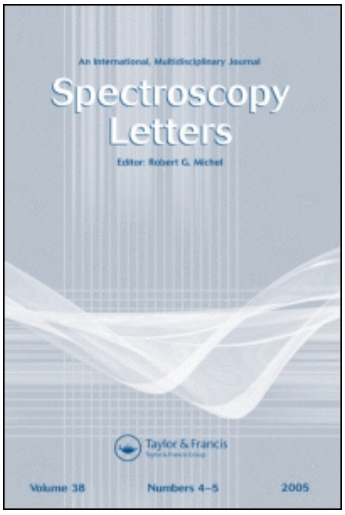

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Rapid and Direct Spectrofluorometric and Chemometrics Methods for the Simultaneous Determination of Two Dansyl Derivatives

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ABSTRACT In this study the simultaneous molecular spectrofluorometric determination of ultratrace amounts of two dansyl chloride derivatives, DMNPS (5-(dimethylamino)naphthalene-1-sulfonyl 4-phenylsemicarbazide) and DMNPH (2-(5-(dimethylamino)naphthalen-1-ylsulfonyl)-N-phenylhydrazinecarbothioamide), was accomplished using a genetic algorithm joint partial least squares (GA-PLS) technique that leads to very low detection limits (lower than 10^{-6} mol/L) The linear dynamic ranges of the compounds were 1–6 μmol L^{-1} and 1–7 μmol L^{-1} for DMNPS and DMNPH, respectively. Quantification was performed using the emission wavelength range from 360 to 600 nm with an optimum calibration sample number of 25 and prediction sample number of 7. The technique was proved to be beneficial.

KEYWORDS chemometrics, dansyl, GA-PLS, molecular fluorescence spectroscopy, simultaneous determination

INTRODUCTION

Spectrofluorometric determination is an attractive detection method not only for the low detection limit and wide linear working range that can be achieved even using relatively simple and inexpensive instrumentation but for the possibility to obtain high accuracy and reproducibility rapidly from a trace or ultratrace amount of samples.[1–3]

Besides, simultaneous determinations of the compounds with the overlapping band spectra by fluorometric methods have been reported less than works have been done by the UV-Vis method.

Recently, much research has been done on the syntheses of highly sensitive and highly selective fluorescence complexing agents[4] as well as studies on the reaction mechanism of the involved fluorescence systems. Research into and application of sensitivity-increasing, stability-increasing, and solubility-increasing mechanisms of the surfactants in fluorescence reactions[5] has led to rapid development of applications of molecular

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spectrofluorometry for both inorganic substances and organic compounds in trace and ultratrace analysis.[6,7]

The molecular fluorescence excitation and/or emission spectra of some organic compounds or complexes of metal ions with similar chemical properties often seriously overlap, leading to interference in the determination of various components. In these cases, because multivariate molecular fluorescence spectrophotometry is similar to multivariate UV-Vis spectrophotometry,[8] coupling the molecular fluorescence spectrophotometry with chemometrics methods is an important advancement in the selectivity of molecular fluorescence spectrophotometry.[9] Employing multivariate calibration methodologies (i.e., partial least squares, PLS) is beneficial in a way that these methods minimize or eliminate sample preparation, avoid a prior separation step in complex matrices,[10] and hence save time. Furthermore, the feasibility of this class of mathematical tools to simultaneously analyze complex mixtures of complexing agents has been proven.[11–16]

The second derivative synchronous fluorescence mode of molecular fluorescence spectral acquisition has been of particular interest in the conventional spectrofluorometry methods[17–19] for the analysis of complex samples with overlapping spectra with $\Delta\lambda_{emission}$ range of 30 to 140 nm. This mode of fluorescence facilitates obtaining higher spectral resolution and helps background reduction, which leads to the possibility of applying the molecular fluorescence technique for the simultaneous determination of multiple analytes in multicomponent samples. Furthermore, this technique can be combined with partial least squares technology to improve the selectivity and sensitivity of molecular fluorescence.

As in this study, the $\Delta\lambda_{emission}$ of fluorescence between DMNPS (5-(dimethylamino)naphthalene-1-sulfonyl 4-phenylsemicarbazide) and DMNPH (2-(5-(dimethylamino)naphthalen-1-ylsulfonyl)-N-phenylhydrazinecarbothioamide) is only 11 nm, so application of the synchronous second-derivative mode of molecular fluorescence is not helpful. Thus, we used genetic algorithm (GA)-PLS as a beneficial chemometrics technique to simultaneously determine these compounds existing together.

