorithm, with different increments of experimental points, between 5 and 25. We have found that the derivative amplitudes decrease when the number of experimental points used increases and a five experimental points window (corresponding to a 24 mV window) has been used to calculate the first-derivative peaks. In Fig. 3, the derivative peaks obtained under these conditions are shown.

The influence of the concentration on the first-derivative peaks of both compounds shows a good linearity between the derivative amplitude (peak-to-peak signal) and the concentration. However, E_p changes with the concentration for each compound,

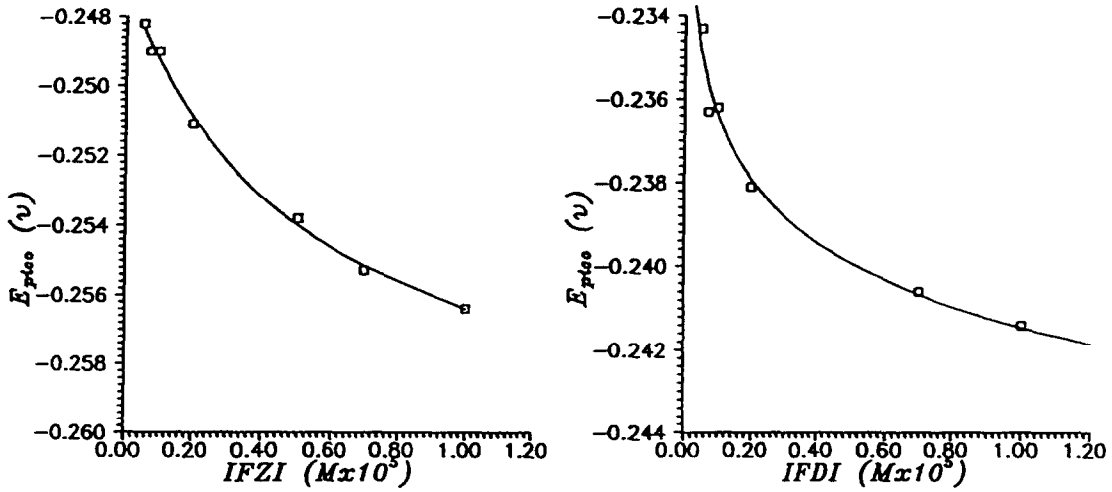

Fig. 4. Variation of E_p (or the zero-crossing potential in the first-derivative peaks) of furazolidone (FZ) and furaltadone (FD) with the concentration.

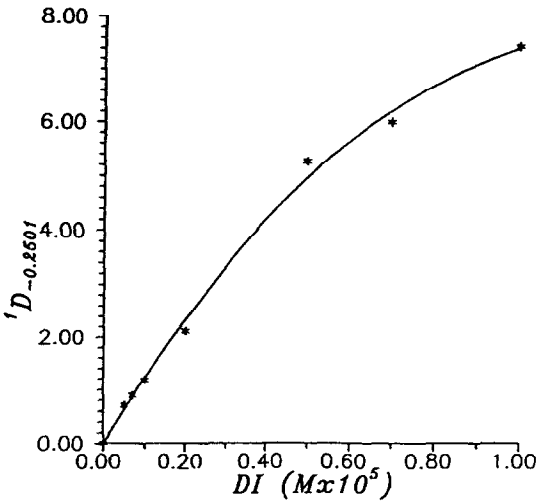

Fig. 5. Variation of the measured first-derivative signal for furaltadone (FD) at a selected potential (near the zero-crossing potential of furazolidone) with the furaltadone concentration.

in irreversible processes, as be can observed in Fig. 4 and also is necessary to take into account that, when the first derivative of the polarogram is obtained, the zero-crossing point corresponds to E_p. As we can see, only for high concentrations of the analyte no significant variation of E_p versus concentration can be observed. This behaviour is characteristic for irreversible electrode processes. Hence, when the value of the derivative signal at a selected potential is chosen as the analytical signal no linearity has necessarily to be observed. This fact can be appreciated in Fig. 5, in which the variation of the derivative signal of furaltadone, at a potential near to the zero-crossing potential of the furazolidone, with the concentration of furaltadone, is represented.

For these reasons, the use of the zero-crossing method is not suitable for the resolution of the overlapped DPP peaks of these two compounds (irreversible systems) by means of differentiation. This has been experimentally proven, by obtaining interactive graphs for the determination of both compounds in synthetic binary mixtures.

3.3. Application of the multivariate methods PLS-1 and PLS-2

As we have mentioned, PLS methods can be considered as "full-voltammogram" methods when electroanalytical techniques are applied.

One of the characteristics of electroanalytical techniques is the wide range of values of the analytical signal that can be measured. Hence, we have designed two training sets of samples in two different concentration ranges between 5×10^{-7} and 5×10^{-6} M (matrix 1: ten samples) and from 1×10^{-6} to 1×10^{-5} M (matrix 2: eleven samples). In Table 1, the composition of the samples prepared for the matrices are shown. The potential region used for the analysis of data is -0.06 to -0.39 V for matrix 1 and -0.09 to -0.44 V for matrix 2, which implies working with 70 experimental points.

To select the number of factors for PLS methods, the cross-validation method, leaving out one sample at a time, has been used [27]. This process was

Table 1
Composition of training sets

Matrix 1			Matrix 2		
Standard	FZ (M) $\times 10^6$	FD (M) $\times 10^6$	Standard	FZ (M) $\times 10^6$	FD (M) $\times 10^6$
m1	0.5	1.0	m1a	0.0	5.0
m2	0.7	1.0	m2a	1.0	5.0
m3	1.0	1.0	m3a	2.5	5.0
m4	2.0	1.0	m4a	5.0	5.0
m5	5.0	1.0	m5a	7.5	5.0
m6	1.0	0.5	m6a	10.0	5.0
m7	1.0	0.7	m7a	5.0	0.0
m8	1.0	1.0	m8a	5.0	1.0
m9	1.0	2.0	m9a	5.0	2.5
m10	1.0	5.0	m10a	5.0	7.5
			m11a	5.0	10.0

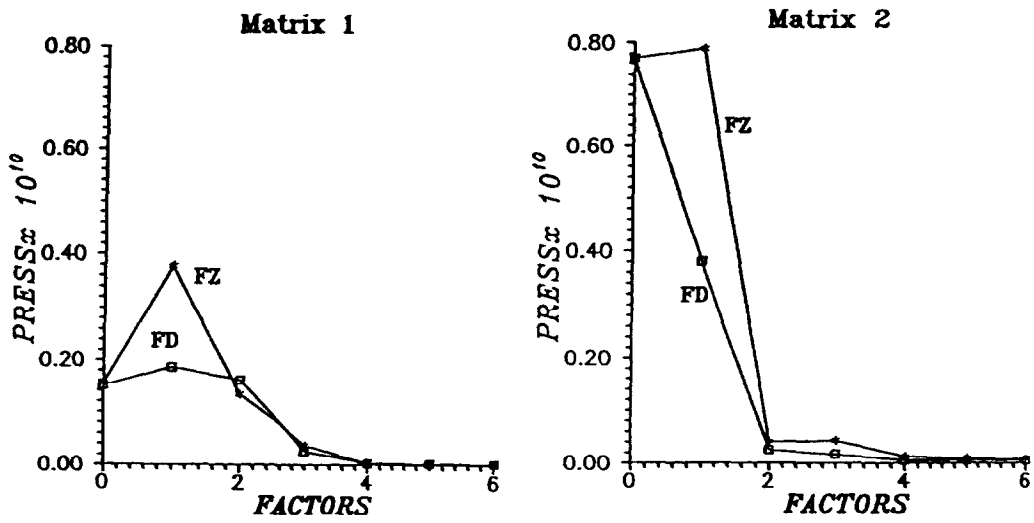

Fig. 6. Obtained PRESS values, by using the PLS-1 method, for the different assayed number of factors.

repeated ten or eleven times, respectively, until each sample had been left out once. The predicted and actual composition of the samples are compared. PRESS (prediction error sum of squares) is expressed as

$$\text{PRESS} = \sum_{i=1}^{N} \sum_{j=1}^{m} (\hat{x}_i - x_i)^2$$

(where $\hat{x}_i$ = predicted concentration and x_i = standard concentration, N = total number of samples and m = total number of components used in the prediction set), and is a measure of how well a particular PLS model fits the concentration data. Another good criterion for selecting the optimum number of factors involves the comparison of PRESS from models (h models) with the model which involves the number of factors yielding the minimum PRESS (h* model). This criterion has been selected by us and the F-snedecor statistic and the Haaland and Thomas criteria [2,3] were used.