Dansyl chloride and its derivatives can be applied as synthetic receptors to selectively bind a wide variety of guest molecules/ions forming host–guest complexes.[20–25] Because dansyl chloride is a good fluorometric detection reagent, it can be used as a fluorophore part in a ligand in order to verify interactions of that ligand with ions of interest such as lanthanide ions. In this work we used dansyl chloride as a fluorophore (signaling moiety) linked to two ionophores (recognition moieties) with very similar structures, which leads to fluoroionophores DMNPS and DMNPH. The inherent fluorescence of DMNPS and DMNPH was obtained at 418 and 431 nm, respectively, in an acetate buffer of pH 6.0 when excited at 325 nm.

Because the simultaneous determination of closely related species is of continuing analytical interest, in this assay we applied the two mentioned derivatives of dansyl chloride that are structurally similar and differ only in one C=O part instead of a C=S one in their structure. So it is probable that they coexist in a media in which a lanthanides determination experiment is being accomplished. Because the excitation–emission of these compounds strongly overlap, their direct determination by conventional fluorometric methods is not possible and they are to be separated by chemometrics methods.

The aim of our research is to present a rapid, direct, precise, and accurate method for the simultaneous determination of DMNPS and DMNPH without separation, using fluorescence spectroscopy coupled with multivariate calibration methodologies. In the present work, a spectrofluorometric method was proposed for direct and simultaneous determination of these chemicals using a full-spectrum

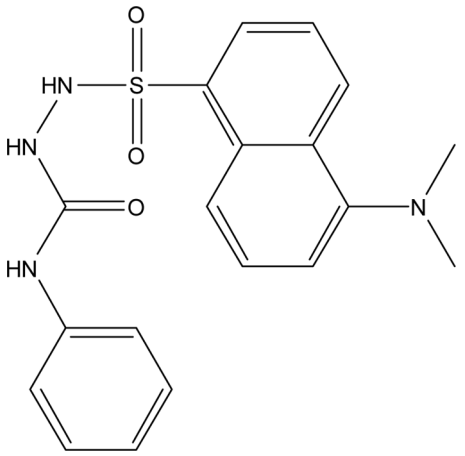

FIGURE 1 Structure of 5-(dimethylamino)naphthalene-1-sulfonyl-4-phenylsemicarbazide (DMNPS).

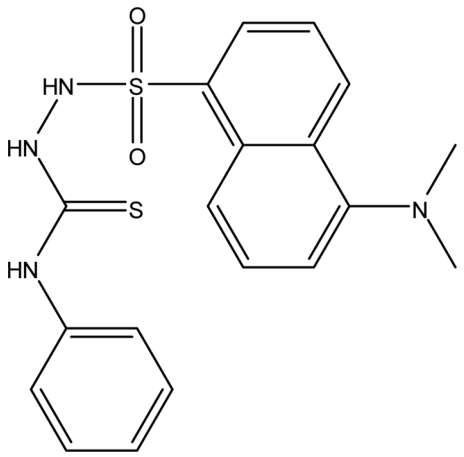

FIGURE 2 **Structure of 2-(5-(dimethylamino)naphthalen-1-ylsulfonyl)-N-phenylhydrazinecarbothioamide (DMNPH).**

multivariate calibration method (PLS) without any pretreatment and separation step. The proposed method is sensitive, simple, fast, reliable, and efficient and has successfully led to quantification of (DMNPS; Fig. 1) and (DMNPH; Fig. 2), based on the measurement of the fluorescence spectra (at $\lambda_{ex} = 325$ nm) in acetonitrile media in a acetate buffer of pH 6.0. To the best of our knowledge, this is the first report on the simultaneous determination of these fluorescent complexing agents using a spectrofluorometric method with joint GA-PLS regression.

EXPERIMENTAL

Chemical Reagents

All the chemicals used were of analytical reagent grade and were used without further purification. Acetonitrile was obtained from Merck (Darmstadt, Germany).

The procedure for synthesizing 5-(dimethylamino) naphthalene-1-sulfonyl-4-phenylsemicarbazide is as follows: the N-phenylhydrazinecarboxamide (2 mmol, 0.302 g) was solved in acetone and three drops of triethylamine was added. Then 5-(dimethylamino)naphthalene-1-sulfonyl chloride (2 mmol, 0.468 g) was added to the solution of N-phenylhydrazinecarboxamide at room temperature. Then, the solid product was crystallized in ethanol.

In order to confirm the DMNPS structure, the relative nuclear magnetic resonance (NMR) spectrum is acquired. ^{1}H NMR (90 MHz, $CDCl_3$): σ_H 3.02 (6H, S, NMe_2), 7.00 (1H, t, J = 7.5 Hz, CH), 7.23 (2H, dd, J = 7.5, 7.8 Hz, 2CH), 7.35 (2H, d, J = 7.6 Hz, 2CH), 7.40 (1H, d, J = 6.4 Hz, CH), 7.56 (1H, dd, J = 6.4, 8.4 Hz, CH), 7.80 (1H, dd, J = 6.6, 8.5 Hz, CH), 8.12 (1H, d, J = 8.5 Hz, CH), 8.22 (1H, d, J = 6.6 Hz, CH), 8.33–8.40 (3H, br, 3NH). ^{13}C NMR (400 MHz, $CDCl_3$): σ_C 39.84 (NMe_2), 116.21, 118.33, 123.60, 124.72 (4CH), 125.91 (C), 126.05, 127.77, 128.70, 131.63, 133.14 (5CH), 134.41, 139.95, 154.39 (3C), 152.55 (C=O).

The procedure for synthesizing of 2-(5-(dimethylamino)naphthalen-1-ylsulfonyl)-N-phenylhydrazine carbothioamide is as follows: the N-phenylhydrazinecarbothioamide (2 mmol, 0.334 g) was solved in acetone and three drops of triethylamine was added; then 5-(dimethylamino)naphthalene-1-sulfonyl chloride (2 mmol, 0.468 g) was added to the solution of N-phenylhydrazinecarbothioamide at room temperature. Then the solid product was crystallized in ethanol.

In order to confirm the DMNPH structure, the relative NMR spectrum is acquired. ^{1}H NMR (90 MHz, $CDCl_3$): σ_H 3.02 (6H, S, NMe_2), 7.00 (1H, t, J = 7.5 Hz, CH), 7.23 (2H, dd, J = 7.5, 7.8 Hz, 2CH), 7.35 (2H, d, J = 7.6 Hz, 2CH), 7.40 (1H, d, J = 6.4 Hz, CH), 7.56 (1H, dd, J = 6.4, 8.4 Hz, CH), 7.80 (1H, dd, J = 6.6, 8.5 Hz, CH), 8.12 (1H, d, J = 8.5 Hz, CH), 8.22 (1H, d, J = 6.6 Hz, CH), 8.33–8.40 (3H, br, 3NH). ^{13}C NMR (400 MHz, $CDCl_3$): σ_C 39.84 (NMe_2), 116.21, 118.33, 123.60, 124.72 (4CH), 125.91 (C), 126.05, 127.77, 128.70, 131.63, 133.14 (5CH), 134.41, 139.95, 154.39 (3C), 173.13 (C=S).

Linear Dynamic Range

The first step for the simultaneous determination of analytes by multivariate calibration methods is to find the dynamic calibration range of each component. One component calibration method was performed here to find the linear dynamic concentration range of each dansyl chloride derivative, by adding different volumes of 10^{-3} mol L^{-1} solution of each compound into different 10.0-mL volumetric flasks in acetonitrile media in an acetate buffer of pH 6.0. Afterward, the emission spectra were recorded over the spectral range of 360–600 nm at $\lambda_{ex} = 325$ nm and the linear dynamic range for each complexing agent (1–6 μ mol L^{-1} and 1–7 μ mol L^{-1} for DMNPS and DMNPH, respectively) were obtained, plotting the fluorescence emission at its λ_{max} versus sample concentration in μ mol L^{-1} at pH = 6 (Fig. 3).