Both PLS types, PLS-1 and PLS-2, give rise to identical optimum number of factors, being four for both compounds, in the two analyzed matrices. In Fig. 6, the obtained PRESS values are plotted versus the assayed number of factors by using PLS-1. It can be observed that the PRESS values obtained for matrix 1 are smaller than those for matrix 2. R^2 and RMSD are used as comparative statistical parameters. They are formulated as

$$R^2 = 1 - \left[\sum_{i=1}^{N} (x_1 - \hat{x}_1)^2 / \sum_{i=1}^{N} (x_i - \bar{x})^2 \right]$$

where $\bar{x}$ = mean of standard concentration

$$\text{RMSD} = \left[1/N \sum_{i=1}^{N} (\hat{x}_i - x_i)^2 \right]^{1/2}$$

In Table 2 the values found by the PLS-1 model for the two training set of standards (matrix 1 and 2) are summarized, the results for furaltadone being

Table 2
Statistical parameters obtained for matrix 1 and 2 by application of PLS1 method

Compound	Matrix 1		Matrix 2	
	R^2	RMSD × 10^5	R^2	RMSD × 10^5
FZ	0.9779	0.0185	0.9839	0.0336
FD	0.9820	0.0167	0.9939	0.0217

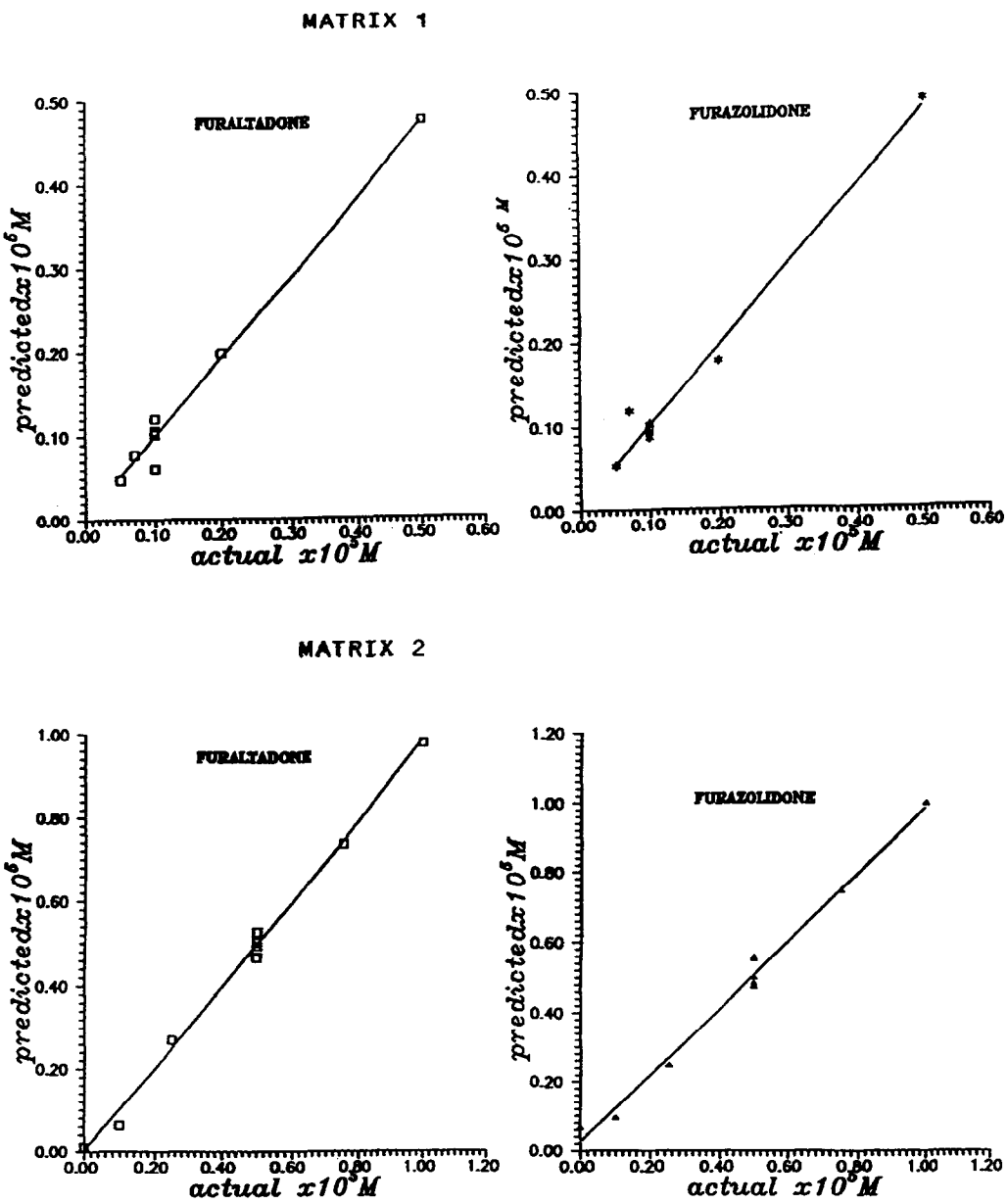

Fig. 7. Predicted versus actual concentration plots for the two training set data by using the optimized matrices.

slightly better. In Fig. 7 a representation of the predicted versus actual concentration values for the two matrices (matrix 1 and 2) are shown. The optimized matrices 1 and 2 have been applied to the resolution of artificial binary mixtures of FD and FZ, in different molar FD/FZ ratios between 0.5 and 2.5. In Tables 3 and 4 the composition of the artificial binary mixtures employed in each case are summarized. A diagrammatical representation of the recovery values for the above mentioned artificial sam-

Table 3
Composition of the artificial binary mixtures resolved by application of matrix 1

Artificial mixture	FD/FZ ratio	FD actual ($M \times 10^5$)	FZ actual ($M \times 10^5$)
P1	2.50	0.15	0.06
P2	2.40	0.12	0.05