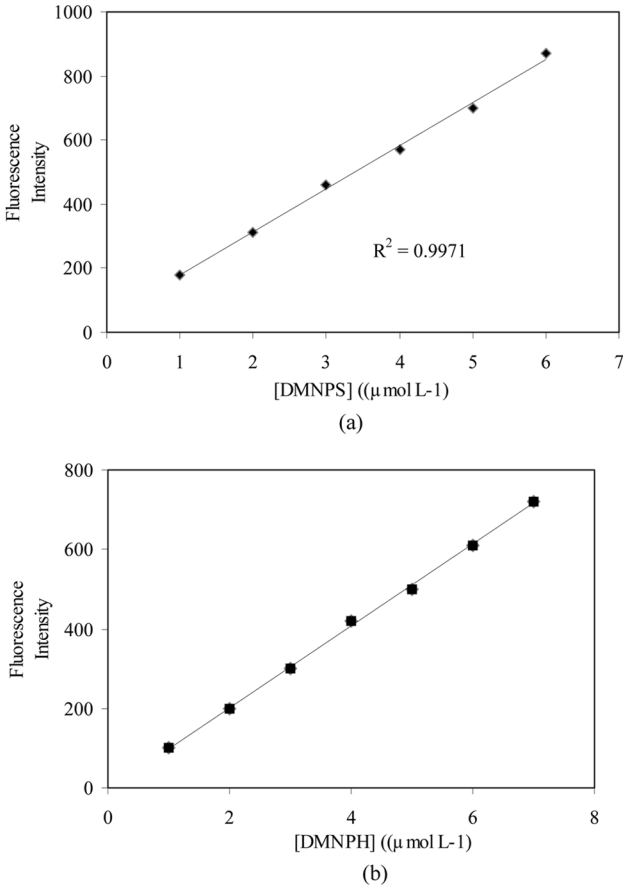

FIGURE 3 **(a) Linear dynamic range for DMNPS plotting the fluorescence emission at its λ_{max} versus sample concentration. (b) Linear dynamic range for DMNPH plotting the fluorescence emission at its λ_{max} versus sample concentration.**

Apparatus and Software

Fluorometric measurements were carried out with a Perkin-Elmer LS50 spectrofluorometer (Beaconsfield, UK). The software used to record fluorescence spectrum was FL WinLab (Beaconsfield, UK). Experiments were carried out at ambient temperature (25°C). The excitation wavelength was 325 nm in all cases with an excitation and emission band pass (slit) of 8 nm and scan rate of 1500 nm/min. The solutions were placed in a 1-cm path-length quartz cell for the fluorescence measurements.

Spectra were acquired over the wavelength range of 360–600 nm. GA-PLS calculations were performed in MATLAB 7.0 software (MathWorks, Natick, MA).

RESULT AND DISCUSSION

pH Optimization

The dependence of the fluorescence intensity on pH was tested for both fluoroionophores in the presence of a specific concentration (3.0×10^{-6} M) of each fluoroionophore. Figures 4a and 4b shows the influence of pH on the spectrofluorometric response for DMNPS and DMNPH, respectively, varying pH from 2.5 up to 10.5. The pH of the test solution was adjusted with nitric acid or sodium hydroxide solutions. As is obvious from Fig. 4, the fluorescence intensity response passes through a more or less plateau region between pH 3.5 and 8.8 for DMNPS and between pH 3.8 and 8.5 for DMNPH and beyond these pH ranges the spectrofluorometric response is decreased. The diminished response at pH < 3.8 could be due to the extraction of H^+ from the test solution and thus protonation of the nitrogen atoms of each ligand, which in turn is expected to change the mobility of π-electrons of the ligand system. Thus, in subsequent experiments,