P3	0.75	0.06	0.08
P4	0.50	0.06	0.12

Table 4
Composition of the artificial binary mixtures resolved by application of matrix 1

Artificial mixture	FD/FZ ratio	FD actual ($M \times 10^5$)	FZ actual ($M \times 10^5$)
P5	2.50	7.5	3.0
P6	2.40	6.0	2.5
P7	1.83	5.5	3.0
P8	1.33	4.0	3.0
P9	0.75	3.0	4.0
P10	0.50	3.0	6.0

Table 5
Simultaneous determination of FD and FZ in Trionic [a]

Found [b] (mg/g), FZ				Found [b] (mg/g), FD			
LC	σ_{n-1}	PLS1 method	σ_{n-1}	LC	σ_{n-1}	PLS1 method	σ_{n-1}
39.10	±0.47	42.93	±0.60	19.98	±0.15	21.00	±0.88

[a] Trionic composition per gram: furazolidone, 40 mg; furaltadone, 20 mg; chloramphenicol, 25 mg; neomycin base, 40 mg; methylescopolamine bromide, 0.2 mg; nicotinamide, 20 mg.
[b] Mean values of three independent samples.

ples are shown in Fig. 8. The results are, in general, acceptable, the worst results being those for a 0.75 FD/FZ molar ratio by application of matrix 2.

3.4. Analysis of a pharmaceutical formulation by the PLS-1 method

Only the optimized matrix 2 has been used to simultaneously analyze FZ and FD in a pharmaceutical formulation (Trionic, from Labiana lab.), to take into account the claimed levels for FD and FZ in this formulation. Trionic contains FD and FZ and chloramphenicol (nitrofuran derivatives) together with other drugs. Previously, we have proved that chloramphenicol and the other drugs do not exhibit any DPP peak in the potential range used for the multivariate analysis. In Table 5, the results obtained by application of matrix 2 are summarized and compared with those obtained by liquid chromatography (LC). Slightly higher values than those obtained with LC are found by application of the proposed method. A lower precision is also obtained. We have statistically treated the results with the object to compare the precision (variance analysis) and the mean values obtained by application of the proposed method with those by LC.

The comparison between the variances for both methods was made using Fisher's F-test and the comparison between the mean values by the Cochran test [28]. Significant statistical differences between mean values have been found for FZ, but not for FD determination. Also, significant statistical differences between the variances have been found for FZ but not for FD.

4. Conclusions

The derivative DPP signals are not suitable for the determination of mixtures of systems exhibiting irre-

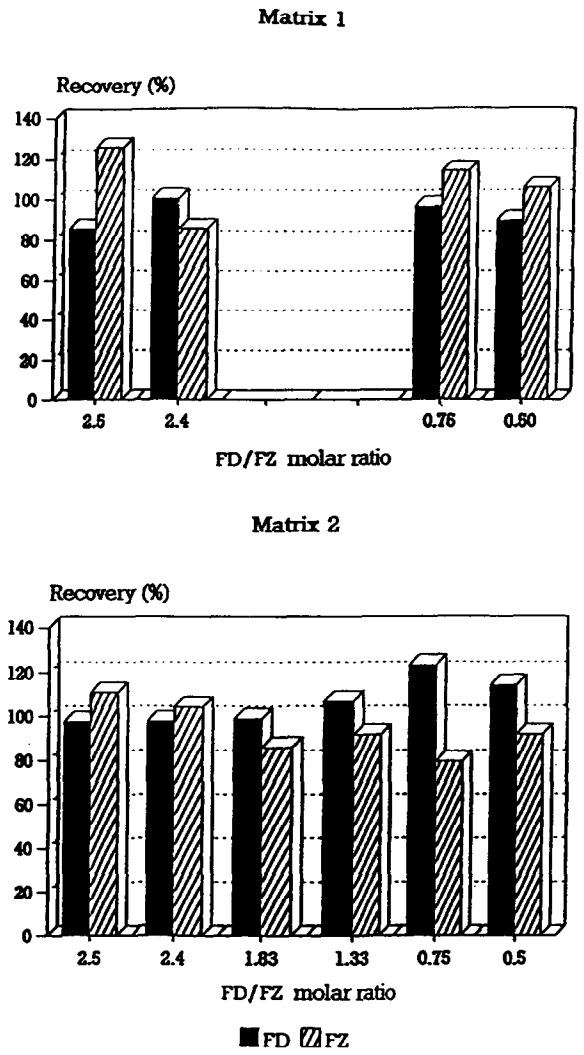

Fig. 8. Diagrammatical representation of the results obtained in the determination of binary mixtures of furazolidone (FZ) and furaltadone (FD) by the PLS-1 method.

versible electrode processes, by application of the zero-crossing method, because the zero-crossing potential value at different concentrations for each component is not constant.

PLS methods have the ability to model the total evolution of the DPP peaks with the concentration. Different matrices in two different concentration range have been designed and satisfactory statistical parameters have been obtained. The resolution of synthetic binary mixtures by the application of the PLS-1 method gives rise to acceptable recovery values. The worst results obtained for a 0.75 FD/FZ molar ratio in matrix 2 (1×10^{-5}–1×10^{-6} M) can be explained by the accordance between I for both compounds in this ratio. According to these results, we conclude that the better approach for resolving overlapping DPP peaks due to irreversible processes, by means of the assayed multicomponent analysis methods, is PLS analysis.

This approach has been applied to the determination of furazolidone and furaltadone in a pharmaceutical formulation.

It must be noticed that in the proposed method prior treatment of the samples is not necessary, while in LC methods previous filtration is always obligatory. On the other hand, the LC methods (spectrophotometric detection) exhibit a lower sensitivity than the electroanalytical techniques (e.g., DPP) and bibliographic data about of the application of LC with electrochemical detection for resolving the FD and FZ mixture have been not reported.

The linearity range in the applied LC method [29] was 2–25 μg ml^{-1} and 2–90 μg ml^{-1} for FD and FZ, respectively (when 10 μl are injected). However, the optimized calibration matrix 2 (used to analyze the Trionic formulation) as well as the other optimized matrix (matrix 1) have been designed for lower concentration levels. Matrix 1 was constructed for 0.06–1.5 μg ml^{-1} and 0.04–1.00 μg ml^{-1} for FD and FZ, respectively, and matrix 2 was constructed for 0.3–3.2 μg ml^{-1} and 0.2–2.2 μg ml^{-1} for FD and FZ, respectively.