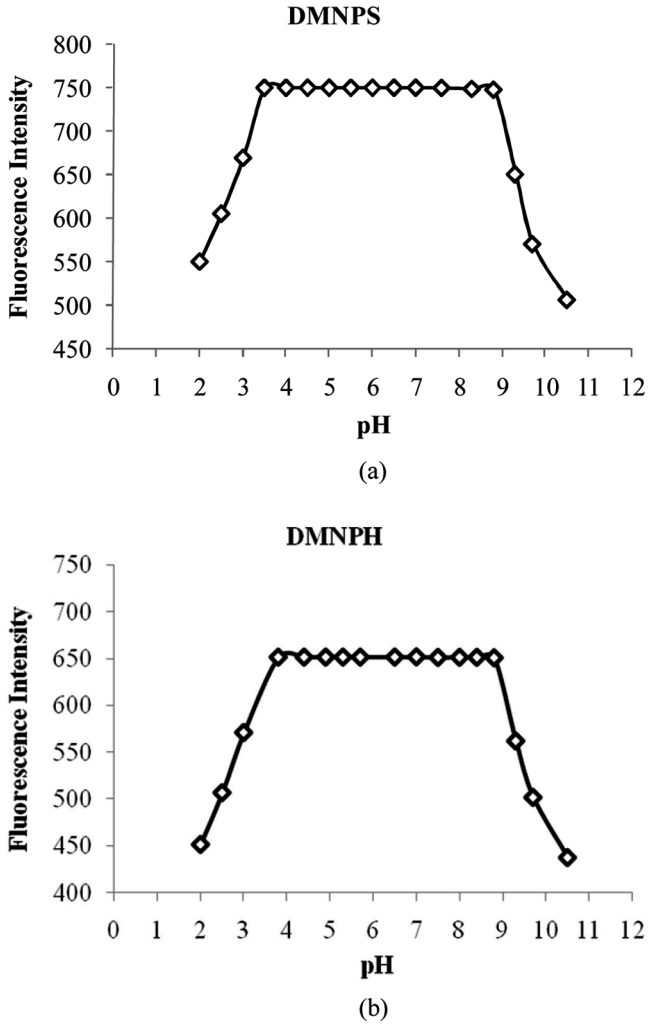

FIGURE 4 **(a) Influence of pH on the spectrofluorometric response of DMNPS at λ_{em} = 325 nm. (b) Influence of pH on the spectrofluorometric response of DMNPH at λ_{em} = 325 nm.**

a solution of pH = 6.0 adjusted by a 0.01 M acetate buffer solution was used for further studies.

Emission Spectra Behavior of DMNPS and DMNPH

The emission spectra of the both studied dansyl chloride derivatives and their mixtures over the 360–600 nm range in an acetate buffer of pH 6.0 are shown in Fig. 5. As can be seen, the spectra of the 3 μ mol L^{-1} of the two compounds excited at 325 nm in a binary mixture displays considerable overlap that conventional spectrofluorometry, using a fluorescence spectrophotometer or synchronous second-derivative mode of molecular fluorescence, is not able to resolve with acceptable accuracy. Therefore, application of a simple and dependable multivariate calibration method such as PLS is necessary for such determination.

Multivariate Calibration Methods

Multivariate calibration approaches are important mathematical tools based on the use of a large number of variables that discriminate species with highly overlapped profiles. In this study, a PLS algorithm was applied to the fluorescence analysis to set up the multicomponent determination prediction model.

Partial least squares modeling is a powerful multivariate statistical tool that has so far been most frequently applied to spectrofluorometry[26–28] and UV–Vis spectroscopy.[29,30] This technique is a multivariate calibration model that involves a two-step procedure: (1) calibration, where the relation between spectra and reference component concentrations is verified from a set of synthesized samples; and (2) prediction, in which the calibration results are used to quantify the components concentrations in unknown samples. The rudimentary feature of PLS regression is that it suggests decomposition of X and Y matrices into two new score and loading matrices using singular value decomposition or principal components analysis. Afterward, the covariance between score vector in X-space and a score vector in Y-space or the size of the loading vector in Y-space derived from the score of the vector in the X-space should be maximized equivalently.

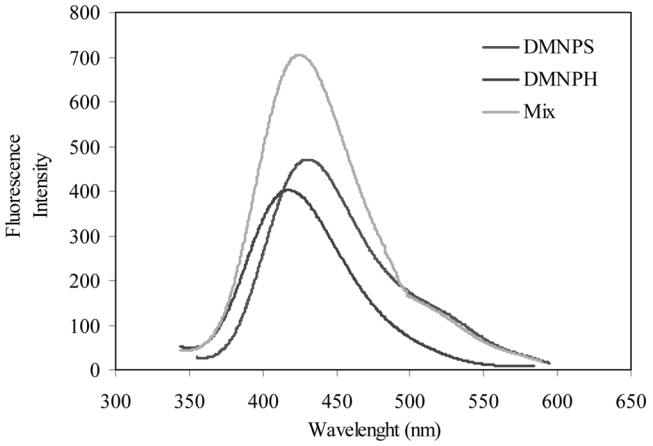

FIGURE 5 Emission spectra of 3 μ mol L^{-1} solutions of DMNPS and DMNPH and their mixture excited at 325 nm.

Selection of the Optimum Number of Factors

A genetic algorithm is a beneficial technique in variable selection problems, because the relationship between the presence/absence of the variables in a calibration model and the prediction ability of the model, specifically for the PLS models, is complicated and the mathematical properties are unknown. It has also been proved to be well suited to spectrophotometric techniques to accurately predict the concentrations of the components in mixtures.[31–40]

A comprehensive discussion of the genetic algorithms can be found in the literature.[41–46] The algorithm used in this article is an evolution of the algorithm described in Leardi and Gonzalez.[47] Selection of the optimum number of PLS factors was done using a GA that has been proved to be superior to other statistical techniques. It is a search paradigm inspired by natural evolution where the variables are represented as genes on a chromosome (model). It is similar to simplex optimization and evolves a group of random initial models (populations) with fitness scores and searches for chromosomes with better fitness functions (response function scores) through natural selection and the genetic operators mutation and recombination. The GA combines genes from two parent chromosomes using the genetic recombination operator to form two new chromosomes that have a high probability of having better fitness than their parents and also explores new response surface through mutation.[48]

To do so, a p-dimensional vector, w, will represent each wavelength subset selected in the emission

spectrum with binary coordinates. If the ith wavelength is selected, then the ith coordinate of w is one, which in the other case is zero. Each w is a chromosome. Given a chromosome (w), a PLS calibration is constructed using from each emission spectrum only the wavelength represented by w. Each chromosome is evaluated using the prediction error sum of squares (PRESS) (w) value reached in the calibration. The genetic algorithm searches for the minimum PRESS (w) in the space of all the possible chromosomes without establishing a priori the latent structure of the calibration. The GA was run for 240 variables (in the range 360–600 nm) using a PLS regression method. The maximum number of factors in this method was the optimal number of components, determined by cross-validation containing all the variables by employing the leave-one-out (LOO) procedure that involves systematically removing one calibration sample at a time and employing the remaining samples for model building. By using this calibration the concentration of the left-out sample is predicted. This process is repeated until each standard is left out once. The selected variables were then used for running PLS.

Wavelength Selection

In order to acquire the optimum wavelength set, the GA procedure was repeated until a wavelength was selected when the percentage of selection for that variable exceeded a critical value. According to the minimum prediction error for each analyte, the thresholds of 83% and 77% were obtained for DMNPS and DMNPH, respectively. The selected wavelengths were 546, 550, and, 554 nm for DMNPS as well as 365, 372, 375, and 379 nm for DMNPH.

GA-PLS Method and Its Verification with Synthetic Mixtures

The second step for the simultaneous determination of analytes by multivariate calibration methods involves designing a calibration matrix for the binary mixtures. Accordingly, a training set of 25 samples was randomly constructed using a five-level orthogonal array design (OAD)[49] by adding appropriate amounts of DMNPS and DMNPH solutions considering the range of their known linear emission–concentration zones to a series of 10-mL volumetric flasks in the acetonitrile media in acetate buffer of pH 5.0. To investigate the accuracy of the obtained models, a prediction set of 7 samples was randomly chosen in a way that the mixtures were not included in the calibration set and were obtained in a way mentioned above; covering the ligand's whole concentration range of interest was prepared. Compositions of the calibration and prediction sets are presented in Tables 1 and 2, respectively. The fluorescence spectra of the mixtures were recorded at the wavelength range of 360–600 nm, and the digitized emission was sampled at 1.0 nm intervals.

The prediction step was carried out applying the constructed model (GA-PLS) for the simultaneous quantification of the two analytes in seven synthetic samples, the concentrations of which were different from those of calibration, and the obtained results are presented in Table 3. Table 3 also shows recoveries and the most relevant statistical parameters that are often used to test the prediction ability of the optimized model for the simultaneous determination

TABLE 1 **Concentration Data of the Different Mixtures Used in the Calibration Set for the Determination of DMNPS and DMNPH with PLS Method**

Sample No.	DMNPS (μ mol L^{-1})	DMNPH (μ mol L^{-1})
1	1	1
2	2	1
3	3	1
4	4	1
5	1	2.5
6	2	2.5
7	3	2.5
8	1	4
9	2	4
10	1	1.5
11	2	1.5
12	3	1.5
13	1	2
14	2	2
15	3	2
16	1	3
17	2	3
18	1	3.5
19	1.5	1
20	2.5	1
21	3.5	1
22	1.5	2
23	2.5	2
24	1	0.5
25	2	0.5