The proposed method can be used without any preconcentration process in other types of samples exhibiting low amounts of these compounds.

Acknowledgements

The author are grateful to Dr. A. Muñoz de la Peña for making the LAB-DU50 convert program. Financial support from DGICYT of Spain (Project PB91-0856) is acknowledged.

References

[1] T.C. O'Haver and G.L. Green, Anal. Chem., 48 (1976) 312.
[2] D.M. Haaland and E.V. Thomas, Anal. Chem., 60 (1988) 1193.

[3] H. Martens, Multivariate calibration, Wiley, New York, 1992.
[4] J.J. Berzas and J. Rodríguez, Fresenius' J. Anal. Chem., 342 (1992) 273.
[5] B. Morelli, Analyst, 108 (1983) 870.
[6] G. Turnes, A. Cladera, E. Gómez, J.M. Estela and V. Cerdá, Electroanal. Chem., 338 (1992) 49.
[7] SCIWARE, Banco de Programas, Association of Environmental Sciences and Techniques, Departamento de Química Analítica, Universidad de las Islas Baleares.
[8] T.F. Brown and S.D. Brown, Anal. Chem., 53 (1981) 1410.
[9] D.P. Binkley and R.E. Dessy, Anal. Chem., 52 (1980) 1335.
[10] B.S. Grabaric, R.J. O'Halloran and D.E. Smith, Anal. Chim. Acta., 133 (1981) 349.
[11] R.W. Gerlach and B.R. Kowalski, Anal. Chim. Acta, 134 (1982) 119.
[12] A. Henrion, R. Henrion, G. Henrion and F. Scholz, Electroanalysis, 2 (1990) 309.
[13] D. Jagner, L. Renman and S.H. Stefansdottir, Anal. Chim Acta, 281 (1992) 315.
[14] P. Geladi and B.R. Kowalski, Anal. Chim. Acta, 185 (1986) 1.
[15] P. McLaurin, P.J. Worsfold, M. Crane and P. Norman, Anal. Proc., 29 (1992) 65.
[16] A. Espinosa Mansilla, A. Muñoz de la Peña, F. Salinas and A. Zamoro, Anal. Chim. Acta, 258 (1992) 47.
[17] A. Espinosa Mansilla, A. Muñoz de la Peña, F. Salinas and M. Martínez Galera, Anal. Chim. Acta, 276 (1993) 141.
[18] H. Wold, in F. David (Ed.), Research Papers in Statistics, Wiley, New York, 1966, pp. 411–444.
[19] H. Wold, in H. Joreskog and H. Wold (Eds.), Systems Under Indirect Observation, Vol. 2, North-Holland, Amsterdam, 1982, pp. 1–54.
[20] S. Wold, H. Martens and H. Wold, in A. Ruhe and B. Kagstrom (Eds.), The Multivariate Calibration Problem in Chemistry Solved by PLS, 'Matrix Pencils' (Lecture Notes in Mathematics), Springer, Heidelberg, 1983, pp. 286–293.
[21] A. Morales, P. Richter and M.I. Toral, Analyst, 112 (1987) 965.
[22] T. Galeano, A. Guiberteau, L. López and F. Salinas, Anal. Chim. Acta, 273 (1993) 351.
[23] Data Leader Software Package, Beckman, Fullerton, CA, 1987.
[24] Lab Calc Software Package, Galactic Industries, Salem, NH, 1989.
[25] A. Saviztky and H. Golay, Anal. Chem., 36 (1964) 1927.
[26] J. Steiniar, Y. Termonia and J. Deltour, Anal. Chem., 44 (1972) 1906.
[27] M.J.R. Stone, Stat. Soc., 36 (1974) 111.
[28] M. Valcarcel and A. Rios, La calidad en los laboratorios analíticos, Edit. Revérte, S.A., 1992, p. 76.
[29] T. Galeano Diaz, L. López-martinez, M. Martinez Galera and F. Salinas, J. Liq. Chromatogr., 17 (1994) 457.