TABLE 2 Predicted Concentrations Obtained by the Application of GA-PLS Method on the Fluorescence Emission Spectra for the Simultaneous Determination of DMNPS (μmol L^{-1}) and DMNPH (μmol L^{-1}) in Binary Mixtures

	Add		Found (GA-PLS)		Recovery (%)	
	DMNPS	DMNPH	DMNPS	DMNPH	DMNPS	DMNPH
	1.5	1.5	1.76	1.36	117.33	90.67
	2.5	2.5	2.75	2.45	110.00	98.00
	3	1.2	2.77	1.17	92.33	97.50
	1.2	3.0	1.17	2.77	97.50	92.33
	2.5	3.0	2.48	2.67	99.20	89.00
	0.5	0.5	0.48	0.45	96.00	90.00
	1.5	0.5	1.45	0.47	96.67	94.00
Mean	—	—	—	—	101.29	93.07
SD			0.1766	0.1771		

of the studied compounds. The root mean square deviation (RMSD) values indicate the average error in the analysis for each component:

$$\mathrm{RMSD} = \left[\frac{1}{n}\sum_{i=1}^{n}(x_i - \hat{x}_i)^2\right]^{0.5} \quad (1)$$

The RMSD values are an estimation of the absolute error of prediction for each compound, which were obtained to be 0.1635 and 0.1640 using the GA-PLS model for DMNPS and DMNPH, respectively.

Another useful parameter is the relative error of prediction (REP) that reveals the predictive ability of each component, calculated as:

$$\mathrm{REP}(\%) = \frac{100}{\bar{x}}\left[\frac{1}{n}\sum_{i=1}^{n}(x_i - \hat{x}_i)^2\right]^{0.5} \quad (2)$$

where x_i is the true concentration of the analyte in the sample i, $\hat{x}_i$ represents the estimated analyte concentration in the sample i, $\bar{x}$ is the mean of the true concentration in the prediction set, and n is the total number of samples used in the prediction set. For the studied compounds, REP% values were obtained to be 9.0136 and 9.4080 via GA-PLS for DMNPS and DMNPH, respectively.

TABLE 3 Statistical Parameters of GA-PLS

Compounds	NPC*[a]	PRESS	RMSD	REP (%)
DMNPS	2	0.1872	0.1635	9.0136
DMNPH	2	0.1882	0.1640	9.4080

[a]NPC* = number of principal components.

CONCLUSION

The method proposed here is a simple, rapid, and precise assay for the simultaneous quantitative determination of DMNPS and DMNPH with very similar structures. It has been used for simultaneous fluorescence spectrophotometric determination of trace or ultratrace amounts of DMNPS and DMNPH. The fluorescence excitation/emission spectra which have seriously overlapped and interfered with each other's, setting up a new fluorescence analysis technique combined with chemometrics methods that could be considered. These methods are faster, dependable, direct, and relatively less expensive alternative for the multicomponent analysis of a mixture. To the best of our knowledge, for the first time we coupled the fluorescence method with a GA-PLS technique as a powerful multivariate statistical tool to simultaneously determine these complexing agents, the results of which had an accuracy, precision, linearity, and sensitivity similar to many available methods or even better, and it is very low cost, fast, and simple.

The $\lambda_{ex(max)}/\lambda_{em(max)}$ values are 320/419 and 330/430 nm for DMNPS and DMNPH, respectively, and their $\lambda_{em(max)}$ values are 419 and 430 nm, respectively, at the same fixed λ_{ex} of 325 nm, indicating their seriously overlapping fluorescence emission spectra ($\Delta\lambda_{emission}$ is only 11 nm) in acetonitrile media in acetate buffer of pH 5.0. Quantification was accomplished using the emission wavelength range from 360 to 600 nm at a fixed λ_{ex} of 325 nm.

According to the obtained results, it can be concluded that a spectrofluorometric method combined with GA-PLS made possible the simultaneous quantification of the studied dansyl chloride derivatives, although the absorption–emission spectrum of the compounds overlapped seriously because of the similarities in these compounds' chemical structures and resulted in reliable outcomes for binary mixtures analysis in prediction samples. In all analyses, the obtained results from GA-PLS method showed good and satisfactory agreement with known values.

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